

# V.B.14 Protic Salt Polymer Membranes: High-Temperature Water-Free Proton-Conducting Membranes

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## Technical Targets

- Membrane conductivity at:
  - Operating temperature, 0.10 S/cm,
  - Room temperature, 0.07 S/cm,
  - T = -20°C, 0.01 S/cm
- Operating temperature, 120°C
- Inlet water vapor partial pressure, 1.5 kPa
- Oxygen and hydrogen cross-over, 2 mA/cm<sup>2</sup>
- Cost, \$40/m<sup>2</sup>
- Durability with cycling
  - At operating temperature of <80°C, 5,000 hours
  - At operating temperature of >80°C, 2,000 hours
- Survivability, -40°C
- Thermal cyclability in the presence of condensed water, yes

## Approach

Proton-conducting polymer electrolyte membranes (PEMs) are being made that are based on protic salt electrolyte concepts. Protic ionic liquids (PILs) will be used to model membranes. Acid and base moieties as well as polymer properties will be systematically varied to optimize properties of a protic salt membrane (PSM). Liquid sorbed membranes and membranes with covalently and electrostatically immobilized ions are being made. The mechanism of proton conduction is being determined to guide electrolyte/membrane making. The first goals are to make stable liquid and then membrane electrolytes with conductivity  $\geq 0.2$  Siemen/cm (S/cm) at operating temperature and  $>0.0005$  S/cm at -20°C. The conductivity and thermal and oxidative stability of these electrolytes are being measured from -20 to 120°C, and the mechanism of transport of protons, anions, and molecules is being investigated. Proton conduction is being characterized by electrochemical impedance spectroscopy (EIS) and three nuclear magnetic resonance (NMR) methods: a) pulse field gradient NMR to determine the diffusivity of ions, b) multipulse solid state NMR to measure the molecular motion and interactions of species in membranes, and c) electrochemical NMR to measure distribution of species during proton conduction.

## Objectives

To make proton-conducting solid polymer electrolyte membrane (PEM) materials having:

- high proton conductance at high temperature (up to 120°C)
- effectively no co-transport of molecular species with proton
- reduction of electrode overpotential
- good mechanical strength and chemical stability

## Technical Barriers

The project addresses technical barriers for proton conducting membranes from the Fuel Cells section (3.4.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan, including:

- (A) Durability
- (C) Electrode Performance

## Accomplishments

Previously, we have found that neat ionic liquids that are protic salts (like ethylammonium nitrate, EAN) have good proton conductivity and have been successfully used as fuel cell electrolytes in short-term fuel cell testing at high temperatures (up to 140°C).

Figure 1 shows that with a neat protic salt electrolyte, liquid EAN, a higher efficiency operation of a hydrogen-oxygen fuel cell results than with an aqueous electrolyte, like phosphoric acid. However, as can be seen from the first 5 scans of the voltammetry of Pt in EAN under oxygen, as shown in Figure 2, EAN

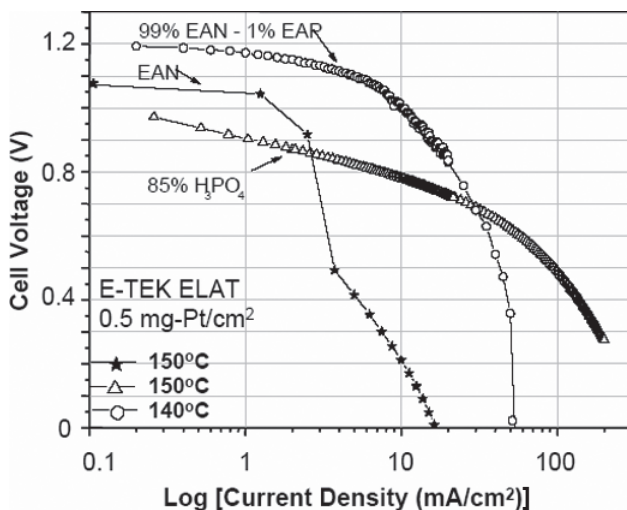


FIGURE 1. Hydrogen – Oxygen Fuel Cell Polarization Curve for Three Liquid Electrolytes

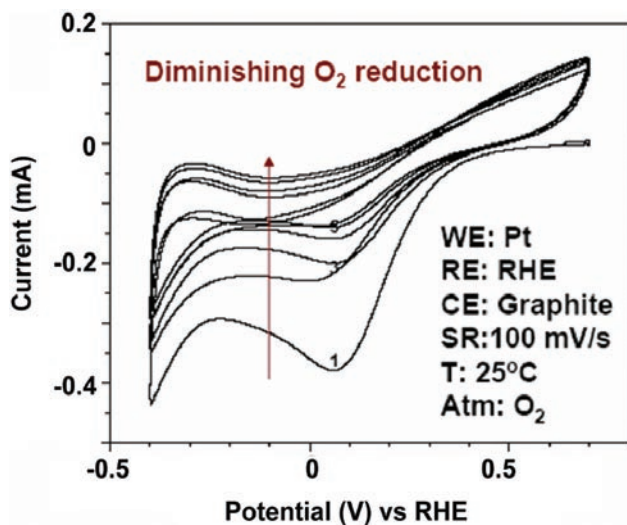


FIGURE 2. Cyclic Voltammogram for Pt in EAN under Oxygen

is oxidatively unstable. EAN is not stable enough for long-term fuel cell operation. The hydrocarbon moieties in tetraethylammonium methane sulfonic (TEAMS) acid are less susceptible to oxidation. Figure 3 shows the voltammograms for Pt in TEAMS compared to the voltammetry of Pt in 85% phosphoric acid. These voltammograms were acquired and were unchanging over a half hour. There are two striking observations: 1) the oxygen reduction activity on Pt is clearly higher with TEAMS versus phosphoric acid as the electrolyte; and 2) the comparison of Figures 2 and 3 illustrates that the stability of protic salt electrolytes can be improved by substituting oxidatively stable moieties (in TEAMS) for oxidatively unstable moieties (in EAN).

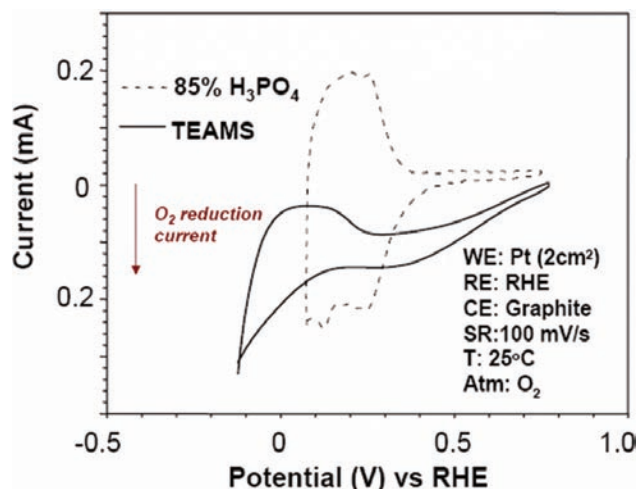


FIGURE 3. Cyclic Voltammogram for Pt in TEAMS under Oxygen

## Special Recognitions & Awards/Patents Issued

1. On September 27, 2005, a provisional patent application was filed with the United States Patent and Trademark Office by AzTE entitled “Materials Having High Ionic Conductivities for a High Temperature Fuel Cell”.

## FY 2006 Publications/Presentations

1. “Fuel Cell based Power-Sources for Airplanes” SAE AE-7 Aerospace Electric Power & Equipment Committee, Embassy Suites Phoenix, 4400 S. Rural Road, Tempe, AZ on April 26, 2006.