

**The American Ceramic Society**

**Materials Challenges in Alternative and  
Renewable Energy 2018**

**ABSTRACT BOOK**

**August 20–23, 2018  
Vancouver, BC, Canada**

# Introduction

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## How to Use the Abstract Book

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Refer to the Table of Contents to determine page numbers on which specific session abstracts begin. At the beginning of each session are headings that list session title, location and session chair. Starting times for presentations and paper numbers precede each paper title. The Author Index lists each author and the page number on which their abstract can be found.

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Monday, August 20, 2018

### Plenary I

Room: Grand Ballroom A & B

Session Chairs: Steven Tidrow, Alfred University; Yoon-Bong Hahn, Chonbuk National University

8:30 AM

#### (MCARE-PLN-001-2018) High Temperature Solid Oxide Fuel Cells for Clean and Efficient Power Generation

S. C. Singhal\*<sup>1</sup>

1. Pacific Northwest National Laboratory, USA

Solid oxide fuel cells (SOFCs), based on an oxide ion conducting ceramic electrolyte such as stabilized-zirconia, offer a clean, low-pollution technology to electrochemically generate electricity at high efficiencies. These cells operate between about 550 and 1000°C, and some hydrocarbon fuels such as natural gas can be reformed within the cell stack eliminating the need for an expensive, external reformer. SOFCs offer important advantages over other kinds of fuel cells, notably their ability to use CO or liquid hydrocarbons as fuel, which makes them ideally suited for commercial, residential, portable, and remote military applications. The most important need to commercialize SOFC technology is to significantly reduce the overall cost of SOFC-based power systems, while maintaining adequate performance and performance stability with time. Reduction of cell operation temperature enables use of low-cost metallic interconnects and a decrease in maintenance costs. This overview focuses on the materials, processing, and performance of solid oxide fuel cells, with relative advantages/disadvantages of different geometries. Stacks and systems built with both tubular and planar geometries are described and their operating experience discussed. Applications of such cells in different market sectors are reviewed and challenges in reducing cell and system costs are summarized.

## SYMPOSIUM 1

### Materials for Solar Fuel Production and Applications I

Room: Grand Ballroom A

Session Chair: Kijung Yong, Pohang University of Science and Technology (POSTECH)

9:30 AM

#### (MCARE-S1-001-2018) Semiconductor Nanoheterostructures for Photoconversion Applications (Invited)

Y. Hsu\*<sup>1</sup>

1. National Chiao Tung University, MSE Department, Taiwan

With the inherently high degree of complexity, nanoheterostructures composed of two or more materials joined in unique architectures may exhibit superior synergetic properties that are difficult or impossible to acquire from their individual constituents. For semiconductor nanoheterostructures, the relative band alignment of the constituents promotes effective charge separation to bring them desirable properties for photoconversion applications. Several representative works from our lab including Au-CdS, Au-ZnS core-shell nanocrystals, Au-decorated ZnO nanocrystals, graphene quantum dot-modified CdSe nanocrystals, and Au@Cu<sub>7</sub>S<sub>4</sub>-decorated TiO<sub>2</sub> nanowires will be introduced to demonstrate the promising potentials of semiconductor nanoheterostructures.

10:00 AM

#### (MCARE-S1-002-2018) Enhancing Long-Term Photostability of BiVO<sub>4</sub> Photoanodes for Solar Water Splitting (Keynote)

D. Lee<sup>1</sup>; D. Lee<sup>1</sup>; K. Choi\*<sup>1</sup>

1. University of Wisconsin-Madison, Chemistry, USA

As the performance of photoelectrodes used in a photoelectrochemical cell (PEC) for water splitting continues to improve, concurrently improving their photostabilities has become an important issue. In this presentation, we report a new strategy to suppress photocorrosion of photoelectrodes using a BiVO<sub>4</sub> photoanode as an example. BiVO<sub>4</sub> has been recently identified as a promising oxide-based photoanodes for solar water splitting owing to many of its uniquely advantageous features. Anodic photocorrosion of BiVO<sub>4</sub> photoanodes involves the loss of V<sup>5+</sup> from the BiVO<sub>4</sub> lattice by dissolution. Any composition change caused by the anodic photocorrosion of BiVO<sub>4</sub> must be coupled with the oxidation of one or more of the elements present in BiVO<sub>4</sub>. Since V<sup>5+</sup> in the BiVO<sub>4</sub> lattice cannot be further oxidized, the dissolution of V<sup>5+</sup> must be linked with the photooxidation of Bi<sup>3+</sup> and/or lattice O<sup>2-</sup> ions. We show that the use of a V<sup>5+</sup>-saturated electrolyte, which inhibits the photooxidation-coupled dissolution of BiVO<sub>4</sub>, can slow down the rate of photocorrosion considerably and serve as a simple yet effective method to suppress anodic photocorrosion of BiVO<sub>4</sub>. The effect of the V<sup>5+</sup> species in the electrolyte on both the long-term photostability of BiVO<sub>4</sub> and the performance of the OEC layer will be discussed in detail.

10:30 AM

#### (MCARE-S1-003-2018) NIR and visible light driven overall water splitting for hydrogen production over CdS/NaYF<sub>4</sub>:Yb<sup>3+</sup>-Er<sup>3+</sup> photocatalysts (Invited)

G. Lu\*<sup>1</sup>

1. Lanzhou Institute of Chemical Physics, China

In this work, we reported a CdS/NaYF<sub>4</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup>/Pt photocatalyst for overall water splitting under near infrared (NIR) and visible light irradiation. By assemble a NIR-to-visible upconversion (UC) component NYF<sub>4</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> (NYF), the effective hydrogen evolution from over-all water splitting under NIR/visible light illumination and the improved stability during the reaction were successfully achieved over the CdS/NYF/Pt. In addition, using the oxygen transfer reagent perfluorodecalin (FDC) can remarkable inhibit the hydrogen-oxygen recombination reaction over the photocatalyst. The highest hydrogen evolution rate of 101.8 μmolg<sup>-1</sup>h<sup>-1</sup> has been achieved under NIR/visible light irradiation. The excited holes in CdS transferred to NYF by taking advantage of inner electric field between them, therefore inhibition of hole oxidation of CdS was fulfilled and better stability of CdS/NYF/Pt was achieved.

11:00 AM

#### (MCARE-S1-004-2018) Construction of three-dimensional nanostructured arrays for efficient solar energy conversion (Invited)

J. Wu\*<sup>1</sup>; J. Yang<sup>1</sup>

1. National Cheng Kung University, Department of Chemical Engineering, Taiwan

To achieve efficient photoelectrochemical (PEC) water splitting for H<sub>2</sub> production, enormous research efforts have been focused on the suppression of charge recombination in photoelectrodes. Nanostructured heterojunction array photoanodes, composed of high electron conductivity semiconductor core (nanostructured array scaffold) and photocatalyst shell, have been demonstrated to enhance the PEC water oxidation efficiency by improving charge separation in the bulk and hole collection on the surface of photoanodes. The array scaffold plays crucial roles both in morphology and interfacial energetic controls for achieving efficient photoanodes. Compared to the one dimensional nanostructured array scaffolds,

the three dimensional (3D) nanostructured array scaffolds exhibit even more significant enhancements in charge separation and photocarrier collection for PEC water splitting. In this presentation, the use of the 3D oxide nanodendrite (ND) arrays as the scaffolds for the constructions of nanostructured heterojunction array photoanodes will be reported. The presence of branches in the ND array scaffold increases the volumes of the depletion regions in both core-shell heterojunction and shell/electrolyte heterojunction, which results in the enhanced charge separation efficiency and therefore photocurrent density in the 3D nanostructured heterojunction array photoanode.

**11:30 AM**

**(MCARE-S1-005-2018) Highly adaptive artificial leaf applicable in various nature environments with floatability and planar design**

S. Kim<sup>\*1</sup>; K. Han<sup>1</sup>; M. Lee<sup>1</sup>; D. Kim<sup>1</sup>; K. Yong<sup>1</sup>

1. Pohang University of Science and Technology(POSTECH), Chemical Engineering, Republic of Korea

Solar energy is the most abundant and sustainable energy on earth, but it is so diffusive. Therefore, it should be converted into storable energies like hydrogen generation from solar water splitting. Nowadays, photo-electrolysis combined with photovoltaic (PV) cell has received great attention as an efficient non-biased water splitting system for solar fuel conversion. Not only for high efficiency, various designs of PV-electrolysis have been studied for convenient and practical usage. In this research, The PV-electrolysis system has been developed as a floatable and planar-compact artificial leaf with unique configuration. The series cell was combined with a 2D-designed electrodes deposited on one face of counter glass substrate, where free air space is adjustable between two substrates. This space enables the module floatable in water-abundant condition, giving several merits like maximizing light absorption without absorption loss by water layer. Also, the 2D-designed single-face electrodes make the water splitting reaction occur on one surface, allowing the device to operate in water-scarce condition like shallow water. Combining these characteristics, our module could be highly adaptive to functioning in various environments.

### Materials for Solar Fuel Production and Applications II

Room: Grand Ballroom A

Session Chairs: Yung-Jung Hsu, National Chiao Tung University; Jih-Jen Wu, National Cheng Kung University

**1:30 PM**

**(MCARE-S1-006-2018) Strongly Facet-Dependent Photocatalytic Properties of Semiconductor Crystals (Invited)**

M. H. Huang<sup>\*1</sup>

1. National Tsing Hua University, Department of Chemistry, Taiwan

Cu<sub>2</sub>O cubes, octahedra, and rhombic dodecahedra exposing respectively {100}, {111}, and {110} faces show facet-dependent photocatalytic activities towards methyl orange degradation. While Cu<sub>2</sub>O RDs are more photocatalytically active than octahedra, Cu<sub>2</sub>O cubes are inactive even after surface Au deposition. These results can be understood from the presence of an ultrathin surface layer with different degrees of band bending for these crystal faces. This thin layer with dissimilar band structures for different faces also explains facet-dependent electrical conductivity and optical properties of Cu<sub>2</sub>O crystals. The photocatalytic inactivity of Cu<sub>2</sub>O cubes has been examined using EPR, electron, hole, and radical scavenger tests, showing lack of photoexcited charge carriers reaching the {100} crystal faces. Ag<sub>2</sub>O crystals having the same crystal structure as Cu<sub>2</sub>O exhibit opposite photocatalytic behaviors for the respective surfaces, showing a modified band diagram is a better way to understand these results than consideration of their surface

structures and surface energies. Photocatalytic inactivity also occurs for ZnO-decorated Cu<sub>2</sub>O cubes and octahedra. Preferential growth of the ZnO (101) planes on the Cu<sub>2</sub>O {111} faces should create a bad heterojunction with unfavorable band alignment causing a dramatic photocatalytic activity suppression. Additional examples of photocatalytic suppression will be presented.

**2:00 PM**

**(MCARE-S1-007-2018) Electrodeposition of copper-cobalt based spinel as highly efficient oxygen evolution catalyst (Invited)**

N. Nath<sup>1</sup>; H. Park<sup>2</sup>; J. Lee<sup>\*1</sup>

1. Dongguk University, Department of Energy & Materials Engineering, Republic of Korea
2. Kyungpook National University, Environmental, and Energy Engineering, Republic of Korea

In the present study, a series of nanostructured copper-cobalt based spinel, Cu<sub>x</sub>Co<sub>3-x</sub>O<sub>4</sub> has been synthesized via a simple and straightforward electrochemically deposition (EC) and applied as catalysts for oxygen evolution reaction (OER). EC was effective to direct growth of electroactive nanostructures of Cu<sub>x</sub>Co<sub>3-x</sub>O<sub>4</sub> (CCO) on the conducting substrate with enhanced intrinsic electrical conductivity and electrochemically active surface area compared with the traditional solid-phase or solvothermal/hydrothermal route. The optimum formula of CCO with flower-like nanostructures showed remarkably lowest overpotential (h) of 250, and 310 mV, at 10, and 20 mA/cm<sup>2</sup>, respectively, which was lower than those of the spinels and noble metal-based oxide catalysts (e.g., RuO<sub>2</sub> and IrO<sub>2</sub>) reported ever. It is attributable to high intrinsic conductivity and high active surface area as well as the fast diffusion of ions and electrons at the interfaces of substrate-CCO-electrolyte.

**2:30 PM**

**(MCARE-S1-008-2018) Complex semi-conductor films, sponges and nano-particles for solar catalysts and solar cells through solution synthesis (Invited)**

G. Westin<sup>\*1</sup>

1. Uppsala University, Sweden

The materials for solar fuels are becoming ever more complex, utilizing nano-crystals, wires and sponges combined with thin- or ultra-thin multi-element oxides and nano-particles. However, the development of such complex multi-functional materials require good understanding of the chemical, optical and electronic processes, which is presently far from enough developed. Often contradictory results are obtained for seemingly the same material, and thus advanced, well-controlled synthesis techniques allowing for series of high quality materials are required. Further, for any societal impact the processes have to be low cost, which are areas of strength for solution based processes. Here we describe solution based synthesis routes using metal alkoxides and organically coordinated metal salts to achieve complex oxides and nano-composites with a focus on materials for photon to electricity or fuel synthesis. Oxides of varying complexities including doped and non-doped Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and WO<sub>3</sub>, ZnO in the forms of films, nano-particles, and nano-sponges have been synthesised achieving very high photo-catalytic rates and improved increased efficiency in solar-cell applications due to increased current by band-broadening. The influence of the precursor, reaction kinetics and thermal treatment will be discussed in relation to the structures and properties obtained.



## Materials for Solar Fuel Production and Applications III

Room: Grand Ballroom A

Session Chairs: Yuanbing Mao, University of Texas Rio Grande Valley; Michael Huang, National Tsing Hua University

### 3:20 PM

#### (MCARE-S1-009-2018) Photocatalytic H<sub>2</sub> Evolution Activity of Dumbbell-shaped Nanocrystals Composed of ZnS-AgInS<sub>2</sub> Solid Solution (Invited)

T. Kameyama<sup>1</sup>; S. Koyama<sup>1</sup>; T. Yamamoto<sup>1</sup>; S. Kuwabata<sup>2</sup>; T. Torimoto<sup>1</sup>

1. Nagoya University, Graduate School of Engineering, Japan
2. Osaka University, Graduate School of Engineering, Japan

Size-quantized semiconductor nanocrystals (NCs) have attracted much attention for the application to solar light-driven photocatalysts because they exhibited controllable size-dependent optical properties due to the quantum size effects. In this study, we report the preparation of ZnS-AgInS<sub>2</sub> (ZAIS) NCs with a dumbbell-shaped heterostructure and investigate their composition-dependent photocatalytic H<sub>2</sub> evolution activity. ZAIS nano-dumbbells (NDs) were prepared via a seeded growth method: rod-shaped ZAIS NCs as seeds were heat-treated at 170 °C for 8 min in an organic solvent containing thiourea and corresponding metal acetate. ZAIS NDs were composed of two ellipsoidal NCs (ca. 4–6 nm in width × 7–11 nm in length) connected by a ZAIS nanorod (ca. 4 nm in width × 16–23 nm in length). The Zn fraction in the ellipsoidal tip parts became smaller than that in the rod part, forming a type-II heterojunction at the interface between rod and tips. The photocatalytic H<sub>2</sub> evolution rates of ZAIS NDs were larger than those of free nano-ellipsoids, the degree being dependent on the chemical composition of ZAIS tip parts in NDs. These results indicated that the type-II heterojunction in dumbbell-shaped NCs induced the effective charge separation of photogenerated electrons and holes, resulting in the increase in reaction probability of photogenerated electrons with H<sup>+</sup> in the solution.

### 3:50 PM

#### (MCARE-S1-010-2018) Z-Scheme Heterostructure Nanowires for Solar Hydrogen Generation

Y. Chiu<sup>\*1</sup>; W. Lin<sup>1</sup>; Y. Hsu<sup>1</sup>

1. National Chiao Tung University, Taiwan

As inspired by the natural photosynthesis, semiconductor heterostructures with the Z-scheme charge transfer mechanism have been regarded as the ideal photocatalyst platform for realizing water splitting. Here, we proposed an advanced Z-scheme mechanism in which two Z-scheme vectorial charge transfer processes occurred cooperatively to render the samples significantly enhanced photocatalytic oxidizing and reducing powers. The samples were prepared by decorating CdS nanowires with Au particles, followed by the respective deposition of ZnO and Cu<sub>2</sub>O on the Au surface, which resulted in the formation of ZnO/Au/CdS/Au/Cu<sub>2</sub>O five-component heterostructure nanowires. The performance of solar hydrogen production was further correlated with the results of charge dynamics measurements, offering insightful information for the design of highly efficient Z-scheme photocatalysts for realizing solar fuel generation.

### 4:10 PM

#### (MCARE-S1-011-2018) Enhancement of Hydrogenation and Thiocyanate Treatments on Ag-Loaded TiO<sub>2</sub> Nanoparticles for Hydrogen Evolution

Y. Lin<sup>1</sup>; M. Lin<sup>2</sup>; L. Hsu<sup>\*1</sup>

1. National Synchrotron Radiation Research Center, Taiwan
2. National Chiao Tung University, Taiwan

H<sub>2</sub> evolution rate enhanced by Ag-loading on 25 nm TiO<sub>2</sub> anatase nanoparticles (denoted as Ag/TiO<sub>2</sub>), Ag-loaded on hydrogenated TiO<sub>2</sub> NPs (Ag/H:TiO<sub>2</sub>), as well as by the treatment of both NPs with potassium thiocyanate (KSCN) solution have been systematically investigated in conjunction with XANES and EXAFS analyses with synchrotron radiation. We have observed a cumulative enhancement effect of these fabrication processes on solar to hydrogen (STH) conversion using a simulating light source. Ag/TiO<sub>2</sub> shows an enhanced visible absorption with 4–5 time increase in H<sub>2</sub> evolution over that of TiO<sub>2</sub> or H:TiO<sub>2</sub> prepared under mild hydrogenation conditions, while Ag/H:TiO<sub>2</sub> exhibits an even greater UV–visible absorption, similar to that of AgSCN/H:TiO<sub>2</sub>, with 3.1 times higher STH than that of Ag/TiO<sub>2</sub>. The treatment of Ag/TiO<sub>2</sub> and Ag/H:TiO<sub>2</sub> NPs with 0.1 mM KSCN solution further increases their STHs by 3.6 and 2.8 times, respectively. The observed synergistic effect of TiO<sub>2</sub> hydrogenation and SCN treatment of the Ag/H:TiO<sub>2</sub> NPs has been corroborated by the results of quantum chemical elucidation of H<sub>2</sub> production mechanism and the photocatalytic effects of Ag/H:TiO<sub>2</sub> and AgSCN/H:TiO<sub>2</sub> NPs revealed by appearances of new sub-band states within the TiO<sub>2</sub> bandgap, as well as by the result of XANES and EXAFS analyses which support the electron-pulling effect of the SCN group attached to Ag.

### 4:30 PM

#### (MCARE-S1-012-2018) Graphene Oxide/Cobalt-based Nanohybrids as Alternative Electrodes for Hydrogen Generation

F. Navarro Pardo<sup>\*1</sup>; H. Zhao<sup>2</sup>; Z. M. Wang<sup>1</sup>; F. Rosei<sup>3</sup>

1. University of Electronic Science and Technology of China, Institute of Fundamental and Frontier Sciences, China
2. Qingdao University, College of Physics and The Cultivation Base for State Key Laboratory, China
3. Institut National de la Recherche Scientifique, Centre for Energy, Materials and Telecommunications, Canada

Recently, there has been tremendous advance in quantum dot (QD)-based PEC cells for H<sub>2</sub> generation. In these systems, when the photoanode (TiO<sub>2</sub>/QDs) is illuminated, redox reactions are driven by generated electron–hole pairs. At the surface of QDs, the holes oxidize the sacrificial agents in the electrolyte and electrons migrate through the TiO<sub>2</sub> and finally toward the counter-electrode (CE) to reduce water and produce H<sub>2</sub>. Most of these devices have been studied with a Pt CE, therefore their widespread application will be compromised by the scarcity and high cost of this electrocatalyst. We have developed graphene oxide(GO)/Co-based nanohybrids as CEs to tackle this disadvantage and to overcome the inherent poisoning of Pt CEs in the presence of the typically used electrolyte in these systems (Na<sub>2</sub>S/Na<sub>2</sub>SO<sub>3</sub>, pH=13). The nanohybrids are initially composed of Co<sub>3</sub>O<sub>4</sub> nanoparticles arranged into a nanoribbon network and electrochemical activation allows the formation of a mixture of cobalt sulfides (Co<sub>2</sub>S<sub>4</sub> and CoS<sub>2</sub>) featuring a nanosheet morphology. We demonstrate that addition of GO can dramatically decrease the charge transfer resistance compared to pristine Co-based nanohybrids. These GO/Co-based nanohybrids represent a plausible pathway for in-situ generation and self-repair of Co-based electrocatalysts and optimized structure for H<sub>2</sub> generation and remarkable long-term stability (for over 40h).

## SYMPOSIUM 3

### Materials Challenges in Perovskite and Next Generation Solar Cells

Room: Grand Ballroom C

Session Chairs: Sang Hyuk Im, Korea University; Vojislav Mitic, Serbian Academy of Sciences

9:30 AM

#### (MCARE-S3-001-2018) Comparative Study of the Output of Amorphous Silicon Photovoltaic Solar Cells when Receiving Direct and Diffused Radiations (Invited)

O. H. David\*<sup>1</sup>

1. Federal Polytechnic Offa, Science Technology, Nigeria

Four amorphous silicon photovoltaic cells rated 12v, 20amps, 30watts DC were subjected to solar radiations study with the aim to determine their output at different positions. The amorphous silicon photovoltaics were paired in two. A pair was placed on a sun tracker while the other was placed on a fixed position. An LDR cell was constructed to control the tracking system while a LED was connected to indicate the radiation intensity at a particular time. The output powers for both arrangements were recorded at 10minutes interval for a period of two months. The data obtained were compared and treated to obtain a model of mean output power at a particular temperature for the two pairs separately. It was observed that the mean output power of the set up on tracking mechanism has a higher mean output power.

9:55 AM

#### (MCARE-S3-002-2018) Unique Semiconducting Organic – Inorganic Halide Perovskite Materials and Their Long-Term Stability in Solar Cell Application (Invited)

H. Shin\*<sup>1</sup>

1. SungKyunKwan University, Department of Energy Science, Republic of Korea

CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> with perovskite crystal structure has attracted considerable interest for high power conversion efficiency. Metal oxide grown via atomic layer deposition (ALD) provides pinhole-free uniform and dense films which are suited to function as passivation layer since ALD is deposited by self-limiting sequential chemical reaction. ALD chemistry for TiO<sub>2</sub> and ZnO are well known and the process requires relatively low deposition temperature as much as ~ 100 °C, which is applicable to deposit onto halide perovskite materials. In this presentation, we report highly efficient perovskite solar cells having a long-term stability that adapts uniform and dense inorganic charge transport layer (NiO and TiO<sub>2</sub> and ZnO) grown by ALD at relatively low temperature. Ultra-thin un-doped NiO films were prepared by ALD with a highly precise control over the thickness. NiO films with the thickness (~ 7 nm) of few times of Debye length (1 ~ 2 nm for NiO) show enough conductivities achieved by overlapping space charge regions, which finally exhibited a highest PCE of 17.40 %. Dense inorganic electron transport layer has been deposited onto perovskite using ALD process at relatively low temperature (100 °C). The devices shows excellent water-resistant properties and long-term stability at 85 °C under illumination compared to devices without ETL grown by ALD.

10:20 AM

#### (MCARE-S3-003-2018) Firing up perovskite solar modules (Invited)

B. Conings\*<sup>1</sup>; A. Babayigit<sup>1</sup>; H. Boyen<sup>1</sup>

1. Hasselt University, Institute for Materials Research, Belgium

A tremendous surge of research in the metal halide perovskite solar cells in the past 5 years has led to an unprecedented rise in power conversion efficiency, as well as environmental and thermal stability.

Arguably the remaining Achilles heel of the technology is that the desirable properties of metal halide perovskites for application in photovoltaics so far have only been achieved with lead (Pb), (and to a lesser extent tin (Sn)) as the metal cation. Consequently, the associated toxicological hazard in case of unintentional liberation of heavy metal containing chemicals into the environment raises concerns in view of the large-scale applicability of perovskite photovoltaics. A relevant scenario that should not be overlooked in this sense, is that of fire. Not only can module encapsulation be severely compromised in such event, possibly setting free toxic compounds in the immediate environment, an additional hazard lies in the exhaust of toxic airborne particles that may travel longer distances. To gain insight in the severity of the danger involved, we have conducted fire simulations on Si-perovskite tandem mini-modules, fabricated according to industry standards. A post-fire chemical analysis is presented of the module as well as downstream fumes. The results of these experiments allow to come closer to an objective assessment of the—hitherto alleged—*inherent* danger associated with perovskite-based solar panels in the case of fire.

10:45 AM

#### (MCARE-S3-004-2018) Solar Energy Fractal Nature and Electronic Ceramics Science (Invited)

V. Mitic\*<sup>1</sup>; G. Lazovic<sup>3</sup>; V. Paunovic<sup>2</sup>; S. Shaikh<sup>5</sup>; S. Veljkovic<sup>1</sup>; B. Vlahovic<sup>4</sup>

1. Serbian Academy of Sciences, Institute of Technical Sciences, Serbia
2. University of Nis, Faculty of Electronic Engineering, Serbia
3. University of Belgrade, Faculty of Mechanical Engineering, Serbia
4. North Carolina Central University, USA
5. Pune University, India

The advance material science faces the lack of energy, incline towards new energy sources. The BaTiO<sub>3</sub> as a perovskite, has fractal configuration based on three different phenomena: grains have fractal shape as a contour in cross section or as a surface, so-called “negative space” made of pores (important role in micro-capacity, microelectronics, PTCR and other), and Brownian micro-particles fractal motion inside the material (ions, atoms and electrons). These triple factors are basic effects for complex fractal correction. The stress is set on inter-granular super micro-capacitors and overall impedances distribution in function of energy harvesting and storage. Fractal nature recognize micro-capacitors with fractal electrodes. Inter-granular permeability is taken as fundamental thermodynamic parameter temperature function. In this paper, for the first time we are successfully involving the fractal correction in electrical current Butler-Volmer equation. This is the new approach within the alternative energy sources by fractal nature corrections.

11:10 AM

#### (MCARE-S3-005-2018) Organic-inorganic hybrid perovskite solar cells (Invited)

S. Im\*<sup>1</sup>; J. Heo<sup>1</sup>

1. Korea University, Republic of Korea

Organic-inorganic hybrid perovskite materials have been of great interest because of their prominent properties such as high absorption coefficient, long charge carrier's diffusion length, ambipolar charge transport, high open circuit voltage, and solution processability. Since Kojima et al reported liquid junction perovskite sensitized solar cells, intensive studies have been done and now its record efficiency reaches over 22 %. However, many issues including further efficiency improvement, stability such as light, air, heat, and humidity, large area coating, modularization, and flexibility should be solved to find commercial application. I would like to discuss these issues and share recent progress of my research group.

11:35 AM

**(MCARE-S3-006-2018) Ambient-air Processed Perovskite Solar Cells with Effective Perovskite-NiO Nanoparticles Composite and Interface Engineering**Y. Wang\*<sup>1</sup>; T. Mahmoudi<sup>1</sup>; H. Yang<sup>1</sup>; K. S. Bhat<sup>1</sup>; Y. Hahn<sup>1</sup>

1. Chonbuk National University, Chemical Engineering, Republic of Korea

Due to poor-stability of lead-halide perovskite materials in ambient condition, often high-quality perovskite films require controlling fabrication and annealing atmosphere. Here we developed solution-processed perovskite-NiO nanoparticles (i.e., MAPbI<sub>3</sub>-NiO NPs and MAPbI<sub>3-x</sub>Cl<sub>x</sub>-NiO NPs) composite films in ambient condition. Firstly, we reported an air-stable, hole-conductor-free (HCF), and high photocurrent PSCs with MAPbI<sub>3</sub>-NiO NPs composite, achieving a high PCE of 12.14 % and excellent air-stability over 60 days. Furthermore, we used MAPbI<sub>3-x</sub>Cl<sub>x</sub>-NiO NPs composites and a simple and effective interfacial engineering with metal oxide nanoparticles, resulting in a high PCE of 18.10 % and a remarkable air-stability over 210 days. Subsequently, we achieved fully-ambient-processed stable and mesoscopic semitransparent PSCs by non-continuous islands-structure-MAPbI<sub>3-x</sub>Cl<sub>x</sub>-NiO NPs composite and interface engineering. The improved performance and air stability of perovskite-NiO composites and interface engineering based PSCs are attributed to the enhanced charge carrier transportation via improving photo-absorption and fast hole-conduction by NiO NPs, and strong chemical interaction between NiO and MAPbI<sub>3</sub> or MAPbI<sub>3-x</sub>Cl<sub>x</sub> molecules, and the lower interface defects.

**SYMPOSIUM 6****Materials for Upconversion, Quantum Cutting and Downshifting I**

Room: Grand Ballroom B

Session Chair: Stefan Fischer, Lawrence Berkeley National Laboratory

9:30 AM

**(MCARE-S6-001-2018) On the upconversion properties of Ln<sup>3+</sup> doped nanoparticles (Invited)**F. C. van Veggel<sup>\*1</sup>

1. University of Victoria, Department of Chemistry, Canada

After briefly discussing the synthesis and characterisation of Ln<sup>3+</sup> doped nanoparticles, such as NaYF<sub>4</sub>, with upconversion properties, I will discuss their optical properties, in particular the upconversion ones. Upconversion is a non-linear process that convert two or more low-energy photon into one of higher energy. Likely the most studied is the conversion of 980 nm light into blue, green, and red. I will spend considerable time on how to measure the upconversion quantum yields (UC-QY) and discuss the challenges and pitfalls. Lastly, I will speculate on possible reasons why the UC-QY of nanoparticles is so much lower than of their bulk analogues.

10:00 AM

**(MCARE-S6-002-2018) Tuning lanthanide luminescence in core-shell nanoparticles (Invited)**F. Wang\*<sup>1</sup>

1. City University of Hong Kong, Department of Materials Science and Materials, Hong Kong

Spectral conversion of light radiation is essential for a variety of modern-day technologies including displays, photovoltaics, data storage, and cancer therapy. In the past decades, a variety of luminescent materials, including organic dyes and semiconductor quantum dots, were developed to realize photon energy conversion in the ultraviolet (UV) to near infrared (NIR) spectral range. However, practical application of these techniques is typically limited by constraints such as toxicity and/or poor stability. In this

regard, lanthanide-doped nanoparticles have been developed as a promising alternative to conventional luminescent nanomaterials. By comparison, these nanoparticles offer low cytotoxicity, sharp emission peaks, long-lived excited electronic states, as well as high stability against photo bleaching and chemical degradation. In this talk, I focus on our recent efforts on lanthanide-doped core-shell nanoparticles that are generally composed of a layer-by-layer structure with a set of lanthanide ions incorporated into separate layer. Examples will be given to demonstrate how to tune the luminescence process and enhance multiphoton upconversion emission for exciting new technological applications.

10:30 AM

**(MCARE-S6-003-2018) Controlling Lanthanide-Doped Nanoparticles for Brighter Luminescence (Invited)**G. Chen\*<sup>1</sup>

1. Harbin Institute of Technology, School of Chemistry and Chemical Engineering, China

Lanthanide-doped upconverting and down-shifting nanoparticles hold promises for applications ranging from bioimaging to solar cells. Yet, their emission brightness are limited by the surface-related quenching effect and the weak narrowband absorption of the doped lanthanide ions. Here, I present our recent progress on exploiting hybrid inorganic-organic systems to address this problem, which consist of an epitaxial core/shell inorganic nanocrystal and near infrared (NIR) dyes anchored on the core/shell nanocrystal surface. The core/shell structure was utilized to suppress surface-related quenching effect, while the dye antenna effect was employed to implement ultrastrong NIR light harvesting. This strategy allows to yield efficient upconversion luminescence (upconversion efficiency of 10-15%), increasing a dye-sensitized solar cell efficiency by 13%, and to produce brighter tunable downshifting photoluminescence for centimeter-deep bioimaging in the second biological window.

11:00 AM

**(MCARE-S6-004-2018) Multi-Doped (Cr:Ce:Yb:Nd) YAG Ceramics for Thermally Enhanced Photoluminescence Applications**B. Ratzker\*<sup>1</sup>; M. Sokol<sup>2</sup>; A. Wagner<sup>1</sup>; S. Kalabukhov<sup>1</sup>; N. Kruger<sup>3</sup>; N. Revivo<sup>4</sup>; C. Rotschild<sup>4</sup>; N. Frage<sup>1</sup>

1. Ben-Gurion University of the Negev, Materials Engineering, Israel
2. Drexel University, Materials Science & Engineering, USA
3. The Nancy and Stephen Grand Technion Energy Program (GTEP), Technion-Israel Institute of Technology, Israel
4. Technion - Israel Institute of Technology, Mechanical Engineering, Israel

Thermally enhanced photoluminescence (TEPL) for heat harvesting in photovoltaics (PV) has recently been proposed. It is a novel approach in which a solar energy converter can exceed the Shockley-Queisser (SQ) limit by utilizing photoluminescence (PL) as an optical heat pump upconverting sub-bandgap photons. Ideally, it will allow to achieve efficiencies up to 70% at the 1000-1500 K temperature range. This approach has been theoretically proven and demonstrated on Cr:Nd:Yb doped glass. It is expected that multi-doped yttrium aluminum garnet (YAG) might be employed as the optical heat pump for a PV cell. Therefore, the optimal combination of doping concentrations of the multiple dopants, which will result in maximum efficiency, must be investigated. Numerous highly transparent polycrystalline YAG samples with varying doping amounts (Cr, Ce, Yb, and Nd at concentrations of 0.1-1 at.%) have been fabricated. The multi-doped YAG powders were synthesized by co-precipitation and consolidated by spark plasma sintering (SPS). The role of each dopant as well as their influence on each other has been examined by PL spectrum measurements and the deduced quantum efficiency (QE). Moreover, the effect of various processing routes (high-pressure SPS, post-processing hot isostatic pressing (HIP) and annealing in an air furnace) on the PL and QE of the YAG ceramics was investigated.

\*Denotes Presenter

11:20 AM

### (MCARE-S6-005-2018) Quantification of Parameters Affecting the Upconversion Luminescence of Lanthanide-Based Upconversion Nanocrystals (Invited)

U. Resch-Genger\*<sup>1</sup>

1. BAM Federal Institute for Materials Research and Testing, Germany

Lanthanide-based upconversion nanoparticles (UCNPs) like hexagonal  $\beta$ -NaYF<sub>4</sub> UCNPs doped with Yb<sup>3+</sup> and Er<sup>3+</sup>, which efficiently convert 976 nm light to ultraviolet, visible, and near infrared photons, offer new strategies for luminescence-based sensing, barcoding, and imaging. The properties of their upconversion (UC) luminescence (UCL) are, however, strongly influenced by particle size, the concentration and spatial arrangement of the dopant ions, surface chemistry including presence and thickness of surface passivation and shielding shells, microenvironment/presence of quenchers with high energy vibrations, and excitation power density (P). We present here a comprehensive study of the influence of UCNP size and particle architecture for Yb<sup>3+</sup> and Er<sup>3+</sup> co-doped NaYF<sub>4</sub> core-only and core-shell nanostructures in the size range of about 5 nm to 50 nm, which underlines the importance of particle synthesis, surface chemistry, and quantitative luminescence measurements for mechanistic insights and the determination of application-relevant matrix- and P-dependent optimum dopand concentrations.

### Materials for Upconversion, Quantum Cutting and Downshifting II

Room: Grand Ballroom B

Session Chair: Eva Hemmer, University of Ottawa

1:30 PM

### (MCARE-S6-006-2018) Perspective on Core/Shell Nanocrystals as Spectral Converters for Solar Energy Applications (Invited)

S. Fischer\*<sup>1</sup>

1. Stanford University, Material Sciences and Engineering, USA

The spectral conversion of photons is a key technology and present in our daily lives because this concept is used in efficient lighting, displays, and lasers, for example. The development of luminescent nanocrystal holds the potential to improve traditional materials used nowadays for spectral conversion and also opens the door for novel applications, whereas the use of luminescent nanoparticles in life sciences or solar energy harvesting are among the most popular ones. Core/shell nanocrystals are very promising candidates for bright, stable, and multi-functional properties with lots of potential applications. The core/shell concepts also allow to design and engineer energy flow within the nanocrystal to achieve new interesting properties. In this presentation, an overview of research on core/shell nanocrystals is given with a focus on lanthanide-based materials for upconversion, downshifting, and downconversion. Furthermore, the current research in our group is presented in which we aim to understand core/shell nanocrystal on a fundamental level to make these materials more efficient and brighter.

