Solid Acid Fuel Cells: Principles, Status, and Outlook

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Solid Acid Electrolytes

Solid acids are compounds whose properties lie between those of a normal acid (H_2SO_4) and a normal salt (Cs_2SO_4). They are comprised of oxyanion tetrahedra, such as sulfates, selenates, phosphates, and arsenates forming a hydrogen-bonded network at room temperature. A subclass of these solid acid compounds is known to undergo a so-called superprotonic phase transition at moderate temperatures (50-250 °C). On heating through the transition, the crystallographic symmetry changes, depending on the specific compound, from a low temperature monoclinic phase to a high temperature cubic, tetragonal, or trigonal phase (Figure 1). Above the transition, the structure is highly disordered with oxyanion groups undergoing rapid reorientation (Figure 2), resulting in proton conductivities (Figure 3) that are several orders of magnitude larger than that of the low temperature phase. CsH_2PO_4, in particular, has been demonstrated as a viable electrolyte for moderate temperature fuel cells (1-3).

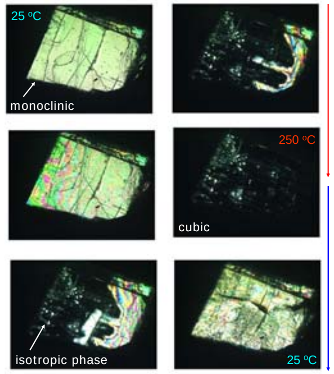


Figure 1. *Polarized light microscopy images of single crystal CsH_2PO_4: heating up to 250 °C and back down to room temperature (4).*

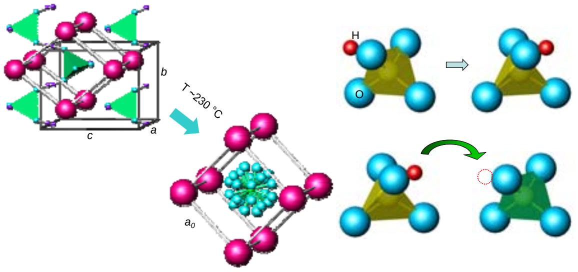


Figure 2. *High Proton Conductivity based on the rapid reorientation of oxyanion tetrahedra with 30 possible orientations in the high temperature cubic lattice.*

The oxyanion tetrahedra reorient ~10^{11} times per second, with a proton transfer frequency of ~10^9 Hertz, resulting in high stoichiometric proton conductivity. Additionally, due to its physical properties such as non-toxicity, easy handling and low cost, CsH_2PO_4 is the material of choice for fuel cells.

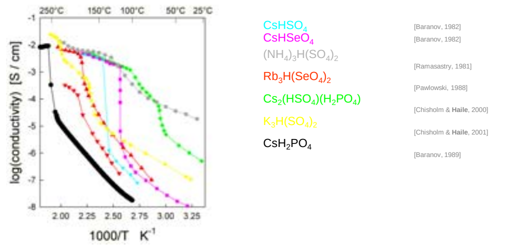


Figure 3. *Conductivity of various solid acids as a function of temperature*

CsH_2PO_4 Electrolyte

A literature debate erupted surrounding the high temperature properties of CsH_2PO_4, based on the decomposition behavior of the material. It has been thought that the dehydration of the compound induces a transient rise in conductivity as water leaves the structure with the absence of a polymorphic phase transition (Figure 4). Thermal analysis experiments, optical cross polarizers and conductivity measurements under controlled atmospheres and water partial pressures verified the existence of a true phase transition. It is believed that while decomposition does interfere with observation of a polymorphic transition, it nevertheless occurs.

