

V.I.1 Resonance-Stabilized Anion Exchange Polymer Electrolytes

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Project Start Date: October 1, 2009
 Project End Date: September 30, 2011

- (A) Durability
- (B) Cost
- (C) Performance

Technical Targets

This project is conducting fundamental aspects of anion exchange membrane fuel cell (AMFCs) for practical use in intermediate (10-50 kW) power applications. Insights gained from these studies will be applied toward the next stage of development of AMFC systems. Since there were no technical targets for AMFCs in the current DOE Fuel Cell Technologies Program, we have proposed the technical targets based on state-of-the-art alkaline fuel cells/materials in the original proposal (2008). Key technical targets, and FY 2011 and 2012 statuses are shown in Table 1.

FY 2011 Accomplishments

- Synthesized highly conductive (0.1 S/cm), chemically stable (>700 h) and mechanically robust poly(phenylene) (PP)-based anion exchange membranes.
- Prepared stable hydrocarbon and perfluorinated-based guanidinium functionalized ionomers having electron donating spacer.
- Measured the oxygen reduction reaction (ORR) kinetics of non-Pt catalysts (Ag, Ni, Pd, and carbon) with KOH and guanidinium electrolytes.
- Demonstrated H₂/O₂ and H₂/air alkaline membrane fuel cell performance at various operating conditions and under steady-state extended term operating conditions.



Fiscal Year (FY) 2011 Objectives

- Synthesize highly conductive and stable anion exchange membranes.
- Prepare highly gas permeable perfluorinated ionomers for electrode layers.
- Develop non-precious metal catalysts for oxygen reduction reactions.
- Demonstrate single-cell performance of alkaline membrane fuel cells.
- Perform an extended term alkaline fuel cell test under steady state conditions.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

Introduction

Current quaternary ammonium-tethered anion exchange polymer electrolytes do not show enough stability under alkaline conditions due to the chemical degradation under highly pH conditions. Furthermore, ionomer used in electrode layers has limited gas permeability that

TABLE 1. Technical Targets and FY 2011 and 2012 Status for the Project

Characteristics	2011 Target	2008 state of the art	LANL 2010 status ^a	LANL 2011 Status ^b
Ion conductivity (mS/cm)	50 (80°C)	27 (20°C)	80 (80°C)	100 (80°C)
Stability (h, at <10% σ loss 1 M NaOH)	500 h	>48 h 1 M KOH at (60°C)	380 h (0.5 M NaOH at 80°C)	700 h (at 60°C, 4 M NaOH)
Maximum power density (mW/cm ² at 80°C) ^c	200 (H ₂ /air)	196 (H ₂ /O ₂)	NA	300 (H ₂ /air)
Fuel cell durability ^d	500 h	NA	NA	300 h

^a as of June 30; ^b as of June 7; ^c platinum-based catalysts; ^d under steady-state conditions; NA: not available

significantly reduces cell performance [1]. In FY 2010, we demonstrated successful synthesis of stable guanidinium functionalized poly(arylene ether)s and initiated synthesis of perfluorinated ionomers for the catalyst layers. In FY 2011, continuing efforts to develop new anion exchange polymer electrolytes and electro-catalysts have been made in order to demonstrate the performance and stability of AMFCs.

Approach

Our approach to achieve high performance AMFCs is to develop new materials which have improved properties and minimal interference between them when the materials are used in membrane electrode assemblies (MEAs). Sandia National Laboratories investigated the properties of PP-based anion exchange membranes for practical use in AMFCs. LANL continued to develop the guanidinium functionalized ionomers for the catalyst layer, which have electron donating stabilizers which may provide good cation stability under high pH conditions. The Jet Propulsion Laboratory (JPL) and LANL investigated the catalytic activity of various catalysts in guanidinium solution in order to screen the best class of catalysts for alkaline membrane fuel cell systems. Extensive efforts on fabrication of AMFC MEAs and fuel cell testing were performed at LANL in order to demonstrate good AMFC performance. The ultimate goal for these approaches is to realize good AMFC performance by integration of these materials into an MEA.

Results

Anion Exchange Polymer Electrolytes

Mechanical properties for both poly(ether sulfone) (PES)- and PP-based anion exchange membranes were investigated as a function of exposure to high pH conditions

in order to gain some insight into the practicality of using these polymers in AMFCs (Figure 1). The PES membranes showed a surprising diminishment of both elongation (strain) and strength (stress) after just 30 minutes in 0.5 M NaOH at 80°C. These effects become more pronounced with increases in both NaOH concentration and temperature, indicating that they are due to degradation of the polymer backbone and not simply the exchange of bromide anions (in the control) for hydroxide anions. This indicates that PES-based polymers lack the chemical stability required for them to be used in AMFCs, an important result given that several recently reported anion exchange membranes and ionomers are based on similar PESs [2,3]. By contrast, the results for the PP-based membranes do not show a continual weakening of the mechanical properties with successive exposures to NaOH. An initial exposure to 0.5 M NaOH at 80°C for 1 hour does result in an elongation decrease of about 40% and a strength decrease of about 10%, but after conversion back to bromide ion form, the curve looks very similar to the control. A second NaOH treatment does not diminish the mechanical properties any more than the first treatment. Thus the shifting of the curves in Figure 1b is indicative of membrane property changes that are due to the identity of the anion present and not due to polymer degradation.

