X-Ray Photoelectron Investigation of Phosphotungstic Acid as a Proton-Conducting Medium in Solid Polymer Electrolytes

Clovis A. Linkous
Stephen L. Rhoden
Florida Solar Energy Center

Kirk Scammon
Advanced Materials Processing and Analysis Center

University of Central Florida
Cocoa, Florida, USA
E-mail: calink@fsec.ucf.edu
Tungsten trioxide, WO$_3$

- Melting point: 1473 K
- Insoluble in mineral acids
- Soluble in alkali
  \[ WO_3 + 2NaOH \rightarrow Na_2WO_4 + H_2O \]
- Formation of phosphotungstic acid, PTA:
  \[ H_3PO_4 + 12WO_3 \rightarrow H_3PW_{12}O_{40-x}H_2O \]
Outline

- PEM fuel cell function
- Conductivity in polymer electrolytes
- Effect of PTA on sulfonic acid polymer membrane conductivity
- XPS observation of W chemical shifts
- Relating chemical shift data to hydration environment
- Thermogravimetry
- Conclusion
- Future work
Polymer Electrolyte Membrane Fuel Cell

Membrane Electrode Assembly (MEA)/Catalyst Coated Membrane (CCM)

ANODE

$\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$

CATHERODE

$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$
Typical Current-Voltage curve for a PEM fuel cell

\[ V = E_0 - \frac{RT}{F} \ln i - R_\alpha i + \frac{RT}{F} \ln \left(1 - \frac{i}{i_t}\right) \]
Membrane Electrode Assembly - the heart of a PEM fuel cell

Polymer membranes with catalyst ink

sprayed catalyst ink layer

MEMbrane

Catalyst

Electrode Assembly

+ 2 GDLs

+ Flow Fields & Hardware Set

MEA in Cell Hardware
Base Polymer of interest: PEEK and PEKK

\[
\left[ \begin{array}{c}
\text{O} \\
(C) \\
\text{O} \\
\end{array} \right]_x (O)_y
\]

\[
\text{poly(aryletherketone)}
\]
Previous work on Nafion® 112 and PTA composite

Comparing Four Electrode Conductivity of NTPA to Nafion®
120 °C, 500 sccm H₂, 230 kPa

Baseline NTPA Wet up at 70% RH 3-16-04
Nafion® 112 Wet up at 70% RH 1-8-04
Solid Acid Additives for Membrane Modification

Keggin structure

Phosphotungstic acid (PTA)

$12\text{WO}_3\cdot\text{H}_3\text{PO}_4\cdot24\text{H}_2\text{O}$
Conductivity vs RH for SPEEK/PTA composite membrane
Effect of Cs+ treatment on PTA/SPEEK composites

SPEEK–PTA Composites at 80°C

Conductivity (S/cm)

RH (%)
Representative W4f spectra

- Na2WO4·2H2O
- Recrystallized PTA
- WO3 Fisher
## Summary of W4f$_{7/2}$ data

<table>
<thead>
<tr>
<th>Sample</th>
<th>Binding Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WO$_3$</td>
<td>35.1</td>
</tr>
<tr>
<td>PTA + Cs$_2$CO$_3$</td>
<td>35.4</td>
</tr>
<tr>
<td>PTA/Cs$^+$/H$_2$SO$_4$</td>
<td>35.6</td>
</tr>
<tr>
<td>SPEEEK/PTA</td>
<td>35.7</td>
</tr>
<tr>
<td>PTA + CsCl</td>
<td>35.8</td>
</tr>
<tr>
<td>Na$_3$PTA</td>
<td>35.9</td>
</tr>
<tr>
<td>PTA-6H$_2$O</td>
<td>36.0</td>
</tr>
<tr>
<td>PTA-EtOH/DMF</td>
<td>36.2</td>
</tr>
<tr>
<td>PTA (anhydrous)</td>
<td>36.2</td>
</tr>
<tr>
<td>PTA – 24H$_2$O (recrystallized)</td>
<td>37.8, 36.0</td>
</tr>
<tr>
<td>Na$_2$WO$_4$-2H$_2$O</td>
<td>36.7</td>
</tr>
<tr>
<td>Cs$_2$WO$_4$ (anhydrous)</td>
<td>37.3, 35.3</td>
</tr>
<tr>
<td>PTA--24H$_2$O (commercial A)</td>
<td>37.5</td>
</tr>
<tr>
<td>PTA--24H$_2$O (commercial B)</td>
<td>37.6</td>
</tr>
<tr>
<td>Cs$_2$WO$_4$-2H$_2$O</td>
<td>37.7</td>
</tr>
</tbody>
</table>
Weight loss thermogram for PTA-24H₂O
Weight loss thermogram for PTA-6H$_2$O
Weight loss thermogram for PTA treated with Cs$_2$CO$_3$
## Summary of W4f$_{7/2}$ data

<table>
<thead>
<tr>
<th>Sample</th>
<th>Binding Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WO$_3$</td>
<td>35.1</td>
</tr>
<tr>
<td>PTA + Cs$_2$CO$_3$</td>
<td>35.4</td>
</tr>
<tr>
<td>PTA/Cs$^+$/$\text{H}_2\text{SO}_4$</td>
<td>35.6</td>
</tr>
<tr>
<td>SPEEK/PTA</td>
<td>35.7</td>
</tr>
<tr>
<td>PTA + CsCl</td>
<td>35.8</td>
</tr>
<tr>
<td>Na$_3$PTA</td>
<td>35.9</td>
</tr>
<tr>
<td>PTA-6H$_2$O</td>
<td>36.0</td>
</tr>
<tr>
<td>PTA-EtOH/DMF</td>
<td>36.2</td>
</tr>
<tr>
<td>PTA (anhydrous)</td>
<td>36.2</td>
</tr>
<tr>
<td>PTA – 24H$_2$O (recrystallized)</td>
<td>37.8, 36.0</td>
</tr>
<tr>
<td>Na$_2$WO$_4$-2H$_2$O</td>
<td>36.7</td>
</tr>
<tr>
<td>Cs$_2$WO$_4$ (anhydrous)</td>
<td>37.3, 35.3</td>
</tr>
<tr>
<td>PTA-24H$_2$O (commercial A)</td>
<td>37.5</td>
</tr>
<tr>
<td>PTA-24H$_2$O (commercial B)</td>
<td>37.6</td>
</tr>
<tr>
<td>Cs$_2$WO$_4$-2H$_2$O</td>
<td>37.7</td>
</tr>
</tbody>
</table>
Conclusion

• Cs$^+$ exchange improves conductivity of SPEEK/PTA composite membranes.
• W chemical shift related to O-bonding geometry (octahedral vs tetrahedral) and waters of hydration.
• Cs$^+$ treatment lowers PTA water content and its enthalpy of hydration.
• Cs$^+$ functions by destabilizing waters of hydration, rendering them more mobile and better able to conduct protons.
Future Work

• XRD of PTA vs water content
• IR analysis of retained hydrogen stretching frequencies
• Obtaining conductivity vs RH curves at temperatures on either side of the TGA water transition.
• Fabricating Pt//SPEEK/PTA//Pt membrane electrode assemblies and deriving fuel cell current voltage curve