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Figure 1. Schematic of the components of a redox flow battery cell. Reproduced from Reference 6.

Flow batteries and energy storage—a new market for ceramics

By Richard Clark

Demand for energy storage technologies is driving dramatic growth in the redox flow battery market, and with it opportunities for the ceramics community.

Redox flow batteries belong to a large and growing group of devices designed for energy storage applications.

Although their origins trace back to a zinc/chlorine flow battery used to power an airship in 1884,¹ rapid, systematic growth in the redox flow battery market has only been apparent within the past decade.

To understand the reasons for this growth and the concurrent opportunities for the ceramics community, it is important to understand several related areas: the energy storage market and its segmentation; the technology behind flow batteries and how it compares to alternatives; and the challenges that need to be addressed to make flow batteries cost-competitive in the market segments where they have an advantage over alternatives.

The energy storage market and the opportunity for redox flow batteries

Widely misunderstood, the energy storage market is highly segmented, with the characteristics required for a given application (primarily discharge time and system power required) having a huge impact on the relative importance of cost. Complicating this market further is the fact that the classification and naming of the segments is not uniform, making comparison of information from multiple sources challenging.

At the top level, the primary categories for energy storage are transportation (mainly electric vehicles) and stationary. While conceptually redox flow batteries can be used for both, practically the only application of note is stationary storage (unless airships make an unexpected comeback) because of the low volumetric energy density of redox flow batteries com-

pared to other technologies, especially the ubiquitous lithium-ion batteries.

Subdivisions for stationary energy storage are generally described by the services they provide as an alternative to conventional grid supply.² These subdivisions are (on-grid) regulation, arbitrage, back-up and reserves, black start, investment deferral, and (off-grid) independent power supply. These subdivisions are variously related to generation, transmission, and distribution as well as end-user markets (residential, commercial, and industrial).

Several competing technologies exist for each of the stationary storage market segments, which are categorized as electrochemical (batteries and supercapacitors), thermal (molten salt), and mechanical (flywheels, compressed air, and pumped storage hydropower), although the specific requirements of each segment preclude all technologies from competing for the entire market. Pumped storage hydropower (PSH) is dominant in the overall space: as of mid-2020, 164 GW of PSH is operational, equivalent to an estimated energy in excess of 17 TWh, with an additional 124 GW in various stages of realization.³ The remaining competition in terms of major market scale is increasingly moving toward lithium-ion and redox flow batteries.

For redox flow batteries, 2021 global sales are projected to reach 350 MWh, with revenue at US\$270 million. However, BloombergNEF predicts that redox flow batteries could compete with lithium-ion batteries for up to 46% (69 GWh) of the total capacity (150 GWh) required for grid-related stationary energy storage in 2030 (defined as being the segment which would be otherwise addressed by lithium-ion batteries).³

In this analysis, redox flow batteries were assumed to have an average system duration of four hours, which makes them particularly favorable for arbitrage (storing energy when the price of electricity is low and releasing it on the grid when high) and peaking capacity (provision of supply to meet the maximum demand of the system, including back-up and reserves and investment deferral applications). If the system duration can be modified significantly from this value,

with appropriate capital and operational economics, then the size of the potential market for redox flow batteries will accordingly increase.

Particularly relevant to redox flow batteries, one of the main drivers behind the growth of the stationary energy storage market is the increasing replacement of fossil fuels with renewable energy sources (most notably wind and solar), which are intermittent and hence not directly coherent with demand. The economics of redox flow batteries are well suited to the relatively long durations required to address this imbalance. They also offer additional benefits such as a high level of safety, long maintenance-free lifecycles, and intrinsic modularity, in that power and energy are decoupled, facilitating customization. In many cases, sustainability issues are also addressed because the chemistries of choice are derived from widely available resources and materials can be readily reused.

A more detailed comparison of redox flow batteries with lithium-ion batteries is provided in Table 1.⁴ By necessity, this table is generalized, and there are exceptions in some cases. Sustainability is not included as a category, mainly because the diversity of chemistries used in redox flow batteries preclude generalization.

However, there are advantages with many of the more popular types, and it is likely to be an increasingly important consideration in the future.

The technology behind redox flow batteries

A redox flow battery is an electrochemical device that uses the potential difference between a set of redox couples, typically solution-based, to transform electrical energy into stored chemical energy and vice versa.⁵ At the most basic level, there are two tanks containing electrolyte connected to a stack of cells where the redox reactions occur. For a single-cell system, a cell would include two current collectors, two bipolar plates, two electrodes, and one membrane, although there are variations on this setup. Cells are usually stacked, so a pair of current collectors would be used for the full stack and bipolar plates would be the components between cells. A schematic of a single cell arrangement is shown in Figure 1.

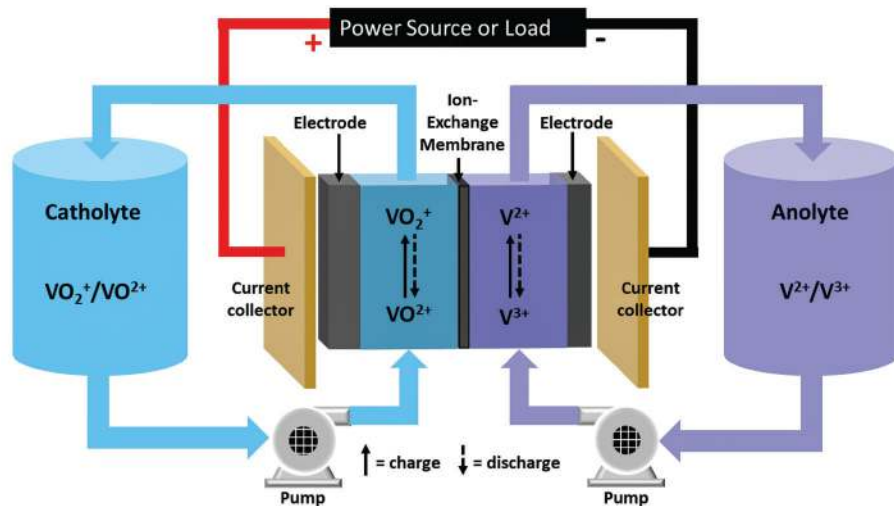
There are a wide variety of systems encapsulated by the general definition, including inorganic aqueous, organic aqueous, and nonaqueous, and the definition is frequently broadened to include membrane-less, metal-air, semi-

Table 1. Comparison of redox flow batteries with lithium-ion batteries. Adapted from Reference 4. Credit: Daggett