LANL continues to develop guanidinium functionalized ionomers for the catalyst layer. Guanidinium functionalized ionomers were synthesized via activated fluorinophenyl-amine reaction [4], followed by the methylation with dimethyl sulfate. The activated fluorine-amine reaction gives precise control of cation functionality without the deleterious side-reactions and allows the direct connection of guanidinium into stable phenyl rings. For perfluorinated ionomer, fluoroaniline or six-membered imides were used as electron donating spacers which reacted with perfluorinated carboxylic acid (equivalent

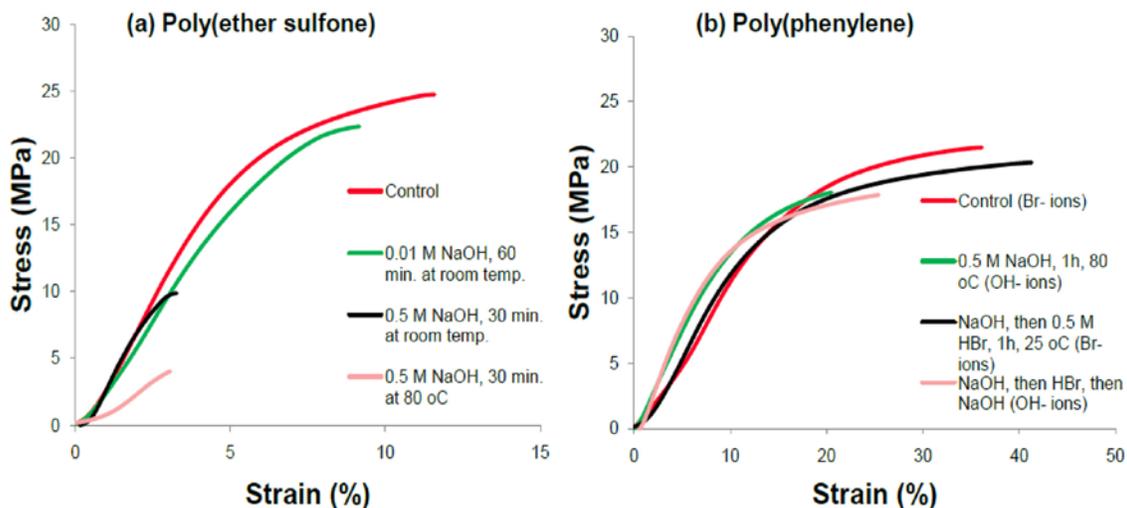


FIGURE 1. Mechanical test results at 50°C and 50% relative humidity for (a) PES-based anion exchange membranes and (b) PP-based anion exchange membranes.

weight=1100). The chemical stability of the ionomer with the electron donating spacers was much improved compared FY 2010 ionomer as it showed less than 10% degradation after soaking the membranes in NaOH solution at 80°C for 100 h. The solubility of the ionomer is good in aprotic solvents such as N-methylpyrrolidone, dimethyl acetamide and high alcohols such as glycerol.

Electro-Catalysts

JPL investigated the reaction kinetics of various electro-catalysts with KOH and guanidinium electrolytes. These experiments were conducted on Pt and Pd surfaces. The Pt surface exhibits H₂O redox processes in 0.1 M tetramethyl guanidine (TMG)_(aq) similar to those in KOH/NaOH electrolytes, and remains highly active for oxygen reduction. Electrochemical tests performed via rotating disk electrode (RDE) measurements on elemental Pt electrodes show that Pt exhibits the major electrochemical reactions: hydrogen evolution reaction (HER), hydrogen oxidation reaction (HOR), hydrogen adsorption and the ORR in 0.1 M TMG and 0.1 M KOH. Surface reconstruction and activity in KOH mirror that of Pt in acids, and in 0.1 M TMG, only (110) crystal plane is active after cycling to 1.1 V (vs. reversible hydrogen electrode, RHE). Electrochemical tests performed via RDE on elemental Pd electrodes show that Pd exhibits HER, H_{upd}, and ORR in 0.1 M TMG and 0.1 M KOH. The ORR current density (at 0.9 V RHE) for Pd surfaces in alkaline electrolytes exceeds that for Pt surfaces in acid solutions, as shown in Figure 2. Thus, Pd or Pd-based alloys are very attractive for use as the cathode in AMFCs. RDE tests on Pd are ongoing to examine potential dependence of surface reconstruction in KOH and TMG electrolytes. To date, in 0.1 M TMG, only (110) crystal plane is active after cycling to 1.1 V (vs. RHE). Our temporal tests have shown that the TMG electrolyte shows remarkable stability after two months, with some signs of