2:00 PM

### (MCARE-S6-007-2018) Combinatorial reactive sputtering of lanthanide doped SiAlON and halide luminescent films for photovoltaic windows based on the LSC principle (Invited)

E. van der Kolk\*<sup>1</sup>

1. Delft University of Technology, Radiation Science and Technology, Netherlands

Photovoltaic windows are currently a holy grail in building-integrated photovoltaics. Luminescent Solar Concentrator (LSC) technology can enable such windows by trapping part of the solar spectrum with a luminescent coating. LSC coatings should absorb the entire visible spectrum, have an efficiency close to unity and show no light scattering, a combination that has not yet been

realised. We report on lanthanide (Ln) doped alkali halide films as well as films based on Si, Al, O and N (SiAlON). We will present off-axis co-sputtering of Si, Al and Eu in an O<sub>2</sub>/N<sub>2</sub>/Ar reactive atmosphere as a technique to explore luminescence properties of films with a large composition gradient. Using xy-scanning of transmission-, emission- and decay spectra, local film properties like intensity, absorption, index of refraction, decay time and thickness could be related to local composition in so-called phase diagrams. This resulted for example in Ln-doped SiAlON films that are both amorphous with low scattering and show efficient luminescence. By tuning the sputter settings, films with both a 2+ and 3+ Ln valence on a single film could be made, with a 2+/3+ ratio that strongly depends on the Si/Al ratio. We will also present Tm<sup>2+</sup> and Eu<sup>2+</sup> doped films with a NaCl-NaBr-NaI composition gradient with a very wide solar absorption range.

2:30 PM

### (MCARE-S6-008-2018) A self-assembled Förster resonance energy transfer system based on upconverting nanoparticles and lanthanide ion complexes

R. Marin\*<sup>1</sup>; D. Errulat<sup>1</sup>; I. Halimi<sup>1</sup>; G. Lucchini<sup>2</sup>; A. Speghini<sup>2</sup>; M. Murugesu<sup>1</sup>; E. Hemmer<sup>1</sup>

1. University of Ottawa, Chemistry and Biomolecular Sciences, Canada

2. Università di Verona, Biotecnologie, Italy

Upconverting nanoparticles (UCNPs) are alluring energy donors in the frame of Förster resonance energy transfer (FRET), due to their chemical and optical stability, long-lived visible emission and near-infrared (NIR) excitation/harvesting capabilities. This latter feature is an asset, for instance, both for photovoltaic and biomedical applications where it allows to minimize autofluorescence and light scattering/absorption phenomena in biological tissues. Despite the promising perspectives, UCNPs have been scarcely investigated as potential FRET donors and their pairing with different type of acceptors is a territory that leaves plenty of room for exploration. In this study, sub-10 nm UCNPs were amalgamated with fluorescent lanthanide complex crystals (FLCs) obtaining a solid state self-assembled hybrid system (HS). This HS is characterized by the absence of chemical bonding among the moieties, yet they can effectively interact via FRET. Said HS features light absorption capabilities both in the ultraviolet and NIR wavelength range, making it a charming system when light harvesting abilities over a broad range are sought after (e.g. preparation of photovoltaic devices). On a more general note, this study shows the possibility to easily obtain functional UCNP-based FRET systems, paving the way for the preparation of novel optical and opto-electronic devices.

### Materials for Upconversion, Quantum Cutting and Downshifting III

Room: Grand Ballroom B

Session Chair: Stefan Fischer, Lawrence Berkeley National Laboratory

3:20 PM

### (MCARE-S6-009-2018) Up-conversion for Solar Cells in Materials Doped with Er/Yb and Tb/Yb by Sol-gel and Ion Implantation (Invited)

R. M. Almeida\*<sup>1</sup>

1. Instituto Superior Técnico, Universidade de Lisboa, CQE, Departamento Engenharia Química, Portugal

A key challenge in solar cell development is to overcome energy losses. In order to minimize transparency losses, the use of frequency converting phosphors is a promising solution. The development of up-conversion (UC) materials for improving the light harvesting efficiency, however, is still a demanding task. Here, we report a low cost sol-gel (SG) technique to deposit SiO<sub>2</sub> - Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> coatings doped with Er/Yb and Tb/Yb with efficient near-infrared to

visible UC photoluminescence (PL). An alternative, direct incorporation of these ions into those matrices has also been achieved by ion implantation, a technique which was also used to dope a-Si:H films prepared by PE-CVD, as an example of second generation solar cell material. Ion beam analysis and XRD were used to study the structural properties of the implanted samples, while PL and Raman spectroscopies were performed to assess the spectroscopic behaviour of the different materials. The UC emission of  $\text{Er}^{3+}$  and  $\text{Tb}^{3+}$  was excited at 980 nm via the  $\text{Yb}^{3+}$  ions. The UC PL results are compared for the different samples, indicating that, although ion implantation is an accurate and controllable doping method, UC emission is superior at present from the films obtained by SG solution doping. Nevertheless, these results provide an additional approach for better understanding the doping parameters needed for high UC PL performance.

**3:50 PM**

**(MCARE-S6-010-2018) Scattering effects in PLQY measurements and design of luminescent devices (Invited)**

J. Marques-Hueso<sup>\*1</sup>

1. Heriot-Watt University, Institute of Sensors, Signals and Systems, United Kingdom

Scattering processes have implications in the measurement of photoluminescent quantum yields (PLQY), and they have to be accounted in order to obtain accurate values. This is especially true in the case of upconversion (UC), because it is a non-linear process and small variations of the pumping intensity can lead to evident modifications of the upconverted signal. An extreme case of scattering is the use of photonic crystals, where the scattering happens repeatedly and in a controlled way, leading to several fold enhancement of the produced signal. These points will be discussed in this talk. Experimental PLQY measurements with embedded  $\text{NaYF}_4:\text{Er}^{3+}, \text{Yb}^{3+}$  phosphors show how the absorbance and the PLQY can vary. These results are relevant not only for the PLQY measurements but also for the design of efficient luminescent devices.

## **SYMPOSIUM 9**

### **Materials for Energy I**

Room: Grand Ballroom D

Session Chairs: Taek-Soo Kim, KITECH; Ryan Ott, Ames Laboratory (USDOE)

**9:30 AM**

**(MCARE-S9-001-2018) Alternative & Renewable Energy Technologies Depend on Critical Material Supply Chains (Invited)**

I. M. London<sup>1</sup>; G. Andrews<sup>\*2</sup>

1. Canadian Rare Earth Elements Network, Canada  
2. Search Minerals Inc., Canada

Critical materials provide essential functionality to a broad suite of engineered products and systems, have few if any easy substitutes, and are subject to supply-chain risks, especially for rapidly developing renewable technologies. The rare earth elements (REEs) possess unique magnetic, luminescent, chemical, mechanical, optical and other properties. REEs contribute to making stronger and smaller magnets, unique phosphor materials, alloying or additive agents, catalysts and polishing materials for aerospace, computing & communications, defense, electronics, clean energy, space, petrochemical, transportation and medical diagnostic and treatment applications. REEs and other critical materials (e.g. cobalt, lithium, niobium, tantalum, zirconium, hafnium, graphite, gallium) are increasingly gaining importance, but pose real supply chain Even rhreats due to limited resources and geopolitical issues. While many tout that supply is promising, the unpredictability of the longer time-horizon development of new resources and their economic

processing is coupled with the unpredictability of advancing technologies demand (including newer technologies disrupting new technologies). Relatively small quantities of the critical materials are required to make larger industrial platforms possible. This keynote address will speak to some of the challenging dynamics being experienced at both ends of the equation.

**10:10 AM**

**(MCARE-S9-002-2018) Secondary and byproduct sources of rare earth metals**

G. Gaustad<sup>\*1</sup>; E. Williams<sup>1</sup>; A. Leader<sup>1</sup>

1. Rochester Institute of Technology, USA

Current concerns about lack of diversity in supply of critical materials have spurred research into utilizing domestic sources, particularly from waste streams. This work combines material flow analysis and techno-economic modelling to explore the resource and economic potential for byproducts (coal combustion products, red mud, etc.) and secondary sources (waste electronics, lighting, etc.) to become a valuable source of rare earth elements (REE). Results show that while REE concentrations in coal ash are significantly lower than currently economically extractable ores in most mines, the magnitude of materials available could meet current REE demand even at fairly low extraction yield rates. For many electronic waste products, the concentration is much higher than economically extractable ores but volumes may not meet demand depending on geographic location. In addition, infrastructure for collection and processing may not be in place. A combination of higher REE commodity prices which seems likely, improved yields, and enhanced infrastructure would be required for economic profitability.

**10:30 AM**

**(MCARE-S9-003-2018) Electrorefining of In from In-Sn metal in the eutectic molten salt systems**

H. Lee<sup>\*1</sup>; K. Park<sup>1</sup>; S. Choi<sup>1</sup>; K. Seo<sup>1</sup>; T. Kim<sup>1</sup>; S. Hyun<sup>2</sup>

1. Korea Institute of Industrial Technology, KIRAM, Republic of Korea  
2. INHA University, Advanced Materials, Republic of Korea

The essentiality of indium in electronic devices has increased in recent past. At the same time indium is rare in natural abundance indium is obtained as a byproduct of zinc metal refining so that the need for recycling of indium has increased dramatically in the near past. Out of other recycling methods, molten salts based electrorefining holds promising future as it provides high conductivity, purity and eco-friendly process. General methods of molten salt electrorefining presents that solid anode and cathode is adapted and handled to get refined metal, but in this study indium(In) and tin(Sn) is used and it shows lower temperature than electrolyte, so electrorefining was carried out using molten anode(In-Sn impure) and cathode(purified In) materials. We report electrorefining of indium at the tungsten(W) and molybdenum(Mo) electrode as anode and cathode, respectively. Process temperature was holded at 700°C and electrolyte is molten LiF-KF eutectic(49 - 51 mol. %). Contents of  $\text{InF}_3$ , initiative compounds was controlled for reducing polarization of electrolytic cell. Fluoride based salts shows high chemical stability with metals and In-Sn alloy was used as raw material and  $\text{Al}_2\text{O}_3$  crucible was utilized for experiments. Concentration of  $\text{InF}_3$  (3~7 wt%) was changed and it was found that the electrochemical reduction of indium at the cathode site and then it was directly move into the bottom crucible.

10:50 AM

### **(MCARE-S9-004-2018) Recovery and purification of lithium carbonate from sulphate solutions by hydrogenation and ion-exchange**

W. Chen<sup>1</sup>; C. Lee<sup>\*1</sup>; H. Ho<sup>1</sup>

1. National Cheng Kung University, Resource Engineering, Taiwan

Purification of lithium carbonate in the battery industry is an important step. In this experiment, the material source mainly comes from sulphate solutions. In this process, we first add sodium carbonate to sulphate solutions to precipitate lithium carbonate. After that, we add CO<sub>2</sub> into the lithium carbonate slurry, and control the aeration of CO<sub>2</sub> and the hydrogenation temperature. In this experiment, we test different ion-exchange resin to remove impurities such as calcium, sodium, and potassium in lithium carbonate. Moreover, we use the adsorption isotherms described by means of the Langmuir and Freundlich isotherms to investigate the ion-exchange behaviors of lithium. After removing the impurities, we test different heating rate to obtain wet lithium carbonate and compare their purity. In the nutshell, this study will show the best condition of CO<sub>2</sub> aeration, hydrogenation temperature, ion-exchange resin and heating rate to get high purity of lithium carbonate.

11:10 AM

### **(MCARE-S9-005-2018) Extraction mechanism of rare earth elements contained in permanent magnet using molten Magnesium**

S. Nam<sup>\*1</sup>; T. Kim<sup>1</sup>; S. Park<sup>1</sup>; B. Kim<sup>1</sup>; D. Kim<sup>2</sup>

1. Korea Institute of Industrial Technology, Korea Institute for Rare Metals, Republic of Korea
2. Yonsei University, Department of Materials Science & Engineering, Republic of Korea

The extraction study of rare earth elements using pyro-metallurgical method such as liquid metal extraction(LME) has been Eco-friendly and efficient than hydrometallurgical route which can make a large amount of waste water including acid/base solutions. However, heavy rare earth element was not extracted by magnesium. In order to study the extraction behavior between the heavy rare earth elements (dysprosium) in permanent magnet and liquid magnesium, it is very important to investigate the characteristics of diffusion of such species in molten magnesium. A measurement of both reaction and diffusion of REE(Nd, and Dy) in molten magnesium was carried out by using a high frequency electric furnace with vacuum chamber. In order to identify the extraction rare and diffusivity, the effects of experimental parameters such as melting temperature (range of 573K to 973K), holding time and distance of magnesium in magnet on the ability of extraction were investigated. The diffusion behaviors were analyzed by Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS), and the constituent phases were characterized using X-Ray Diffraction (XRD). Diffusion of Dy from the REE-Fe-B alloy into molten magnesium was found to occur, and the diffusion rate was varied depending on the temperature and time.

## **JOINT SESSION OF SYMPOSIUM 8 and SYMPOSIUM 9**

### **Materials for Energy II**

Room: Grand Ballroom D

Session Chairs: Gabrielle Gaustad, Rochester Institute of Technology; Soon-Jik Hong, Kongju National University; Kyoung-Tae Park, Korea Institute of Industrial Technology; Ryan Ott, Ames Laboratory (USDOE)

1:30 PM

### **(MCARE-S9-006-2018) Recycling Strategies for Critical Materials (Invited)**

R. T. Ott<sup>\*1</sup>; I. Nlebedim<sup>2</sup>; R. Chaudhary<sup>2</sup>; H. Kim<sup>2</sup>

1. Ames Laboratory (USDOE), Materials Sciences and Engineering, USA
2. Critical Materials Institute, Ames Laboratory, USA

Recycling of critical materials such as Rare Earth (RE) elements is widely accepted as a necessary component of addressing challenges associated with supply and price fluctuations. The optimal approach or technology for recycling in an efficient and economically feasible manner, however, is much less clear. Here we describe different recycling technologies being developed through the Critical Materials Institute (CMI) focused on recovering RE elements from end-of-life products and manufacturing waste. These technologies range from recovering the RE elements in their oxide form to directly reusing the RE-containing alloy in the synthesis of new magnet alloys. The potential benefits and limitations of each process are discussed.

2:00 PM

### **(MCARE-S9-007-2018) Supply Risk Reduction of Critical Materials in Clean Energy Technologies: Case Studies of Li-ion Batteries and Efficient Lighting Devices**

A. Leader<sup>\*1</sup>; G. Gaustad<sup>1</sup>

1. Rochester Institute of Technology, Golisano Institute for Sustainability, USA

A variety of clean energy technologies make use of materials considered critical due to risks in their supply. This work quantifies the material intensities of two case study systems, lithium ion batteries and efficient lighting devices, to better understand how to mitigate these risks. A functional unit approach, inspired by life-cycle assessment, was used to compare performance metrics and material intensities across disparate technologies. Energy and power density, cycle life, and lifespan are among the performance metrics included for Li-ion batteries while lumens, wattage, color rendering index, and lifespan make up those for lighting devices. Criticality of material inputs as well as economic and environmental impacts were also considered. Such an approach allows us to better inform stakeholders in industry of the most strategic paths forward to ensure business continuity in terms of material cost and availability. Results show that next-generation Li-ion battery chemistries that reduce cobalt intensity may mitigate both cost and criticality impacts. For the lighting case, LED bulbs stand out as the technology that most efficiently uses raw materials on a per functional unit basis, and within LED bulbs we identify materials that are hotspots in terms of our criticality, economic, and environmental analyses.

2:20 PM

**(MCARE-S9-008-2018) Manufacturing 4N5 grade Tantalum Wire from tantalum scrap by electron beam melting and drawing techniques**J. Yu<sup>\*1</sup>; K. Park<sup>1</sup>; S. Hyun<sup>2</sup>; T. Kim<sup>1</sup>; J. Sim<sup>1</sup>; J. Lim<sup>1</sup>

1. Korea Institute of Industrial Technology, Republic of Korea
2. University of Inha, Republic of Korea

The electron beam melting (EBM) is known as an outstanding refining techniques that can control melting temperature and speed, is a useful process for obtaining metal of high purity. In addition, high purity tantalum is utilized in the electronic components industry such as sputtering target for semiconductor manufacturing, aerospace parts, medical parts. In this study, the possibility of fabricating tantalum ingot and wire by electron beam melting and drawing process has been investigated. Tantalum scrap (scrap) contained in the exposure lamp, used in the semiconductor process, was used as raw material. Moreover, Mo, Fe, W, Ca, Mg, Na, Th impurities contained in the scrap were removed through pre-treatment by aqua regia treatment. Impurities of scrap were also removed during tantalum melting due to the refining effect of EBM. After tantalum ingot making, glow discharge mass spectrometry (GD-MS) was used to analyze purity of sample. The drawing process was carried out using electron beam melted Ta rod and materials of drawing dies was industrial diamonds. Initial diameter of the tantalum rod was 9 mm. Then, the drawing process of the wires was continuously carried out to diameter of 0.5 mm. Results showed that tantalum scrap is recycle-able using the EBM and the drawing process. The purity of the ingots was analyzed to be more than 4N5 (99.995 %).

2:40 PM

**(MCARE-S8-001-2018) Evaluating the life-cycle environmental impacts of thermoelectric generators for automotive applications**R. Iyer<sup>\*1</sup>; K. Bakthavatchalam<sup>1</sup>; S. Pilla<sup>1</sup>

1. Clemson University, Automotive Engineering, USA

Ever-increasing global energy demand, stringent environmental protection standards, and depleting fossil resources have together resulted in efforts towards energy generation from renewable resources. Amidst this context, thermoelectric generators (TEGs) that harvest anthropogenic waste heat are budding as a technology of focus. However, materials currently used in TEGs have raised apprehensions regarding the toxicity of certain elements used in these systems, posing a challenge to the fundamental notion of TEGs as a "clean and green energy technology". Yet, a thorough assessment of the environmental impacts of TEGs during their lifecycle remains unaccomplished till date. This study marks the first systematic assessment of eco-friendly credentials of TEGs via comprehensive evaluation of their environmental performance. The authors undertake a cradle-to-factory gate life-cycle assessment (LCA) of two automotive TEGs, beginning with raw material extraction and ending with their manufacture. Similar heat-to-electricity conversion efficiency (3.33%) is chosen as the functional unit. The generators are compared on 17 midpoint categories under the hierarchist perspective of ReCiPe midpoint method. Sensitivity analysis is undertaken to assess the validity of results obtained and the extent of reduction achievable for environmental impacts of both TEGs.

3:20 PM

**(MCARE-S9-010-2018) Production of high efficient thermoelectric materials using powder metallurgy processes (Invited)**D. Peyala<sup>1</sup>; C. Lee<sup>1</sup>; S. Hong<sup>\*1</sup>

1. Kongju National University, Republic of Korea

Thermoelectric materials (TE) are playing a crucial role in limiting greenhouse gas emissions, through their unique applications in automobiles, power generators, refrigerators, gas sensors, aerospace

and defense applications. These material performances are directly influenced by fabrication methods. Hence, we are focused on fabrication of efficient materials using high-pressure gas-atomization, it can possible to produce fine, spherical powders with a wide size distribution of 10~200  $\mu\text{m}$ . Gas atomization is well adapted for mass production, especially regarding the powder preparation step. It enables the production of 2-4 Kg/min with a perfect control of size, shape and uniform microstructure. Subsequently, as-prepared powders were compacted by well-known advanced techniques such as spark plasma sintering (SPS), hot isostatic pressing (HIP), magnetic pulsed compaction (MPC), and hot extrusion, techniques. The grain size of TE materials can be easily controlled by using the above-mentioned techniques, which resulted in improved mechanical and thermoelectric properties. By the combination of these techniques, we have been prepared various high efficient  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ ,  $\text{MnSi}$ , and TAGS based materials. Obtained samples were characterized by using sophisticated equipments such as SEM, EBSD, and HRTEM.

3:50 PM

**(MCARE-S9-011-2018) Effect of alloying addition on structural and physical properties of novel  $\text{Ti}_{95-x}\text{Fe}_5\text{Nb}_x$  ternary alloy**M. Haq<sup>\*1</sup>; E. Jeon<sup>2</sup>; B. Lee<sup>2</sup>; B. Kim<sup>2</sup>

1. University of Science and Technology, Republic of Korea
2. Korea Institute of Industrial Technology, Republic of Korea

In this study fast sintering and heat treatment procedures were applied to investigate the microstructural evolution, phase transformation and change in lattice parameter of  $\beta$  phase in  $\text{Ti}_{95-x}\text{Fe}_5\text{Nb}_x$  ternary alloys ( $x = 0, 1, 3$  and  $5$  wt.%). Electron assisted sintering was used to quickly densify the alloy whereas high temperature heat treatment at  $1300^\circ\text{C}$  for short period was employed to improve homogeneity. Microstructural analysis with the increase in Nb content revealed that the size of alpha grains had an inverse relationship with the niobium content. The grain morphology of  $\alpha$ -Ti shifted from plate like for alloys with no Nb content to needle like with maximum Nb content. The length of the grain also decreased concurrently from  $135 \mu\text{m}$  to  $75 \mu\text{m}$ . Furthermore, XRD analysis revealed that the Fe, having lattice parameter less than that of  $\beta$ -Ti, introduced compressive stresses into the  $\beta$ -Ti lattice which shifted its peaks toward a higher value of  $2\theta$ . The lattice parameter contracted in the process. By the introduction of Nb into the system, the lattice expanded and the peaks shifted towards a lower angle. Accumulative influence of the introduction of impurities into Ti matrix resulted in an increase in hardness profile of final alloy.

4:10 PM

**(MCARE-S9-012-2018) Recovery of PGM from spent automotive catalysts with copper anode slimes by solvent extraction**W. Chen<sup>1</sup>; J. Yang<sup>\*1</sup>; C. Lee<sup>1</sup>

1. National Cheng Kung University, Resource Engineering, Taiwan

With the automotive industry booming, the requirement of platinum-group metals (PGM) has been growing rapidly. Therefore, the recovery of the PGMs from the spent automotive catalytic converters should be developed immediately to solve the problem of insufficient resources and can be an important source to obtain these precious metals with environment-friendly technology. In this study, solvent extraction is used as processing the spent automotive catalysts with copper anode slimes; moreover, the PGMs will be extracted and separated successfully to achieve the effect of recycling. To optimize the separation of platinum, palladium and ruthenium, the parameters, such as pH value, concentration of extractant and stripping agents, organic-aqueous ratio and reaction time were investigated. In the future, depending on this study to develop a series of PGM copper anode slimes recycling systems.

4:30 PM

**(MCARE-S8-002-2018) Life-cycles of lithium ion batteries: Understanding impacts from extraction to end-of-life**

G. Gaustad\*<sup>1</sup>; C. Babbitt<sup>1</sup>; E. Olivetti<sup>2</sup>

1. Rochester Institute of Technology, USA
2. Massachusetts Institute of Technology, USA

With the potential for widespread adoption of EVs, key concerns around environmental impacts of LIBs have emerged including resource constraints, use impacts, and end-of-life challenges. Understanding the right path for batteries at their end-of-life is complex given the many options available combined with the rapid technology trajectory of LIBs creating changing volumes, sizes, form factors, and cathode chemistries. This hierarchy of options includes reuse in the original application, cascaded use in other applications, remanufacturing or refurbishment, cathode or anode refunctionalization, recycling, and ultimately, disposal. Any reuse or recycling infrastructure will need to be responsive to a stream of diverse and continually changing materials as a variety of sizes, form factors, cathode chemistries, and morphologies are being used with an even greater variety under development. Results to be shared include compositional characterization of EOL LIBs, economic feasibility of US-based recycling operations given this uncertain waste stream, environmental impacts of cascaded use of EV batteries, policy comparison for EOL LIBs across countries and sectors, criticality and scarcity indicators for LIB materials, and technology development work in the pre-processing and hydrometallurgical extraction field.

4:50 PM

**(MCARE-S9-014-2018) Temperature dependent phase transformation of powder metallurgy processed Nd-Fe-B magnet**

J. Cho\*<sup>1</sup>; S. Nam<sup>1</sup>; S. Abbas<sup>1</sup>; Y. Choa<sup>2</sup>; T. Kim<sup>1</sup>

1. Korea Institute of Industrial Technology, Korea Institute for Rare Metals, Republic of Korea
2. Hanyang University, Republic of Korea

Nd-Fe-B sintered magnet are usually fabricated by pulverized strip and ribbon. But these traditional fabrication methods are complex and fabricated powder can be easily oxidized. Alternatively a novel method about fabrication of Nd-Fe-B magnet is proposed using gas atomized powder. To retain anisotropy plastic deformation of consolidation Nd-Fe-B having composition  $Nd_{12}Fe_{82}B_6$  was performed. Detailed phase transformation was studied. Formability of Nd-Fe-B was observed by hardness with temperature test. The hardness was decrease rapidly with increasing temperature and  $\alpha$ -Fe and  $Nd_2Fe_{14}B$  phase fraction were transformed with temperature. It was found that plastic deformation of in  $Nd_{12}Fe_{82}B_6$  composition enabled  $\alpha$ -Fe phase to precipitate at high temperature followed by its transformation to  $Nd_2Fe_{14}B$  at room temperature.

## SYMPOSIUM 13

### Symposium on Materials for Super Ultra Low Energy and Emission Vehicle

Room: Grand Ballroom C

Session Chair: Kwan-Young Lee, Korea University

1:30 PM

**(MCARE-S13-001-2018) Cu/SSZ-13 Catalysts for the Selective Catalytic Reduction of NOx: Unusual Features of the Complex Redox Reaction Mechanism (Invited)**

C. H. Peden\*<sup>1</sup>; D. Mei<sup>1</sup>; Y. Wang<sup>1</sup>; J. Szanyi<sup>1</sup>; F. Gao<sup>1</sup>

1. Pacific Northwest National Lab, Institute for Integrated Catalysis, USA

Cu-exchanged SSZ-13 materials have recently been commercialized as selective catalytic reduction (SCR) catalysts for diesel engine

exhaust aftertreatment. Active centers in Cu/SSZ-13 SCR catalysts have been identified as isolated  $Cu^{2+}$  and  $[Cu^{II}(OH)]^+$  ions. A redox reaction mechanism has also been established, where Cu-ions cycle between  $Cu^I$  and  $Cu^{II}$  oxidation states during SCR reaction. While the mechanism for the reduction half-cycle ( $Cu^{II} \rightarrow Cu^I$ ) is now reasonably well understood, only very recently have important elements of the oxidation half-cycle ( $Cu^I \rightarrow Cu^{II}$ ) been proposed based on detailed reaction kinetics of low-temperature standard  $NH_3$ -SCR, spectroscopic studies and DFT calculations. In particular, kinetic studies suggested that the low-temperature oxidation half-cycle occurs with the participation of two isolated  $Cu^I$  ions, via formation of a transient  $[Cu^I(NH_3)_2]^+-O_2-[Cu^I(NH_3)_2]^+$  intermediate. Significantly, zeolite structure (topology) plays a central role in enabling this catalytic chemistry. The feasibility of this reaction mechanism was confirmed from DFT calculations, and the simulated energy barriers and rate constants are consistent with experimental findings. Furthermore, this newly proposed low-temperature standard SCR mechanism provides full consistency with detailed low-temperature SCR kinetics.

2:00 PM

**(MCARE-S13-002-2018) Tuning the low temperature catalytic activity of Cu-SSZ-13 over NO SCR: Control of Al content and acidity**

S. Park<sup>2</sup>; H. Jeong<sup>1</sup>; K. Lee<sup>2</sup>; Y. Kim<sup>3</sup>; C. Kim<sup>3</sup>; S. Cho\*<sup>1</sup>

1. Chonnam National University, Chemical Engineering, Republic of Korea
2. Korea University, Republic of Korea
3. Hyundai Motor Group, Advanced Catalysts and Emission-Control Research Laboratory, Republic of Korea

Copper ion exchanged chabazite (CHA) zeolite of high silica (Cu-SSZ-13) has been utilized extensively for selective catalytic reduction of NOx using ammonia. The content of copper and the corresponding location affected the catalytic performance critically and also hydrothermal stability. The ion exchange level of  $Cu^{2+}$  in CHA can be determined with the Si/Al<sub>2</sub> ratio which has been difficult to control because the direct conversion of Y zeolite resulted in the overall Si/Al<sub>2</sub> in addition to the zeolite product yield. In this work, the Si/Al<sub>2</sub> in the CHA zeolite was controlled readily to the range of 8 - 40 while the hydrothermal synthesis condition was varied. The CHA zeolite was synthesized employing trimethyl adamantylammonium ion or benzyltrimethyl ammonium ion as a structure directing agent at 413 K for 4 days under rotation at 40 rpm in the presence or absence of seed zeolite crystals,  $NH_4^+$ -exchanged Y. The CHA zeolite of different Si/Al<sub>2</sub> was also subjected to the Cu ion exchange for further study on the location of Cu, its hydrothermal stability and finally the catalytic performance at low temperature in selective catalytic reduction of NO.

2:20 PM

**(MCARE-S13-003-2018) Facile synthesis of a hierarchically structured MFI and the effect of its physicochemical properties with Cu-loaded MFI on cold-start test**

K. Jinseong\*<sup>1</sup>; C. Jungkyu<sup>1</sup>

1. Korea University, Chemical & Biological Engineering, Republic of Korea

SPP (self-pillared pentasil), a hierarchically structured zeolite, comprised of MFI nanosheet layers has been synthesized in different Si/Al ratios. Mesoporosity of ZSM-5 can be adjusted by synthetic methods like removal of ethanol and/or additional reduction of water. With these SPP particles, we further conducted copper loading on them to use as a hydrocarbon trap. The resulting Cu-SPPs could not only oxidize, but also adsorb hydrocarbons in the exit gas stream including steam. Specifically, Cu-SPP with an actual Si/Al ratio of ~22 and medium mesoporosity performed in cold-start tests; desirably adsorbing propene and toluene even in the presence of 10 vol% steam, retaining their desorption to higher temperature (90 °C for propene and 190 °C for toluene), and furthermore, oxidizing the hydrocarbons. The preferred adsorption can be



attributed to the larger amount of exchanged Cu<sup>2+</sup> ions in SPP particles with a lower Si/Al ratio, while the additional oxidation was due to the CuO particles on the surface of SPP particles. Hydrothermal treatment revealed that the zeolite structure in the Cu-SPPs was transformed into another undesired phase, thus losing the above-mentioned adsorption ability. Nevertheless, oxidation performance of aged SPP was still maintained due to the existence of CuO particles.

### 2:40 PM

#### (MCARE-S13-004-2018) Reducing NO<sub>x</sub> emissions from diesel engines by optimizing the size of SCR reactor with urea injector

B. Lee\*<sup>1</sup>; S. Lim<sup>1</sup>; Y. Kim<sup>1</sup>; T. Park<sup>1</sup>; J. Lee<sup>1</sup>

1. Seoul National University, School of Chemical and Biological Engineering, Republic of Korea

Along with environmental movements, regulations on NO<sub>x</sub> emissions of diesel vehicles have been tightened recently. In order to meet the Euro 6 emissions standards, selective catalytic reduction (SCR) system should be optimized to reduce NO<sub>x</sub> emissions in an efficient and inexpensive manner. In urea-SCR, urea is sprayed from the urea injector, and then thermally decomposed into ammonia under the conditions of high exhaust gas temperature. Generated ammonia is used to convert NO<sub>x</sub> into nitrogen with the help of Cu-ZSM-5 catalyst. Injector-SCR distance and SCR length are important factors for NO<sub>x</sub> removal efficiency, since these are directly related to the amount of generated ammonia and converted nitrogen, respectively. Taking into account these factors, a first-principle model is proposed for the SCR system with urea injector. The model equations that reflect all SCR reactions are solved via the method of lines. By model simulation, the optimal SCR length was obtained at the value of 25 ~ 30cm with the total length of after-treatment system fixed at 40cm, considering NO<sub>x</sub> emissions, ammonia slip, and capital cost. In addition, NO<sub>x</sub> emissions are reduced by about 50%, compared to the commercial SCR. Effects of temperature and catalyst deactivation are also considered in this study, but the optimum value did not change much.

### 3:20 PM

#### (MCARE-S13-005-2018) Catalytic NO reduction by CO over CoO<sub>x</sub>/CeO<sub>2</sub> catalysts (Invited)

T. Kim\*<sup>1</sup>

1. Stony Brook University, Materials Science and Chemical Engineering, USA

Ceria supported Cobalt oxide catalysts (CoO<sub>x</sub>/CeO<sub>2</sub>) are believed to be a promising, more cost-effective candidate to replace platinum group metal catalysts (PGMs) in NO reduction process. However, the molecular/electronic structure-catalytic activity relationship regarding CoO<sub>x</sub> catalysts during the NO reduction by CO reaction remain unknown. A series of CoO<sub>x</sub> catalysts supported on CeO<sub>2</sub> were prepared by the incipient wetness impregnation method. Conventional characterizations (Raman, powder XRD and BET) showed that there are structural changes (e.g., sub-/over-monolayer) as Co loading changed from 0.5wt% to 30wt%. To get a more comprehensive understanding, advanced spectroscopic techniques (e.g., X-ray Absorption Spectroscopy (XAS)) were used under ex-situ/in-situ conditions. We were able to identify an oxidation state change from Co<sup>3+</sup> to Co<sup>2+</sup> as temperature decrease from 300°C to 200°C, which is well matched to the catalytic activity changing in the same temperature ranges. The results provided that Co<sup>3+</sup> ions in the surface species was believed to be the active sites for the NO reduction by CO reactions.

### 3:50 PM

#### (MCARE-S13-006-2018) Re-dispersion of precious metal catalysts for diesel oxidation by hydrothermal treatment

H. Lee\*<sup>1</sup>; H. Jeong<sup>1</sup>; J. Bae<sup>1</sup>; B. Kim<sup>1</sup>

1. Korea Advanced Institute of Science and Engineering (KAIST), Republic of Korea

Ceria-supported nanoparticles of precious metal were known to be efficient catalysts for vehicle exhaust purification, especially diesel oxidation. The exhaust often undergoes harsh conditions, suffering from high temperature up to ~800 °C. These conditions cause the nanoparticles sintered, losing the catalytic active sites. In addition, carbonate and sulfate species might be formed on the catalyst surface, blocking the active sites with degraded activity. Hydrothermal treatment on the M/CeO<sub>2</sub> affected the catalyst structure, resulting in enhanced catalytic activity and durability for CO oxidation. CO conversion approached 100% at the temperature lower than 150 °C even in the presence of propylene or SO<sub>2</sub>. The high activity for CO conversion was changed little for longer reaction time and even for temperature fluctuation up to 850 °C. The promoting effect was obtained due to re-dispersion and surface hydroxyl groups formed after the hydrothermal treatment. The re-dispersion was confirmed by TEM, EXAFS, XRD, in-situ DRIFT, CO chemisorption, and the suppression of surface-poisoning species was investigated using in-situ DRIFT and TPD techniques.

### 4:10 PM

#### (MCARE-S13-007-2018) Effect of the change in Pt-ceria Interaction on CO Oxidation Ability of Pt/CeO<sub>2</sub> Catalysts

J. Lee<sup>1</sup>; Y. Ryou<sup>1</sup>; J. Kim<sup>1</sup>; D. Kim\*<sup>1</sup>

1. Seoul National University, Republic of Korea

Pt/CeO<sub>2</sub> has been studied as a model catalyst on many reactions including the CO oxidation, the CH<sub>4</sub> oxidation and even the electrochemical reactions. CeO<sub>2</sub> is known to interact strongly with Platinum Group Metals (PGMs), and is therefore frequently used as a support material for PGMs. We previously reported that the strong Pt-O-Ce bonds prevent the Pt sintering as well as the CeO<sub>2</sub> agglomeration at the high temperature. However, when Pt species are strongly bonded in the form of Pt<sup>2+</sup>, their intrinsic activity for the CO oxidation is low. In other words, the strong metal-support interaction deteriorated the catalytic activity. Therefore, one strategy to improve the catalytic activity of Pt/CeO<sub>2</sub> would be to control the metal-support interaction to such an extent that Pt species are not too strongly bonded on CeO<sub>2</sub> surface while the Pt sintering is prevented. In this work, we have found that Pt-CeO<sub>2</sub> interaction can be successfully controlled by the thermal treatment of CeO<sub>2</sub> before the Pt loading. The thermal treatment of CeO<sub>2</sub> at the high temperature reduces the defect concentration on CeO<sub>2</sub> surface. The light-off temperature of the CO oxidation of Pt/CeO<sub>2</sub> decreased by more than 70 °C after the thermal treatment. This study clearly shows that catalytic properties can be improved by simply controlling the Pt-CeO<sub>2</sub> interaction.

### 4:30 PM

#### (MCARE-S13-008-2018) Silver loaded macroporous structure CeO<sub>2</sub> catalyst for soot oxidation

J. Lee\*<sup>1</sup>; C. Park<sup>1</sup>; E. Jeong<sup>1</sup>; S. Lee<sup>1</sup>; K. Lee<sup>1</sup>

1. Korea University, Department of Chemical and Biological Engineering, Republic of Korea

Particulate matters (PM) collected in particulate filters are stacked and should be oxidized continuously and removed from the filter to maintain filtration ability. To improve the combustion efficiency, several catalysts have been used, which are usually coated on DPF. Among the catalysts, metal oxides which have high oxygen storage capacity (OSC) could be candidates, and ceria has been widely studied due to its high OSC property and regeneration ability. Also, the catalytic activity could be improved further by increasing the

contact between soot and catalyst surface. The soot particles are difficult to contact with catalyst since the particle size of soot is large. Therefore, the soot combustion temperature substantially depends on contact type between soot and catalyst, and the contact condition is needed to be considered carefully. Thus, in this study, we synthesized macroporous ceria catalyst to improve solid-solid contact and introduced silver metal to enhance the reactive oxygen species generation ability. The silver-loaded macroporous catalysts showed the increased oxidation performance, and the optimum silver loading content was investigated. Also, several analyses were carried out to explain properties of the prepared catalysts. In the catalytic system for the PM combustion, these kinds of catalysts could be used to enhance the oxidation ability at low temperature.