Characteristic	Redox flow batteries (RFB)	Lithium-ion batteries (LIB)
Cycle life	Greater than LIB (e.g., 5x)	Less than RFB
Self-discharge	Near zero	Low
Decoupled energy and power	Feature of most RFB types noted	Not possible
Risk of fire / thermal runaway	Very low / zero	Flammable electrolyte
Safe servicing	Servicing is possible	Cannot discharge and service
Simple monitoring and controls	Cell balancing only for hybrid systems (described below)	Cell balancing required
Accurate measurement of state of charge	Can be done directly	Via voltage/current under load
Complexity of balance of plant	Relatively complex	Liquid-cooled systems complex
Gravimetric energy density	Very low compared to LIB	Much higher than RFB (e.g., 10x)
Volumetric energy density	Very low compared to LIB	Much higher than RFB (e.g., 10x)
Round-trip efficiency	Less than LIB, especially dc	Greater than RFB (e.g., 5 to 10%)
Market penetration	Much less than LIB	Much greater than RFB
Diversity of applications	Many fewer than LIB	Many more than RFB
Cost per kWh	Currently greater than LIB	Currently less than RFB

Green = better option

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Credit: Clemente and Costa-Caselles, Energies (CC BY 4.0)

Figure 2. Schematic of an all-vanadium redox flow battery. Adapted from Reference 8.

are fundamental challenges yet to be overcome, to those which are already launched commercially. Typically, there are multiple chemistries under investigation for each system, and for a given base chemistry, there are alternative systems and approaches. This flexibility offers great opportunities for innovation.

Table 3 provides a summary of the current state of market readiness for the main types of flow battery.⁷ With the exponential growth rate of the energy storage market, the market readiness of each battery is likely to change, and it is quite possible that a technology currently in its infancy could become the dominant force within several years.

Leading commercial redox flow battery systems

All-vanadium redox flow battery (VRFB)

The invention of the all-vanadium redox flow battery (VRFB) is credited to the work of Maria Skyllas-Kazacos and her research team at the University of New South Wales, Australia, in the 1980s. The VRFB electrolyte tanks contain vanadium at four different oxidation states. On the cathode side, vanadium is at +IV (tetravalent) and +V (pentavalent) states within VO^{2+} and VO_2^+ , respectively. On the anode side, vanadium is at +II (bivalent) and +III (trivalent) states. Figure 2 shows a general schematic. Typical materials of construction within the cell include graphite (bipolar plates), graphite felt (electrodes), and membranes based on chemically stabilized perfluorosulfonic acid/polytetrafluoroethylene copolymer acid (PFSA/PTFE), such as Chemour’s Nafion 212.

By using vanadium on both sides of the membrane, contamination issues with cross-over are effectively eliminated, although self-discharge would still occur should cross-over happen. Eliminating the possibility of cross-over contamination helps provide VRFBs with extended cycle life, typically 15,000 to 20,000 cycles,⁹ far above many other chemistries and battery types.

The early work determined suitable, highly reversible redox reactions for vanadium compounds within an aqueous electrolyte containing an appropri-

Table 2. Comparison of types of redox flow battery versus inorganic aqueous systems.

Credit: Clark

System	Proposed differentiation	Example
Inorganic aqueous	Baseline	All-vanadium (VRFB)
Organic aqueous	Abundant precursors, lower cost	Quinone-bromide
Nonaqueous	Improved energy density	All-copper (acetonitrile solvent)
Membrane-less	Lower cost without ion-exchange membrane	Hydrogen-bromine
Metal-air	Improved energy density, lower cost	Zinc-air
Semi-solid (slurry)	No electrolyte solubility limitations	Lithium iron phosphate (LFP)
Electroplated (hybrid)	Improved energy density, lower cost	Zinc-bromine (ZBFB)

solid (slurry), and electroplated redox flow batteries. The latter systems are also termed hybrid redox flow batteries because the total energy storage capacity depends on both the stack size and the size of the electrolyte storage reservoirs. So, energy and power are not fully decoupled, in contrast to more “classi-

cal” types, where decoupling frequently is portrayed as a defining feature. Table 2 provides a summary and an example of each system.

Readers will appreciate that the technologies are in significantly different states of development, from those currently at laboratory scale, where there

Table 3. Market readiness for the main types of flow batteries. Adapted from Reference 7.

Credit: IDTechEx

Chemistry	Example system	Market readiness
All-vanadium (VRFB)	Inorganic aqueous	High
Zinc-bromine (ZBFB)	Electroplated (hybrid)	High
All-iron (Fe-RFB)	Electroplated (hybrid) or semi-solid (slurry)	High
Hydrogen-bromine	Membrane-less	Medium
Organic (ORFB)	Organic aqueous	Medium
Iron-chromium	Inorganic aqueous	Low
Polysulfide-bromide (PSB)	Inorganic aqueous	Low
Vanadium-bromide	Inorganic aqueous	Low
Li-ion RFB	Nonaqueous semi-solid (slurry)	Low

ate level of sulfuric acid, providing ionic conductivity, and stabilizing the reactions. More recent work at Pacific Northwest National Laboratory determined that using a mixed acid (sulfuric and hydrochloric) within the electrolyte increases the solubility of the vanadium ions and improves the battery performance, increasing the specific energy and expanding the operating temperature range.

A VRFB offers some significant benefits in sustainability.¹⁰ First, it has full lifecycle CO₂ emissions lower than other battery technologies—estimated at 27% to 37% lower than standard lithium-ion batteries. Secondly, vanadium is not consumed and does not degrade in a VRFB—so at end of life for one battery, it can be reused in another battery or used for another application such as in steel alloys. Additionally, although China is the leading country for vanadium mining, vanadium is mined in many other countries as well (most notably Russia, South Africa, and Brazil), unlike with lithium-ion batteries, where the raw material supply is dominated by China.

With the experience gained over the past three decades and the other benefits noted, it is not surprising that VRFBs are leading the way for flow batteries commercially. Bushveld Energy reports that there are 25 or more VRFB companies globally and that in China alone they are tracking about 2 GWh of VRFBs under construction.¹⁰ The largest facility is 200 MW/800 MWh in Dalian, China, installed by Rongke Power.¹¹ China is expected to install between 30 GWh and 60 GWh of new energy storage capacity by 2030, and a considerable portion of this storage capacity is likely to be VRFB, providing the economics are suitable.

Vanadium is estimated to be 48% of the cost of the manufacturing cost of a VRFB, and spot pricing of the relevant chemicals in 2021 is still about 50% higher than needed for VRFB to have an economic advantage over lithium-ion batteries, although the other benefits such as increased safety may be sufficient.

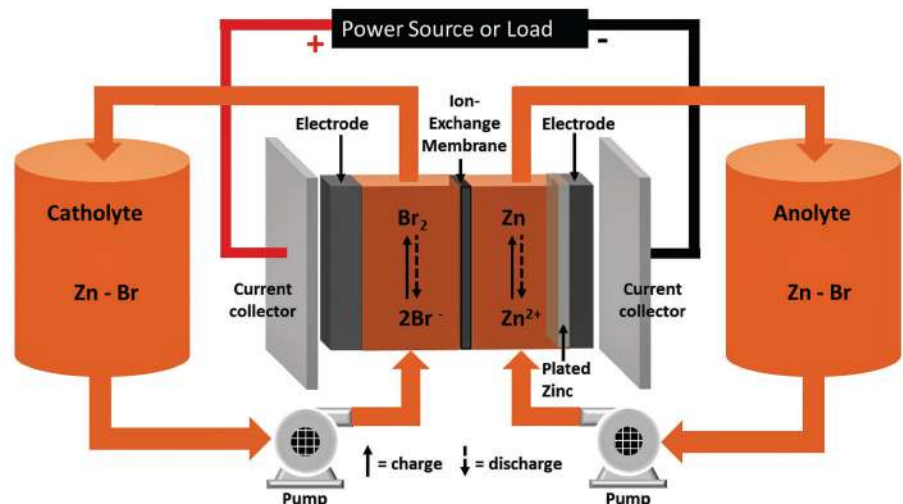


Figure 3. Schematic of zinc-bromine flow battery (ZBFB). Adapted from Reference 8.