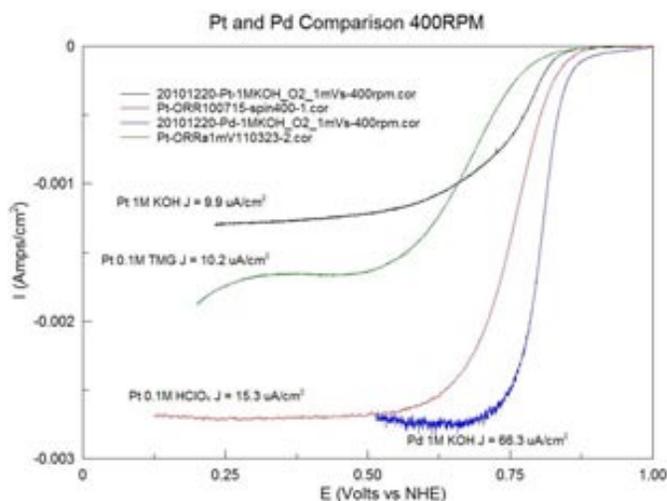


FIGURE 2. Oxygen reduction reaction curves for Pt and Pd surfaces in 0.1 M TMG and 0.1 M KOH electrolytes.

increasing resistivity such as the positive potential shift of the H-desorption peak. TMG and its byproducts can adsorb onto the Pt surface below ~0.8 V, obscuring the transition between typical kinetic and mass-limiting regions during oxygen reduction. This effect is especially pronounced at low rpm (low oxygen concentrations). Though the nature of TMG adsorption onto a polarized Pt electrode needs to be better understood, this study shows that free TMG can be used to support electro-catalytic activity on Pt, in place of NaOH or KOH salts. Because AMFCs require frequent replenishment of metal cation electrolyte to avoid precipitation of bicarbonates, the use of TMG electrolyte could still improve such systems despite its slow degradation. Particularly if it serves to better stabilize functional groups within the membrane, itself.

LANL developed nitrogen-doped carbon-based catalysts. The N-doped carbon-based catalysts showed promising ORR activities ca. half-wave potentials reached up to 0.95 V (vs. RHE) which is superior to the ORR activities of Pt/C catalysts in alkaline media (Figure 3). The durability of the N-doped carbon-based catalysts was measured during potential cycling (0.6-1.0 V vs. RHE) in O₂-saturated electrolytes. The ORR activities were enhanced after 1 k cycles and stabilized after 5 k cycles. The N-doped carbon based catalysts showed good ORR kinetics in guanidinium electrolytes. The onset potential (vs. RHE) of N-doped catalyst (0.2 mg/cm²) in guanidinium 0.1 M aqueous solution is 1.03 V which is same with the Pt/C catalyst (60 μg/cm²) in NaOH and higher than Pt/C in HClO₄.

Fuel Cell Performance

While MEA performance using newly developed catalysts is in progress, AMFC performance using a PP-based membrane, guanidinium functionalized ionomer

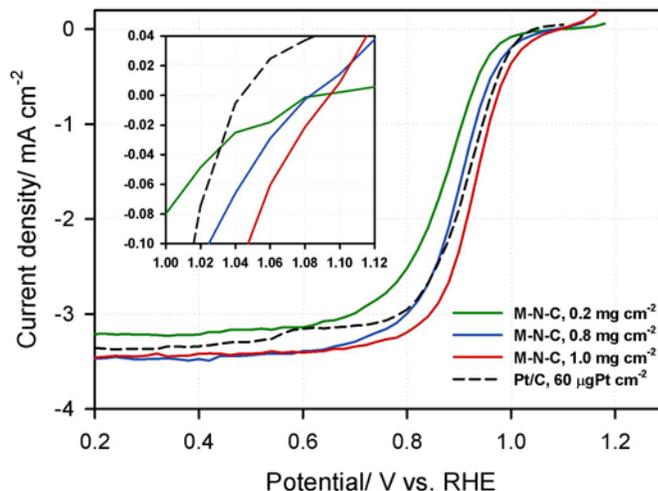


FIGURE 3. ORR activity of M-N-C catalysts in NaOH solution; RDE experimental conditions: 0.1 M NaOH; 900 rpm, room temperature; steady state potential (OCP, 120 s, 20 mV steps, 25 s/step)