### Tuesday, August 21, 2018

#### Plenary II

Room: Grand Ballroom A & B

Session Chair: Sanjay Mathur, University of Cologne

8:30 AM

#### (MCARE-PLEN-002-2018) Metal oxide-based high efficiency and durable perovskite solar cells: Current progress and perspectives

T. Miyasaka\*<sup>1</sup>

1. Tooin University of Yokohama, Faculty of Biomedical Engineering, Japan

Achieving high level of solar power conversion efficiency (PCE >22%) that has exceeded the efficiencies of CIGS and CdTe, perovskite solar cell is required to ensure high durability for practical applications. Although thermal stability of lead halide perovskite materials is determined by their compositions (generally limited to temperature <150°C) and steadily improving, stability of device is highly affected by the kind of carrier transport materials and the quality of interfaces at the perovskite junctions. In perovskite solar cells, all active layers are coated by low cost solution-printing process. Metal oxide electron transport layers (ETLs) generally have advantage in higher thermal stability than organic ETLs. We have been working with TiO<sub>2</sub> ETL-based multi-cation perovskite cells, which yielded efficiency over 21% by low cost ambient air solution processes. Intensity dependence of their V<sub>oc</sub> shows ideality factor low enough (<1.4) for the perovskite device to work as a high voltage power source even under weak light. Such merit enables applications of perovskite device not only for outdoor solar panels but also for indoor power device for currently evolving IoT industries. In such respect, lightweight and flexible thin film perovskite solar cells (fabricated on plastic film) are particularly promising in expanding applications of the device.

### SYMPOSIUM 1

#### Materials for Solar Fuel Production and Applications IV

Room: Grand Ballroom A

Session Chairs: Yung-Jung Hsu, National Chiao Tung University; Doh Lee, Korea Advanced Institute of Science and Engineering (KAIST)

9:30 AM

#### (MCARE-S1-013-2018) Dependence of Oxygen Evolution Reaction Performance on Geometry Factors of Delafossite Copper Gallium Oxide (Invited)

Y. Mao\*<sup>1</sup>; S. Mohan<sup>1</sup>

1. University of Texas Rio Grande Valley, Department of Chemistry, USA

With the recent surge of alternative clean energy with minimal environmental impact, earth-abundant delafossites are potential alternatives for water electrolysis. In this work, we fine-tuned the

synthesis of CuGaO<sub>2</sub> via a surfactant assisted hydrothermal route and investigated the dependence of their (photo)electrochemical properties on geometry factors. The electrocatalytic and photoelectrocatalytic performance of the synthesized CuGaO<sub>2</sub> samples were tested towards oxygen evolution reaction (OER). Based on cyclic voltammetry and electrochemical impedance spectroscopy, their onset potential, current density, Tafel slope, charge transfer resistance, and stability were investigated. In general, the delafossite CuGaO<sub>2</sub> nanoflakes synthesized in the presence of SDS showed better EC and PEC performance and stability for OER than those synthesized without surfactant SDS. It was also found that the synthesized delafossite CuGaO<sub>2</sub> nanoflakes with smallest dimensions exhibited the most superior (photo)electrocatalytic performance. Furthermore, PEC performance was better than the EC performance for the same samples under identical measurement conditions. Thus, this hydrothermal method in combination of surfactant was an efficient approach towards the synthesis of delafossite CuGaO<sub>2</sub> nanostructures with reduced size as cost-effective and high performance (photo)electrocatalysts.

10:00 AM

#### (MCARE-S1-014-2018) Transition Metal Sulfides Prepared by Sequential Gas Phase Deposition as Efficient Electrocatalysts (Invited)

H. Shin\*<sup>1</sup>

1. SungKyunKwan University, Department of Energy Science, Republic of Korea

Metal sulfides have been shown to be efficient electrocatalysts for the hydrogen evolution reaction (HER) replacing expensive noble metals, e.g., Pt, and Ir. When atomic layer deposition (ALD) is applied to layered materials such as MoS<sub>2</sub>, MoS<sub>2</sub> exhibits the non-ideal mode of ALD growth on planar surfaces. The non-ideality does not allow for the conventional linear relationship between the growth thickness and the number of cycles. Instead, it provides the ability to control relative ratios of the edge-sites and basal planes of MoS<sub>2</sub> to the exposed surfaces. When MoS<sub>2</sub> as a representative 2-D material is deposited on self-supported Cu substrates, the sulfidation reactions also occur with Cu. We observed the spontaneous formation of a composite materials that consist of 2-D materials dispersed in bulk, i.e., bulk layered heterojunctions (BLHJs) of Cu-Mo-S that contain MoS<sub>2</sub> flakes inside, which are uniformly dispersed in the Cu<sub>2</sub>S matrix, and their unusual charge transport properties for application in HERs. BLHJ surfaces exhibited the efficient HER performance of approximately 10 mA/cm<sup>2</sup> at a potential of as low as -0.1 V versus a reversible hydrogen electrode. The Tafel slope was approximately 30 to 40 mV/dec. The present strategy was further generalized by demonstrating the formation of BLHJs on other transition metals such as Ni.

10:30 AM

#### (MCARE-S1-015-2018) Catalytic Properties of Mo<sub>2</sub>C - Graphene Oxide Composites for Photocatalytic Water Splitting (Invited)

J. Lee\*<sup>1</sup>

1. University of Pittsburgh, Mechanical Engineering and Materials Science, USA

Molybdenum carbide (mainly referring to Mo<sub>2</sub>C) is important transition metal carbide (TMCs) which shows good catalytic property. Extensive studies have shown that Mo<sub>2</sub>C is active in a variety of catalytic reactions including desulfurization, water - gas shift and hydrogenation reactions. In particular, Mo<sub>2</sub>C is a very active hydrogen evolution reaction (HER) catalyst in both acidic and basic conditions. However, synthesis of Mo<sub>2</sub>C requires high temperature reaction and electrocatalytic property of Mo<sub>2</sub>C itself is not comparable to Pt. This presentation reports facile synthesis of Mo<sub>2</sub>C by microwave-assisted solvothermal (MWSV) reaction and improvement of the electrocatalytic property by hybridizing Mo<sub>2</sub>C with graphene oxide sheets. Crystal structure and catalytic property of

Mo<sub>2</sub>C are sensitive to initial precursor composition. There is an optimum Mo/C ratio that leads to a composite of highly crystalline Mo<sub>2</sub>C and fine graphite particles. In addition, it is found that addition of graphene oxide decreases the size of Mo<sub>2</sub>C nanoparticles, promotes the transport of electrons and increases the area of catalytically active sites. Two-dimensional graphene oxide with open structure tailors Mo<sub>2</sub>C nanoparticles morphology by facilitating heterogeneous nucleation and provides a conductive pathway for rapid electron transport. All of changes of the composites contribute to enhancing HER activity.

**11:00 AM**

**(MCARE-S1-016-2018) Durable and efficient Ni-Mo catalyzed TiO<sub>2</sub>/CdS/CIGS photocathode for solar water splitting under various pH conditions**

M. Baek<sup>\*1</sup>; D. Kim<sup>1</sup>; M. Lee<sup>1</sup>; D. Kim<sup>1</sup>; K. Yong<sup>1</sup>

1. POSTECH, Republic of Korea

CIGS is a promising photocathode material. However, most of CIGS photocathodes have suffered from instability problems for applications in a wide range of pH conditions and also have required rare-earth metal HER catalysts for acquiring high performance to achieve a high performance. Herein, we catalyze the CIGS photocathode with Ni-Mo as a non-noble metal catalyst to enhance the PEC efficiency, and also we employ atomically grown TiO<sub>2</sub> in passivating to passivate the CdS/CIGS surface to improve the stability in under a wide range of pH conditions. Our Ni-Mo alloy exhibits the best HER catalytic activities activity among reported HER catalysts in both acidic and alkaline solutions. The Ni-Mo/CdS/CIGS photocathode yields an open-circuit photovoltage of 0.5 V and a short circuit photocurrent density as high as 15 ~ 25 mA cm<sup>-2</sup> in various pH conditions ranging from 0.4 to 14, which is highly comparable to that of Pt/CdS/CIGS. Furthermore, the passivation of CdS/CIGS with a thin TiO<sub>2</sub> ALD layer effectively prevents the photocorrosion of CdS photocorrosion and also the dissolution of the Mo back contact's dissolution, which are the main causes of photocathode's degradation the degradation of the photocathode. The optimized Ni-Mo/TiO<sub>2</sub>/CdS/CIGS photocathode produces a stable photocurrent density at 0 V<sub>RHE</sub>.

**11:20 AM**

**(MCARE-S1-017-2018) Enhanced Photoelectrochemical Performance of Modified ZnO Nanorod Photoanode under Solar Light**

Y. Lin<sup>\*1</sup>; Y. Lin<sup>2</sup>; L. Hsu<sup>2</sup>; P. Peng<sup>2</sup>; S. Chen<sup>1</sup>

1. National Chiao Tung University, Materials Science and Engineering, Taiwan
2. National Synchrotron Radiation Research Center, Scientific Research Division, Taiwan

The wurtzite-type of ZnO with excellent carrier mobility and thus hold great potential as photoanode for photoelectrochemical (PEC) water splitting. However, the poor absorption of visible light and the prominent surface recombination limited the PEC performance. In this work, the improved UV and visible photocatalytic property can be attributed to improve optical absorption and hindering of the photogenerated electron/hole recombination of V<sub>O</sub> and Zn<sup>+</sup> ions in ZnO NRs created by hydrogenation. The ZnO nanorod photoanodes are well-characterized by UV-vis spectroscopy (UV-vis), Transmission X-ray Microscopy (TXM), X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS), UV Photoelectron Spectroscopy (UPS) and photocatalytic tests. From the photocatalytic results, the ZnO photoanode with growth time 48 hour shows high photocurrent with 0.95 mA/cm<sup>2</sup>. The size of the ZnO nanorods range from 150 to 200 nm in diameter and around 12 μm in height, as determined directly from the SEM micrograph.

## SYMPOSIUM 5

### New Strategies for Advanced Materials in Direct Thermal-to-electrical Energy Conversion

Room: Grand Ballroom D

Session Chairs: Michitaka Ohtaki, Kyushu University; Joseph Poon, University of Virginia

**9:30 AM**

**(MCARE-S5-001-2018) Revisiting Ag<sub>2</sub>Se: A Novel Synthesis Route to High Thermoelectric Performance (Invited)**

J. He<sup>\*1</sup>

1. Clemson University, USA

High performance thermoelectric materials should be developed hand in hand with novel synthesis techniques. Take Ag<sub>2</sub>Se as an example, the volatility of Se, mobile Ag ions above the superionic phase transition at 407 K, an optimal carrier concentration as low as 10<sup>18</sup> cm<sup>-3</sup>, and a weighted majority-to-minority carrier mobility ratio sensitive to both carrier concentration and microstructures make the traditional grow-from-the-melt recipe obsolete. In this presentation we discuss a "flash" self-sustaining room-temperature solvent-less recipe. A systematic study of Ag<sub>2</sub>Q (Q=S, Se, Te) showed that the underlying reaction mechanism is in line with the hard soft acids bases (HSAB) theory, rather than the ordinary oxidation-reduction theory. The final products simultaneously attained rich microstructures, stoichiometry, and compositional homogeneity that in turn led to optimized weighted majority-minority carrier mobility ratio and state of the art figures of merit.

**10:00 AM**

**(MCARE-S5-002-2018) Utilizing Natural Nanostructures to Reduce Thermal Conductivity in Oxide Thermoelectrics**

D. Alvarez-Ruiz<sup>1</sup>; F. Azogh<sup>1</sup>; D. Hernandez-Maldonado<sup>2</sup>; D. Kepaptsoglou<sup>2</sup>; Q. Ramasse<sup>2</sup>; P. Svec<sup>3</sup>; P. Svec<sup>3</sup>; S. Day<sup>4</sup>; R. Freer<sup>\*1</sup>

1. University of Manchester, Materials, United Kingdom
2. STFC Daresbury Campus, SuperSTEM Laboratory, United Kingdom
3. Slovak Academy of Sciences, Institute of Physics, Slovakia
4. Diamond Light Source, United Kingdom

The Ga<sub>2</sub>O<sub>3</sub>(ZnO)<sub>m</sub> family of homologous compounds have been identified as potential thermoelectric materials, but properties are often limited due to low densification. By use of B<sub>2</sub>O<sub>3</sub> as an effective liquid phase sintering aid, high density, high quality ceramic samples of Ga<sub>2</sub>O<sub>3</sub>(ZnO)<sub>9</sub> have been synthesized. X-ray analysis showed that the compound crystallizes in the Cmc21 orthorhombic symmetry. Atomically resolved HAADF-STEM images unambiguously showed the presence of nano-sized, wedge-shaped twin boundaries, parallel to the b-axis. These nano-scale structural features were chemically investigated, for the first time, revealing the exact distributions of Zn and Ga; it was found that Ga ions occupy sites at the interface of twin boundaries and inversion boundaries. HAADF-EDS analysis showed that the calcination step has a significant impact on crystal structure homogeneity. By use of a sintering aid and optimization of processing parameters the ceramics achieved a low thermal conductivity of 1.5 to 2.2 W/m.K (for the temperature range 300 to 900 K), a power factor of 40 to 90 μW/K.m<sup>2</sup>. The work shows a route to exploit nanoscale interface features to reduce the thermal conductivity and thereby enhance the thermoelectric figure of merit in complex thermoelectric materials.

10:20 AM

### (MCARE-S5-003-2018) Thermoelectric properties of polymer-derived SiOCN ceramics

R. Iyer<sup>\*1</sup>; S. Pilla<sup>1</sup>; J. Graser<sup>2</sup>; T. D. Sparks<sup>1</sup>

1. Clemson University, Automotive Engineering, USA
2. University of Utah, Materials Science and Engineering, USA

Increasing stringency of global environmental standards has enhanced focus on improving fuel efficiency via utilization of waste heat across automobiles, industries and thermal power plants. However, existing thermoelectrics suffer from numerous issues, such as high toxicity, poor thermal stability, and observance of optimal thermoelectric performance at temperatures close to melting points, where they also show poor mechanical properties. In this context, this work evaluates the thermoelectric potential of polymer-derived ceramics (PDCs) - a non-toxic set of materials that exhibit high thermal and mechanical stability. Silicon-oxycarbonitride (SiOCN) samples were processed via ceramization at 1000 °C in argon atmosphere, after which they were subjected to pulsed electric current sintering (PECS) at 1500, 1600 and 1700 °C. Thermoelectric properties of PECS-ceramic samples were measured over 0 to 1000 °C. Fourier Transform Infra-red (FTIR) spectroscopy, X-ray Diffractography (XRD) and elemental analysis were undertaken to obtain information on chemical composition and bonding in these samples. Raman spectroscopy was carried out to analyze the amount and nature of free carbon content. Characterization results were analyzed to explain the observed thermoelectric performance of polymer-derived SiOCN samples.

10:40 AM

### (MCARE-S5-004-2018) Anomalous Low Thermal Conductivity of ZnO Along with Extended Solubility Limit of Al + Cu Binary Doping

M. Ohtaki<sup>\*1</sup>; H. Fujiwara<sup>1</sup>; K. Watanabe<sup>2</sup>; K. Suekuni<sup>1</sup>

1. Kyushu University, Interdisciplinary Graduate School of Engineering Sciences, Japan
2. Kyushu University, Transdisciplinary Research and Education Center for Green Technologies, Japan

Although ZnO is one of the most promising n-type oxide candidates in thermoelectrics, a quite high lattice thermal conductivity of ZnO has limited its ZT values below 0.7, despite a number of attempts to enhance phonon scattering in the oxide. Very narrow solubility ranges of major n-type dopants such as Al and Ga in ZnO are the principal reason of the difficulties to reduce the thermal conductivity,  $\kappa$ , and to optimize the carrier concentration in the oxide. In this paper, we report an anomalously low lattice thermal conductivity of ZnO along with an extended solubility limit of equimolar amounts of Al and Cu in the oxide. The ZnO samples doped with equimolar amounts (x at. % to Zn) of Al and Cu showed a significant peak shift in their XRD patterns, which has never been observed on single doping of Al, Ga, or Cu. Moreover, the  $\kappa$  values of the sample at x = 8 was as low as 5 and 1.5 W/Km at room temperature and 800 °C, respectively. By comparing with the  $\kappa$  values of Al-doped ZnO at x = 2 as 40 and 8 W/Km at the corresponding temperatures, a drastic reduction of  $\kappa$  was obvious. It should also be noted that the  $\kappa$  value at 800 °C is very close to the theoretical lower limit,  $\kappa_{\min}$ , of 1.2 W/Km for ZnO above room temperature.

11:00 AM

### (MCARE-S5-005-2018) LANL History of Thermionic Conversion

S. Skaggs<sup>\*1</sup>

1. Retired LANL, USA

My first job at LANL was working under Dr. George Grover in the group that was creating fuel pins that produced electric current/voltage from nuclear heating of UC/ZrC fuel pins. WE began this work in 1960 and pursued it for about 8 years using the Omega West water cooled reactor core as the heat source. I propose to discuss the

evolution of fuel pins from UC/ZrC to MoUO<sub>2</sub> over this period. Allied with that is the use of high temperature ceramic insulators to separate the anode from the cathode. We also did a very comprehensive study of different brazes to bond the metal parts to the ceramics. I can discuss the evolution of various ceramic insulators and the many different high temperature brazes that we used to develop the thermionic diodes. I think the historical perspective of this very early work will be an important contribution to the overall technical program. Ultimately we proposed a development of a series of nuclear reactors to power an ion propulsion system for a Manned Mars Mission in the late 1980's time frame. Details of this may be of interest. I co authored this study along with several members of the Group N-5, most of whom are now deceased.

## SYMPOSIUM 6

### Application-oriented Approaches in Spectral Conversion

Room: Grand Ballroom B

Session Chair: Jose Marques-Hueso, Heriot-Watt University

9:30 AM

### (MCARE-S6-011-2018) Photonic approaches to achieve an optimal performance for perovskite solar cells (Invited)

J. Martorell<sup>\*1</sup>

1. ICFO-The Institute of Photonic Sciences, Spain

As solar cells approach their limit efficiency, photonic considerations to further enhance the performance overtake electronic ones. It has been shown theoretically that with the fully optical combination of a random texturing and a perfectly reflecting mirror, efficiencies close to the Shockley-Queisser limit can be reached even when the absorber layer thickness is just a few hundreds of nano-meters I will present three novel photonic approaches to further increase the efficiency of already very good perovskite solar cells: 1) A two-resonance tapping cavity to reach an optimal broadband confinement for electromagnetic waves. An insulator and a metal are used together to achieve an optical cavity that can be made to resonate at two non-harmonic frequencies. 2) By naturally transferring the perovskite random nano-texturing to the back semiconductor/metal interface, where the contrast in the imaginary part of the refractive index is very large, backscattering reduces light escape, which combined with a coupling to the Au surface plasmon leads to the most effective light absorption. 3) A half photonic fiber plate (h-PFP) is used to effectively trap incident photons which are forced to follow an intermittent chaotic trajectory, leading to an optically ergodic system. The efficiency of a solar cell deposited on the planar side of the h-PFP light absorption is enhanced.

10:00 AM

### (MCARE-S6-012-2018) Towards melanin-based integrated energy conversion/storage devices (Invited)

C. Santato<sup>\*1</sup>

1. Ecole Polytechnique de Montreal, Canada

The United Nations define a sustainable development as “development that meets the needs of the present without compromising the ability of future generations to meet their own needs”. However, the present technologies for electronic and energy storage devices, dominated by inorganic materials, have proven to lack sustainability since (i) they generate colossal amounts of waste of electrical and electronic equipment (WEEE) and (ii) they lead to rapid depletion on natural elements. Due to their ubiquity, batteries are one of the main sources of WEEE. Therefore, new technologies for developing environmental-friendly batteries are highly demanded. Newly designed batteries, making use of carbon-based redox-active electrode materials and aqueous electrolytes, are expected

to be biodegradable within dedicated waste management facilities. In this talk we focus on (i) the study of the charge transfer properties of carbon-based molecular redox active nanomaterials extracted from natural sources, e.g. the biopigment melanin (ii) the exploration of the possibility to augment the autonomy of the melanin-based storage devices using of solar light harvesting electrode materials, with the aim to store the charge not only by conventional electrical charging but also by photocharging.

#### 10:30 AM

##### (MCARE-S6-013-2018) Bridging the gap of photocatalysts by NIR to UV-blue up-conversion for pollutant degradation and H<sub>2</sub> generation

P. Acosta-Mora<sup>\*1</sup>; K. Domen<sup>2</sup>; T. Hisatomi<sup>2</sup>; L. Hao<sup>3</sup>; J. Méndez-Ramos<sup>1</sup>; J. Ruiz-Morales<sup>4</sup>; N. Khaidukov<sup>3</sup>

1. Universidad de La Laguna, Physics, Spain
2. University of Tokyo, Japan
3. Russian Academy of Sciences, Russian Federation
4. Universidad de La Laguna, Chemistry, Spain

Spectral up-conversion (UC) has been attracting growing interest in effective harvesting of the NIR part of sunlight (approx 50% of the total incoming sun's radiation) for photocatalytic hydrogen production and environmental purification. Here we present evidences of NIR to UV-VIS photon conversion for degradation of organic-dyes and hydrogen and oxygen evolution via water-splitting, by TiO<sub>2</sub> and Rh-Cr oxide-loaded SrTiO<sub>3</sub>:Al photocatalysts, respectively. For this aim we have used high intense UV-blue UC emissions in K<sub>2</sub>YbF<sub>5</sub>:Tm<sup>3+</sup> hydrothermal crystals under 980 nm laser excitation to bridge the gaps of efficient photocatalysts. We also have carried out exhaustive control dark experiments and adsorption measurements, to isolate the role of UC effect. These results clearly show that the UC emission can activate photocatalytic processes by itself, without other adsorption or possible side effects due to NIR laser radiation. These results open new ways for photocatalytic wastewater treatment under using cost-effective NIR laser diode arrays and also to split water into hydrogen and oxygen with efficient RhCrO<sub>x</sub>/SrTiO<sub>3</sub>:Al composite catalyst, exclusively excited with NIR laser diodes for the first time, by means of spectral conversion materials.

#### 10:50 AM

##### (MCARE-S6-014-2018) Luminescent solar concentrators for BIPV and mobile electronics (Invited)

A. Menéndez-Velázquez<sup>\*1</sup>

1. ITMA Materials Technology, Spain

The interest in photovoltaic solar energy has grown exponentially in this century. However, the high cost is still a limiting factor for massive uses. Luminescent solar concentrators provide a promising solution for cheaper photovoltaic energy. They also provide an exciting new approach to harvest solar energy in buildings and mobile electronics. A luminescent solar concentrator (LSC) consists of a piece of glass or plastic plate coated with luminescent centers that absorb sunlight and emit it at a longer wavelength. A substantial part of the longer-wavelength light is trapped by total internal reflection and guided to the edges of the LSC plate, where it is absorbed by small area photovoltaic cells. Efforts to translate this technology to the building envelope and electronic displays have been limited due to the performance and visual impact. Several strategies, such as FRET multichromophore systems and vertical aligned dyes have been proposed to increase the performance of LSCs. Photoluminescent polarizers have also been considered to replace conventional polarizers in electronic displays.

#### 11:20 AM

##### (MCARE-S6-015-2018) Luminescent glasses and glass ceramics for white light generation (Invited)

S. Schweizer<sup>\*1</sup>; A. C. Rimbach<sup>2</sup>; B. Ahrens<sup>2</sup>; F. Stuedel<sup>1</sup>; P. W. Nolte<sup>1</sup>

1. Fraunhofer IMWS, Fraunhofer Application Center of Inorganic Phosphors, Germany
2. South Westphalia University of Applied Sciences, Faculty of Electrical Engineering, Germany

Most of the white light emitting diodes (LEDs) currently available on the market consist of a blue LED chip coated with a yellow phosphor-polymer composite. Besides the heat-induced degradation of the phosphor-polymer composite, also the decrease in light output upon increasing temperature is a pressing issue. Lanthanide-doped glasses might represent an attractive alternative as thermally and chemically stable frequency-converter. The emission properties of double- and triple-doped glasses can be tuned over a broad spectral range by varying the lanthanide doping concentrations and ratios accordingly. However, the optical absorption coefficient of the lanthanide ions is low and as such adequate thickness of the glass is needed to guarantee a sufficiently long optical path length. In a subsequent annealing step, the as-made glasses are processed to glass ceramics, which provide a longer optical path length due to scattering at the crystallites in the glass. Apart from the optical properties, the thermal conductivity of the luminescent glasses is of great importance for the practical use in high-power LED applications. Processing of the as-made glass to a glass ceramic enables an increase in thermal conductivity by at least one order of magnitude. In this work, Eu<sup>3+</sup>, Tb<sup>3+</sup>, and Tm<sup>3+</sup> single-, double-, and triple-doped borate glasses are investigated for their potential as frequency-downshifter for LED applications.

#### 11:50 AM

##### (MCARE-S6-016-2018) A Model of Clearness Index using atmospheric parameter for Solar Energy Applications in Offa environment, Nigeria

O. Oyeleke<sup>\*1</sup>

1. Federal Polytechnic, Science Technology Department, Nigeria

Solar energy is the radiant energy from the sun that is harnessed using a range of ever-evolving technologies such as photovoltaic, solar architecture and solar thermal energy. It is a source of renewable energy and its technologies are broadly characterized as passive or active solar techniques depending on how it is obtained and distributed as solar energy or converted to solar power. Clearness index reflects the meteorological variations and climatic changes depending on the location. This study is based on the formulation of a model for clearness index using ambient temperature for solar energy applications in Offa environment (lat.8.9°N, lon4.2°E). The atmospheric parameter was obtained from FEDPOFFA meteorological station at Offa for a period of five months; from 1<sup>ST</sup> June to 30<sup>TH</sup> October, 2016. The performance of this correlated model as global radiation estimator was evaluated by comparing the predicted and measured values. Different statistical analyses were employed to examine the mathematical model. The quadratic equation obtained fits well with the measured data. The quadratic equation obtained was well correlated with the measurement when further comparisons were carried out with the existing equations for tropical environment.

## SYMPOSIUM 10

### Challenges for Sustainable Nuclear Energy

Room: Grand Ballroom C

Session Chair: Shan Sundaram, Alfred University

9:30 AM

#### (MCARE-S10-001-2018) Design and Durability Testing of Advanced Waste Forms (Invited)

C. M. Jantzen\*<sup>1</sup>

1. Savannah River National Laboratory, USA

Future nuclear waste generation is primarily driven by interest in sources of clean energy and this has led to an increased interest in advanced nuclear power production. The development of advanced waste forms is a necessary component of the new nuclear power plant (NPP) flowsheets. Therefore, advanced nuclear waste forms are being designed for robust disposal strategies. A brief summary is given of existing and advanced waste forms: glass, glass-ceramic materials (GCM's), glass composite materials (GCM's), and crystalline ceramic (mineral) waste forms that chemically incorporate radionuclides and hazardous species atomically in their structure. Cementitious, geopolymer, bitumen, and other encapsulant waste-forms and composites that atomically bond and encapsulate wastes are also briefly discussed. The various processing technologies are cross-referenced to the various types of waste forms since often a particular type of waste form can be made by a variety of different processing technologies. Lastly, the existing ASTM durability tests that can be used to determine the leaching mechanism of a given waste form, and thus its long term durability, are discussed. Existing examples will be highlighted.

10:10 AM

#### (MCARE-S10-002-2018) Cesium in Hollandite Ceramics

P. Tumurugoti<sup>1</sup>; S. T. Mixture<sup>1</sup>; S. K. Sundaram\*<sup>1</sup>

1. Alfred University, USA

Hollandite family can be represented with the general formula  $A_xB_yO_{16}$ , with B cations forming the  $BO_6$  oxygen octahedra and A cations occupying the tunnel sites. The hollandite lattice can accommodate monovalent and divalent cations (e.g.  $Li^+$ ,  $Na^+$ ,  $Ba^{2+}$ ,  $Cs^+$ ,  $Rb^+$ ) on the A site and a wide range of elements with varying sizes and oxidation states (e.g.  $Al^{3+}$ ,  $Mg^{2+}$ ,  $Fe^{2+}$ ,  $Fe^{3+}$ ,  $Ti^{3+}$ ,  $Ti^{4+}$ ,  $Ni^{2+}$ ) on the B site. Hollandites of the family  $BaO-M^{3+}_2O_3-TiO_2$  are potential ceramic hosts for radioactive Cs immobilization. With a general composition of the Synroc hollandite  $[Ba_xCs_b][M^{3+}_{2a+b}Ti^{4+}_{8-2a-b}O_{16}]$ , choice of the trivalent cation is crucial because it affects the lateral dimension of the tunnels and thereby influences the amount of Cs loading in the lattice. In addition, the hollandite unit cell symmetry can be tetragonal ( $I4/m$ ) or monoclinic ( $I2/m$ ), depending on the ratio of average radius of tunnel cations (Ba and Cs) and octahedral cations ( $M^{3+}$  and  $Ti^{4+}$ ). We have completed a study of Cs incorporation in the hollandites. We have synthesized phase-pure hollandites adopting monoclinic symmetry ( $I2/m$ ) in the compositional range  $0 \leq x \leq 0.4$  using sol-gel synthesis and characterized using a combination of X-ray, neutron and electron diffraction. Our results show local disorder of Ba/Cs along the tunnel direction in hollandites. These results, our structural models, and interpretation will be presented.

10:30 AM

#### (MCARE-S10-003-2018) ZrN and ZrC nano-phase powders for nuclear fuels by solution chemical processing

S. Naim Katea\*<sup>1</sup>; G. Westin<sup>1</sup>

1. Uppsala University, Chemistry-Ångström, Sweden

ZrN has many extreme properties such as high melting point, hardness, durability, thermal and electric conductivity. ZrN nanophase

powders are required for use in hard cermets and lately ZrN is chosen as the matrix for fuels such as; U, Pu and Am in the Pb and Pb-Bi cooled Gen IV nuclear reactors. The present micron sized and impure ZrN produced through carbothermal nitridation require very high sintering temperatures even with SPS which is not suitable for production. The poor powder quality probably stems from the uneven mixing of the  $ZrO_2$  and carbon black. Here the phase development in a new solution based process to nanophase ZrN based on sucrose-Zr-alkoxide precursors is described in detail with TG-DTA, XRD, IR and Raman spectroscopy SEM-EDS and HR-TEM-EDS/EELS. It was found that an extremely intimate mixing of  $ZrO_x(OH)_y$  and graphenic carbon was obtained at 200°C, and that the Zr-particles were converted to  $ZrO_2$  at 600°C with retained structure at 600°C. The carbothermal nitridation reactions started at 1200°C and were finished at 1500°C, resulting in a phase pure ZrN according to XRD, but TEM showed that the ca 20-30 nm sized particles had a 4-5nm thick amorphous or fine-crystalline shell. The details of this shell are discussed, as well as its formation.

10:50 AM

#### (MCARE-S10-004-2018) Impact of Gamma-Ray Irradiation on Rare-Earth Hafnate Nanocrystals

Y. Mao\*<sup>1</sup>; V. Trummel<sup>1</sup>; S. Gupta<sup>1</sup>; M. Pokhrel<sup>1</sup>; D. Wall<sup>2</sup>

1. University of Texas Rio Grande Valley, Department of Chemistry, USA  
2. Washington State University, Nuclear Radiation Center, USA

Improved methods for nuclear waste disposal are crucial for the long term storage and safety of nuclear high level radioactive waste (NHLW) products. To withstand the harsh effects of  $\gamma$ -ray irradiation, a material must be able to accommodate radiation damage. A proposed method to treating NHLW is to encapsulate it in a matrix made of complex oxide materials. Rare-earth hafnates have the potential due to their desirable properties. In this study, we studied  $RE_2Hf_2O_7:Eu^{3+}$  ( $RE = Y, La, Pr, Gd, Er, Lu$ ) nanocrystals. Raman spectroscopy suggested that  $La_2Hf_2O_7:Eu^{3+}$  and  $Lu_2Hf_2O_7:Eu^{3+}$  underwent the order pyrochlore-disorder fluorite phase transition after exposure to  $\gamma$ -ray irradiation. The excitation spectra depicted a change in position of O-Eu charge transfer band (CTB) as a function of  $\gamma$ -ray dose. The emission spectra revealed that there was no change in the local symmetry of  $Eu^{3+}$  in  $RE_2Hf_2O_7$  ( $RE = Y, Gd$  and  $Lu$ ), but in  $La_2Hf_2O_7:Eu^{3+}$   $\gamma$ -ray dose reduced the  $Eu^{3+}$  symmetry. For  $Y_2Hf_2O_7:Eu^{3+}$  and  $La_2Hf_2O_7:Eu^{3+}$ , the lifetime and emission intensity was found to degrade possibly due to creation of  $\gamma$ -ray-induced defects. Regarding  $Gd_2Hf_2O_7:Eu^{3+}$ , the concentration of oxygen vacancy defects predominated over other defects leading to enhanced emission and lifetime after  $\gamma$ -ray irradiation. This study is of utmost importance for the design of robust pyrochlores as NHLW hosts or  $\gamma$ -ray based scintillator material.

11:10 AM

#### (MCARE-S10-005-2018) Doping induced phase transition in $La_2Hf_2O_7:U$ nanoparticles and its implication on speciation of uranium ion

Y. Mao\*<sup>1</sup>; M. Abdou<sup>1</sup>; S. Gupta<sup>1</sup>; J. Zuniga<sup>1</sup>

1. University of Texas Rio Grande Valley, Department of Chemistry, USA

Solubility and leaching behavior of a particular element is dependent on the oxidation states and the coordination geometry. In this context, speciation studies of actinides in pyrochlore host would give highly scientific insight for their exploration as a nuclear waste host. In this work, for the first time,  $La_2Hf_2O_7:U$  nanoparticles (NPs) has been synthesized and has been characterized systematically using various techniques. Uranium is stabilized as both  $U^{4+}$  and  $U^{6+}$  (in octahedral uranate  $UO_6^{6-}$  form) oxidation state in these  $La_2Hf_2O_7$  NPs. Lifetime spectroscopy suggested the stabilization of  $U^{4+}$  at  $Hf^{6+}$  site with a lifetime of  $\sim 1.0 \mu s$  and  $U^{6+}$  at  $La^{3+}$  site with a lifetime of  $\sim 9.0 \mu s$ . More interestingly, concentration dependent study indicated that the proportion of  $U^{4+}$  in the  $La_2Hf_2O_7$  NPs was greater than that of  $U^{6+}$  at low doping level, but at the doping level  $> 2.5\%$ ,

the fraction of  $U^{6+}$  was greater than that of  $U^{4+}$ . Such optical variation was successfully explained based on Raman spectroscopy results. Order pyrochlore phase favors  $U^{4+}$  whereas disordered cotunnite phase favors  $UO_6^{6+}$ . This work is important from nuclear industry perspective, but also opens up a new avenue for research areas, such as fundamental solid state spectroscopy of uranium, doping induced phase transition, and structure-optical property correlation for doped  $A_2B_2O_7$  composition.

## Wednesday, August 22, 2018

### Plenary III

Room: Grand Ballroom A & B

Session Chair: Gabrielle Gaustad, Rochester Institute of Technology

#### 8:30 AM

#### (MCARE-PLN-003-2018) High-Energy Ni-Rich $Li[Ni_xCo_yMn_z]O_2$ Cathodes via Compositional Partitioning for Next-Generation Electric Vehicles

Y. Sun\*<sup>1</sup>

1. Hanyang University, Republic of Korea

The ability of Li-ion batteries (LIBs) to provide portable high-density energy sources with outstanding cycle life has led to their deployment in recent electric vehicles (EVs). For wider consumer acceptance of EVs, however, the current state-of-the-art LIBs face formidable technological challenges, including concerns related to the battery cost, durability, and driving range. Resolving these hurdles requires substantial improvements in energy density, cycle life, and safety of current LIBs. Compared to the most widely accepted anode, graphite, cathodes suffer from inferior capacity, poor cycle life, thermal characteristics, and high cost. As a result, high-energy cathodes enabling a long cycle life and reliable safety need to be developed. One of the most promising oxides is full concentration gradient (FCG) lithium nickel-cobalt-manganese oxide composed of a Mn-rich outer surface providing excellent safety and Ni-rich center achieving high capacity. We further report a new novel  $Li[Ni_xCo_yMn_z]O_2$  cathode with two-sloped full concentration gradients (TSFCG) of Ni, Co, and Mn ions. The TSFCG delivers a high discharge capacity with excellent cycle life and thermal stability. Comparison of electrochemical and thermal properties of the TSFCG with those of NCA and conventional cathode  $Li[Ni_xCo_yMn_z]O_2$  is presented.