Zinc-bromine flow battery (ZBFB or ZBB)

Development of the zinc-bromine flow battery (ZBFB) in its current form is attributed to work at Exxon in the early 1970s. Unlike most other redox flow battery types, the ZBFB is a hybrid system, in that the total energy stored is not purely proportional to the volume of electrolyte but instead depends on both the volume of electrolyte and the electrode area because zinc metal is plated onto the anode during charge. Concurrently, bromide ions are oxidized to bromine on the other side of the membrane. During discharge, the zinc metal oxidizes to Zn²⁺ and dissolves into the electrolyte, and the bromine is reduced to bromide ions.

Figure 3 shows a general schematic of ZBFBs. The figure does not depict some additional requirements related to bromine. One, bromine has limited solubility in water, so a complexing agent is needed on the cathode side to prevent its release. With bromine's high toxicity, it is essential to maintain certain conditions such as moderate system temperature to maintain the stability of the complex. Two, with bromine being highly oxidative, system components need to be specially selected, which can add to cost. There are also challenges on the anode side. Repeated plating of the zinc can cause uneven deposition and eventually dendrites of zinc can puncture

the membrane. Pulsed discharge during charge may be required.

Despite these challenges, two significant benefits of a ZBFB are the high voltage and high energy density for flow batteries, associated with the two electrons per atom of zinc that are engaged in the charge-discharge process. Typical materials of construction within the cell include carbon-filled plastic (bipolar plates), carbon felt (electrodes), and membranes based on a PFSA/PTFE copolymer/polymer composite.

Conceptually, ZBFBs could be very low cost because of the raw materials, but dealing with the issues noted above frequently offsets this benefit. The potential cost reduction continues to drive work in this space (i.e., to solve or mitigate the issues and realize the benefits of the lower cost raw materials), and there are already several companies selling ZBFBs to end users. One recent development, arising from work at the University of Sydney, Australia, is the use of gel electrolytes replacing the liquid electrolytes.

All-iron flow battery (Fe-RFB)

The earliest work on the all-iron flow battery (Fe-RFB) is attributed to L. W. Hruska and R. F. Savinell in Ohio, with their first major publication on the subject in January 1981.¹² The Fe-RFB follows similar principles to those of the VRFB in that by using

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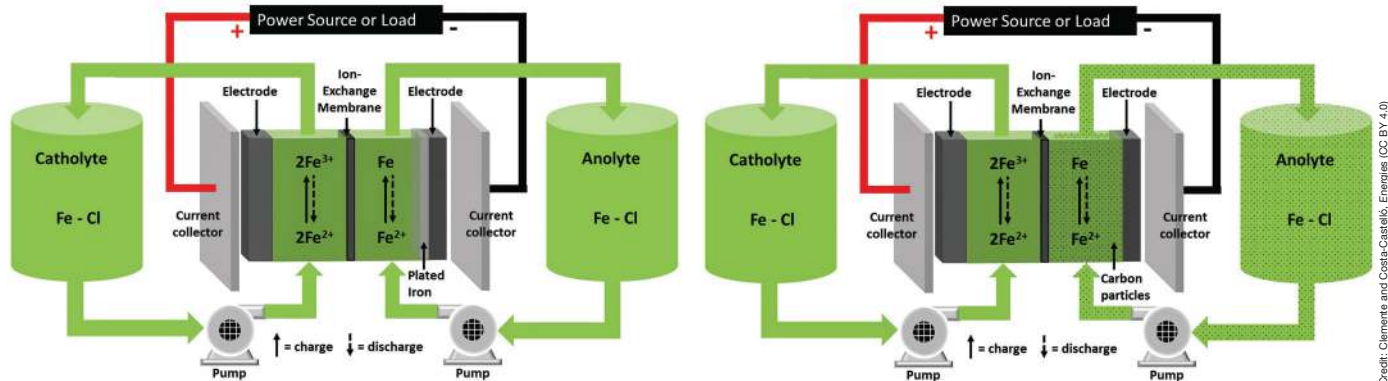


Figure 4. a) Schematic of an all-iron flow battery (Fe-RFB) (hybrid). b) Schematic of an all-iron flow battery (Fe-RFB) (slurry). Adapted from Reference 8.

the same element with multiple valence states on either side of the membrane, losses associated with cross-over contamination can be eliminated.

During charging, Fe^{2+} oxidizes to Fe^{3+} on the cathode side and Fe^{2+} reduces to iron metal on the anode side. During discharging, the reverse is true. Additionally, iron is abundant, inexpensive, and nontoxic.

While these characteristics would appear to make Fe-RFBs the ideal flow batteries, there is a major challenge caused by hydrogen generation, and frequent electrolyte rebalancing is required. Recent work at Case Western Reserve University in Cleveland, Ohio, demonstrated that a sealed Fe-RFB is possible with internal rebalancing, hence facilitating desired maintenance-free operation.¹³

As well as hydrogen evolution, other challenges include dendrite formation during iron plating and a relatively low cell voltage. Typical materials of construction within the cell include graphite (bipolar plates), carbon or graphite felt (electrodes), and microporous polyethylene (membrane).

In addition to the hybrid version of the Fe-RFB (depicted in Figure 4a), an alternative system uses a slurry at the anode side, in which the iron metal deposits on carbon particles (depicted in Figure 4b). As well as the obvious benefit of fully decoupling energy and power, this system also extends the capacity of the cell because the surface area of 3D carbon particles can be made much larger than the area of the negative electrode. This system has its own challenges, however, in that the slurry rheol-

ogy must be maintained for extended periods and at different states of charge, and iron must deposit uniformly onto the particles.

There are at least three companies currently engaged in commercializing the Fe-RFB technology.

Opportunities for the ceramics community and conclusion

This period is one of rapid growth for energy storage, and redox flow batteries are likely to play an increasingly significant role. Large energy storage installations are very expensive, and already companies have experienced significant losses caused by lithium-ion battery-related fires in energy storage system (ESS) facilities in Australia, Belgium, China, England, South Korea, and the United States. The fires are difficult and dangerous to extinguish, and in at least one case resulted in loss of life.¹⁴ While safety standards for electric vehicles are designed to allow sufficient time for occupants to leave vehicles after initiation of battery thermal events, these standards are not as relevant for ESS installations, where prevention of propagation of thermal runaway is the only acceptable solution. Lithium-ion batteries containing solid-state electrolytes will provide a solution in the future, but there are still technical and commercial hurdles to overcome before these solutions will be widely used in cost-sensitive markets.