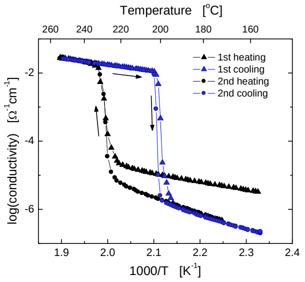


Figure 4. *Conductivity of CsH_2PO_4 vs. temperature (4)*

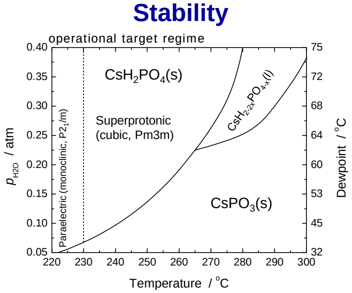

Stability

Figure 5. *Phase diagram of CDP (5)*

Fuel cell polarization curves for humidified H_2/O_2 feed gas

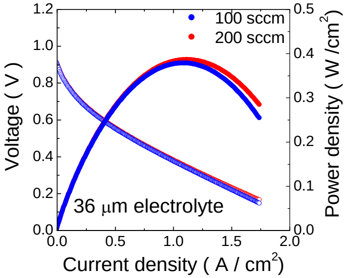


Figure 6. *Solid acid fuel cell performance in pure hydrogen and oxygen (6)*

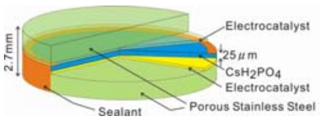
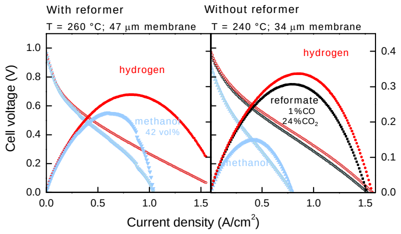


Figure 7. *Solid acid fuel cell membrane assembly. The stainless steel gas diffusion layer provides mechanical support for the thin electrolyte.*

Performance of “direct” methanol fuel cell



- Methanol power ~ 85% H_2 power
- For polymer fuel cells ~ 10%
- Ethanol power ~40% H_2 power

- Reformate power ~ 90% H_2 power
- Methanol power ~ 45% H_2 power

Figure 8. *Solid acid fuel cell performance with various inlet fuels (7)*

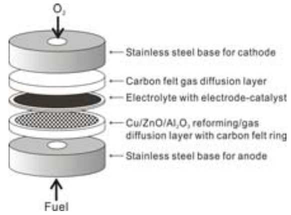


Figure 9. *Solid acid fuel cell membrane assembly with incorporated reformer (7)*

Electrocatalysis

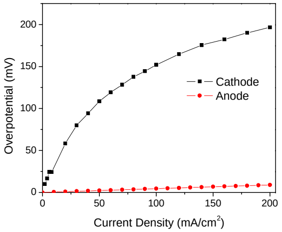


Figure 10. *Overpotential losses at anode and cathode*

Three point measurements of standard platinum-based composite electrodes reveal electrode losses are dominated by the cathode. Non-platinum electrodes could potentially reduce both overpotentials and cost. Currently, both new materials and new composite fabrication methods are being explored.

Platinum electrode performance is limited by the triple phase boundary of the microstructure. While PEM fuel cell electrode performance is optimized through maximizing catalyst surface area, solid electrolyte fuel cell electrocatalysis is more dependent on the interplay between electrode and electrolyte feature sizes.

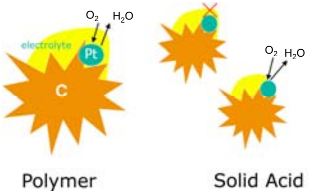
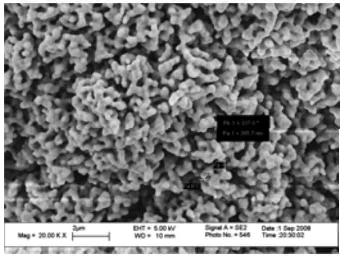


Figure 11. *Schematic depicting difference in reaction pathway*



State of the art electrode composites employ nanoscale electrolyte particles, obtained by new synthesis methods. An interconnected three dimensional nanostructure with feature sizes of 250nm was obtained via electrospray deposition.

Figure 12. *SEM micrograph of fine featured CsH_2PO_4*

Conclusion

Solid acid fuel cells and CsH_2PO_4 in particular represent an exciting new alternative to conventional fuel cells; combining the fuel flexibility an increased electrode kinetics of solid oxide fuel cells, with the lower temperature advantages of PEM fuel cells. Current research is focused on engineering improved electrode microstructures and characterization of intrinsic electrode material properties.

Acknowledgments

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References

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