## SYMPOSIUM 1

### Materials for Solar Fuel Production and Applications V

Room: Grand Ballroom A

Session Chairs: Yuanbing Mao, University of Texas Rio Grande Valley; Jung-Kun Lee, University of Pittsburgh

#### 9:30 AM

#### (MCARE-S1-018-2018) Challenges and Opportunities in Photocatalysis: Catalyst Design, Reaction Engineering, and Emerging Substrates (Invited)

J. Vela\*<sup>1</sup>

1. Iowa State University, Chemistry, USA

True photocatalysis offers the promise of performing clean room-temperature reactions that are driven by a cheap and abundant energy source: sunlight. Recent developments in the soft synthesis of new materials, as well as in high resolution optical and electron microscopy allow to revisit long standing challenges in photocatalysis. These include the role of catalyst design and structure on photocatalytic activity and selectivity, the atomic level

mechanism of photocatalysis, and the application of photocatalysis to a growing body of possible substrates and chemical processes. In this invited talk, we present our group's recent contributions to the development of heavy-metal free, greener photocatalysts; the controlled photo-fabrication of semiconductor-metal heterostructures; the understanding of microstructure effects on the water oxidation activity of  $Co_3O_4$ -porous silica nanoparticles; and the super-resolution mapping of photo-generated electron and hole separation in single metal-semiconductor nanocatalysts. We also present our work on solar-to-chemical, photocatalytic conversion of emerging substrates such as alcohols from biomass, as well as nitrate.

#### 10:00 AM

#### (MCARE-S1-019-2018) Surface Chemistry Approaches to Stabilizing Organo-metal Halide Perovskites for Soar Energy Conversion (Keynote)

J. Z. Zhang\*<sup>1</sup>

1. UCSC, Chemistry and Biochemistry, USA

Organo-metal halide (OMH) perovskites have shown great promise for various applications including photovoltaic solar cells and light emitting diodes (LEDs) due to their unique optical and electronic properties. However, instability towards factors such as light, oxygen, water, temperature, and oxide layers used in devices presents a major challenge for practical applications. We use OMH perovskite quantum dots (PQDs) as a model system to understand the origin of the material instability and to develop strategies to enhance stability using surface passivation with special molecular ligands to reduce surface defects or trap states. We also developed and evaluated several strategies to passivate surface states including the use of cone-shaped ligands. One important finding is that ammonium ions ( $-NH_3^+$ ) and carboxylate groups ( $-COO^-$ ) have synergistic effects on surface passivation, attributed to simultaneous passivation of both anions ( $X^-$ ) and cations ( $Pb^{2+}$  or  $MA^+$ ) on the surface. We have also shown that bifunctional peptides can serve as bidentate ligands for effective surface passivation. Furthermore, we compare different strategies for passivating PQDs vs bulk films. These studies demonstrate that surface chemistry approaches are highly effective in stabilizing OMH perovskites.

#### 10:30 AM

#### (MCARE-S1-020-2018) Design of Heterostructure Alloy Nanoparticles for Photocatalysis of $CO_2$ Reduction (Invited)

D. C. Lee\*<sup>1</sup>

1. Korea Advanced Institute of Science and Engineering (KAIST), Republic of Korea

Semiconductor nanocrystals of size in the strong quantum confinement regime, or quantum dots, exhibit size-dependent energy gap. The size-tunable shift of band-edge states can be a powerful tool in the control of exciton dynamics. For example, heterostructure nanocrystals with mere changes in geometric dimensions can lead to the band alignment from type I to type II, which could dramatically increase the exciton recombination lifetime. In this presentation, I describe the design of heterostructure nanocrystals showing long exciton recombination lifetime. For the study, we synthesized various core/shell composite particles and introduced CdS outer-most shell with varying thickness and morphology. These heterostructure nanoparticles with prolonged exciton lifetime result in efficient photocatalysis of methylene blue reduction and hydrogen evolution from water. In the way of addressing the heterostructures, we stumbled upon the observation that metal cocatalysts and surface can be engineered with relatively simple chemical approaches, rendering new photocatalytic systems suited in photocatalytic reduction of  $CO_2$  in gas phase.

11:00 AM

### (MCARE-S1-021-2018) Effects of Nanoscale Interfacial Design on Enhanced Photoelectrocatalytic Activity at Modified Photoelectrodes

Y. Lin\*<sup>1</sup>

1. National Synchrotron Radiation Research Center, Taiwan

Sunlight's conversion to hydrogen has been considered an ideal solution to counter the depletion and environmental problems of fossil fuels. Photoelectrochemical (PEC) water splitting is an ideal technology for the purpose, since H<sub>2</sub> could be produced directly from abundant and renewable water and solar light from the process. The key to the technology is photoelectrodes made of small band gap semiconductors of photocatalytic properties. The materials should have high efficiency, high stability, and low cost. In addition of the discovery of new materials, the structure and morphology of the known materials could be controlled to enhance the performance of the photoelectrodes. In this talk, the concepts of materials design and their examples will be proposed for efficient photoelectrodes of PEC cells for visible light water splitting. Particularly, We will discuss the material designs including i) p-n heterojunction photoanodes for effective electron-hole separation, ii) electron highway to facilitate interparticle electron transfer, iii) metal or anion doping to improve conductivity of the semiconductor and to extend the range of light absorption, iv) one-dimensional nanomaterials to secure a short hole diffusion distance and vectoral electron transfer, and v) loading co-catalysts for facile charge separation.

11:20 AM

### (MCARE-S1-022-2018) TiO<sub>2</sub> Nanorods-Supported In<sub>2</sub>S<sub>3</sub> Nanostructures for Solar Hydrogen Production

P. Hsieh\*<sup>1</sup>, Y. Hsu<sup>1</sup>

1. National Chiao Tung University, Materials Science and Engineering, Taiwan

Sulfides have been extensively used in photoelectrochemical (PEC) water splitting for more than two decades.  $\beta$ -In<sub>2</sub>S<sub>3</sub> is particularly appealing by virtue of its fascinating materials properties such as narrow bandgap and favourable band levels. However, the severe photocorrosion of sulfur moieties remains a potential threat to the widespread applications. In this work, TiO<sub>2</sub> nanorods-supported In<sub>2</sub>S<sub>3</sub> nanostructures were prepared and employed as photoanodes for conducting PEC hydrogen production. With the mediation of the underneath TiO<sub>2</sub>, In<sub>2</sub>S<sub>3</sub> showed enhanced photocurrent generation of hydrogen production as well as improved long-term stability. Time-resolved photoluminescence data suggested the prevalence of interfacial charge transfer at the TiO<sub>2</sub>/In<sub>2</sub>S<sub>3</sub> interface, which eased the hole accumulation on In<sub>2</sub>S<sub>3</sub> to retard the photocorrosion. Hydrogen evolution tests demonstrated the practical efficacy for TiO<sub>2</sub>-supported In<sub>2</sub>S<sub>3</sub> photoanodes for realizing solar hydrogen production, showing five times improvement in hydrogen evolution rate over pure In<sub>2</sub>S<sub>3</sub>.

## SYMPOSIUM 2

### Advanced Electrochemical Materials for Energy Storage I

Room: Grand Ballroom B

Session Chairs: Mickael Dollé, Université de Montreal; Philippe Knauth, Aix Marseille University

1:30 PM

### (MCARE-S2-001-2018) Electropolymerization of ionomers for all-solid-state Microbatteries and micro-fuel cells (Invited)

P. Knauth\*<sup>1</sup>; M. Di Vona<sup>2</sup>

1. Aix Marseille University, France
2. University di Roma Tor Vergata, Italy

Electrochemical synthesis is a powerful tool for the preparation of conformal, thin solid electrolyte membranes directly on the electrodes, particularly with complex shapes, such as nanotubes. Such separators should present the highest possible conductivity by the electrochemically active ions, negligible electronic conductivity combined with high chemical and mechanical stability. Thin ionomers separators are important for the realization of micropower devices, such as microbatteries and fuel cells. Aromatic polymers with grafted ionogenic groups (such as sulfonic acid and quaternary ammonium) present excellent mechanical properties (large stiffness and strength); they can block dendrite growth in microbatteries. Single-ion conductivity is assured by grafting the counter-ions on the polymer chain, reducing polarization phenomena during cycling. 1. Cation-conducting membranes We synthesized several ionomers containing grafted sulfonate groups, including poly(styrene sulfonate), which can be used for proton exchange membrane fuel cells and Li batteries. 2. Anion-conducting membranes These ionomers contain quaternary ammonium as fixed cationic groups and can be applied for example in anion exchange membrane fuel cells. In the talk, I will present examples of electrodeposition and report structural and electrical properties of the ionomers, including Li battery cycling.

2:00 PM

### (MCARE-S2-002-2018) First-Principles Density Functional Theory based Screening of High Performance ABO<sub>3</sub> Type Oxides

S. Kang\*<sup>1</sup>

1. University of Ulsan, Chemical Engineering, Republic of Korea

First-principles density functional theory (DFT) calculations were carried out to identify the useful dopants for the chemical stability and the proton conductivity of A-site or B-site doped BaZrO<sub>3</sub>. Notably, the tradeoff relationship between chemical stability and proton conductivity was observed in the B-site doped studies. On the other hand, a linear relationship between the chemical stability and the proton conductivity was found in the A-site doped studies. These computational studies will provide valuable ideas for efficiently designing promising proton-conducting perovskites.

2:20 PM

### (MCARE-S2-003-2018) Flexible Thin Film Batteries for Smart Lens Applications

H. Lee\*<sup>1</sup>; K. Kim<sup>2</sup>; J. Choi<sup>1</sup>

1. Korea Institute of Science and Technology, Center for Electronic Materials, Republic of Korea
2. Yonsei University, Department of Material Science and Engineering, Republic of Korea

Following portable devices, wearable devices recently have been actively developed. The wearable devices have been applied to various areas such as hat, glasses, belt, gloves, watch, and clothes. Among various wearable devices, the smart lens is a wearable device most closed to human living. The smart lens system may serve as



the ultimate wearable electronics platform in the near future, yet its advance has been bottlenecked by the development of suitable batteries. The batteries must be flexible, durable, non-toxic and scalable in fabrication processes. The flexible batteries developed so far has been relying on costly lift-off processes, significantly hindering the scalability of the battery fabrication. In this work, we design a novel fabrication technique that allows the entire thin film batteries to be developed on flexible substrates without the complication of lift-off processes. The thin film batteries applied to contact lens form-factor demonstrates the energy storage capacity of 35  $\mu$ Wh and single-step annealing at 400°C. We also demonstrate the battery operation under wet condition, successfully lighting a light emitting diode.

**2:40 PM**

**(MCARE-S2-004-2018) Garnet Type Solid State Electrolyte of Li-ion Battery**

R. Liu<sup>\*1</sup>; S. Hu<sup>2</sup>

1. National Taiwan University, Department of Chemistry, Taiwan
2. National Taiwan Normal University, Department of Physics, Taiwan

In the present report, Al-doped  $\text{Li}_x\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO) has been found to be more ionic conductive after applying voltammetric cycles to the solid electrolyte with  $\text{Li}|\text{LLZO}|\text{Li}$  configuration. Li deposition-dissolution signal was observed in I-V curves. Electrochemical impedance spectroscopy and Arrhenius plots were employed to test the electrochemical properties. Neutron diffraction techniques and X-ray photoelectron spectroscopy show the structural evolution of LLZO during the voltammetric process. Increase in Li occupancy and rearrangement of O are the two conspicuous changes and they may be the mechanism behind the conductivity enhancement of LLZO. Cyclic voltammetry (CV) process can be a potential technique to replace expensive doping method to boost the electrochemical performance of LLZO and applicable to all solid-state Li-ion batteries.

**3:20 PM**

**(MCARE-S2-005-2018) Synthesis, Structure and Electrochemical Properties of New Lithium Iron Vanadates (Invited)**

Y. Benabed<sup>1</sup>; M. Dollé<sup>\*1</sup>

1. Université de Montreal, Chemistry, Canada

Iron vanadates have been widely explored as possible electrode material for Li batteries. Up to recently, the ternary  $\text{Li}_2\text{O}-\text{Fe}_2\text{O}_3-\text{V}_2\text{O}_5$  phase diagram only displays two lithium iron vanadium oxides with a similar spinel structure. Our recent investigations allowed us to identify two new phases in this system. These two compounds will be discussed in this presentation starting with their synthesis and their thermal properties. Single crystal diffraction data were collected at room temperature and the structure was refined. Mössbauer and magnetic measurements were also used to check the oxidation state of iron ions, to support the obtained crystal structure and to consider any possible structural/magnetic transitions. A specific emphasis will be given to the interesting electrochemical properties of these new phases.

**3:50 PM**

**(MCARE-S2-006-2018) Novel  $\text{SiO}_2$ -based ternary nanocomposite anode material for lithium-ion batteries**

M. Babaa<sup>\*1</sup>; M. Karim<sup>3</sup>; A. Molkenova<sup>1</sup>; A. Terechshenko<sup>1</sup>; I. Kurmanbayeva<sup>2</sup>; Z. Bakenov<sup>1</sup>

1. Nazarbayev University, Chemical Engineering Department, Kazakhstan
2. Institute of Batteries, Kazakhstan
3. Skolkovo Institute of Science and Technology, Center for Electrochemical Energy Storage, Russian Federation

Composites of  $\text{SiO}_2$  nanospheres/Carbon nanotubes/Graphene ( $\text{SiO}_2/\text{MWCNT}/\text{G}$ ) were synthesized and evaluated as electrode materials for lithium-ion batteries.  $\text{SiO}_2$  nanoparticles with an

average diameter of 60 nm and narrow size distribution were obtained using ultrasonically assisted sol-gel method.  $\text{SiO}_2/\text{MWCNT}/\text{G}$  composites was synthesized by high energy ball milling. The electrochemical properties of the composites with different weight ratio were investigated as anode material over a potential range of 0.01 - 3.0 V versus  $\text{Li}^+/\text{Li}$ . The improvement of the electrochemical properties were associated with the highly conductive 3D network consisting MWCNT and graphene, which provides structural integrity to the composite anode and reduces the volume change during charge/discharge and diminishes its effect on cyclability

**4:10 PM**

**(MCARE-S2-007-2018) Ab initio modeling and design of vanadia based electrode materials for post-Li batteries (Invited)**

D. Koch<sup>1</sup>; V. V. Kulish<sup>1</sup>; S. Manzhos<sup>\*1</sup>

1. National University of Singapore, Mechanical Engineering, Singapore

Vanadium oxides (VO) are promising electrode materials that work with many cations (Li, Na, K, Mg, Al...). VOs can be stabilized in many stoichiometries and phases, which creates many possibilities of design but makes rational choice of phase tedious. We present results of ab initio modeling of multiple VO phases which helps select promising phases for a specific type of battery. We also address the problem of low voltages achieved in polyvalent batteries with 3 strategies: (i) computational prescreening of interaction of Mg, Al etc. with multiple VOs; (ii) p-doping; (iii) amorphization. We previously showed that p-doping of (organic and inorganic) semiconductor electrode materials has the potential to improve the voltage significantly. Here, we present results of ab initio modeling of doped VO which establish that p-doping of this popular material for Mg ion and Al ion batteries can substantially increase the voltage and thereby energy density. We also previously showed that amorphization can be used to substantially increase the voltage. Here, we will show our recent results showing a similar effect in VO.

**4:40 PM**

**(MCARE-S2-008-2018) Rational design approaches for organic magnesium ion cathode materials**

J. Lueder<sup>1</sup>; Y. Chen<sup>1</sup>; S. Manzhos<sup>\*1</sup>

1. National University of Singapore, Mechanical Engineering, Singapore

Using magnesium metal as anode material, high volumetric capacity and specific energy can be achieved. Moreover, its safe dendrite-free electrochemical deposition, low cost and natural abundance make Mg an excellent choice of metal for metal ion batteries. This scalability could be married to sustainability and environment-friendliness if organic cathodes were available. While a number of efficient organic electrodes have been reported for Li and Na ion batteries, few organic cathode materials have been identified so far, most of them are quinone-based with voltage plateaus of ca. 2 V (vs.  $\text{Mg}^{2+}/\text{Mg}$ ) and capacities of ca. 200  $\text{mAh g}^{-1}$ . Higher capacities and voltages are desired. Therefore, detailed understanding of rational design strategies for organic Mg ion batteries is required to design materials with improved performance. In this work, we systematically study the interaction between molecules and Mg atoms by means of Density Functional Theory calculations. Our calculations show how electronic, strain, and solvent effects as well as chemical environment influence this interaction, and we determine how design strategies can increase the interaction between them as well as some of the limitations of such strategies. We furthermore demonstrate how the interaction with Mg can be strengthened corresponding to an increase in voltage of several volts for a single molecule.

### JOINT SESSION OF SYMPOSIUM 4 and SYMPOSIUM 12

#### **Ferroelectrics and Multiferroics for Energy Generation, Conversion and Storage / Young Scientist Forum**

Room: Grand Ballroom A

Session Chairs: Soutik Betal, Alfred University; Ram S. Katiyar, University of Puerto Rico

##### **1:30 PM**

#### **(MCARE-S4-001-2018) Magnetic Behavior of Near Room temperature Multiferroic Gallium Ferrite And it's Application**

S. Dugu<sup>\*1</sup>; K. K. Mishra<sup>1</sup>; D. K. Pradhan<sup>2</sup>; S. Kumari<sup>3</sup>; M. K. Bhattarai<sup>1</sup>; R. S. Katiyar<sup>1</sup>

1. University of Puerto-Rico, Department of Physics, USA
2. Geophysical Laboratory, USA
3. West Virginia University, USA

Because of the technological importance and novel applications, such as sensors, logic and memories, multiferroic materials are quite promising. Gallium Ferrite (GaFeO<sub>3</sub>, GFO) is known to be piezoelectric and near-room temperature ferrimagnetic with significant magnetoelectric (ME) coupling (10<sup>-11</sup> s/m at 4.2 K). XRD pattern of polycrystalline ceramics of GFO, prepared by solid state reaction method, shows orthorhombic phase with space group Pc2<sub>1</sub>n at room temperature. M(T) measurements is carried out with external magnetic field of 100, 500 and 1000 Oe in temperature range of 5-395 K. Large bifurcation on ZFC curve indicates the spin glass like behavior. In the M(H) curve, initial magnetization increases sharply followed by slow increase in magnetization indicating the presence of both hard and soft magnets. Phonon frequencies and their line-widths exhibit anomaly across T<sub>N</sub> (225 K). The observed changes in phonon frequencies in Raman scattering are explained based on spin-lattice coupling in the low temperature ferromagnetic phase. Ferroelectric behavior has also been studied in epitaxial thin film of GFO grown on STO (111) substrate. The butterfly loop was observed on piezoelectric response study that is measured by Piezo Force Microscopy (PFM) spectroscopy. The detailed experimental results and their physical correlation with possible applications in energy storage will be presented.

##### **1:50 PM**

#### **(MCARE-S4-002-2018) Barium titanate nanoparticles: Short-range lattice distortions with long-range cubic order**

R. C. Haskell<sup>\*1</sup>; C. Shi<sup>2</sup>; S. J. Billinge<sup>2</sup>; E. Puma<sup>3</sup>; S. Bang<sup>4</sup>; N. J. Bean<sup>1</sup>; J. de Sugny<sup>4</sup>; R. G. Gambee<sup>4</sup>; A. Hightower<sup>4</sup>; T. C. Monson<sup>5</sup>

1. Harvey Mudd College, Physics, USA
2. Columbia University, Applied Physics & Applied Mathematics, USA
3. Pomona College, Physics, USA
4. Harvey Mudd College, Engineering, USA
5. Sandia National Laboratories, Nanoscale Sciences, USA

Barium titanate (BTO) nanoparticles (sizes 10 to 500 nm) exhibit a displacement of the Ti atom from the center of the Perovskite unit cell as inferred from synchrotron X-ray diffraction patterns (XRD) analyzed using atomic pair distribution functions (PDFs). Fits to PDFs acquired at temperatures of 20° to 220°C indicate that these Ti displacements (~0.1 Å) are comparable to or even greater than those in the bulk material. Moreover, these displacements persist at temperatures well above 120°C where the tetragonal to pseudo-cubic phase transition occurs in the bulk. Tetragonal Raman spectral lines were observed for all sizes of these BTO nanoparticles and confirm a distorted unit cell up to 120°C. Above 120°C, the small BTO nanoparticles (10, 50, 100 nm) continue to display tetragonal Raman lines, though with slowly decreasing amplitudes as the temperature rises. In contrast, the tetragonal Raman lines of large BTO

nanoparticles (300, 400, 500 nm) disappear abruptly above 120°C, suggestive of bulk material. By combining information from X-ray PDFs, Raman spectra, and Bragg peak profiles, we conclude that small BTO nanoparticles exhibit both short-range (unit-cell) distortion and long-range (mesoscale) cubic order from 20° to 220°C, while the large nanoparticles behave as bulk material, exhibiting a mesoscale structural phase change at 120°C.

##### **2:10 PM**

#### **(MCARE-S4-003-2018) Dielectric and Ferroelectric Properties of La<sup>3+</sup> and Sc<sup>3+</sup> Doped Lead Zirconate Titanate Thin Films**

M. K. Bhattarai<sup>\*1</sup>; A. A. Instan Ballesteros<sup>1</sup>; K. K. Mishra<sup>1</sup>; S. Dugu<sup>1</sup>; R. S. Katiyar<sup>1</sup>

1. University of Puerto Rico, Physics, USA

Single phase of polycrystalline zirconate titanate 0.90[PbZr<sub>0.53</sub>Ti<sub>0.47</sub>]0.10[La<sub>0.80</sub>Sc<sub>0.20</sub>]O<sub>3-δ</sub> (PLZTS) targets were synthesized using a solid-state reaction method. Highly oriented PLZTS thin films were deposited on La<sub>0.67</sub>Sr<sub>0.33</sub>MnO<sub>3</sub> (LSMO) coated MgO(100) substrates employing laser ablation process in oxygen atmosphere using Pulsed Laser deposition technique. The composite films exhibited tetragonal structure at ambient temperature. The dielectric and electrical measurements on metal-ferroelectric-metal capacitors of Pt/PLZTS/LSMO thin films measured in the temperature range 100-600 K and frequencies 10<sup>2</sup>-10<sup>6</sup> Hz exhibited high dielectric constant having broad features with a clear frequency dispersion. P-E hysteresis loop measurements using an electrometer shows slim loop on PLZTS thin films indicating relaxor behavior. These films were investigated for their applications as high energy density capacitors. The details of the findings will be discussed.

##### **2:30 PM**

#### **(MCARE-S4-004-2018) Micro plasma based surface modification of ZnO and Graphene based flexibe thin films**

A. Katakam<sup>1</sup>; S. Ahmed<sup>\*2</sup>; S. Banerjee<sup>1</sup>

1. California State University, Fresno, Mechanical Engineering, USA
2. Portland State University, Mechanical and Materials Engineering, USA

The current work involves the use of atmospheric pressure and ambient temperature plasmas for enhancement of dielectric and piezoelectric properties of ZnO and Graphene based composite thin films. Interaction with micro-plasma discharges such as corona discharge and dielectric barrier discharge leads to modification of enhancement in surface energy by chain polymerization of the surface in organic composite thin films that changes the surface bonding characteristics. The current work focuses on the development and use of a corona discharge setup for surface modification of piezoelectric flexible composites. ZnO-Epoxy-Graphene composites are prepared with varying ZnO volume fraction from 30% - 50% and a constant Graphene volume fraction of 1%. Four different plasma regimes, including three stable voltage driven regimes, and one pulsed current driven regime are used to modify the surface properties of the thin films. The samples are tested for dielectric and electrical characteristics such as capacitance, resistance, and impedance. For the plasma regime with a voltage of 10 kV and a current of 0.02 mA, the dielectric constant increases up to 6 times over a frequency range from 200 Hz to 10 MHz. A similar trend can be observed for other plasma regimes. The micro-structural and elemental properties of the thin films are characterized using an SEM and EDS respectively.

2:50 PM

**(MCARE-S4-005-2018) Structural, dielectric, ferroelectric ordering and high energy storage capacity in (100) oriented lead-free Ba(Zr<sub>0.2</sub>Ti<sub>0.8</sub>)O<sub>3</sub> thin film**A. A. Instan Ballesteros<sup>1</sup>; K. K. Mishra<sup>1</sup>; R. S. Katiyar<sup>1</sup>

1. Universidad de Puerto Rico Rio Piedras, Physics, USA

Structural, dielectric and ferroelectric ordering in Zr-substituted relaxor Ba(Zr<sub>x</sub>Ti<sub>1-x</sub>)O<sub>3</sub> (BZT) (100) oriented thin film with  $x = 0.2$  are investigated using x-ray diffraction, Raman, dielectric, and polarization measurements. Highly textured thin films were deposited on La<sub>0.67</sub>Sr<sub>0.33</sub>MnO<sub>3</sub> (LSMO) coated MgO (100) substrates using laser ablation process in an oxygen atmosphere using a pulsed laser deposition technique. X-ray diffraction results indicates that the titular thin film stabilizes at tetragonal phase with (100) orientation. Broad Raman features are found to be insensitive to finite temperature down to 80 K. The dielectric measurements on capacitor sandwiched as Pt/Ba(Zr<sub>0.2</sub>Ti<sub>0.8</sub>)O<sub>3</sub>/LSMO thin film in the temperature range 85-650 K and frequencies 10<sup>2</sup>-10<sup>6</sup> Hz suggests a high dielectric constants with broad features with dielectric maximum ( $T_{max}$ ) at ~265 K. A slim P-E loop with  $P_R \sim 93 \mu\text{C}/\text{cm}^2$ ,  $P_S \sim 166 \mu\text{C}/\text{cm}^2$ ,  $E_c \sim 0.3 \text{ MV}/\text{cm}$  are observed from polarization measurements. Large polarization and existence of broad Raman bands even at lowest temperature are explained on the basis of formation of polar nanoregions, which leads to relaxor behavior in the film. The larger electrostatic energy densities efficiency of ~72% is estimated from its stored and recoverable P-E curves. The detailed finding will be presented later.

3:30 PM

**(MCARE-S4-006-2018) Magnetic and Dielectric properties of LuFe<sub>2</sub>O<sub>4</sub> prepared by high-temperature solid state reaction**R. C. Rai<sup>1</sup>; J. Pawlak<sup>1</sup>; J. Hinz<sup>1</sup>; M. Pascolini<sup>1</sup>; M. DeMarco<sup>1</sup>

1. SUNY Buffalo State College, Physics, USA

We present structural, resistivity, magnetic, and dielectric properties of a polycrystalline LuFe<sub>2</sub>O<sub>4</sub> prepared by an electron-beam assisted solid state reaction. The x-ray diffraction of LuFe<sub>2</sub>O<sub>4</sub> shows single phase sample with a small amount of impurities. Resistivity of LuFe<sub>2</sub>O<sub>4</sub> shows two distinct activation energies above and below 310 K, possibly indicating the charge-order state. The ferrimagnetic transition temperature of LuFe<sub>2</sub>O<sub>4</sub> was measured at 241 K, followed by the two low-temperature transitions at 210 K and 140 K, respectively. Mossbauer measurements at 300 K and 78 K indicate the presence of Fe<sup>2+</sup> and Fe<sup>3+</sup> ions in the sample. We also present the magnetoresistance data of LuFe<sub>2</sub>O<sub>4</sub>. The M-H hysteresis loops exhibit a strong temperature dependence with the strongest coercive field and residual magnetization between 100 K and 125 K. In addition, temperature dependence of the magnetic properties suggests that LuFe<sub>2</sub>O<sub>4</sub> enters into a spin-glass state below 100 K. We found that the frequency-dependent complex dielectric constant was strongly influenced by the contact effects, and the intrinsic ferroelectricity of LuFe<sub>2</sub>O<sub>4</sub> could not be ascertained.

3:50 PM

**(MCARE-S4-007-2018) Enhancing Energy Storage Density of BaTiO<sub>3</sub> Based Capacitors Using Dipole Engineering at the Nanoscale**S. Betal<sup>1</sup>; D. Travis<sup>1</sup>; J. Scoones<sup>1</sup>; W. A. Schulze<sup>1</sup>; S. M. Pilgrim<sup>1</sup>; S. Tidrow<sup>1</sup>

1. Alfred University, USA

By optimization of relative permittivity and electric-field breakdown strength, amongst other factors, the energy storage density of BaTiO<sub>3</sub> based ceramic capacitors can be increased. Further, the length of time that such an energy density can be stored within BaTiO<sub>3</sub> can be increased by optimizing resistivity and relative permittivity. Each of these factors, relative permittivity, electric-field breakdown strength and resistivity depend upon controlling the local electric field(s). The designed engineering of local electric fields, through

atomic substitutes, dilute dipole-like substitutions, within "simple" and "simply" mixed perovskites, including BaTiO<sub>3</sub>, are discussed. The design methodology is based upon the new "simple" material model (NSMM) which is a temperature dependent construct and which has been shown to significantly outperform Goldschmidt's tolerance factor formalism at room temperature and over extended temperature ranges. Experimental results indicate that resistivity and electric-field breakdown strength can be enhanced by order(s) of magnitude while the relative permittivity of the material can be maintained at relatively high levels to provide significant increases, order(s) of magnitude, of both energy storage density and length of time that such energy storage density can be maintained within BaTiO<sub>3</sub> based devices.

4:10 PM

**(MCARE-S12-001-2018) Nanostructured Carbon Yarn Based Optoelectronic Rods for Efficient Energy Generation and Structural Protection**M. Uddin<sup>1</sup>; J. Jaksik<sup>1</sup>; I. Martinez<sup>1</sup>; H. Moore<sup>1</sup>

1. University of Texas RGV, Chemistry, USA

The past 25 years has seen great development in the use of carbon nanotubes (CNTs) including their application in solar cells. CNT based devices could provide energy to individuals in remote locations and complex structures without the difficulty of care and handling. CNTs can be formed into ultra-aligned intertwined yarns, which were used to synthesize optoelectronic rod for highly flexible super strong power wire. The application of CNT based energy yarn for use in photovoltaic system (PVS) provides a new surface for the support of dye-loaded TiO<sub>2</sub> nanoparticles as a base for photovoltaic cells that are flexible and easily transported. These fiber based solar cells have enhanced (7%) power conversion efficiency that is independent of the location of the light source and are generally referred to as 3D power wires. We propose these flexible smart wires for aerospace and naval structures for advanced energy generation and structural protection.

4:30 PM

**(MCARE-S12-002-2018) Enhancing capacitive thermal-to-electric energy conversion devices**J. Scoones<sup>1</sup>; D. Travis<sup>1</sup>; S. Betal<sup>1</sup>; W. A. Schulze<sup>1</sup>; S. M. Pilgrim<sup>1</sup>; S. Tidrow<sup>1</sup>

1. Alfred University, USA

A direct thermal-to-electric energy conversion device based on capacitors is discussed. By loading and isolating the charge on a high resistance, long time constant and highly temperature dependent dielectric capacitor, a change in temperature can be used to increase the voltage of the charge residing on the isolated capacitor to "effectively" increase the electrical energy stored on the capacitor. The charge on the capacitor can then be immediately utilized or off-loaded to another energy storage or energy conversion device. The temperature of the discharged capacitor can then be returned to its initial state where charge can be uploaded on the capacitor with the process repeated over the lifetime, structural and electrical, of the device. The theory of the thermal-to-electric capacitive energy conversion device is presented along with experimental data showing conversion of thermal energy to electric-potential energy. Theoretically, the efficiency of capacitive thermal-to-electric energy conversion devices significantly exceed those of currently demonstrated thermoelectric Peltier, Seebeck, and Thomson based converters.

## SYMPOSIUM 5

### High-efficiency Bulk Thermoelectric Materials

Room: Grand Ballroom D

Session Chairs: Jian He, Clemson University; Robert Freer, University of Manchester

9:30 AM

#### (MCARE-S5-006-2018) Half Heuslers as Prospective Mid-To-High Temperature Thermoelectric Alloys (Invited)

J. Poon<sup>\*1</sup>; J. He<sup>2</sup>; T. Tritt<sup>2</sup>

1. University of Virginia, Physics, USA
2. Clemson University, Physics, USA

Half-Heusler (HH) alloys are one of the leading classes of thermoelectric (TE) alloys for converting heat to electricity in the 400-1000°C domain. HH phases exhibit good thermal stability and are scalable. TE generators based on HH modules exhibit power density outputs of several W/cm<sup>2</sup>. For many years, the highest dimensionless figure of merit (ZT) of HH alloys has stayed near 1, obtained largely via nanostructuring.<sup>4</sup> Recently, several groups have reported HH alloys with ZT > 1 and as high as 1.5. This talk reviews the various physics and engineering approaches in achieving high ZT in HH alloys. In particular, we will focus on our approach that involves structural order<sup>6</sup> and resonant electronic states in attaining ZT above 1.3. The combination of enhanced Seebeck coefficient and reduced thermal conductivity due to the presence of resonant states has led to the high ZT observed. Opportunities for further development of this class of practical thermoelectric materials will be discussed.

10:00 AM

#### (MCARE-S5-007-2018) Electronic Mechanisms for Optimizing the Thermoelectric Properties of PbTe/SnTe alloys

D. Ben Ayoun<sup>\*1</sup>; Y. Gelbstein<sup>1</sup>

1. Ben-Gurion University of the Negev, Department of Materials Engineering, Israel

The demand for energy efficiency was motivated many researchers to seek for novel methods capable of enhancing the conversion efficiency of heat to electricity. Most of the recently published methods for thermoelectric (TE) enhancement are mainly attributed to the reduction of the lattice thermal conductivity, with a limited focus on efficiency enhancement due to an improved electronic optimization. This is attributed mainly to the fact that the electronic properties are correlated and opposing each other upon increasing the carrier concentration. PbTe alloys considered among the most efficient TE compositions for temperatures of up to ~450°C. In the current research, BiTe- and Cu-co-doping of PbTe is reported while incorporation of Cu electron donors into PbTe-BiTe vacancies results in an effective compensation of the original high holes' concentration of PbTe toward the optimal TE range. Cu-doped (PbTe)<sub>1-x</sub>(BiTe)<sub>x</sub> alloys with different x values were examined, expecting to yield improved TE performance due to an enhanced electronic doping mechanism. Compare to PbTe, SnTe is receiving an extensive attention due to its eco-friendly nature. Intrinsic SnTe has inherent Sn vacancies and a high hole concentration leading to degraded ZT. However, with the effective electronic approaches, related to co-doping of Bi and another effective donor-type impurity, significant improvements can be achieved.

10:20 AM

#### (MCARE-S5-008-2018) Influence of Ball Milling on Microstructure and Thermoelectric Properties of n- and p-Type Half-Heusler Materials

N. Farahi<sup>\*1</sup>; C. Stiewe<sup>1</sup>; D. Truong<sup>1</sup>; J. de Boor<sup>1</sup>; E. Müller<sup>1</sup>

1. German Aerospace Center (DLR), Institute of Materials Research, Germany

Half-Heusler (HH) materials are promising candidates for thermoelectric (TE) generators in medium temperature range, i.e. hot side temperatures varying from 600 K to 900 K. These materials provide a wide range of compositions, which can be utilized to tailor the TE properties. A major hurdle in the synthesis of commonly known HH materials, is stemmed from the high melting points of the constituent elements such as Hf, Zr, Nb. Consequently, synthesis of these materials usually comprises a melting step. Nevertheless, differences in vapour pressures and melting temperatures of the individual elements may induce loss through evaporation, leading to an undesirable stoichiometry changes in the material. Moreover, several re-melting attempts of the ingot followed by long time annealing are generally required, for complete homogenization. In this study, we investigate the micro-structure and TE properties of n- and p-type half-Heusler TE materials, synthesized by high energy ball-milling of pure elements succeeded by current-assisted direct sintering of the powders. No secondary phase was observed in the X-ray patterns of the samples. A power factor of 34  $\mu\text{Wcm}^{-1}\text{K}^{-2}$  and 42  $\mu\text{Wcm}^{-1}\text{K}^{-2}$  were obtained at 800 K for the n-type  $\text{Ti}_{0.5}\text{Hf}_{0.5}\text{NiSn}_{0.98}\text{Sb}_{0.02}$  and p-type  $\text{FeNb}_{0.9}\text{Hf}_{0.1}\text{Sb}$  composition, respectively, which resulted in a ZT of 0.7 for both compounds at the same temperature.

## SYMPOSIUM 6

### Development of Novel Optical Materials

Room: Grand Ballroom B

Session Chair: Riccardo Marin, University of Ottawa

9:30 AM

#### (MCARE-S6-017-2018) Complex materials for energy applications through solution synthesis (Invited)

G. Westin<sup>\*1</sup>

1. Uppsala University, Sweden

There is great interest to enhance materials using solar energy by up- and down-converting energy and thereby increase the efficiency of solar cells and photo-catalysts. However, these processes are highly sensitive to the local structure of the converting, normally Ln-ions, which calls for improved synthesis techniques that allows for designing local structures in complex materials, allowing for increased understanding of the photonic processes, as well as making materials for applications. Here solution based synthesis routes using metal alkoxides and organically coordinated metal salts have the greatest possibilities. Ways to efficiently synthesise complex oxides and nano-composites as thin- and ultra-thin films, nano particles and nano-sponges will be shown. The influence of the precursor, reaction kinetics and thermal treatment will be discussed in relation to the structures and properties obtained, including the possible synthesis of oxides with extended doping range or locally designed metastable dopings are described. The syntheses and products were studied with; SEM, TEM, XRD, TGA, DSC and, IR and Raman spectroscopy.