With ESS applications, redox flow batteries offer an immediate alternative to lithium-ion batteries, and the benefit of safety far outweighs the downside

of the low energy density. Solutions already exist to the main technical challenges, and if it is possible to reduce cost as well (in US\$/kWh), redox flow batteries can take the leading position in this market.

Already, according to detailed estimates from the U.S. Department of Energy,¹⁵ costs are relatively similar for longer duration systems when comparing higher energy lithium-ion battery installations versus VRFB. For example, for a 10 MW installation and 10-hour duration, total installed cost for an NMC-cathode lithium-ion battery system would be US\$387/kWh and for a VRFB it would be US\$426/kWh. However, the ongoing reduction of lithium-ion battery costs also needs to be considered, and it may be more difficult to reduce costs of redox flow batteries once a large scale (GWh) is reached because of the increasing relative dominance of the chemicals.

For a given redox flow battery chemistry, there are several ways in which cost can be addressed. The first and most obvious is replacement of current materials of battery construction with lower cost substitutes (lower US\$, same kWh). A second way is to replace these materials with alternatives that provide improved system characteristics (same US\$, higher kWh). For example, increasing the energy density of the stack will mean the total cost of the other system components will be lower on a system energy basis. A third way is to use materials that allow lower cost system design, for example, by combining components.

Bipolar plates and electrodes are usually made from carbon or graphite in

a solid or flexible form. Bipolar plates by necessity must be impermeable. Electrodes can be made of flexible or rigid (porous) material, with some benefits offered by each, most notably cost for flexible materials and more uniform flow and extended life for solid ones. The membrane is highly engineered and can dominate stack component costs, particularly if it is based on a PFSA/PTFE copolymer or an equivalent polymer. Finding an alternative high-performance and lower-cost ion exchange membrane may prove to be the key to ongoing widescale commercial success for redox flow batteries, and hence presents an excellent opportunity for ceramics.

The membrane in a redox flow battery has some characteristics not significant for other battery types: it must deal with ion cross-over, i.e., selectively allowing counter-ions to pass through, but not allowing active species the same passage; it must limit water transport; it must have a low areal resistance; it must resist fouling; and it must be stable in whichever chemistry is present and at whatever pH is used to stabilize the system.

Despite their attractive properties (high proton conductivity and chemical stability), even PFSA/PTFE copolymer-based membranes are not ideal—aside from the cost, they are also selectively permeable to water and allow some cross-over of active species. One example of a ceramic which may prove suitable as a membrane in flow batteries is NaSICON, as demonstrated in recent work at Sandia National Laboratories by Eric Allcorn and others.¹⁶ Other work identified sol-gel as a possible process route for fabrication of low-cost silica-based membranes.¹⁷

As we progress in this dynamic growth period for energy storage, many options are conceptually possible. However, commercialization of any new technology and scaling it to GWh level takes many years, typically decades. The two most likely systems to capture the new space are lithium-ion batteries and redox flow batteries, which have each matured sufficiently to be scalable to the required level. Although there are advan-

tages and disadvantages of each, there is no dispute that redox flow batteries are safer from the perspective of minimizing battery-related fires.

The three chemistries of redox flow batteries which are furthest advanced are all-vanadium, zinc-bromine, and all-iron. There is yet no clear winner among these, but in each case, innovation will help to realize the potential. If a suitable membrane can be part of the fulfillment, redox flow batteries will be a major new market for the ceramics industry.

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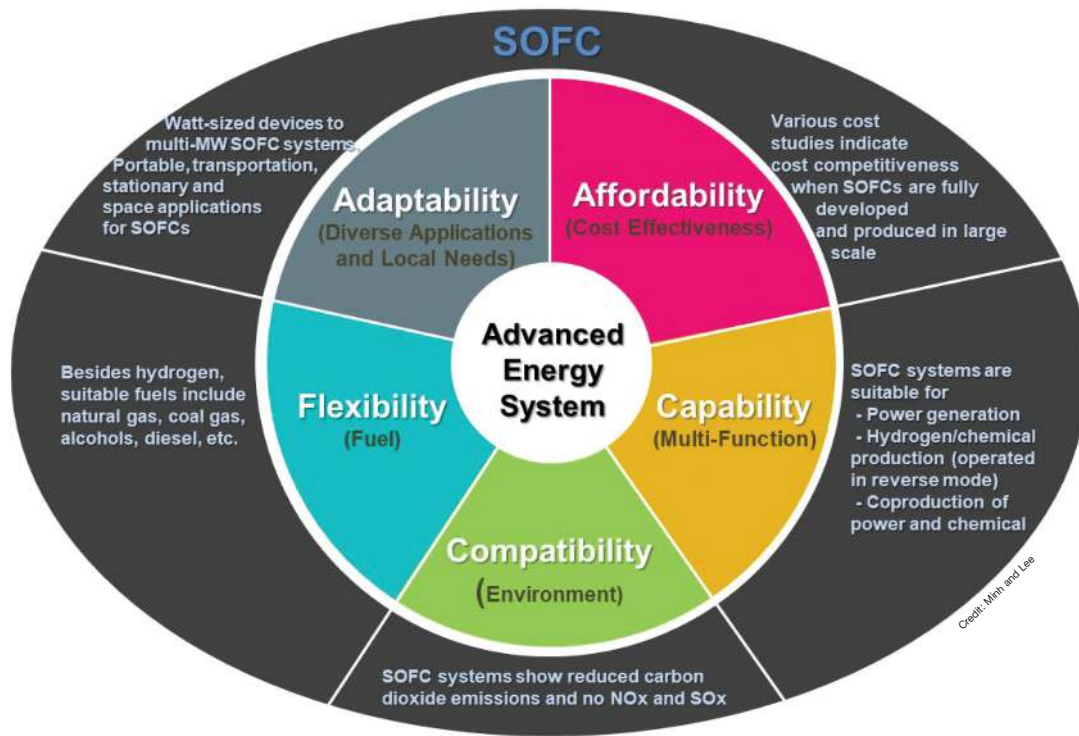


Figure 1. Characteristics of future energy systems and solid oxide fuel cell (SOFC) technology.

Solid oxide fuel cell technology for the future

By Nguyen Q. Minh and Yoon Ho Lee

Solid oxide fuel cells possess all the characteristics desired for future advanced energy systems—and recent technological advances have helped move the technology toward widespread applications.