and Pt black catalyst was measured under various conditions. The electrode composition and humidification were optimized. Degrees of anode flooding and cathode dehydration strongly depend on membrane and ionomer type and fuel cell operating conditions. After the optimization process, maximum power density of 500 and 300 mW/cm² was achieved for the MEAs at 80°C and under H₂/O₂ and H₂/air conditions, respectively (Figure 4). Much inferior performance was obtained when tetraalkyl ammonium functionalized poly(phenylene) polymers were used as electrode ionomer (e.g. maximum power density of 200 mW/cm² under H₂/O₂ condition). Guanidinium functionalized ionomer also showed promising durability during a 300 h AMFC operation at 60°C and constant voltage of 0.3 V. Tafel-slope of internal resistance-free polarization curves before and after lifetime test changed from 62.4 to 69.6 mV/decade (24 μV/dec h), indicating that minimal ionomer degradation occurred during the lifetime test while more than six times faster degradation rate was observed for tetraalkylammonium functionalized ionomer.

Conclusions and Future Directions

- Newly synthesized PP-based anion exchange membranes exhibited excellent chemical stability after immersion in 0.5 M NaOH solution. Stable guanidinium functionalized perfluorinated ionomers with electron donating spacer were prepared in liquid dispersion.
- Catalytic activities of Pt, Pd and N-doped carbon-based electro-catalysts showed excellent ORR kinetics in KOH and guanidinium solution. The N-doped carbon-based catalysts showed unprecedented activity (ca. half-wave potentials reached up to 0.95 V [vs. RHE]) in alkaline conditions.

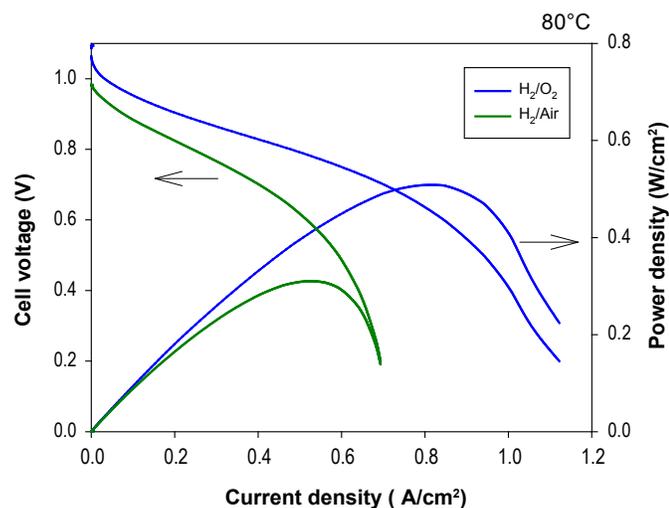


FIGURE 4. H₂/O₂ and H₂/air AMFC performance at T_{cell} = 80°C under fully hydrated conditions

- The maximum power density of alkaline membrane fuel cells under H₂/O₂ and H₂/air conditions reached to 500 and 300 mW/cm² which exceeded the project target performance. The preliminary extended term life test indicated that only minimal degradation of ionomer (24 μV/dec h) occurred during steady-state AMFC operation.
- AMFC performance tests using non-precious metal catalysts are yet to be assessed. Longer term test up to 800 h is under investigation.

Patents Issued

- Solid State Alkaline Fuel Cells, DOE S-121,575 Patent pending (2011).
- Anion Exchange Polymer Electrolytes, DOE S-121589 Patent pending (2011).
- Fuel Cell Catalysts, DOE S-121083 Patent pending (2010).

FY 2011 Publications/Presentations

- D.S. Kim, A. Labouriau, M.D. Guiver, Y.S. Kim, Guanidinium Functionalized Anion Exchange Polymer Electrolytes via Activated Fluorophenyl-Amine Reaction, *Chemistry of Materials*, 2011, 23, 3795.
- M. Hibbs, C.H. Fujimoto, T. Lambert, D.S. Kim, Y.S. Kim, Poly(phenylene)-based anion exchange membranes for alkaline fuel cells, NAMS meeting, Las Vegas, June (2011).
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- D. Konopka, M.A. Johnson, M. Errico, P. Bahrami, and C.C. Hays, ECS 220 Meeting, Boston, MA October (2011).
- D. Konopka, M.A. Johnson, M. Errico, P. Bahrami, and C.C. Hays, Oxidation and oxygen reduction on polycrystalline platinum in aqueous tetramethylguanidine alkaline electrolyte, (Manuscript to be submitted to *Electrochemical and Solid-State Letters*).

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- J. Wang, S. Li, S. Zhang, "Novel hydroxide-conducting polyelectrolyte composed of an poly(arylene ether sulfone) containing pendant quaternary guanidinium groups for alkaline fuel cell applications" *Macromolecules* 2010, 43, 3890.
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