10:00 AM

**(MCARE-S6-018-2018) La/Eu doped Zr(O,N) via a solution chemical method**S. Naim Katea<sup>1</sup>; G. Westin<sup>1</sup>

1. Uppsala University, Chemistry-Ångström, Sweden

Zr-based ceramics has many interesting properties and is therefore used in a wide range of applications. In this work nitridation of Zr-carbon-gels to La/Eu doped Zr(O,N) is presented. Traditional powder based carbothermal processes give poor mixing of the constituent compounds which results in high synthesis temperatures and long annealing times, yielding large and extensively agglomerated powders. A solution chemical based method using sucrose-Zr-La-alkoxide and sucrose-Zr-Eu-alkoxide precursors is described in detail, using TG-DTA, IR, XRD, Raman, SEM-EDS, TEM-EDS.

**Plasmonics**

Room: Grand Ballroom B

Session Chair: Eva Hemmer, University of Ottawa

10:20 AM

**(MCARE-S6-019-2018) Optimizing the efficiency of plasmonically enhanced upconversion by nano-particle design (Invited)**P. Balling<sup>1</sup>; J. Christiansen<sup>1</sup>; R. E. Christiansen<sup>4</sup>; E. Eriksen<sup>1</sup>; H. Lakhotiya<sup>1</sup>; M. Mirsafaei<sup>3</sup>; S. Møller<sup>1</sup>; A. Nazir<sup>1</sup>; J. Vester-Petersen<sup>3</sup>; B. Jeppesen<sup>2</sup>; P. Bomholt<sup>2</sup>; J. L. Hansen<sup>2</sup>; S. Ram<sup>1</sup>; O. Sigmund<sup>4</sup>; M. Madsen<sup>5</sup>; A. N. Larsen<sup>1</sup>; S. Madsen<sup>3</sup>; B. Julsgaard<sup>1</sup>

1. Aarhus University, Dept. of Physics and Astronomy, Denmark
2. Aarhus University, Interdisciplinary Nanoscience Center, Denmark
3. Aarhus University, Dept. of Engineering, Denmark
4. Technical University of Denmark, Dept. of Mechanical Engineering, Denmark
5. University of Southern Denmark, NanoSYD, Denmark

One of the fundamental limits on the efficiency of solar cells is their inability to absorb sunlight of wavelengths longer than that corresponding to the band gap of the absorber material. In the well-known crystalline silicon solar cells, this effect is responsible for losing about 20 % of the energy from the sun. A potential solution to this problem is the process of upconversion, where two (or more) long-wavelength photons are converted to a photon with energy exceeding the band gap. This is inherently a non-linear process, which occurs with low probability under solar intensities. An alternative to external focusing of the sunlight is the application of field enhancements by local (nano-) optical design. In this presentation, we will discuss the use of plasmonic near-field enhancement as a tool for enhancing the upconversion probability. Upconversion is driven in the well-known  $\text{Er}^{3+}$  system embedded in thin films of two different matrices –  $\text{TiO}_2$  and  $\text{NaYF}_4$ . The control of plasmonic nano-particle geometries is very flexible as they are defined by electron-beam lithography. Initial geometries, using simple circular gold disks, have been optimized to enhance the upconversion yield by a factor of 7. For further improvements, we are currently employing the technique of topological optimization, which is a method for unrestricted searches of optimized design (within a certain design domain).

10:50 AM

**(MCARE-S6-020-2018) Toward efficient photon upconversion: Plasmonic and covalent tethering strategies (Invited)**T. Kelly<sup>\*1</sup>

1. University of Saskatchewan, Department of Chemistry, Canada

Non-coherent photon upconversion processes have been proposed as a means of circumventing the Shockley-Queisser limit on the efficiency of single junction photovoltaic devices; however, despite

this promise, the quantum yield of most upconversion processes is still too low to make a meaningful contribution to the overall power conversion efficiency. In this presentation, I will discuss some of our research group's efforts to improve the efficiency of triplet-triplet annihilation processes. This includes plasmonic approaches, which make use of the high absorption cross-section and strong near-field effects of triangular silver nanoprisms, and covalent tethering strategies, whereby the triplet sensitizer and fluorescent emitter are bound together in close proximity.

11:20 AM

**(MCARE-S6-021-2018) More Efficient Photon Harvesting by Designing Nanostructures (Invited)**D. Ma<sup>\*1</sup>

1. INRS, University of Quebec, Canada

Harvesting photons at longer wavelengths in the visible and near infrared (NIR) ranges represents an attractive approach to improve the power conversion efficiency of photocatalysis and photovoltaics. Plasmonic and upconverting nanostructures are promising in boosting and broadening photon harvesting and have been recently explored for enhancing the efficiency of solar cells and photocatalysis. Herein, I will present some of our most recent development in plasmonic and upconverting nanostructures and their applications in photocatalysis and solar cells. One example is novel, plasmonic Au nanoparticle (NP) decorated  $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}, \text{Tm}^{3+}$  (denoted as NYF) – core @ porous- $\text{TiO}_2$ -shell microspheres, which can harvest solar photons over a wide spectral range from ultraviolet to NIR for efficient photocatalysis, significantly better than the benchmark Degussa P25. Another example is about the development of a simple method for combing Au NPs and NYF microspheres with two-dimensional graphitic  $\text{C}_3\text{N}_4$  (g- $\text{C}_3\text{N}_4$ ) nanosheets (Au-NYF/g- $\text{C}_3\text{N}_4$ ). The Au-NYF/g- $\text{C}_3\text{N}_4$  structure exhibits excellent stability, wide photoresponse from the ultraviolet to NIR regions, and prominently enhanced photocatalytic activities compared with the plain g- $\text{C}_3\text{N}_4$  sample in the degradation of methyl orange. If time allows, I will also briefly introduce the development of multifunctional nanoparticles involving the NIR-emitting components for bioimaging.

**SYMPOSIUM 7****Advanced Materials for SOFC I**

Room: Grand Ballroom C

Session Chairs: Sun Jae Kim, Kyushu University; Tae Ho Shin, Korea Institute of Ceramic Engineering &amp; Technology

9:30 AM

**(MCARE-S7-001-2018) Steam electrolysis cells with proton-conducting  $\text{BaZr}_{0.6}\text{Ce}_{0.2}\text{Y}_{0.2}\text{O}_{3-\delta}$  electrolytes (Invited)**Y. Aoki<sup>\*1</sup>; H. Toriumi<sup>1</sup>; H. Habazaki<sup>1</sup>

1. Hokkaido University, Faculty of Engineering, Japan

Anodic reaction pathways in proton-conducting solid oxide electrolyzer [A1] cells ( $\text{H}^+$ -SOECs) were investigated using electrochemical impedance spectroscopy with a cell structure of  $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$  (anode) |  $\text{BaZr}_{0.6}\text{Ce}_{0.2}\text{Y}_{0.2}\text{O}_{3-\delta}$  | Pt (cathode). Densely sintered  $\text{BaZr}_{0.6}\text{Ce}_{0.2}\text{Y}_{0.2}\text{O}_{3-\delta}$  ceramics (>97% relative density) were fabricated by a reactive sintering process with a 2 mol%  $\text{Zn}(\text{NO}_3)_2$  additive and were applied as the electrolyte. The impedance spectra were measured while the oxygen ( $p_{\text{O}_2}$ ) and water partial pressures ( $p_{\text{H}_2\text{O}}$ ) in the anode side were systematically varied, which revealed that the SOECs have two polarization resistances at the anode side, one proportional to  $p_{\text{O}_2}^{-1/4}$  and  $p_{\text{H}_2\text{O}}^0$  and another insensitive to  $p_{\text{O}_2}$  and  $p_{\text{H}_2\text{O}}$ . A comparison between the experimental results and elementary step modeling revealed that the actual anode reactions could be described by the reverse mode  $\text{H}^+$ -SOFC cathode reactions, and, thus, the elementary steps dominating the anodic polarization resistance were assigned.

10:00 AM

**(MCARE-S7-002-2018) Characterization of Proton Uptake through Air Electrode Materials for Electrochemical devices**

K. Leonard<sup>\*1</sup>; V. Thoréton<sup>1</sup>; J. Druce<sup>1</sup>; J. Kilner<sup>2</sup>; H. Matsumoto<sup>1</sup>

1. International Institute for Carbon-Neutral Energy Research Center (WPI-I2CNER) Kyushu University, Electrochemical Energy Conversion, Japan
2. Imperial College London, Department of Materials, United Kingdom

Low temperature operation of solid oxide electrochemical devices such as fuel cell and electrolyzers can reduce the cost of such systems. Proton-conducting electrolytes offer many unique merits for Low temperature operation. However, a key factor limiting progress in this area is the sluggish catalytic activity of the air/oxygen electrodes. Some double perovskite oxide like BaGd<sub>0.8</sub>La<sub>0.2</sub>Co<sub>2</sub>O<sub>6-δ</sub> (BGLC) has been reported to exhibit, electronic (p-type), oxygen ion and protonic conduction. In this paper, a combination of Isotope exchange experiments (<sup>18</sup>O and <sup>2</sup>H<sub>2</sub>O tracers), Tritium imaging and Time-of-Flight Secondary Ion Mass Spectrometry depth profiling were used to study the proton uptake in the dense ceramic pellets of Ba<sub>0.5</sub>La<sub>0.5</sub>CoO<sub>3</sub> BLC and BGLC as a means of broadening current knowledge on the availability of protons. The BGLC <sup>2</sup>H distribution, as inferred from the <sup>2</sup>H<sub>2</sub><sup>16</sup>O<sup>-</sup> signal, shows an apparent depth profile which could be interpreted as <sup>2</sup>H diffusion. Our data also suggest BGLC can indeed incorporate protons in the bulk relative to BLC at 300 °C and that both materials retains appreciable mixed oxygen ion/electron conduction behavior. Tritium imaging however showed similar levels of protons in both materials (~5x10<sup>-8</sup> mol H/g) at 600°C. These results will be presented together with recent work on protonic electrolysis cells.

11:20 AM

**(MCARE-S7-003-2018) Processing Ceramic Proton conductor for Intermediate temperature Steam Electrolysis (Invited)**

H. Matsumoto<sup>\*1</sup>; Y. Lee<sup>1</sup>; M. Ivanova<sup>2</sup>; K. Leonard<sup>1</sup>; W. Deibert<sup>2</sup>; W. Meulenber<sup>2</sup>

1. International Institute for Carbon-Neutral Energy Research Center (WPI-I2CNER) Kyushu University, Electrochemical Energy Conversion, Japan
2. Institute of Energy and Climate Research IEK-1, Forschungszentrum Jülich GmbH, Germany

Proton-conducting solid oxide electrolyzers can efficiently electrolyze steam and separately produce hydrogen at the anode under external electrical voltages. We have made significant progresses in the development of our steam electrolysis devices. BaZr<sub>0.44</sub>Ce<sub>0.36</sub>Y<sub>0.2</sub>O<sub>3-δ</sub> our state-of-the-art electrolyte retained a conductivity of 1.44 × 10<sup>-2</sup> Scm<sup>-1</sup> in wet 1 % H<sub>2</sub> at 600°C. A cell terminal voltage of 1.45V at a current density of 500mA cm<sup>-2</sup> with ~86% current efficiency was obtained. In this presentation we present some of the challenges of proton conductors particularly for electrolysis operation. On the anode side, Several transition metal containing perovskites, such as Sm<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3</sub> (SSC55) used as electrode, but these materials are not sufficiently durable against high steam concentration at intermediate temperature. Another issue is the inter-diffusion of transition metal species from the electrodes to the electrolyte causing a decrease in proton conductivity. We examined the impact of several transition metals by introducing them as part of the B-site component of AB<sub>0.9</sub>Y<sub>0.1</sub>O<sub>3-δ</sub> (A=Ba, Sr; B=Ce, Zr) and found that proton conductivity is more or less reduced by the transition metal incorporation. Finally, preliminary results of our recent efforts in fabricating and scaling up our protonic membrane devices by sequential tape casting will be presented.

10:50 AM

**(MCARE-S7-004-2018) Insights on the proton dissolution behaviour of acceptor-doped perovskite oxides by in-situ diffuse reflectance FT-IR spectroscopy (Invited)**

T. Ishiyama<sup>\*1</sup>; H. Kishimoto<sup>1</sup>; K. Develos-Bagarinao<sup>1</sup>; K. Yamaji<sup>1</sup>; T. Yamaguchi<sup>1</sup>; Y. Fujishiro<sup>1</sup>

1. National Institute of Advanced Industrial Science and Technology (AIST), Japan

Acceptor-doped perovskite oxides are known as alternative electrolyte materials for proton conducting fuel cells (PCFCs). Recently, it has been suggested that PCFC can improve the electrical power generation efficiency as compared to SOFC with an oxide ion conductor as electrolyte material, because it is able to increase the fuel utilization due to the absence of hydrogen fuel dilution during the cell operation. However, electrolyte materials such as barium zirconate and barium cerate exhibit not only proton conductivity but also oxide ion and electron hole conductivities depending on the atmosphere and temperature. These electronic conductive properties are strongly related with the defect chemistry in the oxides. In this study, proton dissolution behavior was investigated by in-situ diffuse reflectance Fourier-Transform infrared (FT-IR) spectroscopy with controlled temperature and atmosphere. We will discuss the correlation between proton dissolution behaviour and electrical conductivity as a new insight obtained using in-situ FT-IR technique.

11:20 AM

**(MCARE-S7-005-2018) Dynamic Response of Solid Oxide Fuel Cell: The Effect of Anode Microstructure on Transport Phenomena under Electrical Load Change (Invited)**

Y. Bae<sup>\*1</sup>; S. Lee<sup>2</sup>; K. Yoon<sup>3</sup>; J. Lee<sup>3</sup>; J. Honh<sup>1</sup>

1. Yonsei University, Mechanical Engineering, Republic of Korea
2. Korea University, Mechanical Engineering, Republic of Korea
3. Korea Institute of Science and Technology, High-Temperature Energy Materials Research Center, Republic of Korea

The transient behavior of thermodynamic variables in a solid oxide fuel cell upon electrical load change is examined by elucidating the effect of microstructure on transport processes. Local thermodynamic states and thermo-fluid environment are resolved by dynamic 3-D numerical simulation. A high-fidelity physical model is developed, which is used to investigate fundamental physical, electrochemical processes occurring at electrodes upon electrical load change. Especially, the effect of cell microstructure (i.e., porosity and tortuosity) on transport phenomena on the anode is discussed in detail. Results show that the electrical current responds excessively to potential steps and recovers asymptotically to the quasi-steady state with a relaxation time. This is explained by time-dependent variation of an electrochemical reaction zone and species transport in the anode. The former reacts quickly to electrical load change, influencing hydrogen concentration, while the latter shows time-delay, affecting the diffusion of hydrogen between the reaction zone and fuel channel. This indicates that the overall transient behavior is governed by species diffusion in the anode. The parametric study with respect to cell microstructure also shows that the transient behavior can be controlled within a safety margin by designing the optimal electrode microstructure.

11:50 AM

**(MCARE-S7-006-2018) Fabrication of lanthanum strontium cobaltite-infiltrated lanthanum strontium cobalt ferrite cathodes for high performance solid oxide fuel cells**

M. Kim<sup>\*1</sup>; G. Han<sup>1</sup>; H. Choi<sup>1</sup>; J. Kim<sup>1</sup>; H. Choi<sup>1</sup>; K. Bae<sup>2</sup>; J. Shim<sup>1</sup>

1. Korea University, Mechanical Engineering, Republic of Korea
2. Stanford University, Mechanical Engineering, USA

Surface modification has been applied as an effective method for the fabrication of heterogeneous electrodes for solid oxide fuel cells (SOFCs). The application of the heterogeneous electrode is

particularly useful for increasing the rate of the oxygen reduction reaction (ORR) of the cathode requiring high catalytic activity at the surface. For example, lanthanum strontium cobalt ferrite (LSCF) can be used effectively in SOFCs operable at intermediate temperatures through simultaneous conduction of oxygen ions and electrons, but there is a problem of low surface catalytic activity. In this case, modifying the LSCF surface with a material having excellent catalytic properties can improve the surface reactivity and enhance the ORR rate. With respect to this, we fabricated surface modified LSCF cathode by penetrating lanthanum strontium cobalt (LSC) having excellent in surface diffusion and charge transfer kinetics. This surface modification was conveniently accomplished using commercially available inkjet printer and LSC was uniformly dispersed the LSCF backbone. Electrochemical impedance spectra (EIS) shows that the polarization resistance significantly reduced after surface modification of LSCF cathode using LSC. As a result, the performance of LSC-infiltrated cell was increased by 45.7% compared to the bare cell measured at 600°C.

## Advanced Materials for SOFC II

Room: Grand Ballroom C

Session Chairs: Yoshio Matsuzaki, Tokyo Gas; Taner Akbay, Kyushu University

### 1:30 PM

#### (MCARE-S7-007-2018) Strain-Driven Control of B-metal Exsolution on Perovskite Oxides: A Case Study on $\text{SrTi}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ (Invited)

K. Kim<sup>\*1</sup>; J. Han<sup>1</sup>; W. Jung<sup>2</sup>; B. Koo<sup>2</sup>

1. Pohang University of Science and Technology (POSTECH), Chemical Engineering, Republic of Korea
2. Korea Advanced Institute of Science and Engineering (KAIST), Materials Science & Engineering, Republic of Korea

The exsolution phenomena of B-site cation metals have great potential to synthesize well-distributed metal nanoparticles (NPs) on the surface of oxide support materials for various applications. In particular, it has been widely reported that B-metal exsolution occurs under SOFC anode environment (reducing environment). However, the ways to control the exsolution on perovskite oxides are not clear yet. In this study, we chose Co-doped  $\text{SrTiO}_3$  (STC) as a model system to find out how to control the B-metal exsolution phenomena. Interestingly, we found that Co exsolution can be facilitated by biaxial tensile strain. It is demonstrated that the weaker bond strength of Co-O under the applied tensile strain destabilizes Co atoms within the lattice of bulk perovskite, thereby inducing the segregation toward the surface. To realize this concept in practical electrodes, we employed doping of A-site cation with the larger ionic radius than Sr host cation in STC to induce the tensile strain around Co. We confirmed that the exsolution of Co is more preferred at the doped STC. This study will provide a useful insight to control the exsolution behavior on perovskite oxides not only for SOFC electrodes but also for a variety of catalytic applications.

### 2:00 PM

#### (MCARE-S7-008-2018) Strain Effects on Oxygen Dissociation Activity of $\text{Pr}_2\text{NiO}_4$ Dispersed with Au

S. Kim<sup>\*2</sup>; T. Ishihara<sup>1</sup>

1. Kyushu University, International Institute for Carbon-Neutral Energy Research, Japan
2. Kyushu University, Department of Applied Chemistry, Faculty of Engineering, Japan

For increasing power density at low operating temperature, electrochemical performance of cathode is required to increase because activity loss is occurred more significant than that of anode by larger activation energy. In our previous study,  $\text{Pr}_{1.9}\text{Ni}_{0.71}\text{Cu}_{0.41}\text{Ga}_{0.05}\text{O}_{4+\delta}$  (PNCG) which shows superior mixed ionic and electronic conductor

(MIEC) is expected as superior cathode, however, surface activity to oxygen dissociation is low. In this study, introduction of tensile strain into PNCG by mismatch in thermal expansion coefficient (TEC) between metal and metal oxide on cathodic property for increasing power density at decreased temperature. Strain induction into PNCG by Au dispersion was confirmed by using XRD peak shift and apply into this powder for SOFC. In case of PNCG cathode, there are large overpotential of cathode observed suggesting the insufficient surface activity to oxygen dissociation. However, by addition of 3 mol% Au dispersed into PNCG cathode, cathodic overpotential was significantly decreased resulting in the increase in maximum power density 2.5 times higher than that of the cell using PNCG without Au.

### 2:20 PM

#### (MCARE-S7-009-2018) Suppression of cation segregation in $(\text{La,Sr})\text{CoO}_{3-\delta}$ by elastic energy minimization

J. Koo<sup>\*1</sup>; H. Kwon<sup>4</sup>; M. Ahn<sup>1</sup>; M. Choi<sup>1</sup>; J. Son<sup>3</sup>; J. Han<sup>2</sup>; W. Lee<sup>1</sup>

1. SungKyunKwan University, School of Mechanical Engineering, Republic of Korea
2. Pohang University of Science and Technology (POSTECH), Republic of Korea
3. Korea Institute of Science and Technology, Republic of Korea
4. University of Seoul, Republic of Korea

Solid oxide fuel cells (SOFCs) are thought of promising energy devices because of the advantages like a high power density, and fuel flexibility, etc. However, the high operating temperature (>800 °C) of SOFCs has been a critical technical obstacle, and especially, a chemical stability caused by strontium segregation at cathode surfaces is a significant issue in SOFCs. The strontium segregation aggravates the oxygen reduction reaction at cathodes, and that causes decreased the long-term stability of SOFCs. The elastic interactions of A-site dopant cations reported to significantly affect the degree of dopant segregation. In this study, we suggest the fractional free volume as a new indicator with a quantitative assessment for the elastic energy in the perovskite. To prove a new elastic model, three samples were applied with different A-site dopants:  $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ ,  $\text{La}_{0.6}\text{Sr}_{0.2}\text{Ca}_{0.2}\text{CoO}_{3-\delta}$ , and  $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_{3-\delta}$ . The dopant segregation was estimated and evaluated by the segregation energy and oxide formation energy calculated by DFT simulations, and the structural, chemical, and electrochemical changes at the surfaces measured by AFM, AR-XPS, and EIS. These results were well explained by a new elastic model. Our results can provide insight into designing the chemically stable cathode materials for SOFCs from the elastic energy perspective.

### 2:40 PM

#### (MCARE-S7-010-2018) Nickelate as an Active and Durable Electrode for Oxygen Reduction and Oxygen Evolution Reactions

X. Zhou<sup>\*1</sup>; Y. Wang<sup>1</sup>; J. Wilson<sup>1</sup>

1. University of Louisiana at Lafayette, Chemical Engineering, USA

Nickelates (e.g.  $\text{Pr}_2\text{NiO}_4$ ) exhibit a greater surface exchange coefficient and a diffusion coefficient than these of perovskite-type oxides (e.g. LSCF) over a wide temperature regime (500 – 900 °C). As a result,  $\text{Pr}_2\text{NiO}_4$ -based compounds are considered as an attractive candidate for oxygen reduction electrode in solid oxide fuel cells (SOFCs) and oxygen evolution electrode in solid oxide electrolysis cells (SOECs). In this presentation, we will discuss the phase stability, electrocatalytic activity, and performance durability for the parent  $\text{Pr}_2\text{NiO}_4$  and doped  $\text{Pr}_2\text{NiO}_4$ . In addition, we will elucidate the role of interlayer on the electrode activity and stability measured over a long period. Gas bubbles are formed in SOECs, which is influenced by the chemistry of interlayer. Distribution of Relaxation Times (DRT) Analysis is carried out to decouple the mechanical and electrochemical processes.

### Advanced Materials for SOFC III

Room: Grand Ballroom C

Session Chairs: Hiroshige Matsumoto, Kyushu University; Yoshitaka Aoki, Hokkaido University

**3:20 PM**

#### (MCARE-S7-011-2018) Oxygen Reduction Reaction on Strained Surfaces of $\text{La}_2\text{NiO}_4$ (Invited)

T. Akbay\*<sup>1</sup>; A. Staykov<sup>1</sup>; J. Kilner<sup>2</sup>; T. Ishihara<sup>1</sup>

1. Kyushu University, Japan

2. Imperial College London, United Kingdom

Facile kinetics of air electrode reactions in solid oxide fuel and/or electrolyser cells limits the use of such devices in low temperature electrochemical energy conversion/storage applications. Rare-earth metal oxides with  $\text{K}_2\text{NiF}_4$ -type perovskite-related crystal structures are promising candidates as air electrode materials for these devices owing to their mixed ionic and electronic conduction properties. In addition to the high charge carrier mobility, the surface structure and chemistry of these materials plays a critical role in determining the kinetics of oxygen reduction and exchange reactions. Among various candidates, certain members of the Ruddlesden-Popper series, such as  $\text{La}_2\text{NiO}_4$ , have been identified as active for surface oxygen interactions. The structure and composition of the outermost layers of this material have recently been identified as LaO rather than  $\text{NiO}_2$  terminated. In our earlier study, the changes in the electronic structure and the energetics of surface interactions on the transition metal free surfaces of  $\text{La}_2\text{NiO}_4$  were analysed by using ab initio techniques. Our calculations substantiated that the LaO-terminated surfaces participate in the formation of surface superoxo species owing to the d-electron(s) of the lanthanide atoms. In this contribution, the effect of lattice strain on the surface reconstruction and the catalytic O-O bond cleavage will be presented.

**3:50 PM**

#### (MCARE-S7-012-2018) Designing the metallic grids using electrohydrodynamic (EHD) jet printing for enhanced interfacial properties of IT-SOFC

M. Choi\*<sup>1</sup>; S. Hwang<sup>1</sup>; D. Byun<sup>1</sup>; W. Lee<sup>1</sup>

1. SungKyunKwan University, Mechanical Engineering, Republic of Korea

Interface engineering at electrolyte/cathode is one of the most crucial issue to achieve the highly performing solid oxide fuel cell (IT-SOFC). Among the various technic to conduct the interface engineering, we approached the precisely printed metallic grids in a pitch size of  $\sim 50 \mu\text{m}$  with various metals such as Silver (Ag), Nickel (Ni), and Aluminum (Al) using electrohydrodynamic (EHD) jet printing process which was previously commercialized printing process on the large scale application. To assess the effect of those metallic grid structure on the interfacial properties, we performed the electrochemical impedance spectroscopy (EIS) in the IT regime of 650-500 °C, resulting the substantially reduced polarization resistance of 2-8 fold compared with non-printed cathode. In addition, electrochemical analysis involving the tafel analysis, activation energy, and careful impedance fitting with distribution of relaxation times (DRT) analysis were performed and it could specifically regulate that the roles of metallic grids on the oxygen reduction reactions can be specified with electrical conductivity and catalytic effect of each metal. Through those results, it can provide the in-depth understanding of role of metallic grids on the oxygen reduction reactions at interface and promise of grid structure with various metals for highly performing cathode of IT-SOFC.

**4:10 PM**

#### (MCARE-S7-013-2018) Multiscale design of composite nanofibers by one-step fabrication for high-performing solid oxide fuel cells

M. Ahn\*<sup>1</sup>; W. Lee<sup>1</sup>

1. SungKyunKwan University, Mechanical Engineering, Republic of Korea

We report the substantially improved electrochemical performance of  $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$  (SSC) and  $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$  (GDC) composite nanofiber-based cathodes for intermediate temperature solid oxide fuel cells fabricated by one-step electrospinning with a cathode area-specific resistance of  $0.051 \Omega\text{cm}^2$  at 650 °C. On the basis of the composite configuration and the nanofiber structure, desired structural properties including maximized heterointerfaces between electrode and electrolyte materials, increased grain boundary density, and tensile strained state are achieved to promote sluggish oxygen reduction reactions at the cathodes. Our results can provide a design guideline to utilize the nanostructured composite electrodes by engineering the structural properties with superior long-term stability.

**4:30 PM**

#### (MCARE-S7-014-2018) Improving thermal shock resistance in yttria stabilized zirconia (YSZ) by tungsten addition for rapid startup of solid oxide fuel cells (SOFC)

H. Hayun\*<sup>1</sup>; C. Barad<sup>1</sup>; Y. Gelbstein<sup>1</sup>

1. Ben-Gurion University of the Negev, Materials Engineering, Israel

SOFCs are promising energy conversion devices showing very high efficiencies and low emissions. Despite their many advantages they remain mostly unimplemented in the industry. This research aims to solve one issue hindering the commercialization of SOFCs. The high operating temperature limits the startup time of the cell considerably, due to thermal stress in the ceramic electrolyte (YSZ) which is prone to thermal shock and will crack when subjected to other than extremely slow heating rates ( $<2^\circ\text{C}/\text{min}$ ). Reducing the starting time may open the possibility to use SOFCs in the automotive industries. Zirconia ( $\text{ZrO}_2$ ) and tungsten oxide ( $\text{WO}_3$ ) when heat treated together may form zirconium tungstate ( $\text{ZrW}_2\text{O}_8$ ), which is well-known for its negative thermal expansion behavior. Upon adding small amounts of tungsten to cubic YSZ the thermal expansion is reduced without altering its mechanical properties, resulting in better thermal shock resistance. The effect of tungsten addition was tested in the range of 1-6at%. The obtained electrolytes were synthesized using sol-gel and sintered by hot pressing resulting in fully dense samples. Extensive thermal analysis was conducted to determine the thermal shock resistance. The electrolytes were tested in EIS at high temperatures to denote the effect of the addition on the performance of the YSZ electrolyte.

## SYMPOSIUM 11

### Metal Oxides: Fundamental Studies and Applications

Room: Grand Ballroom D

Session Chairs: Wenzhuo Wu, Purdue University; Ji-Won Choi, Korea Institute of Science and Technology

**1:30 PM**

#### (MCARE-S11-001-2018) Large-area solution-manufactured air-stable 2D material for high-performance electronics and smart sensors (Invited)

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1. Purdue University, School of Industrial Engineering, Birck Nanotechnology Center, Regenstrief Center for Healthcare Engineering, USA

The reliable production of two-dimensional (2D) crystals is essential for exploring new science and implementing novel technologies in the 2D limit. However, ongoing efforts are limited by the vague



potential in scaling-up, restrictions on growth substrates and conditions, small sizes and/or instability of synthesized materials. In this talk, I will discuss our recent progress in the fabrication of large-area, high-quality 2D material by a substrate-free solution process. The crystals exhibit process-tunable thicknesses from a mono-layer, bi-layer, tri-layer to tens of nanometers, and lateral sizes ~ 100  $\mu\text{m}$ . Our prototypical 2D transistor device, which is air-stable, shows an excellent all-around figure of merits compared to existing 2D materials. We further carry out the first experimental exploration of piezotronic effect in such solution-grown 2D material and systematically investigate the piezotronic transport properties. The coupling between the piezoelectric and semiconductor properties in such material system enables the design and implementation of novel electronic devices and smart sensors that can interact with the mechanical stimuli. Our approach has the potential to produce stable, high-quality, ultrathin semiconductors with a good control of composition, structure, and dimensions for applications in electronics, optoelectronics, and energy devices.

2:00 PM

**(MCARE-S11-002-2018) Controlling the polarizability of high-k dielectric 2D nanosheets using A-site modification**

J. Choi\*<sup>1</sup>

1. Korea Institute of Science and Technology, Republic of Korea

The demand for size-reduction of the electronic devices have been continuously increased the requirement of two-dimensional (2D) dielectric materials such as  $\text{Ti}_2\text{NbO}_7$ ,  $\text{Ca}_2\text{Nb}_3\text{O}_{10}$ , and  $\text{Sr}_2\text{Nb}_3\text{O}_{10}$ . These 2D materials show a stable dielectric permittivity invariant with thickness and great thermal stability. However, dielectric permittivity is still far below than bulk value. Therefore, we developed new high-k dielectric materials as substituting A-site of  $\text{Sr}_2\text{Nb}_3\text{O}_{10}$  nanosheets. The nanosheets have been prepared by 2-step cation exchanging process and deposited by Langmuir-Blodgett method on Nb-doped  $\text{SrTiO}_3$  substrate. The microstructure and structural properties are investigated by XRD, RAMAN, and TEM. These A-site modified  $\text{Sr}_2\text{Nb}_3\text{O}_{10}$  nanosheets show the high permittivity and low dielectric loss in the ultrathin film region. We expect that this novel materials can be emerging materials for of next-generation capacitor for smart devices.

2:20 PM

**(MCARE-S11-003-2018) Interaction of Light Illumination and Dielectric Charge Trapping in Zinc Tin Oxide (ZTO) Thin Film Transistor**

J. Chen\*<sup>1</sup>; Y. Hsiao<sup>1</sup>; C. Chang<sup>1</sup>; J. Li<sup>1</sup>

1. National Cheng Kung University, Materials Science and Engineering, Taiwan

Zinc tin oxide (ZTO) is a transparent semiconductor based on earth-abundant elements. In this work, ZTO films prepared by spin coating via a solution route have been applied as the active semiconductor layer in a thin film transistor (TFT) with  $\text{SiO}_2$  dielectrics and Si gate. With thickness less than 10 nm, the ZTO film exhibits a good field-effect mobility of  $\sim 10$   $\text{cm}^2/\text{Vs}$ , small subthreshold slope of  $\sim 0.5$  V/decade and high on/off current ratio of  $\sim 10^7$ . Under light illumination of 405 nm wavelength (below ZTO bandgap), the photoresponse of ZTO TFT is related to the ionization of neutral oxygen vacancies to positively-charged oxygen vacancies, which simultaneously produce photogenerated electron carriers. The light responsibility of ZTO TFT reaches around 740 A/W with power density  $\sim 1$   $\text{mW}/\text{cm}^2$ . Moreover, the  $\text{SiO}_2$  dielectric layer is modified to a sandwich stack of  $\text{Al}_2\text{O}_3/\text{AZO}$  (Al-doped zinc oxide) nanoparticles/ $\text{SiO}_2$ , where the AZO nanoparticles act as the charge trapping medium. With the addition of AZO charge trapping layer, electrons in the ZTO active layer can be trapped under positive gate bias. The trapped electrons will then interact with ionized oxygen vacancies generated by light illumination. Consequently, the light

responsibility of ZTO TFT can be further modulated with different gate biases during light illumination.

2:40 PM

**(MCARE-S11-004-2018) Solution-processed flexible and transparent high-k dielectric thin films**

H. Yim\*<sup>1</sup>; J. Choi<sup>1</sup>

1. Korea Institute of Science and Technology, Republic of Korea

The search for 2D high-k dielectric nanosheets materials have been actively researched due to a versatile properties such as high dielectric permittivity and great thermal stability. In addition, the development of flexible and transparent electronics required the advanced dielectric materials. 2D Dion-Jacobson phase nanosheets have been shown high-k dielectric permittivity properties, which are undisturbed for the thickness, even for thickness down to 20 nm. Moreover, these nanosheets are transparent and don't require to do a post annealing process, so 2D nanosheets can be deposited on flexible substrate. Here, we firstly demonstrate the effect of A-site modified Dion-Jacobson phases layered perovskites  $\text{Sr}_2\text{Nb}_3\text{O}_{10}$  nanosheets to enhance their dielectric properties and realize flexible dielectric thin films on polymer substrate in MIM structure. Oxide/metal/oxide multilayer electrodes are deposited as top and bottom electrodes, and the nanosheets thin films are grown by Langmuir-Blodgett method in room temperature. This new and simply fabricated high-k dielectric thin film can be a new tool to develop next-generation flexible electronics.

3:20 PM

**(MCARE-S11-005-2018) Mitochondria-Reactive Oxygen Species Targeting Surface Modified Ceria-Zirconia Nanoparticles as Antioxidants for Hepatic Cirrhosis**

S. Hong\*<sup>1</sup>; S. Choi<sup>1</sup>; O. Kim<sup>2</sup>; H. Hong<sup>2</sup>; S. Kim<sup>2</sup>; K. Yoon<sup>1</sup>

1. Hannam University, Department of Chemistry, Republic of Korea  
2. Catholic University of Korea, Central Laboratory of Surgery, Republic of Korea

Reactive Oxygen Species (ROS) in the mitochondria are a important pathologic factor in liver diseases, including cirrhosis. Ceria nanoparticles (CNPs) have two oxidation states,  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$  which have stimulated researchers to study CNPs as therapeutic agents for treating numerous diseases, including cancer. The 2 nm ceria-zirconia nanoparticles (CZ NPs) are control a higher  $\text{Ce}^{3+}/\text{Ce}^{4+}$  ratio and faster change from  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$  that those indicated by ceria nanoparticles. Consequently, targeting surface modified CZ NPs selectively to ROS might be a potential of therapeutic apply to generally liver diseases. Herein, we report the synthesis of surface modified CZ NPs that localize to mitochondria and inhibit hepatocellular death in a hepatic cirrhosis disease mouse model. The physicochemical properties were analysed by FE-TEM (Field-emission Transmission Electron Microscope), EDS (Energy Dispersive X-ray Spectroscopy), FT-IR (Fourier Transform Infrared Spectroscopy), DLS (Dynamic Light Scattering), TGA (Thermogravimetric Analysis),  $^1\text{H-NMR}$  ( $^1\text{H}$  Nuclear Magnetic Resonance).