According to the U.S. Department of Energy’s Energy Information Administration (EIA), world energy consumption will increase to about 740 quadrillion Btu in 2040, rising 28% between 2015 and 2040.¹

The EIA projects that increases in consumption will affect all energy sources—fossil (petroleum and other liquids, natural gas), renewables (solar, wind, hydro), and nuclear—except coal, which is estimated to remain flat. Although renewables are the world’s fastest growing form of energy, fossil fuels are expected to continue supplying most of the energy used worldwide. As use of fossil fuels increases, it is projected that world energy-related carbon dioxide emissions will grow from about 34 billion metric tons in 2015 to about 40 billion metric tons in 2040 (an average of 0.6%/year).¹

To meet this energy growth while limiting carbon dioxide emissions, future advanced energy systems should possess two key characteristics: flexibility (i.e., fuel flexible, suitable for efficient operation on a variety of practical fuels from fossil to renewable fuels) and compatibility (i.e., environmentally compatible, operable with reduced carbon dioxide emissions). In addition, other desirable characteristics for such a system include capability (i.e., multifunctional), adaptability (i.e., appropriate for diverse applications and versatile to local energy needs), and affordability (i.e., cost effective and cost competitive)² (Figure 1).

Solid oxide fuel cells (SOFCs) are one example of technology suitable to serve as a technology base for future energy systems. SOFCs are energy conversion devices that produce electricity by electrochemical combination of a fuel with air across an oxide electrolyte. The key features of an SOFC are its solid-state construction (ceramics and metals) and high operating temperature (typically 600–1,000°C). The combination of these two features leads to several advantages for SOFCs, including cell and stack design flexibility, multiple cell fabrication options, multifuel capability, and operating temperature range.

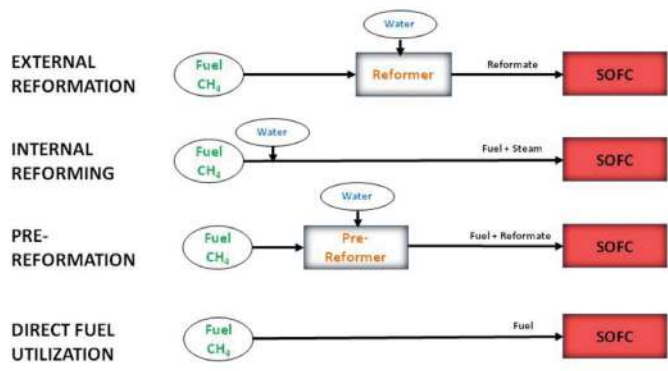


Figure 2. SOFC operating options with hydrocarbon and alcohol fuels (written for methane and steam reformer/pre-reformer).

At present, the most common SOFC materials are yttria stabilized zirconia (YSZ) for the electrolyte, nickel-YSZ (Ni-YSZ) for the anode, and lanthanum strontium cobalt iron perovskite-YSZ (LSCF-YSZ) for the cathode. For multicell stacks, stainless steels are commonly used for the interconnect (to connect single cells in electrical series in a stack) and glasses for gas sealing.³ Many other materials (e.g., oxygen ion conducting perovskites, proton conducting oxides for the electrolyte) have been considered and evaluated for SOFCs as well.

SOFCs possess all the characteristics given above for future advanced energy systems. Its fuel flexibility, adaptability, and capability in particular set the SOFC apart from many energy technologies, especially other fuel cell technologies.

Flexibility

SOFCs are fuel flexible. Like other types of fuel cells, the primary fuel for an SOFC is hydrogen. However, suitable fuels for SOFCs also include natural gas, biogas, coal gas, alcohols, and diesel. It should be noted that use of these fuels requires removal of certain contaminants, such as sulfur, and appropriate ways to prevent carbon deposition.

For fuels, especially light hydrocarbons and alcohols such as natural gas, biogas, and ethanol, an SOFC can operate with four fuel input options that incorporate different ways of fuel reforming (Figure 2). Reforming is a catalytic process that converts an input fuel, such as methane, to carbon monoxide and hydrogen. Each option has advantages and disadvantages, and selection very much depends on many factors including specific applications and requirements, designs, and operating conditions.

- *External reforming:* SOFCs can operate directly on reformates from external reformation of the fuel. No clean-up of carbon monoxide and carbon dioxide in the reformate is needed.

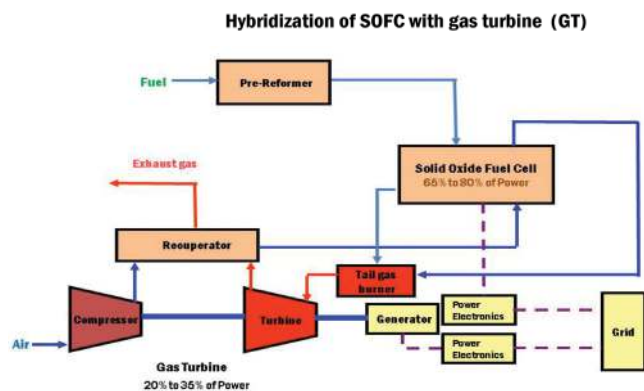


Figure 4. Hybridization of SOFC with gas turbine.

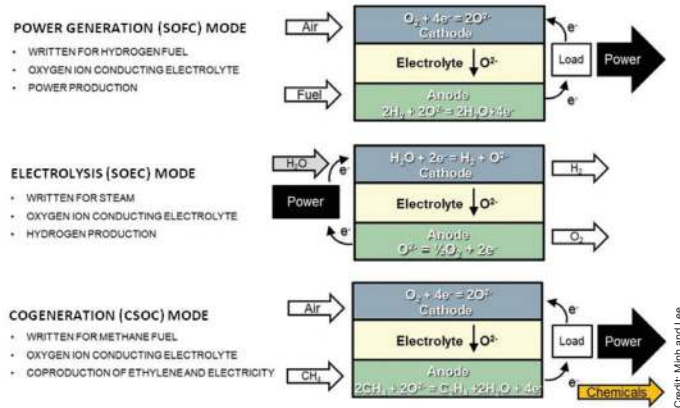


Figure 3. SOFC operation modes.

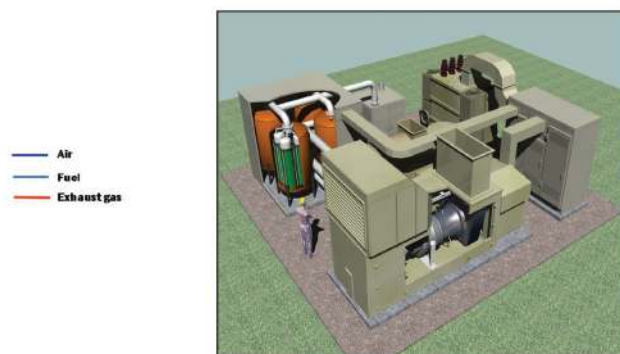
mate is needed. In fact, dry CO can serve as fuel for the SOFC, and in the case of wet CO, the CO reacts to generate hydrogen fuel within the fuel cell via the water-gas shift reaction. In this mode, the SOFC operates in conjunction with an external reformer (steam reformer, autothermal reformer, or catalytic partial oxidation reformer).