3:40 PM

**(MCARE-S11-006-2018) Thermal Barrier Coating of YSZ Aerogel Composite**

S. Yoon\*<sup>1</sup>; J. Kim<sup>1</sup>; G. Han<sup>1</sup>; H. Choi<sup>1</sup>; J. Shim<sup>1</sup>

1. Korea University, Mechanical Engineering, Republic of Korea

Yttria stabilized zirconia (YSZ) is commonly used for thermal barrier coating (TBC) at high temperature due to its good thermal and chemical stability at high temperature with low thermal conductivity. Aerogel is the lightest solid material in the world and has low thermal conductivity and large surface area. These characteristics are originated from the fact that most of the internal microstructure of aerogel is comprised of nano-sized pores and linked with primary

particles. In this work, we synthesized the YSZ aerogel using sol-gel method and supercritical drying step. To enhance the thermal stability at high temperature, we mixed sodium silicate based inorganic binder. Thermal conductivity of YSZ aerogel and composite was measured by laser flash method. We coated the YSZ aerogel slurry on the superalloy specimen, and then found out better thermal insulating performance than conventional YSZ thermal barrier. These results indicate that the YSZ aerogel composite can improve the thermal endurance of thermal barrier at high temperature.

### Poster Session

Room: Grand Ballroom Foyer

5:30 PM

#### (MCARE-P001-2018) Evaluation of the Photoelectrochemical Properties of Manganese Oxide/Cobalt Oxide Thin Films

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1. National Taipei University of Technology, Chemical Engineering and Biotechnology, Taiwan

Mesoporous manganese oxide/cobalt oxide ( $\text{Mn}_2\text{O}_3/\text{Co}_3\text{O}_4$ ) thin films were fabricated on stainless steel (SS) substrates by using electrodeposition. In this work, the electrodeposition solutions containing manganese acetate, cobalt acetate, and sodium sulfate under acidic conditions were used. The structural and photoelectrochemical properties of the thin films were investigated by a number of techniques, such as X-ray diffraction (XRD), BET specific surface area, field emission scanning electron microscopy (FESEM), energy dispersive analysis of X-ray (EDX) and Mott-Schottky measurement. The XRD, FESEM and EDX showed the formation of a dual phase mixture consisting of interconnected pores. The band gaps  $\text{Mn}_2\text{O}_3$ ,  $\text{Co}_3\text{O}_4$  and  $\text{Mn}_2\text{O}_3/\text{Co}_3\text{O}_4$  determined from the PL spectra were in the range of 2.58-2.70 eV, corresponding to absorption wavelengths of 459-480 nm. The flat band potentials of these samples were located between -0.218 and +0.319 V versus Ag/AgCl electrode by using the Mott-Schottky measurements. The maximum photocurrent density was found to be  $1.72 \text{ mA cm}^{-2}$  in 0.1 M potassium hydroxide on the  $\text{Mn}_2\text{O}_3/\text{Co}_3\text{O}_4$  thin film under the illumination using a 300 Xenon lamp system with the light intensity kept at  $100 \text{ mW cm}^{-2}$ . These visible light responsive thin films are capable for various industrial applications such as methanol and hydrogen production.

#### (MCARE-P002-2018) In-situ Growth Nano-catalyst for Diverse Energy Devices

Y. Kim<sup>\*1</sup>; J. Myung<sup>1</sup>

1. Incheon National University, Department of Materials Science and Engineering, United Kingdom

Facilitating chemical and electrochemical reactions requires well-designed catalysts where transition metal nanoparticles are deposited on high-surface supports. Various preparation methods have been developed to enhance the catalytic activity for the reactions, such as impregnation or several types of deposition methods. However, they still have the limited control over distribution and anchorage of the deposited particles during preparation or ageing, which causes that metal particles away from oxide supports are agglomerated. Recently, In-situ metal exsolution from A-site deficient perovskite has been recently reported to use as high-temperature catalysts for solid oxide cells (SOCs). It show to prevent metal agglomerations by highly dispersed metal nanoparticles anchored on the perovskite supports, but the metal-exsolved perovskites have been only applied to high-temperature electrochemical systems. In this study, the perovskites which can exsolute Ni, Ni-Fe Alloy, Fe metals, were prepared to show the metal-exsolved perovskites are effective for the OER catalysts. The Ni-Fe alloy was formed from perovskite after reduction process, which exhibited more reduced overpotential than the single Ni and Fe nanoparticles exsolved on the perovskites. The

results suggest that the Ni-Fe alloy exsolved on the perovskites is a promising catalyst for low-temperature electrochemical reactions.

#### (MCARE-P003-2018) Preparation of Si/C Anode Material with PVA Nanocomposite for Lithium-ion Battery by Electrospinning

S. Choi<sup>\*1</sup>

1. Pukyong National University, Republic of Korea

Anode materials of rechargeable lithium-ion batteries have been developed to have high power density and long cycle life. Among them, silicon (Si) is considered to be a promising anode material for lithium-ion batteries (LIBs) with its high capacity of 4,200 mAh/g ( $\text{Li}_{4.4}\text{Si}$  phase). However, the large volume expansion and contraction of Si during lithiation and delithiation leads to rapid capacity decrease. Meanwhile, a binder is homogeneously mixed with active materials to maintain electrical contact. Polyvinyl alcohol (PVA) is known to form a hydrogen bonding with partially hydrolyzed silicon oxide layer on Si nanoparticles. The decrease of its cohesiveness followed by the large volume change of Si also remains unsolved. Thus, we have introduced the electrospinning method to weave active materials in a stable nanofibrous PVA structure, where stresses from the repeated volume change of Si could be contained. It was confirmed that the capacity retention of Si-based LIBs using electrospun PVA matrix is higher compared to those prepared by the conservative method (dissolved in slurry only); the 15<sup>th</sup> cycle capacity retention ratio based on the 2<sup>nd</sup> cycle was 55% for the electrode with electrospun PVA matrix, compared to 38% and 23% for the electrodes with PVdF and PVA binders only.

#### (MCARE-P004-2018) Molecular Precursor Approach to Lithium-vanadate Nanorods as Anode Materials for Lithium-Ion Batteries

O. Ojelere<sup>\*1</sup>; S. Mathur<sup>1</sup>

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One of the biggest and critical problems researchers attempt to solve in lithium-ion batteries is the dendrite formation that develops after repeated charges, causing batteries to short-circuit and sometimes explode. To approach this,  $\text{Li}_3\text{VO}_4$  with working voltage between 0.5~0.8 V (vs  $\text{Li}^+/\text{Li}$ ) is being considered as an option to avoid lithium dendrite growth. In this study, highly crystalline nanosized  $\text{Li}_3\text{VO}_4$  has been synthesized from novel bimetallic complexes containing both vanadium and lithium with molecular formula  $[\text{LiV}(\text{O}^t\text{Bu})_4\text{LiN}[\text{Si}(\text{CH}_3)_3]]$  (1) and  $[\text{V}_8\text{Li}_2\text{O}_2(\text{OMe})_{26}]$  (2) (where Me = methyl and Bu = tertbutyl). The chemical identity of the synthesized complexes was established by single-crystal X-ray diffraction studies, cyclic voltammetry, and spectrometric studies. The crystal structure and phase purity of the synthesized  $\text{Li}_3\text{VO}_4$  were examined by powder X-ray diffraction while Transmission electron microscopy and X-ray photoelectron spectroscopy data confirmed the morphology and chemical composition respectively.

#### (MCARE-P005-2018) Composite membrane with low permeability based on sulfonated poly(phenylene oxide) (sPPO) and sulfonated silica for vanadium redox flow battery

H. Jung<sup>\*1</sup>

1. Chonnam National University, Environment and Energy, Republic of Korea

The composite membrane based on sulfonated poly(phenylene oxide) (sPPO) and sulfonated silica ( $\text{sSiO}_2$ ) is synthesized for the application of redox flow battery (RFB). The introduction of a sulfonic acid functional group to PPO and  $\text{SiO}_2$  is confirmed by Fourier Transform Infrared Spectroscopy (FT-IR). The proton conductivities of the sPPO and composite membranes are 0.050 and 0.077 S/cm, respectively. The increased proton conductivity of the composite membrane can be attributed to the introduction of sulfonic acid functional group in the membranes. In addition, inorganic silica particles can be used as a barrier for vanadium permeation through the membrane. Permeabilities of Nafion 212 and composite membranes are  $2.22 \times 10^{-7}$ , and  $4.76 \times 10^{-9} \text{ cm}^2 \text{ min}^{-1}$ ,

respectively. Based on those experimental results, low cost composite membrane can be a candidate for RFB system.

#### (MCARE-P006-2018) Electrochemical characterization of Graphite/Sulfur dye mixtures

W. Lee\*<sup>1</sup>; M. Kim<sup>1</sup>; M. Kim<sup>1</sup>; V. M. Nagulapati<sup>1</sup>; K. Kim<sup>2</sup>; S. Lee<sup>1</sup>

1. Pusan National University, Department of Organic Material Science & Engineering, Republic of Korea
2. Pusan National University, School of Materials Science and Engineering, Republic of Korea

Lithium-ion batteries are commercially applied in mobile applications such as portable electronic devices, electric vehicles, as well as large-scale energy storage. For enhanced anode, doping specific materials, such as sulfur, nitrogen, phosphorus, and tin on the graphite or graphene is studied conventionally. Although these kinds of studies lead to development of lithium-ion batteries, the related methods are still too complex for mass production and need high temperature. Herein, we report a mixture of graphite and dyestuff, which containing nitrogen and sulfur, to substitute for doped anode. The electrochemical performance is significantly improved by simple mixing. We demonstrated that optimum amount of additional agent composed with nitrogen and sulfur to enhance electrode's columbic efficiency and specific capacity. We also investigated the mechanism of adsorption processes by density functional theory calculations. Acknowledgement This research was supported by Global Frontier Program through the Global Frontier Hybrid Interface Materials (GFHIM) of the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT and Future Planning (No. 2013M3A6B1078882). This research was supported by the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (NRF-2016M1A2A2937151 and NRF-2015M1A2A2057129).

#### (MCARE-P007-2018) Investigation of electrochemical performance of TiC supported antimony-tellurium bimetallic anodes

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3. Gachon University, Department of Chemical and Biological Engineering, Republic of Korea

Lithium-ion batteries (LIBs) are one of the most popular rechargeable batteries for electronic devices such as portable devices, electric vehicles, and energy storage system. Graphite has theoretical capacity 372mAh g<sup>-1</sup>, but it is not suitable for large-scale devices due to low theoretical capacity. Non-graphite anode materials show volume expansion and it leads to pulverization of the electrode that causes drop the stability. Considering these problems, electrochemically inactive Titanium Carbide (TiC) is used as reinforcing phase and buffer material, which has been effective improving the stability as well as mitigates the volume expansion. In this study, we investigated SbTe-TiC-C bimetallic anode using high energy mechanical milling (HEMM) and evaluated electrochemical performance with different contents of TiC through cycle performance, electrochemical impedance spectroscopy (EIS) and rate capability test. Acknowledgement This research was supported by Global Frontier Program through the Global Frontier Hybrid Interface Materials (GFHIM) of the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT and Future Planning (No. 2013M3A6B1078882). This research was supported by the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (NRF-2016M1A2A2937151 and NRF-2015M1A2A2057129).

#### (MCARE-P008-2018) Electrochemical performance of Sb<sub>2</sub>Te<sub>3</sub>-TiC anode material for sodium-ion batteries

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In the search for alternative storage options, sodium ion batteries are attracting a lot of interest due to its abundance and the fact that they apply the same technique as the current lithium ion batteries. However, volume change and cyclability remain major hurdles and since sodium ion is larger than lithium ion the problem is further intensified. One of the method suggested to solve this problem is bi-metallic compounds, by introduction of a second element which buffers the volume changes. In this work Sb<sub>2</sub>Te<sub>3</sub> bi metallic compound is prepared with TiC using high energy machine milling (HEMM) method. TiC is used as it is denser and more electrically conductive than carbon. The as prepared Sb<sub>2</sub>Te<sub>3</sub>-TiC bi-metallic compound exhibits reversible capacity of around 380mAh g<sup>-1</sup> with capacity retention of 99% after 100 cycles. We further investigated the effect of binder and FEC electrolyte additive on the stability, performance and cyclability of the electrode. Acknowledgement This research was supported by Global Frontier Program through the Global Frontier Hybrid Interface Materials (GFHIM) of the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT and Future Planning (No. 2013M3A6B1078882). This research was supported by the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (NRF-2016M1A2A2937151 and NRF-2015M1A2A2057129).

#### (MCARE-P009-2018) Fast Li-Ion Conduction of Chemically Evolved Lithium Thiophosphates with Nickel Sulfides

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The development and application of all-solid-state batteries (ASSBs) with a fast Li-ion conductor are hampered by structural instability and rigid stoichiometry restrictions. Also, the most approaches for improving conductivity have relied on the same principle, which is to control the concentration and mobility of the mobile carrier (here, Li<sup>+</sup> cation). To overcome the limitations of the conventional Li-ion conductors beyond the conventional paradigm, we demonstrate here a lithium thiophosphate prototype with via a novel principle, the control of sulfur deficiencies, for high Li-ion conduction and distinct electrochemical stability under the extended material library. The Li-ion conductivity of the solid electrolyte consisting of thiophosphate matrices is significantly enhanced by the control of sulfur deficiencies with the addition of nickel sulfide based additives. Sulfur deficiency of Li<sub>3</sub>PS<sub>4</sub> matrix controlled by nickel sulfide results in the increase of Li-ion conductivity (~2×10 mS/cm at 25°C). This new thiophosphate matrix, when integrated as a solid electrolyte in an ASSB, is also demonstrated to exhibit discharge capacities of ~116 mAh/g for LiNi<sub>0.6</sub>Co<sub>0.2</sub>Mn<sub>0.2</sub>O<sub>2</sub> cathode composites at 25°C. We believe our study makes a significant contribution to the literature because it details new solutions to problems associated with the transport of Li-ions in existing ASSBs.

### (MCARE-P010-2018) Synthesis and Characterization of a Crosslinkable Non-Conjugated Polyelectrolyte for Optoelectronic Applications

Y. Kim<sup>\*1</sup>; H. Jeong<sup>1</sup>; T. Kim<sup>1</sup>

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To avoid thermal annealing of interlayers and improve their compatibility with organic active layer, Polyelectrolyte that can be solution-process have been used as interface materials for improving solar cell, OTFT and OFET performance. Non-conjugated polyelectrolytes (NCPEs) with charged ionic groups in their structures can also be employed to tune work functions so as to reduce interfacial energy barriers and increase the built-in potential of inverted devices. Here we report an optically crosslinkable polyelectrolyte suitable for inverted PSCs. This new interlayer material allows us to better processability for high efficiency inverted PSCs from PTB7-Th:PC71BM systems. PMAB, A crosslinkable non-conjugated polyelectrolyte, was designed and applied to polymer solar cell as a buffer layer. The crosslinkable nature of PMAB was good for fabricating the devices with well-defined interface and investigating the long term stability of highly efficient polymer solar cells. After optimization of the device structures, The device of ITO/ZnO/PMAB/PTB7-Th:PC71BM/MoO<sub>3</sub>/Ag showed highly efficient power conversion efficiency (PCE), 8.78 %, with 0.81 of Voc, 15.27 mA/cm<sup>2</sup> of Jsc, and 0.71 of FF.

### (MCARE-P011-2018) Modulation of Perovskite Structures by Changing Length of Alkylammonium

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Organic lead halide (APbX<sub>3</sub>) perovskites have characteristics that make them attractive for inclusion in several optoelectronic devices, such as solar cells, photodetectors and light-emitting diodes as well as lasing applications. Especially MAPbI<sub>3</sub> (Methylammonium lead iodide) has excellent properties for the photo-absorption layer of solar cell including high extinction coefficient, middle band-gap and small exciton binding energy. However MAPbI<sub>3</sub> has a fatal disadvantage in long-term lifetime because it is sensitive to humidity and high temperature by having three-dimension structure. To overcome these drawback we manufactured 2D and quasi-2D Perovskite structures by mixing MA (Methyl Ammonium ion) and PA (Propyl Ammonium ion) and confirmed structure of 2D and quasi-2D Perovskites by using X-ray diffraction.

### (MCARE-P012-2018) Exploration M-doped SnO<sub>2</sub> to apply for OMO multilayer in order to advanced transparent conductive electrode

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There is increasing attention to improving transparent conductive electrodes for next generation displays that are being developed for energy and electronics. The advanced devices require new electrodes with lower resistivity and higher transmittance previously achieved. In addition, flexibility is demanded. The oxide-metal-oxide(OMO) multilayer structure has been studied because it can be obtained low resistivity, high transmittance as well as flexibility. The oxide layer in OMO multilayer is important factor due to obtaining high transmittance by anti-reflective effect and protecting metal layer from oxidation. In addition, it assists to obtain thin and smooth metal layer. As an oxide layer, SnO<sub>2</sub> based films have been researched because is inexpensive and has wide band gap (3.6 eV). In this work, we optimized M-doped SnO<sub>2</sub> composition using continuous composition spread(CCS) method and proceeded optical simulation using Essential Macleod Program (EMP). Subsequently, we fabricated

the M-doped SnO<sub>2</sub>/Ag/ M-doped SnO<sub>2</sub> multilayer structure. The composition of M-doped SnO<sub>2</sub> was confirmed. Electrical and optical properties of M-doped SnO<sub>2</sub>/Ag/M-doped SnO<sub>2</sub> deposited on PET were measured by 4 point probe and UV-Visible spectroscopy, respectively.

### (MCARE-P013-2018) Study of photovoltaic cells with active layer consist of hybrid compounds

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The aim of this work is present of the influences of composition of the material and manufacturing conditions of the photovoltaics cells (OPv) with the hybrid bulk heterojunctins. The layers were produced by use small molecular compounds: the metal-phthalocyanine (MePc) and perylene derivatives (PTCDA) with the addition of semiconducting dioxides nanoparticles. Two kinds of metal phthalocyanines (NiPc, TiOPc) were used as donor material and as a acceptor was used perylenetetra-carboxylic dianhydride (PTCDA). The used depositing technique allows to using thin layers of materials in a fast deposition process. The research was based on the estimate of composition of bulk heterojunction, the examination of the optical properties studies of the heterojunction and its implementation to photovoltaic architecture surface. The produced photovoltaic cells parametres were determined on the basis of current - voltage characteristics. The researches of structure of obtained layers were conducted by usingscannind electron microscope (SEM). The quantitative determination of surface topography by determining RMS and R<sub>a</sub> coefficients were perform by atomic force microscopy (AFM). In order to determining the optical properties of films the UV-Visible spectroscope have been utilize. Current - voltage characteristics were to determine the basic photovoltaic parameters using a dedicated device.

### (MCARE-P014-2018) Researches of photovoltaic cells with hybrid active structures containing low molecular materials and nanoparticles

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In this paper the aim of Athors was obtaining getting the highest possible efficiency of hybrid organic - inorganic solar cells and examination the influence of conditions of manufacturing technology as well as composition of the materials and the parameters of photovoltaics devices. The hybrid structure was fabricated by use molecular compound (metal-phthalocyanine (MePc)) used as donor material, and the nanoparticles of metal oxides (Bi<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZnO) used as acceptor materials. The heterojunction thin films were used in the structure of photovoltaic cells of ITO/PEDOT:PSS/nanoparticle - MePc /Al, and compared to organic cells with structure ITO/PEDOT:PSS/ perylene derivative-MePc /Al. The analysis carried out included the results of the research of properties of active layers as composition, surface morphology and structure and optical properties of the obtain thin films. Based on the results of these studies, the manufacturing process of thin films that forms the hybrid heterojunction has been optimized. The resultant performance of produced photovoltaic cells have been determined on the basis of current-voltage characteristics. The proposed novelty is the production of new hybrid organic-inorganic connections as well as the use of a combination of different types of nanoparticles allowing the use of differences in their optical properties and particle size.

**(MCARE-P015-2018) Study of photoanodes consisting of ceramic nanowires**T. Tanski<sup>\*1</sup>; P. Jarka<sup>1</sup>; M. Szindler<sup>1</sup>; W. Matysiak<sup>1</sup>

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The purpose of the work was to produce photoanodes with low interfacial electron recombination and fast electron transport. This is the result of the use of photoanode material with a very large specific surface area. In the first stage of anodes manufacturing is the depositing of the nanostructured materials with use a doctor blading technique on a glass substrate with a fluorine doped tin oxide layer (FTO). That prepared layers were subjected to annealing process at the oven temperature to remove organic components. Then on the prepared medium has been deposited a N3 dye. In order to determine the surface of layers, the following tests were carried out: topographic studies using a stereoscopic microscope, surface morphology tests scanning electron microscope, qualitative studies of the chemical composition using the energy dispersive spectrometer (EDS). Investigations of optical properties of layers were made using the spectrophotometer equipped with a xenon lamp with a wavelength range from 190 to 1110 nm. Absorbance of the layers was measured before and after dye deposition. The research has shown the prospect of using nanowires in the architecture of photoanodes. The absorption spectra of structures shows the additional absorption bands that testify to optical transitions in the visible spectrum, in which the charge from the highest occupied molecular orbital is transferred to the lowest unoccupied molecular orbital.

**(MCARE-P016-2018) Optimization of hybrid structures for improving efficiency of photovoltaic devices**T. Tanski<sup>\*1</sup>; P. Jarka<sup>1</sup>; W. Matysiak<sup>1</sup>

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In this paper Authors focused on production of the hybrid structures containing organic layered or bulk donor-acceptor interfaces enriched with inorganic nanoparticles. The aim of this work has been the obtaining high efficiencies of solar energy conversion of photovoltaic cells containing Poly(3-hexylthiophene)/Phenyl-C61-butyric acid methyl ester organic heterojunction. The work related to insertion of inorganic nanoparticles (ZnO, Bi<sub>2</sub>O<sub>3</sub>) in the interface between the donor and acceptor materials. Manufactured in this way organic - inorganic hybrid structure improving the formation and transport of the excitons. The final product was a hybrid cell containing the anode in the form of indium tin oxide layer (ITO) thinning), poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT PSS) hole transporting layer (HTL), P3HT PCBM heterojunction with nanoparticles, lithium fluoride (LiF) electron transporting layer and silver (Ag) cathode. The studies have included structure and surface morphology of produced layers as well as optical and electrical properties. Next the obtaining cells has been subjected the tests of electrical properties and current-voltage characteristics. In this work the proposed innovation is the creating the hybrid structure by the application organic-inorganic connections in donor-acceptor junctions and also new is the use of modern nanoparticles (Bi<sub>2</sub>O<sub>3</sub>).

**(MCARE-P017-2018) Nanopatterning hole extraction layer for inverted planar perovskite solar cells**H. Yang<sup>\*1</sup>; Y. Wang<sup>1</sup>; W. Rho<sup>2</sup>; T. Mahmoudi<sup>1</sup>; Y. Hahn<sup>1</sup>1. Chonbuk National University, School of Semiconductor and Chemical Engineering, Republic of Korea  
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Organometal halide perovskite solar cells (PSCs) have exhibited a rapid increase in energy conversion efficiency. PSCs are emerging as one of the most promising candidates for next-generation photovoltaic technology due to strong absorption over the incident solar

spectrum, high carrier mobility, and simple processes such as solution techniques at low temperatures. The increasing light harvesting is the best way to improve the energy conversion efficiency of solar cells. Because the perovskite device consist of thin film layers, it is difficult to adapt the light harvesting materials in perovskite solar cells with well crystal quality of perovskite film. Nanoimprinting technique has been regarded as an effective method to construct nanostructures for improving light absorption in optoelectronic devices. Here we used nanoimprint lithography technique to form highly uniform and well-designed nanopatterning hole-extraction layer in inverted planar perovskite solar cells. Compared to the plain layer of hole-extraction layer, the nanopatterned device resulted in high photocurrent density and thus improvement of light harvesting efficiency.

**(MCARE-P018-2018) Ambient-air-solution-processed efficient and highly stable perovskite solar cells based on CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>Cl<sub>x</sub>-NiO composite with Al<sub>2</sub>O<sub>3</sub>/NiO interfacial engineering**Y. Wang<sup>\*1</sup>; T. Mahmoudi<sup>1</sup>; H. Yang<sup>1</sup>; K. S. Bhat<sup>1</sup>; Y. Hahn<sup>1</sup>

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The poor air-stability and reproducibility of perovskite solar cells (PSCs) have prevented the practical applications of the devices that can withstand sustained operation under ambient air conditions. Here, we report all-ambient-air-solution-processed PSCs based on CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>Cl<sub>x</sub>-NiO composite film with inserting Al<sub>2</sub>O<sub>3</sub>/NiO at the TiO<sub>2</sub>/perovskite interface in a cell configuration of FTO/c-TiO<sub>2</sub>/mp-TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>/NiO/MAPbI<sub>3-x</sub>Cl<sub>x</sub>-NiO/spiro-OMeTAD/Au. The interface engineering with Al<sub>2</sub>O<sub>3</sub>/NiO not only improves crystalline quality of perovskite films and enhances charge transport, but also effectively suppresses carrier recombination. This composite-based interface engineering PSCs showed a high power conversion efficiency (PCE) of 18.14 % and excellent reproducibility with average 16-18 % PCE for 35 devices. More importantly, the devices without encapsulation showed a significant enhancement in long-term air-stability; the device photovoltaic parameters stabilized after 20 days and sustained its stability over 210 days with retaining ~100% of its original V<sub>oc</sub>, ~94% of J<sub>sc</sub>, ~91% of FF and ~86% of PCE in an ambient environment.

**(MCARE-P019-2018) Spontaneous etching of oxide and sulfide underlayers during Cu<sub>2-x</sub>S ALD**R. E. Agbenyeye<sup>\*1</sup>; B. Park<sup>1</sup>; T. Chung<sup>1</sup>; C. Kim<sup>1</sup>; J. Han<sup>2</sup>1. Korea University of Science and Technology, KRICT School, Advanced Materials Department, Republic of Korea  
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The high diffusivity of Cu<sup>+</sup> ions in the hexagonal-close-packed structure of Cu<sub>2-x</sub>S often leads to interesting and sometimes unexpected observations. Herein, we present the etching of oxide and sulfide thin film underlayers during the atomic layer deposition of Cu<sub>2-x</sub>S. Infiltration of the underlayers by highly mobile Cu<sup>+</sup> ions was identified as an essential step that precedes the etching process. However, it is suspected that the eventual etching of the underlayer, and the etch rate strongly depend on the lattice or bond dissociation energy of the underlayer material. Thin films of ZnS, ZnO, SnS, and SnO were etched to different degrees during the deposition of Cu<sub>2-x</sub>S while SnO<sub>2</sub> exhibited a high resistance to etching. Interestingly, a selective removal of Zn<sup>2+</sup> was observed when a ternary Zn<sub>1-x</sub>Sn<sub>x</sub>O film was used as underlayer. Based on XPS results, and the observations from other supplementary experiments, a possible reaction mechanism for the etching process was proposed. Finally, the etching phenomenon was extended to the synthesis of Cu<sub>2-x</sub>S 3D structures (nanowires) which have the potential of being employed as effective absorbers for photovoltaic cells.

## (MCARE-P020-2018) Highly oriented BiFeO<sub>3</sub> films grown by atomic layer deposition with great performance of ferroelectric properties

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BiFeO<sub>3</sub> (BFO) ultrathin films with total thickness less than 10 nm were deposited on LaNiO<sub>3</sub>-coated Si (001) substrates by atomic layer deposition (ALD) at temperature range of 480°C-550°C. For comparison, a sample fabricated by radio frequency (RF) magnetron sputtering with the same thickness also prepared. The x-ray diffraction investigated the crystalline present only BFO phase in the films. Synchrotron X-ray diffraction anomalous fine structure (DAFS) also certified well valence bonding through BFO (001) diffraction peak. The stoichiometric of BFO from XPS indicated ALD has much better proportion ratio than RF which also agreement to synchrotron X-ray DAFS results. Moreover, the layer structure and morphology from the high-resolution TEM and AFM showed ALD sample presented fairly good coverage and conformal than RF sample. In the results, the BFO films by ALD shows excellent leakage for at least 1000 times improvement respect to RF, which is suitable for ferroelectric random-access memories devices fabrication. The highest remanent polarization value was observed from the hysteresis loop with  $2Pr=2.0 \mu\text{C cm}^{-2}$  for the BFO thin film prepared at 500°C. This remanent polarization value shows strong correlation on growth rate; the highest crystalline quality appeared while the growth rate closely to theoretical value with proper temperature.

## (MCARE-P021-2018) Development and Evaluation of Energy Harvester in Alarm System for Movement Status Monitoring of Rotating Machines

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A self-powered piezoelectric energy harvester was developed for application in a wireless sensor node. The energy harvester was evaluated using the power generation characteristics of the wireless sensor node for structural diagnosis of the rotating machines. The self-powered wireless sensor node was set to measure the temperature and vibration frequency of the rotating machines. However, in most practical scenarios, ambient vibrations vary in terms of frequency varying and are sometimes completely random, with energy distributed over a wide frequency range. Therefore, it is necessary to increase the bandwidth of the energy harvester. For this purpose, a bender-type harvester was designed. The experimental results demonstrated that the bender-type energy harvester could generate a maximum output power of 6.42 mW, with an acceleration of 1.0 g ( $1 \text{ g} = 9.8 \text{ m/s}^2$ ) and frequency of 28 Hz. The piezoelectric energy harvester was placed on the surface of a rotating machine. In this work, we show the results of making and evaluating a unit module for piezoelectric energy harvesters for diagnosis of a vibrating rotating machine.

## (MCARE-P022-2018) Ceramics materials structures, energy and fractal frontiers

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In science and technology, tools are always adjusted to the problem, i.e. orderly packed atomic structures suits Euclidian geometry, which is not suitable for rather characterized particles flows and irregular structures. It is fact that energy transformations are permitted on a small scale. The modern Material Science faces new frontiers priorities which opens directions within deeper structure knowledge down to nano and towards new and alternative energy sources. Through our research, we recognize that BaTiO<sub>3</sub> and other ceramics have fractal configuration nature based on three phenomena. Ceramic

grains fractal shape, so called "negative space" (pores), Brownian fractal particles motions. The stress in this note is set on super inter-granular capacity in function of higher energy harvesting and energy storage. Constructive fractal theory recognize microcapacitors with fractal electrodes. The method is based on iterative process of interpolation. Intergranular permeability is a function of fundamental thermodynamic parameters (temperature, Gibbs free energy).

## (MCARE-P023-2018) Barium-titanate ceramics microstructure Minkowski hull analysis

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Technological parameters and different additives can be used to control BaTiO<sub>3</sub> based materials structure. In this paper, Yb<sub>2</sub>O<sub>3</sub> doped BaTiO<sub>3</sub>, sintered from 1320 to 1380 °C, microstructure (by using SEM/EDS and quantitative metallography) and dielectric properties have been investigated. Correlation between microstructure and dielectric properties, based on fractal geometry and micro-contact surfaces, has been developed. Using the fractal descriptors of the grains contact surface, a reconstruction of microstructure configurations (grains shapes, intergranular contacts), has been successfully done. Obtained results indicated that fractal analysis of different shapes contact surfaces, are important for BaTiO<sub>3</sub>-ceramics microstructure and dielectric properties prognosis. The ceramics grain's morphology pointed out developing new structure analytical methods validity. Model based on Minkowski hull is presented as new tool for structure research. Materials properties prognosis is determined by correlations synthesis-structure-property. The fractal BaTiO<sub>3</sub>-ceramic grains investigation, concerning the relationship between temperature and contact surface area is also introduced.

## (MCARE-P024-2018) Structural, optical, and electrical behaviors in lead free [KNbO<sub>3</sub>]<sub>1-x</sub>[(BaNi<sub>1/2</sub>Nb<sub>1/2</sub>O<sub>3-δ</sub>)]<sub>x</sub> electroceramics

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Herein, we present our results on structural, optical, dielectric, charge transport and ferroelectric behavior of a solid solution  $[\text{KNbO}_3]_{1-x}[(\text{BaNi}_{1/2}\text{Nb}_{1/2}\text{O}_{3-\delta})]_x$  for  $x = 0.1$  and  $\delta = 0.25$  (KBNNO). The samples were prepared by standard solid-state reaction method. Formation of ferroelectric orthorhombic phase of the as synthesized samples were confirmed using x-ray diffractometry. T-dependent Raman spectra measured up to 800 K suggest absence of any structural phase transition. A direct optical band gap  $E_g$  of 3.16 eV was estimated from analyses of the diffuse reflectance spectra. Investigations on T-dependent dielectric behaviors on a metal-ferroelectric-metal capacitor suggests a broad peak with discernible dispersive features with frequencies indicating its relaxor-like behavior. A slim P-E loop measured up to 2000 V corroborates its relaxor behaviors. The frequency dependence of AC conductivity showed typical features of universal dynamic response and satisfy the known power law,  $\sigma_{ac} = \sigma_{dc} + A\omega^n$ . The I-V characteristic curves measured in between  $\pm 600$  V at several temperatures (100-500 K) suggest a typical Schottky type (diode) behavior. The vibrating sample magnetometer results at room temperature show a linear magnetization curve with negative slope indicating its diamagnetic behavior. Our studies reveal KBNNO has the potential for ferroelectric device applications.

## (MCARE-P025-2018) Preparation of Ni-based alloy electrodes for high-performance thermoelectric Mg<sub>2</sub>Si modules

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Magnesium silicide (Mg<sub>2</sub>Si), owing to its non-toxicity, light weight, low cost, and composition based on elements that are abundant

in the Earth's crust, has been identified as a promising candidate for developing mid-temperature thermoelectric materials. For the industrialization of this material, the reduction of the contact resistance between the electrodes and Mg<sub>2</sub>Si-based thermoelectric elements is essential. We have previously reported the synthesis of a series of Ni electrodes using a monobloc sintering technique with a low contact resistivity of 10<sup>-10</sup> Ω m<sup>2</sup>. However, the contact resistivity was found to increase by heating with air at practical operating temperatures (~900 K) in a few tens of hours. For practical applications, especially for vehicles, the preparation of electrodes with lower contact resistivity and high temperature durability is vital for the fabrication of high-performance Mg<sub>2</sub>Si thermoelectric modules. In this report, the heat durability and the reduction of the contact resistance of Ni-based alloy electrodes are examined. These electrodes were fabricated by the conventional paste printing method. The resulting Ni-Au, Ni-Pd, and Ni-Al alloy electrodes exhibited a lower contact resistance value of approximately 10<sup>-11</sup> Ω m<sup>2</sup>. Experimental information on the degradation of the contact resistivity associated with interdiffusion and oxidation will also be discussed.

**(MCARE-P026-2018) Electronic thermal transport behavior of metal-dispersed Ti<sub>2</sub>O<sub>3</sub> composites by metal-insulator transition**

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Recently, concerns regarding global warming and fossil fuel depletion have been growing as a result of the increase in the consumption of fossil fuel-derived energy. For the realization of a sustainable society, thermal energy must be effectively utilized. In this regard, the development of advanced thermal management materials for the control of phonons can be envisaged as a plausible solution. The relationship between thermal energy transfer, electronic properties, and atomic- to macro-scale material structures has been intensively studied to integrate this fundamental knowledge to the thermal management field. In recent years, heat transfer control based on electronic and structural phase transitions has been investigated using metal-insulator transition (MIT) materials. In general, the changes in the electron thermal conductivity triggered by MIT are estimated to be of the order of several W/mK. Therefore, a significant increase in the effect on electronic thermal conductivity induced by MIT is essential for thermal switch applications. In this work, we report the increase in the MIT-induced effect on the electronic thermal conductivity of microstructure-controlled Ti<sub>2</sub>O<sub>3</sub>-metal composites at approximately 450 K. Details of the relationship between the thermal transport change of MIT and the microstructure will also be discussed.

**(MCARE-P027-2018) Preparation of Highly Textured and Porous Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> Ceramics for Thermoelectric Applications Using a Topotactic Solid-State Reaction**

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Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> (CCO) is regarded as an alternative to heavy-metal-based thermoelectric materials. Recently, porous CCO ceramics with a relative density of 65% and a Lotgering factor *f* of 0.21 exhibited a superior thermoelectric performance. In this work, we have fabricated porous CCO ceramics with a higher *f* value by a topotactic solid-state reaction. Co(OH)<sub>2</sub> synthesized by a precipitation method was used as a template to form textured CCO ceramics. A mixed powder of Co(OH)<sub>2</sub> and CaCO<sub>3</sub> was uniaxially pressed into pellets under a pressure of 500 MPa and then converted into a single phase of CCO by a heat treatment at 900 °C for 8 h under flowing O<sub>2</sub>. The (001) plane of Co(OH)<sub>2</sub> in the green compact was found to be oriented perpendicular to the pressing direction. The resulting CCO ceramics were also highly oriented and showed a high *f* value of 0.70 for the (001) planes. Because both Co(OH)<sub>2</sub> and CCO have similar edge-sharing CoO<sub>2</sub> layers, (001)-oriented CCO ceramics were obtained via a topotactic reaction. Despite the porous structure

(relative density = 56%), the sample exhibited relatively low resistivity of 26.0 mΩ•cm and high Seebeck coefficient of 176 μVK<sup>-1</sup> at 920 K. From Eucken model, thermal conductivity and ZT value of the porous CCO at 920 K were estimated to be 0.964 Wm<sup>-1</sup>K<sup>-1</sup> and 0.11, respectively.

**(MCARE-P028-2018) New luminescent molecules with novel structure: Design, synthesis, spectral characterization and application in cell imaging**

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In this work, a series of new functional BODIPY derivatives with indole moieties containing different substituted groups have been synthesized and characterized by NMR, FTIR and HRMS measurements. These new compounds exhibited the different UV-vis and PL spectral phenomena due to their varied molecular structures in various solvents with different polarities, suggesting presence of positive solvatochromism. Theoretical calculations and CV results showed that the electron-withdrawing group located in indole moiety contributed to increase of the oxidation potential of the whole molecular system, while the electron-donating group was the opposite. Due to influences of the different substituents at 5-position of indole such as methyl, 3-thiophene, bromine, nitro and amido etc, the resulted functional BODIPY derivatives indicated a different sensitivity to pH changes. Moreover, they could also be appropriately applied as cell imaging materials due to their good physical chemical characteristics and excellent biocompatibility. Especially, the fluorescence spectra of BODIPY derivatives showed a linear increased relationship between logarithms of fluorescence intensity and solvent viscosity, implying its potential application to test the intracellular viscosity changes of the living cell for disease diagnosis. (NSFC NO.21374046)

**(MCARE-P029-2018) Mesoporous Ni/MgO-MgAl<sub>2</sub>O<sub>4</sub> Catalyst Promoted by Samarium-Stabilized Ceria for Steam-CO<sub>2</sub> Reforming of Methane**

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Ni/MgO-MgAl<sub>2</sub>O<sub>4</sub> catalysts with mesoporous structure for steam-CO<sub>2</sub> reforming of methane (SCR), as promoted and unpromoted by ceria and samarium-stabilized ceria (SSC), were fabricated by the co-impregnation method, and their catalytic activities were compared. Promotion by SSC remarkably enhanced the catalytic activity and stability of the mesoporous catalysts in the SCR reaction. The conversion rate of CH<sub>4</sub> and CO<sub>2</sub> by the SDC-promoted catalyst significantly increased, yielding results that were 13.4% and 69.1% higher than those of the non-promoted catalyst even under the harsh condition at 650 °C for 20 h, with a gas hourly space velocity of 20,000 h<sup>-1</sup>, where the carbon deposition is thermodynamically more favorable. The enhanced conversion rates were mainly affected by the basicity of the SDC-promoted catalyst. The total amount of coke formation by the SDC-promoted catalyst greatly decreased by approximately 72.5% from that produced by the non-promoted catalyst. As a result, the long-term stability in the SCR was significantly enhanced by the high carbon resistance of catalysts promoted by Sm-stabilized ceria with high oxygen-storage capacity.

**(MCARE-P030-2018) Polyvinylpyrrolidone nanofibers filled by TiO<sub>2</sub> NWs: Synthesis, structural and optical investigation of the novel type of nanocomposite material**

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The aim of study was prepare the polyvinylpyrrolidone (PVP) nanofibers filled by titanium oxides (TiO<sub>2</sub>) nanowires and investigation of their morphology, structure and optical properties. The polymer and composites nanofibers were obtained using electrospinning method

from PVP/EtOH solutions doped by nanofillers. The investigations of influence of process parameters on the morphology obtained fibrous mats were carried out on the basis of their images of surface topography obtained using SEM. The incorporation of used TiO<sub>2</sub> nanowires in the volume of PVP nanofibers were confirmed by EDX. A TEM was used along with XRD in order to analyze the structure of obtained materials. Using the modified Swanepoel method, which the authors proposed, and the recorded absorbance spectra determined the banded refractive index  $n$ , real  $n'$  and imaginary  $k$  part of the refractive index as a function of the wavelength, complex dielectric permeability  $\epsilon$ , real and imaginary part  $\epsilon_r$  and  $\epsilon_i$  of the dielectric permeability as a function of the radiation energy of the produced composite materials. The analysis of the energy gap of the prepared PVP/TiO<sub>2</sub> NWs composite nanofibers were determined by spectral analysis of the absorbance in the function of the energy of radiation carry out using a UV-Vis spectrophotometer.

### (MCARE-P031-2018) Novel types of the polymer nanocomposites with 0D and 1D SiO<sub>2</sub>, TiO<sub>2</sub> and Bi<sub>2</sub>O<sub>3</sub> nanostructures

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Subject of the research are innovative composite nanostructured materials with polymer matrix, which are reinforcement by the use ceramic phase in the form of composite bimodal ceramic nanowires of TiO<sub>2</sub>, SiO<sub>2</sub>, Bi<sub>2</sub>O<sub>3</sub>, and the manufacturing process of these materials, with these composite materials exhibit unique physical properties, including electrical properties. The electrospun 1D nanostructures were studied using scanning electron microscope (SEM) and transmission electron microscope (TEM) to analyse the influence of used temperature on the morphology and structures obtained ceramic nanomaterials. In order to examine the chemical structure of nanowires, the energy dispersive spectrometry (EDS) was used. Optical property analysis was performed on the basis of UV-Vis spectra of absorbance as a function of wavelength. Thanks to application of reinforcement phase developed by authors and precise control of their concentration in obtained composite materials, it is possible to change properties of the material to obtain dielectric materials or semiconductors. This materials can be successfully applied in process of production of advanced electronic and electrical components such as thin film transistors or supercapacitors, thanks to which big-scale energy storage is possible.

### (MCARE-P032-2018) Design and Fabrication of Antireflective Luminescent Coatings by Liquid Processes

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Transparent thin-film phosphors have attracted attention for practical and potential applications including spectral converters. Due to the fundamental characteristics of optical thin films, however, thin-film phosphors are usually less bright because of multiple internal reflection of emitted light. Lanthanide-doped phosphors commonly have higher refractive indices which also cause surface Fresnel reflection of incident light. We report here our attempts to develop highly luminescent thin-film phosphors by introducing multilayered structures, surface nanostructures, or composite structures. All the thin films studied were fabricated by combining liquid processes. Transparent bi-layer coatings consisting of a dense Y<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup>,Bi<sup>3+</sup> phosphor layer and a porous SiO<sub>2</sub> layer showed an excellent antireflective (AR) effect as well as luminescence enhancement. Moth-eye-type coatings composed of a YVO<sub>4</sub>:Eu<sup>3+</sup>,Bi<sup>3+</sup> phosphor and an Al<sub>2</sub>O<sub>3</sub> morphology modifier had the gradually changing film density and refractive index, which caused luminescence enhancement with the AR effect. The introduction of Ag nanoparticles into the moth-eye-type coatings further increased luminescence intensity without losing the AR effect, as evidenced for a CaMoO<sub>4</sub>:Eu<sup>3+</sup> phosphor with the Al<sub>2</sub>O<sub>3</sub> modifier. Our results demonstrate that the AR coatings composed of the thin-film phosphors are promising for spectral converters.

### (MCARE-P033-2018) Thermally Stable Silver Cathode for High-Performance Low Temperature Solid Oxide Fuel Cells

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Silver (Ag) is a promising catalyst candidate for solid oxide fuel cell (SOFC) cathodes in the low operating temperature range (<500°C) thanks to its high oxygen solubility, diffusivity and low cost. However, the thermal agglomeration of Ag can be severe at SOFC operating temperatures, reducing the number of active sites for oxygen reduction reactions. In this study, Ag coated with Scandia-stabilized zirconia (ScSZ) nanoparticles was proposed as a thermally stable metal cathode for low temperature SOFC. The ScSZ surface coating on the Ag cathode was performed by the DC sputtering method followed by an oxidation step at 450°C. The STEM-EDX results show that ScSZ nanoparticles uniformly cover the Ag cathode surface. As a result, the optimal amount of ScSZ coating (10 nm) recorded a higher peak power density than samples with bare Ag and Pt cathodes. The electrochemical impedance spectroscopy indicates that the polarization resistance of ScSZ coated Ag is lower than bare Ag. After long term test, the ScSZ coated Ag cathode maintained a nanoporous structure, while the bare Ag and Pt were agglomerated severely. These results indicate that the surface ScSZ coating can improve the electrochemical activity of the cathode by preventing agglomeration of the Ag cathode.

### (MCARE-P034-2018) Fabrication of composite cathode for high performance solid oxide fuel cell using a low-price commercial inkjet printer

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Inkjet printing has received a lot of attention as a useful way to quickly prototype functional ceramic materials into their desired geometry. In particular, inkjet printing has an advantage in that a functional composite material having a desired structure and composition can be easily manufactured through synthesis of inks containing raw materials and adjustment of printing parameters including color level. Recently, our group demonstrated that inkjet printing technique can be used effectively to optimize the microstructure and composition of SOFC composite cathodes. We succeeded in synthesizing lanthanum strontium cobalt ferrite (LSCF) and gadolinium-doped ceria (GDC) inks, respectively, with suitable fluidic properties for inkjet printing process. The LSCF-GDC composite cathodes were fabricated using a low-price commercial HP inkjet printer, and the composition ratio of LSCF and GDC was controlled via two color-level adjustments within the MS Publisher program. Anode-supported SOFC stack with optimized LSCF-GDC composite cathode reached a high power output above 570 mW cm<sup>-2</sup> at 650 °C. We anticipate that this study will help in the rapid prototyping and evaluation of SOFC samples that require a variety of composite electrode materials.

### (MCARE-P035-2018) Ionic conductivity in nanocrystalline ceramic electrolytes for solid oxide fuel cells (SOFC)

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Nanocrystalline ceramics are promising in their mechanical and optical properties, however effects in the nanoscale influencing the ionic conductivity are still controversial. Nanostructured electrolytes might prove to be a suitable candidate for SOFCs operating at intermediate temperatures. While some studies have shown an increase in the total conductivity due to enhanced conductivity in the grain boundaries, other studies have showed the opposite, attributed to an increase in space charge in the grain boundaries. This research aims to deepen the understanding and clarify the behavior of different ionic conductors with nanocrystalline grains using electronic impedance spectroscopy (EIS). The investigated materials will range from classic to contemporary ion conductors namely yttria stabilized



zirconia (YSZ), gadolinium doped YSZ, gadolinium doped ceria (GDC), samarium doped ceria (SDC). Fully dense nanocrystalline ceramics were obtained by a unique high-pressure spark plasma sintering (HPSPS) approach. The ionic conductivity was investigated as well as the influence of post-sintering annealing.

**(MCARE-P036-2018) A Novel Approach to Atomic-Layer-Deposited Zinc Oxide Thin Film Analysis Using Resonance Raman Scattering**

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High-performance transistors with high electron mobility and reliability are prerequisites to the design of next-generation displays. This has inspired many researchers to focus on oxide thin film transistors having excellent electrical and optical characteristics. Among popular materials used, ZnO belongs to the family of compound semiconductors with a wide band gap of about 3.4 eV. ZnO is transparent to visible light, and serves as a suitable material for devices such as lasers and LEDs. In addition, ZnO thin films have the advantage of possessing high mobilities even at low temperatures. In this study, thin films of ZnO with various thicknesses were deposited using atomic layer deposition below 404.15K. Atomic force microscopic analysis was performed to elicit information on the interface states and bonding stress within the silicon substrate as also data on surface morphology of the ZnO thin film. The phase of each deposited sample was analyzed by X-ray diffraction. Unlike X-ray diffraction, Raman spectroscopy is a technique that measures the inelastic scattering of photons, and probe the surface and molecular structure. In this study, resonant Raman spectroscopy was resorted to facilitate characterization of ultra-thin (<100 nm) films of ZnO.

**(MCARE-P037-2018) Computational Design of Electrocatalyst for High-Temperature Co-Electrolysis**

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High-temperature co-electrolysis system can solve environmental issues by reducing carbon dioxide emissions without modifying the existing infrastructure. The high-temperature technology is promising because of its high selectivity and conversion efficiency toward the products. In addition, the products, hydrogen and carbon monoxide, can also be further converted into very useful synthetic fuels. In this study, to improve conventional nickel catalysts in solid oxide electrolyzer cells (SOECs), we have derived the volcano plots of the electrolysis of carbon dioxide and steam on various transition metals through microkinetic analysis combined with DFT calculations. Based on our results, we have further investigated the nickel-based alloy materials for reverse water gas shift reaction where carbon dioxide mainly converts into carbon dioxide. From this study, we could suggest good candidates of nickel-based alloy materials with excellent activities in both electrochemical and thermochemical reactions. Our result will provide great insight to improve the high-temperature co-electrolysis system.

**(MCARE-P038-2018) Innovative approach for nano-metal particles soaked electrode of solid oxide cells**

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Reversible solid oxide cells (RSOCs) operated in severe conditions (low/high Po<sub>2</sub>, high temperature, high steam), the ideal fuel electrode materials has not been found yet to accomplish of its requirements such as electronic and ionic conductivity, and catalytic activity with strong stability in redox condition. Conventional

Ni-YSZ cermet has been regarded as the embodiment of these functionalities, but the electrode still suffered from agglomeration and oxidation during redox condition. Recent nano-structured electrode designs have been developed to microstructures consisting of a porous mixed ionic electronic conductor backbone decorated with metallic nanoparticles by impregnation method. However, these are still hindered by the lack of cost and time-effective methods. Here, a simpler alternative, will be introduced, exsolution whereby the catalytically active metal is substituted in the crystal lattice of the backbone in oxidizing conditions and exsolved on the surface as designed metal particles under reduction condition. Here I demonstrated a simple and highly effective in situ method for producing nanostructured electrodes capable of delivering high performances in both fuel cell and electrolysis mode.

**(MCARE-P039-2018) High-Throughput Study of Conduction Mechanisms in Triple Conducting Oxides**

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Although proton conducting fuel cells (PCFCs) are gaining interest for intermediate-temperature (400-600°C) electrochemical energy conversion, the high polarization resistance and decreased oxygen reduction activity in traditional cathodes at these temperatures have impeded PCFC development. Triple conducting oxides (TCOs) address these issues by rendering triple phase boundaries obsolete and enabling the cathode reaction throughout the bulk. The present work explores Ba(Co,Fe,Zr,Y)O<sub>3</sub>, a perovskite material system that includes a proven TCO, BaCo<sub>0.4</sub>Fe<sub>0.4</sub>Zr<sub>0.1</sub>Y<sub>0.1</sub>O<sub>3-δ</sub>, which transports electron holes, protons, and oxide ions. Conductivity of each type is modulated by structural variables, such as unit cell volume, as well as chemical variables, such as oxygen vacancy concentration and transition metal oxidation states. Combinatorial pulsed laser deposition of thin films is combined with high-throughput characterization methods to explore composition-induced variation in these parameters. The films' chemistry and structure are correlated to transport properties as analyzed by high-throughput electrochemical impedance spectroscopy in dry and wet (3% H<sub>2</sub>O) air at temperatures up to 500°C. These relationships contribute to fundamental understanding of mixed species transport and design of future mixed conducting oxides.

**(MCARE-P040-2018) Liquid and solid phase sintering of Ta-Cu composite for electric contact materials**

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Tantalum-Copper (Ta-Cu) composite material has shown strength to be used as electrical contact material owing to its combination of high melting point for stable thermal ability and excellent electrical properties for their better work. In this work, Ta-(50~90)Cu wt% mixture was used as raw material to manufacture Ta-Cu composite. Two solid phase pressure sintering and liquid phase sintering was carried out to fabricate bulk materials. To produce sintered Ta-Cu, SPS, Hot Press and Heat treatment were selected to manufacture each solid phase pressure and liquid phase sintering, respectively. Each samples was obtained electrical/thermal conductivity and mechanical properties by using each measuring instrument. And then sample was plastic deformed by rolling process. It is difficult to build homogeneous microstructure because of immiscible properties of Ta and Cu. Microstructure analysis of as-sintered Ta-Cu bulk materials was showed for uniform dispersion of each raw material. The decrease of Electrical and thermal conductivity values have found by decreasing Cu content.

### (MCARE-P041-2018) Fabrication of 3D Ceramic Structures via Binder Jetting Additive Manufacturing Process

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Polymers are the most utilized class of materials for 3D additive manufacturing (AM) process, however, ceramic based AM process has been considered attractive and practical recently. In this research, we have studied the production of ceramic ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and  $\text{TiO}_2$ ) based structures fabricated with the binder jetting (BJ) AM process. In the case of 3D printing made from ceramics, it is difficult to maintain the shape and strength of the product during the sintering process because of the minimum additives. Polyvinylpyrrolidone (1, 1.5 and 2 wt% of PVP) was used as an aqueous binder containing the optimum solute component, and the jetting was easily controlled by using the surfactant (0.05 wt%). The ceramic ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and  $\text{TiO}_2$ ) particles calcined at 500 °C exhibited various shrinkage and strength change because the raw materials were densified and assembled during calcination process. The ceramic structures fabricated with 1.5wt% of PVP exhibited less shrinkage and cracking compared with the ones synthesized with 1 and 2 wt% of PVP. The optimal processing parameters were successfully determined for BJ AM process to minimize shrinkage and eliminate cracking for sintering strength.

### (MCARE-P042-2018) Synthesis of Akaganeite/ $\epsilon$ - $\text{Fe}_2\text{O}_3$ Nanorods: Tuning the Concentration of Phases for Spintronic Based Applications

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Iron oxide with its high natural abundance and low cost comes out as a replacement of critical materials in various field especially in biomedical, ion exchanging and spintronic. Akaganeite ( $\beta$ - $\text{FeO}(\text{OH})$ ) although have antiferromagnetic behavior, however, shape anisotropic 1-D akaganeite induces weak ferromagnetism via uncompensated spins. But akaganeite in 1-D forms show only weak ferromagnetism and therefore coercivity is low. In this study akaganeite nanorods were synthesized and further heat-treated to transform from akaganeite to  $\epsilon$ - $\text{Fe}_2\text{O}_3$  (hard magnet phase). Heat treatment was done in the argon atmosphere at a range of temperature to synthesize different concentration of  $\beta$ - $\text{FeO}(\text{OH})/\epsilon$ - $\text{Fe}_2\text{O}_3$  samples. Exchange bias effect of different sample with varying concentration of phases were analyzed and parameter were optimized in order to achieve exchange bias near to room temperature. This increase in exchange bias was correlated with phase concentration and these arguments were well supported using TEM, FE-SEM, and XRD. Magnetic properties were analyzed using vibrating sample magnetometer (VSM). Iron oxide nanorods with near room temperature exchange bias properties may finds its application in read/write read of HDD, MRAM and magnetic sensors.

### (MCARE-P043-2018) Conversion of $\text{CO}_2$ to cyclic carbonates using a multi-ligand MOF $\text{Cu}(\text{L-Asp})(4,4'\text{-Bpy})$

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Metal-organic frameworks (MOFs) are prominent catalysts due to their porous nature, richness in metal/inherent functional groups, their synthetic or post-synthetic customizability etc. Besides, MOFs are excellent materials for  $\text{CO}_2$  capture. Amino acid based AA-MOFs are attractive catalysts, owing to their richness in acid-base sites. Henceforth, their efficacy in  $\text{CO}_2$  capture makes them prospective candidates for  $\text{CO}_2$  transformation. In this study, a multi-ligand MOF with the formula  $\{[\text{Cu}(\text{L-Asp})(4,4'\text{-Bpy})_{0.5}]\cdot\text{H}_2\text{O}\}_n$  ( $\text{CuAspBpy}$ ), was employed as a catalyst for cyclic carbonate

synthesis from epoxides and  $\text{CO}_2$  in association with quaternary ammonium halide ionic liquid co-catalyst. They showed excellent catalytic activity at mild reaction conditions without use of any solvent. They also exhibited good recyclability for several consecutive uses. DFT calculations were performed to investigate the mechanistic pathways including intermediates and transition states.

### (MCARE-P044-2018) Effect of stabilizing agents on particle size and distribution of Pt

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Pt supported catalysts have been investigated for chemical industry due to high activity in many reaction. Among them, Pt/C catalysts are most widely used in various fields such as hydrogenation and methanol oxidation. It is well known that catalyst activity is affect to particle size and distribution which are determined to preparation method and conditions. Herein, we investigated the effect of support properties and stabilizer agents on particle size and distribution of Pt. Activated carbon pre-treated was performed by acid pre-treatment. Different concentration of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  mixed solution was used for chemical treatment. The Pt/C catalyst prepared by polyol method using the sodium acetate (SA), sodium tartrate (ST), and tartaric acid (TA). All catalysts were dried at 378 K for 12 h, affording catalysts denoted as Pt/C(A\_B) (A: Concentration of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ ; B: stabilizer agents). The prepared Pt/C catalyst characterized by XRD,  $\text{N}_2$ -physisorption, FT-IR, CO-chemisorption, and FE-TEM. The CO-chemisorption results showed that Pt/C(4M\_SA) catalyst has the highest Pt dispersion of 45.2%. At the results of FE-TEM image shows that Pt/C(4M\_SA) catalyst has small particle size and uniform distribution of Pt. The results suggest that the acetate anion are strongly affects to particle size and distribution of Pt.

### (MCARE-P045-2018) Study on basic sensing principle of ion-sensitive semiconductor nanowire devices using 3D numerical device simulation

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High-performance semiconductor nanowire ion-sensitive field effect transistor (NW-ISFET) has attracted considerable attention as a next-generation device for chemical and biological sensors in the sensor field. Despite their potential applications, this technology has been limited to only academic research field due to the absence of the cost-effective and highly reliable fabrication routes. To make matters worse, lack of understanding of sensing mechanism is regarded as one of the bottleneck for a wide range of applications. To address these issues, we performed 3D device simulations of NW-ISFET based on ion-screening effect and site binding model of the electrical double layer at insulator/electrolyte interface for the ion-sensing mechanism. The simulation results are verified through comparison of our experimental data. Finally, the detailed phenomena are discussed to illuminate the origin of sensing mechanism using nanowire field effect transistor and to suggest how to enhance sensing performance. We believe that this work will support better insights to overcome bottlenecks of nanowire sensors concerning the commercialization of these technologies.

### (MCARE-P046-2018) Highly Flexible Poly(dimethylsiloxane) Nanofiber Reconstructive Electrode by Electrospinning

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Highly elastic polydimethylsiloxane (PDMS) fiber has extensive applications in various area including membrane technologies for artificial skin, wounding healing, filtration, energy generation,

sensors, catalysis, and functional textile. The liquid PDMS precursor was crosslinked in situ to form a solid core when the electrospun core shell nanofibers were deposited onto a hot-plate electrode collector. After dissolving the shell layer off the finers. We demonstrated that improved mechanical properties of PDMS nanofiber is controlled with thickness of nanofiber mats, various ratio mixed polymer solution and lay by layer. The resulted PDMS nanofiber mats were successfully evaluation used as substrates for stretchable electrode. The physicochemical properties of the PDMS nanofibers were confirmed by FE-SEM (Field-emission Scanning Electron Microscope), FE-TEM (Filed-emission Transmission Electron Microscope), EDS (Energy Dispersive X-ray Spectroscopy), FT-IR (Fourier Transform Infrared Spectroscopy), TGA (Thermogravimetric Analysis), DSC (Different Scanning Calorimetry), Tensile strength analyses.

**(MCARE-P047-2018) Effects of NiS for hematite photo anodes in Photorelectrochemical water splitting**

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Iron Oxide (Hematite) is considered as a promising photo anode for hydrogen production using solar irradiation due to its strong light absorption properties. However, the intrinsic drawbacks like low photo voltage generation, low carrier life time and high electron-hole recombination hinders its application in photo electrochemical water splitting. To overcome the issues, we proposed the novel structure combined hematite with NiS catalyst. In the photo electrochemical measurement, the onset potential of this electrode is starched in negative direction due to the enhancement in photo voltage and interface properties caused by NiS. Beyond that the formation p-n junction the interface enhances the charge separation by suppressing the carrier recombination.

**(MCARE-P048-2018) A transparent nanowire film fabricated by facile sintering process for flexible smart nanodevices**

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Wearable storage devices can malfunction due to various mechanical stresses applied over a long period of time. Therefore, there is a growing need for a flexible strategy for future flexible storage devices. Consequently, herein, we prepared a transparent acrylic polymer-coated/graphene oxide/silver nanowire (Ag NW) (A/GO/SAW) EM interference (EMI) shielding film via liquid-to-vapor pressure-assisted wet sintering. The film exhibited enhanced Ag NW network formation and antireflection (AR) effects. The wet-sintered Ag NW film had a threshold radius of curvature (ROC) of 0.31 mm, demonstrating its high flexibility, while the conventional indium tin oxide (ITO) film had a threshold ROC of ~5 mm and a thickness of 100  $\mu\text{m}$ . The EMI shielding effectiveness (SE) of the A/GO/SAW film was twice that of the ITO film at a similar transmittance (84%–85%). The optical reflectance of the Ag NW layer was reduced due to the AR effect, and the visible light transmittance was considerably improved owing to the different refractive indexes in the multilayer film. As the acrylic coating layer had a high contact angle, the film exhibited durability with little change in the SE over 500 h at 85 °C and 85% relative humidity. The multilayer film comprising wet-sintered Ag NW exhibited high flexibility and durability, making it highly applicable for use as a transparent flexible smart film.

**(MCARE-P049-2018) 3D Numerical Simulation of Solid State Hydrogen Storage System using Sodium Aluminum Hydride**

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Solid-state hydrogen storage with chemical hydride is a challenge for next-generation fuel-cell-powered transportation applications. Heat management in this system is a significant issue due to the low thermal conductivity of chemical hydride. Recently, a compressed hydride with materials of high thermal conductivity has been researched. In this work, we performed a 3D heat and mass transfer simulation to design effective solid-state hydrogen storage tanks using a compressed NaAlH<sub>x</sub> material with expanded natural graphite and graphene. Chemical kinetics and phase equilibrium are considered for chemical hydride regarded as a porous medium in hydrogen storage tank. Through this simulation, optimum design parameters of heat exchange system will be discussed.

**(MCARE-P050-2018) Computational validation of the degradation of radiation grafted anion exchange membrane via removal of vinylbenzyl trimethylammonium hydroxide**

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We have previously reported that in close to neutral and low alkalinity solutions, typical of that in alkaline anion exchange membrane fuel cells (AEMFC) and electrolyser (AEMWE) applications, degradation of the fabricated LDPE-based AEMs in terms of ion exchange capacity (IEC) loss was not mainly due to OH<sup>-</sup> ion attack on the trimethylamine (TMA) functional groups, but mainly due to the removal of the vinylbenzyl trimethylammonium hydroxide (VBTMA-OH) group as a whole via nucleophilic and peroxide radical attack, and the same was observed with other tethered amine functionalities. To validate the observed experimental data, computational methods of membrane degradation mechanism was performed using Orca program package (freeware) using B3LYP hybrid functional method. Geometry optimisation was performed on each polymer structure and frequency analysis was employed on all optimised single molecule structures to ensure that there were no imaginary frequencies. Solvent effects where incorporated in the calculation wherein water was used as implicit solvent. Both nucleophile (OH<sup>-</sup>) and peroxide radical were introduced to a VBTMA-OH dimer and the energy changes (activation energy profile) along the degradation pathway were obtained from the reaction path calculations.

**(MCARE-P051-2018) Synthesis of Graphite/Metal Nanoparticle Composites and Its Properties**

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Composites between metal nanoparticles and inorganic substrates have attracted wide attention because of their potential to yield desirable properties coming from different nano scale building blocks that possess specific mechanical, optical, electronic, or physical properties. The synthesis of valuable composites is a desirable approach to exploring their properties and applications. It is of critical interest if metal nanoparticles can be integrated with carbon-based materials to form a composite. Among the metal nanoparticle composites, it is desirable to explore the creation of synergy effects between expanded graphite (EG) and metal nanoparticles. We proposed a simple approach for the synthesis of EG/Ag nanoparticle composites by the chemical reduction of Ag ions followed by the addition of EG to the solution. We demonstrated that the EG/Ag nanoparticle composites had uniform dispersion of Ag nanoparticles on the surface of EG. In this study, we performed and evaluated the synthesis of EG/Ag nanoparticle composites by chemical reduction

of Ag ions in a reductive solution. The Ag nanoparticle size, the dispersion profile on the EG and other properties are reported according to the process conditions. We measured and discussed the thermal properties of the composites.

### (MCARE-P052-2018) Capacitive constant voltage/current source

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Discharge from a capacitor depends upon the RC time constant. Using a capacitive direct thermal-to-electric energy conversion device, which does not operate on the well-known thermoelectric Peltier, Thomson or Seebeck effects, we demonstrate that a capacitive constant voltage/current source can be fabricated. By controlling the heating profile of a direct thermal-to-electric capacitive energy conversion device, it is shown that the discharge of a capacitor can be used to provide a constant voltage/current source. By loading and isolating the charge on a high resistance, long time constant and temperature dependent high relative permittivity dielectric capacitor, a systematic change in temperature can be used to maintain the charge residing on the capacitor at constant voltage; thereby, providing a capacitive constant voltage source. Using an appropriate heat ramped capacitive thermal-to-electric energy conversion device, a constant current can be provided to the constant load circuit. Hence, by controlling the temperature profile, the direct thermal-to-electric capacitive energy conversion device can act as either a constant voltage or constant current source. The theory of the capacitive thermal-to-electric energy conversion device is presented along with experimental data showing conversion of thermal energy to electric-potential energy.

### (MCARE-P053-2018) Effect of reduced graphene oxide as a V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>-TiO<sub>2</sub> catalyst support for enhancement catalytic activity

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Nitrogen oxide (NO<sub>x</sub>) produced during the combustion of fossil fuels is a major cause for air pollution and there are many studies to control NO<sub>x</sub>. Among them, V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst is one of the most widely used technology due to good properties such as a high catalytic activity and a sulfur resistance. However, it is a challenge to reduce the amount of V<sub>2</sub>O<sub>5</sub> and WO<sub>3</sub> for the SCR catalyst while maintaining the activity, because V<sub>2</sub>O<sub>5</sub> and WO<sub>3</sub> nanoparticles are harmful to human. In this study, we presented reduced graphene oxide (rGO) using as a support of the V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>-TiO<sub>2</sub> catalyst. The rGO support provided functional sites for the well-dispersed nanoparticles on the surface, and it leads to the formation of the catalysts with increased specific surface area. The specific surface area was measured 15% higher by using rGO as a support. The rGO supported catalysts exhibited improved catalytic activity with reduced contents of V<sub>2</sub>O<sub>5</sub> and WO<sub>3</sub>. The catalytic activity was measured in a fixed-bed reactor at the operation temperature 250 – 500 °C. The activity of the catalysts using rGO were about 10 % higher than the catalyst without rGO which is the same amount of the materials in. In addition, the uniform dispersion of the materials on the rGO surface of the catalysts was shown by TEM, and detailed measurements of the acid site analyzed by FTIR and NH<sub>3</sub>-TPD.

### (MCARE-P054-2018) NO<sub>x</sub> adsorption/desorption performance on copper oxide and barium oxide co-impregnated Y-Al<sub>2</sub>O<sub>3</sub>

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Lean-burn engine technology has been widely applied for increasing fuel efficiency while decreasing the amount of emitted CO<sub>2</sub>. However, using lean-burn engine for automobile not only increases NO<sub>x</sub> emissions but also reduces the NO<sub>x</sub> removal efficiency of conventional catalytic converter. In order to develop

vehicles having both low energy and low emission, lean-NO<sub>x</sub> trap (LNT) with improved adsorption performance for NO<sub>x</sub> gas at low temperature (the emission condition of a lean-burn engine) should be developed. In this study, we developed LNT adsorbent in which CuO was co-impregnated with BaO in Y-Al<sub>2</sub>O<sub>3</sub> and evaluated its NO<sub>x</sub> adsorption/desorption performance. The characterization of the adsorbents was performed using X-ray diffraction (XRD) and nitrogen adsorption analysis. The adsorption capacity of the adsorbents was measured by a breakthrough test using a quartz flow reactor with NO<sub>x</sub> analyzer, and the desorption temperature was figured out by temperature programmed desorption (TPD). Also, the surface change of adsorbents during the adsorption/desorption was observed by in-situ FT-IR.

### (MCARE-P055-2018) Influence of Size and Surface Structure of Co<sub>3</sub>O<sub>4</sub>-supported Pd Nano-particles on CO Oxidation Activity

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Palladium(Pd) is well-known as an effective catalyst for CO oxidation while Co<sub>3</sub>O<sub>4</sub> is expected to be a good support because relatively weak Co-O bond leads to easily provide the reactive oxygen. In former studies, we synthesized various sizes of Pd particles from 2 nm to 15 nm by controlling the multiple synthesis factors and had proved that optimum Pd particle size existed for the excellent reaction activity. To reveal more intrinsic relationship between Pd particle size and the catalytic activity, we hypothesized that there is an effect of the surface structure of Pd nanoparticle with regard to its size on the reaction activity. Our density functional theory(DFT) calculation results verified that the catalytic activity of CO oxidation is changed with the surface structure of Pd. This relationship we elucidated in this study will be useful to design the highly efficient catalyst for CO oxidation.

### (MCARE-P056-2018) Rational Design of Catalyst for CO Oxidation on Transition Metal Co-doped Ceria

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As the regulations for automobile emission are strengthened, there is a growing demand for highly efficient catalysis at low temperatures. The automobile vehicles release mainly three pollutants, NO<sub>x</sub>, CO, and hydrocarbons, into the atmosphere. In this study, suitable catalysts have been developed to remove the CO. The precious metals often have high activity of CO conversion, but they are uneconomical due to the high cost. The lattice substitution with inexpensive metals into ceria (CeO<sub>2</sub>) support can be one route to increase the low temperature activity with economical consideration. In this study, we designed the enhanced catalysts for CO oxidation by means of co-doping of transition metals on CeO<sub>2</sub>. We firstly screened 13 dopant metals (8-11 groups, 4-6 periods elements, and Mn) and their combinations of co-doping through density functional theory (DFT) calculations. Then, CeO<sub>2</sub> nanoparticles co-doped with the selected transition metals (TMs) (Ce<sub>0.95</sub>TM<sup>1</sup>TM<sup>2</sup><sub>0.05</sub>O<sub>2.8</sub>) were synthesized by EDTA-citrate complexing method, which were then characterized by XRD, TEM, BET measurement. In addition, low-temperature activity was demonstrated by O<sub>2</sub>-TPD, H<sub>2</sub>-TPR, and GC. From first-principles calculations to the experimental validation, we demonstrated a good example of reasonable catalyst search to improve the low-temperature catalytic activity of CO oxidation.

**(MCARE-P057-2018) A DFT Search for High Performance Nitrogen Oxide Adsorbents among the Alkaline Earth and Transition Metal Oxides**

J. Lim<sup>\*1</sup>; J. Han<sup>2</sup>

1. University of Seoul, Chemical Engineering, Republic of Korea
2. Pohang University of Science and Technology(POSTECH), Chemical Engineering, Republic of Korea

Nitrogen oxides (NO<sub>x</sub>) are one of the main sources of air pollution, which are produced from automotive exhaust gas. To reduce NO<sub>x</sub>, Selective Catalytic Reduction (SCR) or Lean NO<sub>x</sub> Trap (LNT) is used to convert the NO<sub>x</sub> into harmless components like N<sub>2</sub>. The materials used as the adsorbents in the conversion process are mainly expensive noble metals. It is therefore necessary to reduce the costs. In this study, alkaline earth metal oxides (MgO, CaO, SrO, BaO), transition metals (Ag, Au, Cu, Ir, Ni, Pd, Pt, Rh, Fe, Ru, Co), and transition metal oxides were investigated to find out which elements are good candidates for the adsorbents of NO<sub>x</sub>. We firstly screened the adsorption energies on the most stable surfaces of those materials. Good adsorbent materials should not have too strong or too weak interaction with NO<sub>x</sub>. If the interaction is weak, the adsorbent will not bind to the catalyst, where no reaction will occur. If the interaction is strong, the product cannot be separated from the surface. Then, we investigated NO<sub>x</sub> conversion reactions on the selected materials. Our results will provide a useful insight for designing the adsorbents for NO<sub>x</sub> conversion.

**(MCARE-P058-2018) Enhanced Catalytic Activity of CO Oxidation on M/metal-doped CeO<sub>2</sub> (M = Pt, Pd, Cu, and Ni)**

M. Jang<sup>\*1</sup>; J. Han<sup>2</sup>

1. University of Seoul, Chemical Engineering, Republic of Korea
2. Pohang University of Science and Technology(POSTECH), Republic of Korea

As environmental pollution which is considerably caused by automobile exhaust gas becomes serious, the development of catalysts for reducing the pollution is actively pursued. Ceria has been widely studied because it has made a great contribution as a support for CO oxidation reaction. To improve the CO oxidation activity on CeO<sub>2</sub>, we have previously screened good dopant candidates for CeO<sub>2</sub> from all of transition and rare-earth metals. In this study, we impregnated several metals onto the metal-doped CeO<sub>2</sub> to further enhance the activity of CO oxidation. The characteristics of the catalysts were analyzed by BET, XRD, TEM, TPD, and TPR. In addition, their activities were compared by GC measurement. By comparing M/doped CeO<sub>2</sub> with M/CeO<sub>2</sub>, the interaction between the dopants and the impregnated particles was identified. There were no different peaks between M/CeO<sub>2</sub> and M/doped CeO<sub>2</sub> in XRD data because the influence of dopants in the lattice of CeO<sub>2</sub> is weak. However, we found that their combinations that are metal particles impregnated onto metal-doped CeO<sub>2</sub> further increases the CO oxidation activity compared to only the metal-doped one. Especially, Cu/Cu-doped CeO<sub>2</sub> and Cu/La-doped CeO<sub>2</sub> showed relatively high activity for CO oxidation.