- *Internal reforming:* In this operating option, fuel with significant amounts of water or carbon dioxide is fed to the SOFC and reformed on the anode of the fuel cell. This internal reforming approach can be employed to eliminate the need of an external reformer and to use the endothermic reforming reactions to reduce cooling requirements in thermal management of the SOFC. This option may require development of suitable schemes to distribute the reformation to minimize temperature gradients within the fuel cell.

- *Prereformation:* This operating option combines external reformation and stack internal reforming. In this option, only a portion of the fuel is reformed in an external reformer (in this case, referred to as a prereformer), and the resulting reformat plus the remaining fuel are fed to the SOFC, where the fuel is internally reformed (via steam reforming) within the stack. This operating option permits smaller reformers (due to partial external reformation) and improves thermal management of the fuel cell (due to internal reforming).

- *Direct fuel utilization:* The SOFC is shown to have the capability for direct fuel utilization of hydrocarbons and alcohols, meaning it can operate directly on these fuel feeds. This operating option is similar to but different from the internal reforming mode in that the fuel feed contains no water or

5 MW SOFC/GT hybrid system concept



Solid oxide fuel cell technology for the future

carbon dioxide. Direct utilization of hydrocarbons and alcohols in the SOFC requires modifications of the Ni-YSZ anode or use of alternative materials to prevent carbon deposition.

Capability

SOFCs are multifunctional. These devices can operate in fuel cell or SOFC mode (power generation), electrolysis or solid oxide electrolysis cell (SOEC) mode (chemical production), and cogeneration or CSOC mode (coproduction of power and chemical)⁴ (Figure 3). Among these operating modes, the SOFC is the most technologically advanced. The SOEC and CSOC are based fundamentally on the SOFC, and their development to date depends on leveraging progress in SOFC technology.

SOFCs have been developed for a broad spectrum of power generation systems, ranging from watt-size devices to multimegawatt power plants that operate on a variety of fuels. The SOEC has been evaluated for hydrogen production from steam at different sizes—from distributed plants (e.g., 1,500 kg H₂/day) to central stations (e.g., 150,000 kg H₂/day), production of syngas (mixtures of H₂ and CO₂) for industrial uses, and oxygen generation/recovery from air or CO₂. The CSOC, currently at its conceptual and research stage, is considered for production of valued chemicals, e.g., ethylene from methane.

SOFC and SOEC operation modes can be combined in a unit. In other words, the unit can operate efficiently in both fuel

cell and electrolysis modes, referred to as a reversible solid oxide cell (RSOC).

A special application of the SOEC is its deployment for oxygen production in space exploration. The SOEC developed for NASA’s Mars Oxygen In-Situ Resource Utilization Experiment (MOXIE) instrument was included in the rover and sent to the Martian surface to explore the planet, paving the way for future human missions. This SOEC uses solar energy to convert some of the thin, carbon dioxide-rich Mars atmosphere into oxygen, which will then be used for propellant and human breathing. The MOXIE instrument aboard on the NASA Perseverance rover demonstrated oxygen production on Mars for the first time in April 2021.⁵

Adaptability

Examples of SOFC power systems and their applications and development/commercialization status are given in Table 1.⁶

An attractive attribute of SOFCs is the possible hybridization of the fuel cell with another power generating equipment such as a gas turbine (GT) to improve system performance.⁷ In SOFC/GT hybrids, the tail gas from the SOFC is combined with ambient air and fed to the turbine section of the GT to generate additional electricity (Figure 4). An example of a 5 MW SOFC/GT system concept is also shown in Figure 4. In a generic SOFC/GT hybrid design, the SOFC produces about 65–80% of the power and about 20–35% is from the GT. Hybridization of the SOFC with

Table 1. Markets and applications of selected SOFC power systems. Adapted from Reference 6. Credit: Minh, Fuel Cell Science and Engineering

Market	Application	Power level	Readiness level
Portable	Consumer electronic devices, portable power	1–100 W	Demonstration, precommercial, commercial
	Portable power, battery chargers	200–500 W	Demonstration, precommercial, commercial
Transportation	Range extenders, automobile and truck auxiliary power units	5–50 kW	Demonstration
	Aircraft auxiliary power units, aircraft power	100 kW–30 MW	Concept
Stationary	Residential, micro combined heat and power, uninterruptible	1–10 kW	Demonstration, precommercial, commercial
	Micro combined heat and power, distributed generation	100 kW–1 MW	Demonstration, precommercial, commercial
	Baseload	100–500 MW	Concept

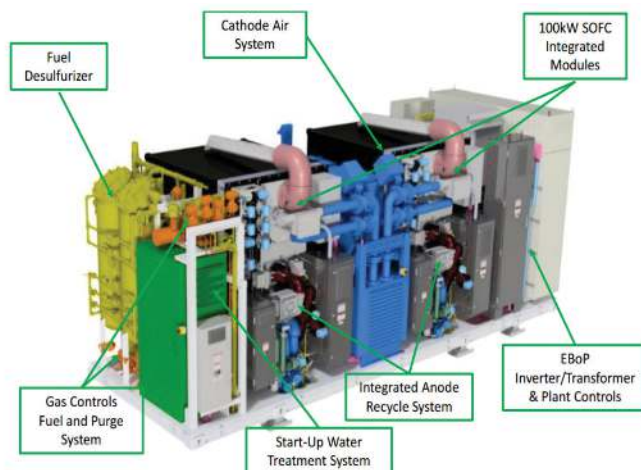


Figure 5. 200 kW SOFC demonstration system. Adapted from Reference 9.

a GT significantly improves system efficiency and can be beneficial for use in large (\geq hundreds of kilowatts) power plants. Researchers have validated operation of SOFC/GT hybrids in several demonstration systems.⁷ For the SOEC, integration of SOEC systems with nuclear energy using process steam/process heat/electricity from the nuclear reactor was envisioned.⁸

Advances in design, engineering, materials, and manufacturing of SOFC technology

SOFCs are considered and developed for a wide range of applications and markets, as shown in Table 1. To date, many of the applications for SOFCs have progressed to hardware demonstration and prototype/precommercial/commercial stages with systems of power level up to 200 kW; several applications, especially those with large power outputs, are at the conceptual/design stage. Figure 5 shows an example of a 200 kW SOFC demonstration system.⁹

Significant advancements were made in the past few years in several technological areas critical to the development of SOFCs. However, further improvements are needed in several areas for cells and stacks, relating to the key drivers (efficiency, reliability, and cost) to enable commercialization. At present, SOFCs show efficiency and performance levels suitable for many applications. Reliability and durability of SOFCs demonstrated to date is adequate, although improvements in performance degradation rates, especially under practical operating conditions, are desirable.

The current critical issue facing the technology is cost. Reduction in the cost of SOFCs requires not only high-volume production but also significant changes in the materials, design, and engineering of current technology.

If the issues facing the technology are resolved, future SOFCs are expected to be an efficient, reliable, and cost-effective clean energy system that is fuel flexible and versatile in applications when fully developed. Recent innovations in design, engineering, materials, and manufacturing could help to move SOFCs toward this expectation. Selected examples of recent technology advances include development of advanced multicell stack designs, electrode microstructural engineering, application of digital manufacturing, fabrication of thin-film SOFCs, incorporation of nanomaterials and nanostructures, and direct utilization of hydrocarbons and other fuels. The following discussion and examples are based mainly on the on-going efforts at the University of California, San Diego on design, research, and concept development for SOFC technology.

Advanced multicell stack design

One recent development in SOFC stack technology is the design concept based on a prime surface interconnect configuration. The key feature of this configuration is a one-piece metallic interconnect that incorporates both fuel and oxidant flow fields, with peaks on one side of the interconnect serving as flow channels (valleys) on the other side.¹⁰

Figure 6 shows an example schematic stack concept, including the prime-surface interconnect configuration with an egg carton shaped flow field. This stack concept has several attractive features, including reduced weight and volume, flexibility

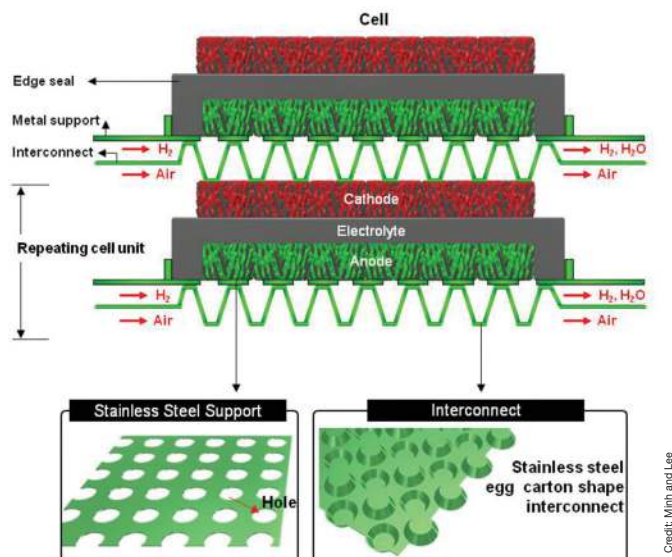


Figure 6. Stack design concept incorporating egg carton shaped prime surface interconnect.

in gas flow configuration, minimal stacking performance losses, and improved sealing. These features lead to lower cost, better performance, and enhanced reliability for the stack. Another important attribute of this stack concept is its versatility in incorporating different types of cell construction (e.g., conventional sintered cells, such as sintered anode-supported cells, and metal-supported cells). The metal-supported cell configuration permits thin cell components, facilitates cell scale-up, and can be designed for reduced temperature operation, all of which reduce cost and increase reliability and durability.

Electrode microstructure engineering

An example in this area is engineering the anode microstructure to prevent the anode's redox instability (chemomechanical instability of the anode under oxygen partial pressure changes during redox cycles at high temperatures).

Current SOFC cells based on YSZ electrolytes use almost exclusively Ni-YSZ compositions for the anode. The Ni-YSZ anode can become unstable because of the oxidation of the nickel (i.e., redox instability) if fuel supply is interrupted, the cell is operated under extremely high fuel utilization/high current conditions, or seal leakage occurs. Oxidation of the nickel increases the volume of the anode, and the volume expansion creates stresses in the layers (compression in the anode and tension in the electrolyte), which can cause cracks in the electrolyte, especially the thin electrolyte in the case of anode-supported cells.

At UCSD, researchers proposed an engineered structure concept to enhance robustness, reliability, and endurance of

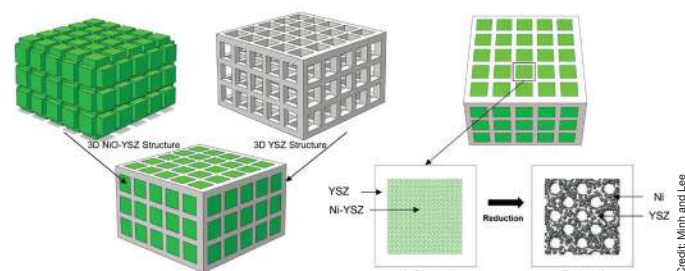


Figure 7. Proposed engineered Ni-YSZ anode microstructure concept

Solid oxide fuel cell technology for the future

SOFC Ni-YSZ anodes. SOFC anodes of this engineered microstructure consist of specifically designed 3D networks of nickel and YSZ, with each phase topologically connected throughout the anode. Figure 7 schematically shows an example of such an engineered microstructure (with nickel(II) oxide in oxidation state and nickel in reduction state). The controlled connectivity and the engineered microstructure, especially of the YSZ, in contrast to the random connection and microstructure in conventional nickel-based anodes, strengthen the anode structure and prevent dimensional changes during anode reduction and oxidation, thus significantly increasing robustness and enhancing reliability and endurance of the anode.

Digital manufacturing

Additive manufacturing shows promise for fabrication of complex SOFC structures, such as the proposed engineered anode structure discussed above.

An additive manufacturing process constructs parts with intricate shapes from 3D model data, usually layer by layer. As opposed to subtractive manufacturing (e.g., machining) and formative manufacturing (e.g., casting), the additive manufacturing process does not penalize complexity of design with additional equipment or labor costs.

The anode structure can be fabricated by a variety of additive manufacturing techniques, including 3D microextrusion, aerosol jet, or inkjet printing.

Thin-film technology

Thin-film SOFCs were recently developed for miniaturization of the fuel cell (for applications requiring small size and light weight) and for efficient operation at lower temperatures (400–600°C). Operating the SOFC at lower temperatures while maintaining adequate cell performance provides several benefits, such as decreased deleterious chemical interactions and reduced thermal stresses, and thus increased cell reliability.

Researchers have used different deposition processes to fabricate components for thin-film SOFCs. Among various physical vapor deposition processes, sputtering is a versatile technique commonly used in mass production as it can create either porous or dense films just by changing the deposition conditions.

Figure 8 presents typical micrographs of SOFC components

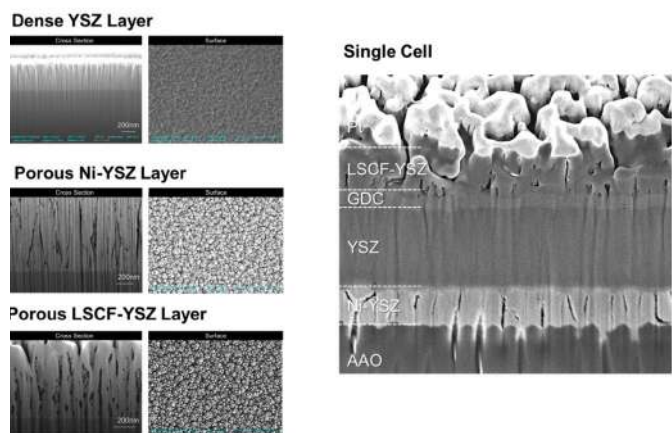


Figure 8. Micrographs of sputtered SOFC components and single cell. Adapted from Reference 11.

and a thin-film cell made by sputtering on anodized aluminum oxide (AAO) substrate. This cell has a gadolinium doped ceria, or GDC, interlayer between the electrolyte and cathode to minimize interactions between LSCF and YSZ. As seen from the figure, the sputtered components have the desired density/porosity characteristics: fully dense electrolyte, fully dense interlayer, porous anode, and porous cathode layer. Examination and characterization of single cells indicate uniform layer thickness, well-defined interfaces, and excellent adherence between layers.