**(MCARE-P059-2018) Ce-Pr mixed oxide catalysts with fibrous morphology for diesel soot (PM) combustion**

E. Jeong<sup>\*1</sup>; S. Lee<sup>2</sup>; J. Lee<sup>1</sup>; C. Park<sup>1</sup>; K. Lee<sup>1</sup>

1. Korea University, Department of Chemical and Biological Engineering, Republic of Korea
2. Korea University, Republic of Korea

PM generated by combustion of automobile engine is separated physically and burned periodically by DPF (Diesel Particulate Filter). Oxidation catalysts can be used to increase the oxidation rate of filter traps at low temperature, and oxygen storage capacity (OSC) of catalysts plays the crucial role. Ceria has been widely used for soot oxidation catalyst since it has high OSC property, and Ce-Pr mixed oxides are well known for more improved oxidation ability. Therefore, Ce-Pr based catalysts could be substitutes for pure ceria

in soot oxidation. Also, the contact between soot and catalyst is important, and morphology -controlled structure is considered to enhance catalytic performance. Fiber structure catalysts show high activity for oxidation of soot due to the network with surrounded soot particles, and could increase the number of contact points. Thus, in this study, Ce-Pr metal mixed oxide catalyst with fibrous morphology was synthesized and analyzed by TGA and several characterizations. The increased exposure of external surface and contact site between PM and catalyst decreased soot combustion temperature. Also, the optimum ratio of Ce-Pr was verified, since the doping of Pr generates more oxygen ions vacancies, which hereby affects the catalysts behavior significantly. The correlation between the activity and characterization results will be discussed further.

**(MCARE-P060-2018) Effect of calcination temperature on NO<sub>x</sub> uptake of cobalt-incorporated mixed oxides derived from layered double hydroxides**

Y. Choi<sup>\*1</sup>; K. Lee<sup>1</sup>

1. Korea University, Republic of Korea

One way to improve the fuel efficiency and reduce the CO<sub>2</sub> emissions from vehicles is to operate the engine under an excess of oxygen (lean conditions). However, the presence of excess oxygen in the exhaust gas significantly reduces the catalytic activity for nitrogen oxides (NO<sub>x</sub>) decomposition. NO<sub>x</sub> gas reacts to form photochemical smog and acid rain, so effective technology for NO<sub>x</sub> removal from vehicles is required. Lean NO<sub>x</sub> trap (LNT) is one of promising NO<sub>x</sub> removal technologies. Under lean conditions, NO<sub>x</sub> is oxidized and stored as nitrate species; under rich conditions, nitrate species are released and subsequently reduced. Therefore, to enhance the performance of LNT, development of effective NO<sub>x</sub> adsorbents is essential. Layered double hydroxides (LDHs) consist of metal hydroxide layers, interlayer anions and water. Mixed oxides derived from LDHs by thermal treatment are widely used as adsorbents and catalysts due to its high specific area, high dispersion of metal oxides and basicity. In this study, we prepared Co-Mg-Al hydroxalcalite-like compounds as precursors of NO<sub>x</sub> adsorbents using a co-precipitation method and calcined them at various temperatures between 550 and 850 °C to investigate the effect of calcination temperature on NO<sub>x</sub> uptake. NO<sub>x</sub> uptake tests were performed in a quartz flow reactor with gas mixtures of NO and O<sub>2</sub> at 150 °C.

**(MCARE-P061-2018) Rheological analysis of aluminum oxide suspensions: Effect of particle shape and pH conditions**

G. Lee<sup>1</sup>; D. Lee<sup>1</sup>; K. Jung<sup>1</sup>; T. Yoo<sup>1</sup>; B. Chun<sup>1</sup>; H. Jung<sup>\*1</sup>

1. Korea University, Chemical and Biological Engineering, Republic of Korea

Aluminum oxide is one of the typical ceramic catalyst supports used in various fields such as exhaust gas filters, improving the durability and activity of catalysts as the carrier for precious metal catalysts. To uniformly deposit catalytic suspensions or slurries on a filter substrate, their macro-/micro-rheological analysis should be well scrutinized. Rheological properties of aluminum oxide suspensions, such as viscosity, surface tension and particle motion, are significantly influenced by the internal structure and dispersion stability of particles dispersed in a continuous medium. In suspension systems, Van der Waals force and electrostatic force are applied between particles, depending on the surface charge of particles and their structures. In this study, coating suspensions with rod-like boehmite and spherical alumina particles were prepared under different pH conditions. To investigate the effect of particle shape and pH condition, various macro-rheological properties of suspensions (e.g., shear viscosity and elastic/viscous moduli) were measured using a rotational rheometer. The particle size distribution and particle motions were identified by using dynamic light scattering (DLS) and multi-speckle diffusing wave spectroscopy (MSDWS).

### (MCARE-P062-2018) Molecular Modeling Study on the Adsorption of Hydrocarbons (Propylene, n-butane and Toluene) on Metal Cation-exchanged ZSM-5 Zeolites

K. Kim\*<sup>1</sup>

1. Pukyong National University, Chemical Engineering, Republic of Korea

Hydrocarbon (HC) traps have to perform its role of preventing hydrocarbon emissions until three-way catalysts (TWCs) are activated in vehicle emission gas consecration system, because 70~80% of total HCs are emitted during this cold-emission period. In this study, the adsorption characteristics of HCs in HC trap was computationally investigated. The adsorbents and adsorbates were cation-exchanged ZSM-5 zeolites and three selected hydrocarbons (propylene, n-butane, toluene), respectively. Cations such as lanthanum (La), potassium (K), and silver (Ag) were used for cation exchange to provide hydrothermal stability to ZSM-5 zeolites. A DFT-based cluster approximation, where the catalytic site is cleaved out from the zeolite structure, was employed to save the computational capacity. Experimental results obtained by TPD (thermal programmed desorption) and TGA (thermogravimetric analysis) were then successfully explained by the calculated binding energies for the physisorption between HCs and the cluster. The hydrothermal stability of cation-exchanged ZSM-5 zeolites was also supported by the calculated geometrical factors of the cluster.

### (MCARE-P063-2018) Genetic Algorithm Using Statistical Clustering with Flexible Reliability

T. Park<sup>1</sup>; Y. Kim<sup>1</sup>; S. Lim<sup>1</sup>; B. Lee\*<sup>1</sup>; J. Lee<sup>1</sup>

1. Seoul National University, Republic of Korea

Genetic algorithm(GA) has been used to solve various problems based on its versatility. It requires long calculation time, however, when the number of variables and inter-variable dependency are high. In addition, there is a lack of reliability for determining whether the obtained solution is optimal or not. A new algorithm is developed to increase the efficiency and reliability of the LNT-pSCR exhaust gas aftertreatment system in diesel vehicles. Unlike the general GA where all the generated populations are handled, the algorithm proposed in this study classifies the population into clusters based on the statistical estimation. Through this method, the computation speed is about three times faster than the previous GA, and the error with the known optimal solution also converges to a smaller value in a shorter time. Compared with other algorithms that combine GA and clustering, the proposed algorithm shows the fastest speed, and it can perform the most iterative solving within the same time, resulting in high robustness and shortening the time to reach the optimal solution.

## Thursday, August 23, 2018

### Plenary IV

Room: Grand Ballroom A & B

Session Chair: Michitaka Ohtaki, Kyushu University

8:30 AM

### (MCARE-PLN-004-2018) Creation of active functionality utilizing abundant elements

H. Hosono\*<sup>1</sup>

1. Tokyo Institute of Technology, Materials Research Center for Element Strategy, Japan

In this talk I introduce our approach to electro-active functionality in oxide-based materials focusing on electron and hydrogen as anions. Crystals in which electrons serve as anions are called electride, which may be regarded as the crystalline form of solvated electrons. The first electride was synthesized by J.Dye in 1983 using crown-ether. The fatal drawback was extreme sensitivity to temperature

and air. It was thus a long standing issue to realize RT-stable electride since then. We reported RT stable electride C12A7:e- in 2003 using  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ (C12A7). Since then, unique electronic structure and physical properties have been elucidated; insulator-metal-superconductor transition and very low work function (but chemical inertness) are typical examples. In addition, metallic conduction at molten state is found. Recently, we reported two novel findings: Ru-loaded C12A7:e works as efficient ammonia synthesis at mild conditions and 2-dimensional electride  $\text{Ca}_2\text{N}$  and  $\text{Y}_2\text{C}$  with exceptional properties. Another focus is hydrogen anion  $\text{H}^-$  in oxides. We reported the incorporation of  $\text{H}^-$  ions in C12A7 in place of  $\text{O}^{2-}$  ions and found the UV-induced insulator – electronic conductor conversion. If  $\text{O}^{2-}$  ion sites are replaced by  $\text{H}^-$  ion,  $\text{H}^-$  would work as an electron donor. This approach has succeeded in heavy electron doping to iron-based superconductor  $\text{LaFeAsO}_{1-x}\text{H}_x$  and two Tc-dome structure has been found.

## SYMPOSIUM 2

### Advanced Electrochemical Materials for Energy Storage II

Room: Grand Ballroom B

Session Chairs: Maria Luisa Di Vona, University of Rome Tor Vergata; Aitana Tamayo, Institute of Ceramics and Glass, CSIC

9:30 AM

### (MCARE-S2-009-2018) Preparation of Nitrogen-doped Ordered Mesoporous Carbon Containing $\text{SeS}_2$ as a Cathode Materials for the Lithium-Sulfur Battery

S. Lee\*<sup>1</sup>; J. Lee<sup>2</sup>; S. Lee<sup>2</sup>; W. Kim<sup>2</sup>; H. Kim<sup>2</sup>; K. Eom<sup>1</sup>; C. Pak<sup>2</sup>

1. Gwangju Institute of Science and Technology, School of Materials Science and Engineering, Republic of Korea
2. Gwangju Institute of Science and Technology, Graduate Program of Energy Technology, School of Integrated Technology, Institute of Integrated Technology, Republic of Korea

There are many efforts to develop the post-Li battery, which can be overcome the limitations of present Li-ion battery, One important approach is to combine a Li metal negative electrode with a high capacity positive electrode such as sulfur and oxygen. However, the Li-S battery is still suffering from polysulfide dissolution, which resulted in the fast degradation. Thus, a paradigm shift is required to increase the energy density and durability of the Li-S battery. In this study, a novel cathode composed of selenium-sulfide( $\text{SeS}_2$ ), which is recently suggested for the Si- $\text{SeS}_2$  battery, and nitrogen-doped ordered mesoporous carbon (N-OMC) for the Li-S battery is investigated. The N-OMC synthesized using the 1,10-phenanthroline by the nano-template method. The N-OMC contains total 3.9 at% of N, which present as pyrrolic and pyridinic N. The  $\text{SeS}_2$ /N-OMC was prepared by infiltration of  $\text{SeS}_2$  into the N-OMC, which has 4.8 nm mesopore arranged by carbon nanorod. The novel composite showed almost 99.999% of capacity retention during 500 cycles at 0.15 A/g rate, which may come from the confinement effect of the mesopore and exit of N atom that can effectively hold the lithium-polysulfides and lithium-polyselenides. To elucidate the effect of N atom, the N-OMC with different amount of N atom will be investigated as a host material for the cathode and discussed.

9:50 AM

### (MCARE-S2-010-2018) Cation permeability of protonic, anionic and ampholytic membranes for all vanadium redox flow batteries

M. Di Vona\*<sup>1</sup>

1. University of Rome Tor Vergata, Industrial Engineering, Italy

Ion exchange membranes have many applications in electrochemical energy technologies, such as fuel cells and redox flow batteries. In most of these applications, the separator membrane must impede

the cross-mixing of ionic solutions. Important properties that an ion exchange membrane should present are i) high ion conductivity, required to minimize the Ohmic loss and to increase the voltage efficiency in batteries, ii) high ion selectivity: the separator must be permeable to the charge balancing ions of the supporting electrolyte (e.g. protons, hydrogensulfate ions or others), but must prevent permeation of the electrochemically active ions, which leads to self-discharge in the case of the redox flow battery and reduces the Coulombic efficiency. In this presentation we discuss the vanadium permeability and the ionic conductivity of various ion exchange membranes, including protonic, anionic, and amphoteric ionomers. The relationship with the type of grafted ionic groups (sulfonic acid, sulfammonium, quaternary ammonium) and the type of polymer backbone, such as poly(ether ether ketone) (PEEK) or polysulfone (PSU) are presented. Both aromatic polymers have a large strength and stiffness due to the rigid phenyl rings in the macromolecule. PEEK presents a slightly higher stiffness than PSU, due to the quaternary carbon in the PSU structure that increases the backbone flexibility.

#### 10:10 AM

##### (MCARE-S2-011-2018) Performance of Co@CNOs prepared from Co-containing preceramic polymers as supercapacitor electrodes

A. Tamayo<sup>\*1</sup>; F. Rubio<sup>1</sup>; C. Arroyo<sup>2</sup>; M. Rodriguez<sup>2</sup>

1. Institute of Ceramics and Glass, CSIC, Spain
2. University of Extremadura, Faculty of Sciences, Spain

Carbon nano onions (CNOs) represent a nanophase of carbon material that consists of multilayered quasi-spherical and polyhedral shaped shells. The main synthetic methods to synthesize CNOs in general require high energy input yet have a very low yield of CNOs. We report on a facile synthesis route to produce Co encapsulated into carbon nano onions (CNO@Co) from SiOC polymeric precursors. To fabricate the electrodes for supercapacitors, we have treated the polymeric precursors at temperatures below the ceramic conversion and removed the undesired phases (SiO<sub>2</sub> derivatives) by HF etching at room temperature. Metallic cobalt and cobalt carbide (Co<sub>2</sub>C and Co<sub>3</sub>C) phases are developed during the heat treatment although they decompose at temperatures above 700 °C. In spite of the poor stability of these carbides, the siloxane network (from the partial mineralization of the preceramic polymer) prevents the carbides from decomposition. The CNOs possess highly graphitized walls and are probably formed from the diffusion of C through the Co nanoparticles during the carbide decomposition. The Co@CNOs have been characterized through Raman an IR spectroscopy, XRD, SEM, TEM and thermogravimetric methods. Their performance as electrodes for supercapacitors was evaluated by cyclic voltammetry, galvanostatic charge-discharge measurements, and electrochemical impedance spectroscopy.

#### 10:30 AM

##### (MCARE-S2-012-2018) Study on the chemical durability of ion selective electrode based on chalcogenide glass

G. Chen<sup>\*1</sup>; L. Li<sup>1</sup>

1. East China University of Science and Technology, China

In this study, the water stability of chalcogenide (ChH) glass based ion-selective electrode (ISE) are investigated in different electrolyte solutions considering requirements for onsite real-time analysis in the harsh environments. ChH glass samples were prepared from Ge, Se, Ag and AgCl. The samples were heated at 950 °C for 10 hrs. Melts were quenched in the water from 800 °C to RT. Bulk glasses were cut into discs as electrode membranes and thoroughly polished with fine abrasive powder, then a silver wire had been soldered to the membranes inner surface to making a solid contact electrode. The ChH glass based ISEs were then immersed in different aqueous solutions for different times. The analytical characteristics of ChH glass based ISEs before and after soaking were measured. Changes of the surface morphology was confirmed from SEM images. In acidic and

alkaline aqueous solutions, the electrical conductivity of the ChH glass based ISEs changed with immersion period, and the significant changes of the surface morphology were observed after long immersion, which indicates that the ChH glass based ISEs are not stable in the strong acidic and alkaline aqueous solutions. Structural changes and corrosion mechanisms are studied with high-resolution XPS.

#### 10:50 AM

##### (MCARE-S2-013-2018) Oxide-based all-solid-state batteries: Prospects and challenges (Invited)

M. Finsterbusch<sup>\*1</sup>; Y. Arinicheva<sup>1</sup>; A. Windmueller<sup>1</sup>; S. Moeller<sup>1</sup>; C-L. Tsai<sup>1</sup>; S. Lobe<sup>1</sup>; C. Dellen<sup>1</sup>; S. Uhlenbruck<sup>1</sup>; D. Fattakhova-Rohlfing<sup>1</sup>; O. Guillon<sup>2</sup>

1. Institute of Energy and Climate Research, Materials Synthesis and Processing (IEK-1), Forschungszentrum Jülich GmbH, Germany
2. Jülich Aachen Research Alliance: JARA-Energy, Germany

Li-ion batteries dominate the portable electronics market due to their high energy and power density, fast charging capabilities, low self-discharge and long cycle life. However, improvements are needed in order keep track with the ever increasing energy demand and to enter new large scale markets like stationary storage or electric vehicles. As evolutionary development of organic liquid electrolyte based batteries seems to be limited to around 350 Wh/kg, evolutionary chemistries and systems need to be researched in order to further increase the energy density as well as tailor or improve other specification to the specific needs of the respective applications. The use of Li-metal anodes, high voltage cathodes and solid-state electrolytes is thus a major topic in battery research worldwide. Ceramic All-solid-state batteries are currently seen as a highly promising way to improve several aspects at once, leading to inherently safe cells with practical energy densities around 500 Wh/kg, large operating temperatures of up to 150 °C and low calendaric aging. However, main challenges like Li-dendrites during fast charging, short cycle life as well as scalable production still need to be overcome. Current achievements and limitations for completely inorganic all-solid-state cells as well as prospects of achievable performance will be discussed.

## SYMPOSIUM 7

### Advanced Materials for SOFC IV

Room: Grand Ballroom C

Session Chairs: Taner Akbay, Kyushu University; Kwati Leonard, International Institute for Carbon-Neutral Energy Research Center (WPI-I2CNER) Kyushu University; Tatsumi Ishihara, Kyushu University

#### 9:30 AM

##### (MCARE-S7-015-2018) Active Perovskite Oxide Cathode Materials for High Temperature CO<sub>2</sub> Electrolysis Cells using Solid Oxide Conductor (Invited)

T. Shin<sup>\*1</sup>; H. Kim<sup>1</sup>; K. Hwang<sup>1</sup>; J. Irvine<sup>2</sup>

1. Korea Institute of Ceramic Engineering & Technology, Republic of Korea
2. University of St Andrews, School of Chemistry, United Kingdom

Recycling or reuse of CO<sub>2</sub> could be an effective approach for accessing a new form of energy carrier and enabling a carbon-neutral cycle. In particular, electrochemical reduction of CO<sub>2</sub> into CO fuel with renewable electricity has been proposed as an alternative method to store this energy, overcoming the inherent problems with intermittency and geographical distribution of renewable energy sources. Thus a solid oxide electrolysis cells for reducing CO<sub>2</sub> into CO have been recently studied using various potential ceramic cathode materials as a potential cathode for good redox stability with tolerance to coking in high temperature CO<sub>2</sub> electrolysis operation. However, electrochemical performance of the ceramic electrodes is still smaller than that using a metal based catalytic electrode, due to

insufficient electrical conductivity and low electrocatalytic activity. Here we shows that robust transition Cu metal nano complex grown in situ from specifically designed nonstoichiometric perovskites or extreme nano ceria share a uniquely strong interaction with the parent support and form a well-functioning SOEC, with good stability even after several redox cycles. It was found that Cu ex-soluted ceramic cathode with La(Sr)Ga(Mg)O<sub>3</sub> electrolyte exhibits a performance with a current density of c.a 0.6 A cm<sup>-2</sup> at 1.5 V and 850°C and electrochemical property also was evaluated.

**10:00 AM**

**(MCARE-S7-016-2018) CuFe<sub>2</sub>O<sub>4</sub> Spinel-based Oxide Cathode used for CO<sub>2</sub>/H<sub>2</sub>O High-Temperature electrolysis**

K. Wu<sup>2</sup>; T. Ishihara<sup>\*1</sup>

1. Kyushu University, International Institute for Carbon-Neutral Energy Research, Japan
2. Kyushu University, Applied Chemistry, Japan

Reducing CO<sub>2</sub> emissions and converting it into useful fuels by renewable energy has been an attractive approach, and application of solid oxide electrolysis cells (SOECs) is expecting as a promising high efficient electrolyzer. This allows not only effectively reduce climate impact, but also produce useful fuels (such as syngas and hydrocarbon source). High activity and low degradation rate are essential required for potential cathodes in the application for CO<sub>2</sub> electrolyzer. To improve the stability, perovskite oxides as fuel electrodes recently has been widely studied instead of conventional metallic-based electrodes (for example, Ni-based oxide). In this study, we proposed to use spinel oxides, a general formula AB<sub>2</sub>O<sub>4</sub>, which are composed of two transition metals. This type of material is expected to provide a higher current density of electrolysis and possess a mixed termination of transition metals as active roles to facilitate the reduction of CO<sub>2</sub> and H<sub>2</sub>O. In this study, we investigate a number of spinel oxides as cathodes applied in the electrolysis of CO<sub>2</sub>/steam co-electrolysis using LSGM as the electrolyte and it was found that CuFe<sub>2</sub>O<sub>4</sub> shows high activity to CO<sub>2</sub>/H<sub>2</sub>O co-electrolysis. Surface composition of CuFe<sub>2</sub>O<sub>4</sub> will also be mentioned.

**10:20 AM**

**(MCARE-S7-017-2018) Reduction in CO<sub>2</sub> Emissions from Methane Fueled SOFCs (Invited)**

Y. Matsuzaki<sup>\*1</sup>; M. Keller<sup>2</sup>; J. Otomo<sup>2</sup>

1. Tokyo Gas, Fundamental Technology Dept., Japan
2. The University of Tokyo, Japan

While the CO<sub>2</sub> emission coefficient of the electrical power from methane fueled SOFCs will decrease with increasing the electrical efficiency, it remains to have non-negligible value even at the considerably high efficiency. Recently thermal decomposition and catalytic thermal decomposition of methane have attracted attentions as advanced technologies producing CO<sub>x</sub>-free hydrogen, which are simple ways to reduce the CO<sub>2</sub> emission caused by methane fuel. We have conducted feasibility study and catalyst evaluation for the innovative low-carbon methane-fueled SOFCs, in which methane was partly decomposed to form hydrogen and solid carbon before power generation, and a mixture of the generated hydrogen and undecomposed methane was used as a fuel. The solid carbon deposited by the decomposition will be able to be utilized as carbon materials such as carbon black and carbon fiber, or source material of syngas which leads to liquid chemicals. Thus by using this system, carbon fixation in methane fueled power generation will be materialized through forming the co-products such as solid carbon, syngas, and/or liquid organic compounds.

**10:50 AM**

**(MCARE-S7-018-2018) Highly Conductive and Stable Bismuth Oxide-Based Electrolytes for Lower Temperature Solid Oxide Fuel Cells**

K. Lee<sup>\*1</sup>

1. DGIST, Energy Science & Engineering, Republic of Korea

The erbia-stabilized Bi<sub>2</sub>O<sub>3</sub> (ESB) is known as a great oxide ion conductor for an SOFC electrolyte material due to its excellent ionic conductivity compared to other conventional oxide ion conductors such as doped CeO<sub>2</sub> and stabilized ZrO<sub>2</sub>. Despite its superior ionic conductivity at reduced operating temperatures below 700 °C, ESB has not been a practical choice for an electrolyte material for SOFCs because its time-dependent conductivity degradation below 650 °C. In this work, we developed highly stable stabilized bismuth oxides via substituting Bi<sup>3+</sup> with very small amounts of the secondary aliovalent dopant. In order to investigate the effect of the aliovalent dopants on suppressing the kinetic degradation mechanism, the cation diffusivity of the samples was evaluated by Boltzmann-Matano method, and chemical and structural changes by extended annealing were also investigated. Moreover, our novel double-doped stabilized bismuth oxides were incorporated into a conventional yttria-stabilized zirconia (YSZ)-based SOFC. The electrochemical performance and the stability of the SOFCs with our novel bismuth oxides were evaluated with I-V characteristics and impedance spectroscopy.

**11:10 AM**

**(MCARE-S7-019-2018) Effect of Ageing on the Integrity of an Electrolyte-Supported SOC**

A. Masini<sup>\*1</sup>; Z. Chlup<sup>1</sup>; I. Dlouhy<sup>1</sup>

1. Institute of Physics of Materials, AS CR, Brittle Fracture Group, Italy

A critical issue for the reliability and efficiency of SOC is the structural integrity of the ceramic cells embedded in the stack. The local loss of integrity causing bridging fault of the cell or complete mechanical failure of one single cell could lead to a lower efficiency and eventually to the end of service of the whole device. Therefore, it is of high importance to gain knowledge on the mechanical properties of the cells, such as elastic behaviour and fracture characteristics. In this contribution, the flexural strength and Young's modulus of a state of the art electrolyte-supported cell have been investigated. Tests have been performed on cells extracted from stacks operated for a different amount of hours; this way, it has been possible to assess the effect of ageing on the mechanical response. Comparing experimental results with those obtained for as-sintered cells, an embrittlement effect has been observed with the increasing service time. Possible causes of observed changes have been discussed and analysed.

**11:30 AM**

**(MCARE-S7-020-2018) Investigation of cost-effective potassium doped strontium silicate (Sr<sub>1-x</sub>K<sub>x</sub>SiO<sub>3-0.5x</sub>) as a solid electrolyte for IT-SOFC application**

R. Pandey<sup>\*1</sup>; P. Singh<sup>2</sup>

1. A.R.S.D. College, University of Delhi, New Delhi, Department of Physics, India
2. Indian Institute of Technology (BHU) Varanasi, Department of Physics, India

The demand for clean, secure, and renewable energy has stimulated great interest in fuel cells. Of the many types of fuel cells, solid oxide fuel cells (SOFCs) have attracted much attention because of their potential of providing an efficient, environmentally benign power generation system. A solid oxide fuel cell is an electrochemical conversion device that produces electricity directly from oxidizing a fuel. Solid oxide fuel cells are a class of fuel cells characterized by the use of a solid oxide material as the electrolyte. Conventional electrolyte materials yttria-stabilized zirconia (YSZ) operates at a very



high temperature ( $\sim 1000$  °C) in order to produce sufficient ionic conductivity for SOFC. Therefore, a key issue to develop intermediate temperature solid oxide fuel cells (ITSOFCs) which can operate between 400-800 °C, led to the investigation of new electrolyte materials with enhanced ionic conductivity intermediate temperature range. Recently, the sodium doped strontium silicate ( $\text{Sr}_{1-x}\text{Na}_x\text{SiO}_{3-0.5x}$ ) is gathering attention as a fast ion conductor in the intermediate temperature range (500 - 600 °C). In this study, we investigated the potassium doped strontium silicate ( $\text{Sr}_{1-x}\text{K}_x\text{SiO}_{3-0.5x}$ ) as promising material to get the optimal fabrication condition with composition and to minimize several issues on this material.

11:50 AM

**(MCARE-S7-021-2018) Studies on hybrid composite membranes for fuel cell applications**

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Proton exchange membrane (PEM), as proton conductive material, is a key component for transferring protons from the anode to cathode as well as providing a barrier to the fuel gas cross-leaks between the electrodes. The recent trend of researches is to develop the membrane of organic-inorganic material. Several efforts have been made to develop proton-conducting membranes. However, PEMFCs using membranes of the perfluorosulfonated polymer Nafion cannot operate at temperatures above 100 °C because the low-water content in the membrane decreases its proton conductivity and consequently its performance. For this reason, a number of studies have been carried out to develop alternative membrane materials. One interesting alternative is hybrid organic/inorganic membranes with the potential to provide unique combinations of organic and inorganic component properties. The membranes of inorganic material ( $\text{SiO}_2/\text{P}_2\text{O}_5$ ) have been developed by the sol-gel method. The hybrid composite material contains polymer, the polyvinylpyrrolidone (PVP) has good film-forming and adhesive behaviour on many solid substrates. The hybrid composites of different composition of inorganic and organic compounds were characterized to study the structural, thermal and electrical conductivity by SEM, TGA, NMR, FTIR and conductivity measurements.

## SYMPOSIUM 11

### Novel Materials, Organic and Hybrid Materials, Fundamental Studies

Room: Grand Ballroom D

Session Chairs: Yongchai Kwon, Seoul National University of Science and Technology; Dahl-Young Khang, Yonsei University

9:30 AM

**(MCARE-S11-007-2018) Enzymatic biofuel cells using biocatalysts (Invited)**

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Enzymatic biofuel cells (EBC) using glucose and oxygen fuels are devices converting chemical energy of the fuels to electrical energy by enzyme based biocatalysts. Since the EBC can operate even in physiological conditions, glucose and oxygen that are contained in human body fluid can be considered for the target and implantable devices using electrical energy produced by EBC can be incorporated. However, in spite of that, there are still problems to be addressed. Most of all, slow reaction rate of the biocatalyst is the dominant issue. To alleviate the problem, the employment of new mediator into the biocatalyst can be properly applied. As the mediator is embedded into the biocatalyst, electron transfer for both anodic and

cathodic reactions is promoted and the associated reaction rates are also enhanced. Here, we suggest new mediator embedded biocatalysts and how they affect EBC performance, while their reaction mechanisms are explained. When it comes to anode, glucose oxidase (GOx) enzyme and dye mediator are used and as for cathode, bi-enzyme structure fabricated by cascade type are used. By the use of the redox couple, the activity of the corresponding and the performance of EBCs using the biocatalysts are excellent.

10:00 AM

**(MCARE-S11-008-2018) High efficiency (>17%) Si-organic hybrid solar cells by concurrent structural, electrical, and interfacial optimization via low temperature processes (Invited)**

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Si-organic hybrid solar cells have been expected to be low cost and high efficiency photovoltaics (PVs) due to synergistic combination of organics and inorganics. The actual device performance, however, seems to be rather stagnant at  $\sim 15\%$  power conversion efficiency (PCE). The efficiency can further be improved by optimizing various elements in the cell. Here we show high (>17%) efficiency Si-organic solar cells based on concurrent engineering of surface structure, electrical property of organic material, and interface treatment. Especially, the sheet resistance of organic PEDOT:PSS, together with electrical conductivity, is the primary parameter of interest in the cell. Simple contact-printing of siloxane oligomers at interfaces has resulted in the suppression of charge recombination, thus enhancing solar cell performance greatly. It is notable that the contact-printing can be done at room temperature, contrary to high-temperature doping or additional wet or vacuum processes for the interfacial layer.

10:30 AM

**(MCARE-S11-009-2018) Graphene analogues Two Dimensional Transition Metal Chalcogenides for electrochemical sensor Applications**

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Graphene analogues two dimensional (2D) transition metal dichalcogenides (TMCs), with the chemical formula  $\text{MX}_2$ , where M is a transition metal and X is a chalcogen (S, Se, Te) have gained wide attention in electrochemical sensor applications due to their exceptional layer dependent physical and chemical properties. In specific, their high electrical conductivity, large surface to volume ratio, high signal-to-noise ratio and more importantly their fast electron transfer kinetics make TMCs the suitable material for electrochemical sensors. Till date, there have been many TMCs including  $\text{MoS}_2$ ,  $\text{WS}_2$ ,  $\text{SnS}_2$ ,  $\text{CuS}$ ,  $\text{NiS}$  and  $\text{Ni}_3\text{S}_2$  are reported as an active material in electrochemical sensors. Very recently, binary TMCs such as  $\text{NiMoS}_4$ ,  $\text{CoMoS}_4$  are emerged as an alternative to simple TMCs and employed in various electrochemical applications because of their enriched redox reactions. In this presentation, we will discuss the recent progress on the use of various TMCs in electrochemical sensor applications. In addition to that, we will also present the detailed study on the non-enzymatic glucose sensing properties of two different binary TMCs viz.  $\text{NiCo}_2\text{S}_4$  and  $\text{Ni}_2\text{FeS}_4$ .

10:50 AM

**(MCARE-S11-010-2018) Qualification of silver-nanowire networks as an alternative transparent electrode to indium-tin-oxide thin film**

S. Ham\*<sup>1</sup>; M. Kim<sup>1</sup>; C. Kim<sup>1</sup>; G. Han<sup>1</sup>; S. Cho<sup>1</sup>

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Indium-tin oxide (ITO) or fluorine-doped tin oxide (FTO) has been predominantly utilized as a transparent electrode for various energy devices such as photovoltaic cells since it offers good optical

transparency, low sheet resistance, chemical stability, and mechanical durability. In recent years, various studies have been made to replace the rigid metal oxide transparent electrodes with flexible transparent electrode as the necessity of flexible devices increases. A silver nanowire (AgNW) network electrode is a candidate of the flexible transparent electrodes. In this presentation, The performance of the AgNW electrode is compared with that of the ITO electrode in terms of transparency, sheet resistance, price, durability, and stability, using an organic light-emitting diode (OLED) device as a qualification platform. All the performance of the AgNW electrode using OLED as the platform was almost similar to that of the ITO electrode while the price of AgNW was much lower than ITO. This AgNW transparent electrode seems to have sufficient performance as an alternative electrode for flexible energy devices such as photovoltaic cells and is expected to be used in various ways in the future.

**11:10 AM**

### **(MCARE-S11-011-2018) Electrospun Ceramic Nanofibers for Energy Harvesting and Conversion**

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Ceramic nanofibers provide advantageous chemical and physical properties beneficial for energy harvesting and storage applications. Electrospinning offers a simple and robust way to produce nanofibers with controlled morphology and varied compositions. Electrospun nanofibers were synthesized in three different systems: Lead zirconate titanate (PZT), iron-based and titanium-based nanofibers. In the first system, PZT particles are integrated with a polymer to produce flexible energy generator device. In the second system, unique lamellar-like porous nanofibers are designated to be used as a selective catalyst for converting carbon dioxide and hydrogen into liquid hydrocarbons. The structure is obtained by reordering of an initially uniform fiber consisting of two metals coordination complexes (Al/Fe(acac)<sub>3</sub>) and a polymer. A general mechanism for the morphology formation is suggested, where the final structure depends greatly on the heating stage and chemical composition of the metal oxide precursors and polymer matrix. In the third system, titanium-based nanofiber with added aluminium designated for photocatalytic degradation of organic pollutions and thermal conversion reactions was investigated. Changing the aluminium content influence the obtained morphology from non-porous to porous. The presented processes to obtain nanofibrous mats with designated properties is highly promising in material research.

**11:30 AM**

### **(MCARE-S11-012-2018) A Nickel catalyst supported on phosphate modified hierarchically macro-mesoporous alumina for effective hydrogen production by steam methane reforming**

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A nickel catalyst has been mainly used in steam methane reforming to produce the hydrogen. A nickel catalyst has advantages like low cost, broad application, and high catalytic activity. The drawbacks, nevertheless, are need to overcome such as carbon coking and sintering at high temperature. In this study, we focused on developing the phosphate modified macro-mesoporous alumina support to maximize the activity of nickel catalyst in steam methane reforming. A series of support modified was prepared by a polymeric template and a non-ionic surfactant-template for producing macropores and mesopores, respectively. A nickel as active site was loaded on the modified alumina support by an impregnation method, and

steam methane reforming reaction was performed during 12 hours. The developed support was characterized the highly ordered mesopores (<5 nm) and macropores (>300 nm) by TEM images. The nickel catalyst based on developed support showed the highest methane conversion in steam methane reforming. These results might be attributed to the effect of support morphology and addition of phosphate. The macro-mesoporous phosphate modified alumina had not only increased of surface area also enhanced mass transport ability. Furthermore, phosphate acted as an electron donor, thus carbon deposition can be reduced in steam methane reforming.

**11:50 AM**

### **(MCARE-S11-013-2018) Electrocatalytic Activity and Stability of Nb-TiO<sub>2</sub> supported Pt Nanocatalyst**

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Fuel cells are regarded as an environmental friendly energy conversion device. In a typical fuel cell, oxygen reduction reaction (ORR) is one of the most important electrochemical reactions occurring at the cathode of fuel cells. As a candidate support material, Nb-doped TiO<sub>2</sub> nanotube has attracted the attention as a novel support material due to the stability under fuel cell operation condition and controllability of its shape and structure. The Nb dopant whose atomic radius is similar to that of Ti can increase the electrical conductivity of TiO<sub>2</sub>. In this study, using the hydrothermal process, we synthesized TiO<sub>2</sub> nanotube that is a 1D structure of TiO<sub>2</sub> nanoparticle suitable for a catalyst support due to the high surface area. We confirmed that doping Nb into the TiO<sub>2</sub> nanotube leads to a drastic increase in electrical conductivity with doping level of up to 25at%. In addition, we loaded Pt nanoparticles up to 20wt% on the Nb-TiO<sub>2</sub> nanotube. The electrocatalytic activity and stability of the synthesized nanocatalysts were compared with the commercial carbon black (Pt/C) during an accelerated stress test (AST) for a conventional three-electrode cell. We could identify the optimal loading amount of Pt nanoparticles on the Nb-TiO<sub>2</sub> support catalyst, which results in the high corrosion resistance of Nb-TiO<sub>2</sub> as well as the strong interaction between Pt and TiO<sub>2</sub> for the stabilized electrocatalytic activities.

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