Nanomaterials and nanostructures

In recent years, a major development in SOFC R&D work is the demonstration of using nanomaterials to modify electrode microstructure, thus electroactivity, as a potent means for performance enhancement. As the operating temperature of the fuel cell is reduced, it is more feasible to incorporate nanomaterials and nanostructures in SOFCs due to their improved long-term stability.

Nanomaterials and nanostructures can be introduced into the cell by adding the material to existing porous electrode structures (for example, by infiltration of a precursor solution followed by decomposition), by forming from elements present in existing structures (for example, by exsolution), or by depositing using different deposition techniques.

Figure 9 shows an example of the cathode and anode nanostructures made by sputter deposition. The electrodes in this case are made of a columnar nanostructure with a diameter of about tens of nanometers with nanofiber-like branches growing onto the columnar structure. This type of nanostructure significantly enlarges electrode active areas, resulting in exceptionally high-power densities for the cell that can be as high as 3W/cm² at 650°C depending on cell configurations and electrode materials.¹² As an example, a sputtered cell incorporating such electrodes exhibits excellent performance at reduced temperatures of 550–650°C (versus 800–1,000°C for conventional SOFCs) as shown in Figure 10.

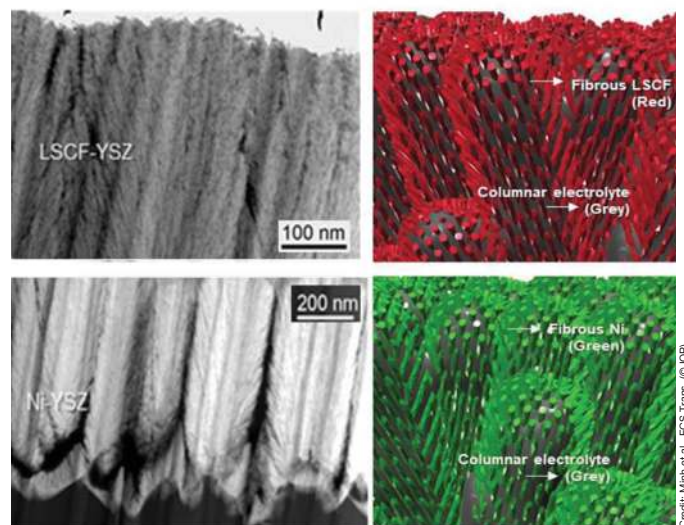


Figure 9. Sputtered electrode nanostructure. Adapted from Reference 11.

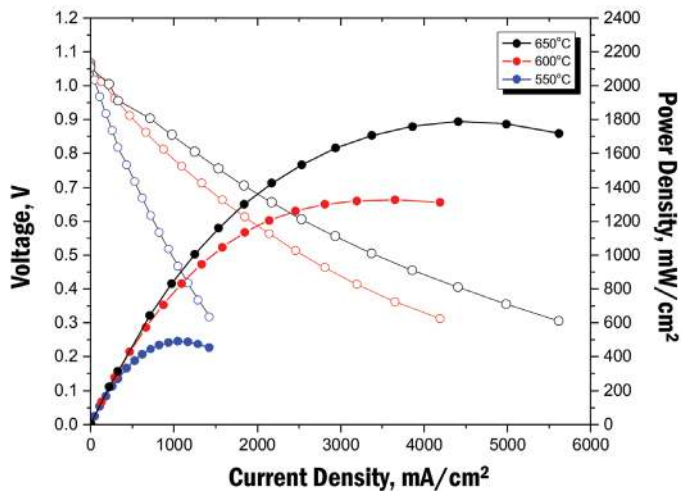


Figure 10. Performance of cell LSCF-YSZ/GDC/YSZ/Ni-YSZ featuring sputtered nanoscale electrodes.

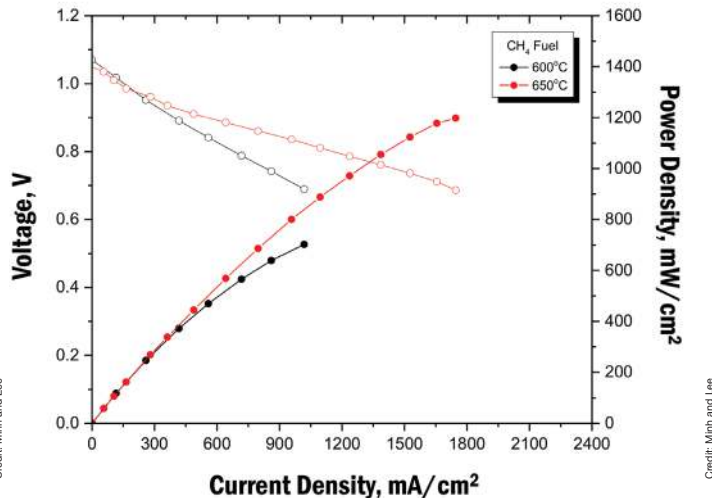


Figure 11. Performance of sputtered thin-film SOFC on dry methane.

Direct fuel utilization

One example in this area is the recent demonstration at UCSD of direct operation of the SOFC with excellent performance using dry methane. As discussed earlier, for fuels other than hydrogen, SOFCs can operate directly on the fuel (Figure 2). Direct fuel utilization is the preferred approach to operating SOFCs with fuels like hydrocarbons and alcohols because it removes the need for an external reformer in such a power system. This absence of an external reformer reduces cooling requirements due to less heat generated by direct oxidation of the fuel, and it can lead to higher system efficiency and lower system cost if adequate performance is maintained for the fuel cell. (In other words, if performance of the fuel cell with direct fuel utilization matches the performance level of fuel cells using externally reformed fuel.)

Researchers have demonstrated the feasibility of direct-fueled SOFCs. Figure 11 shows an example of direct methane utilization in a sputtered thin-film SOFC cell tested at UCSD. The cell performance indicates a superior power density of about 1,200 mW/cm² at the temperature of 650°C. The issues of carbon deposition and long-term durability of course need to be addressed in this case.

Concluding remarks

SOFCs have the potential to serve as a base technology for future energy systems, as it has all the desirable attributes of compatibility (environment), flexibility (fuel), capability (multiple function), adaptability (diverse application), and

affordability (cost effectiveness). SOFC technology has made significant progress toward commercialization, with several applications (buildings/facilities, residential CHPs, portable power) at precommercial or commercial stages. Recent technological advances have helped to improve the performance, reliability, and cost of the technology. However, significant challenges, especially in the area of cost, must be addressed and resolved to move the SOFC toward widespread applications in the future.

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