

V.N.2 Resonance-Stabilized Anion Exchange Polymer Electrolytes

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Objectives

- Develop new anion exchange polymer electrolytes that have high hydroxyl conductivity and stability under alkaline conditions.
- Demonstrate an improved single-cell performance of solid-state alkaline fuel cells using the polymer electrolytes and non-precious metal catalysts.

Technical Barriers

- (A) Durability: stability of fuel cells under highly basic conditions is not well understood. Strategies for mitigating performance loss over time are needed.
- (B) Cost: material costs for platinum-based catalysts and membranes are the major barriers for fuel cell commercialization.
- (C) Performance: anode and cathode performance depends on electrode structure and interactions between electrode materials.

Technical Targets

This project is conducting fundamental aspects of solid state alkaline fuel cells for practical use in transport applications. Insights gained from these studies will be applied toward next stage of development of alkaline fuel cell systems. Since there were no technical targets for solid state alkaline fuel cells provided by the current U.S. DOE Fuel Cell Technologies Program, we propose

technical targets based on state-of-the-art alkaline fuel cells/materials in the original proposal. Key technical targets and current status are shown in Table 1.

TABLE 1. Technical Targets and Current Status for Solid State Alkaline Fuel Cells

Characteristics	State-of-the-art	2011 Target	LANL 2010 Status
Ion conductivity (mS/cm)	27 (20°C)	50 (80°C)	80 (80°C)
Stability (hour at 10% conductivity loss at 80°C in 1M KOH)	>48 h 1 M KOH at (60°C)	500 h 1 M KOH at (80°C)	380 h 0.5 M NaOH at 80°C (42% loss)
Fuel Cell Performance	196 mW/cm ² H ₂ /O ₂ (80°C)	200 mW/cm ² H ₂ /air at (80°C)	NA

NA: Not available

Accomplishments

- Discovered that traditional aqueous quaternization produces incomplete amination due to undesirable alcohol formation while non-aqueous quaternization provides precise control of amination without forming alcohol.
- Prepared hydrocarbon-based guanidine base (HCGB) homopolymer which has extremely low water uptake (9%) with reasonable anion conductivity (35 mS/cm at 80°C) and stability (ca. 380 h in 0.5 M NaOH at 80°C).
- Prepared perfluorinated guanidine base (PFGB) polymer electrolyte. The anion conductivity of this material met the 2011 conductivity target (80 mS/cm at 80°C) but showed limited stability.
- Identified the degradation mechanism for PFGB polymer electrolytes and discovered that the electrolyte stability can be significantly improved by having an electron donating group next to the cation functional group.
- Prepared nano-structured whiskers for electrode supporting materials. This material will be used as a high surface area support for alkaline fuel cell electrodes.



Introduction

Recently, renewed interest has grown in the development of solid-state alkaline fuel cells, since the efficiency of oxygen reduction reaction of electrocatalysts in an alkaline environment is likely greater than

in acidic conditions and therefore, expensive platinum-based catalysts can be replaced with inexpensive ones such as nickel, silver and carbon [1,2]. However, current quaternary ammonium-tethered anion exchange polymer electrolytes do not show enough stability under alkaline conditions due to the nucleophilic substitution reaction under highly basic conditions [3]. Furthermore, ionomer used in electrode layers have limited gas permeability that significantly reduces cell performance.

Approach

Our approach to achieve stable anion exchange polymer electrolytes is to use highly basic cation functional groups instead of traditional tetra-methyl ammonium group. Tetramethyl guanidine (TMG) has high basicity (i.e. $pK_a=13.6$) and formed resonance structure which contributes further stabilization of cation through uniform electron distribution. In order to maximize the fuel cell performance, anion exchange membranes and ionomeric binders should be designed in a separate manner, as the requirements for each role are somewhat different. Another key approach is to prepare perfluorinated ionomer for electrode binding material that has significantly higher gas permeability. An alternative approach is to prepare nano-structured thin film electrodes which do not need an ionomeric binder which minimizes the limited gas permeability problem.

Results

One of the technical barriers for anion exchange polymer electrolytes is poor synthetic control of cationic functional groups [4]. We found that when quaternization was accomplished by soaking halogenated polymer electrolytes in aqueous trialkylamine, hydroxide ions can act as nucleophiles and compete with alkyl amines to produce primary alcohols in addition to alkylammonium salts. Once alcohols are formed in polymer chains, the ion exchange capacity of the polymer is reduced, and water sorption is increased which dilutes the concentration of cation functional groups and gives a significant impact on ion conductivity and water uptake. Figure 1 compares the water uptake and ion conductivity of aqueous quaternized and non-aqueous quaternized anion exchange polymer electrolytes. It is noted that much higher water uptake and lower proton conductivity was achieved with aqueous quaternized anion exchange polymer electrolytes. Non-aqueous quaternization improves hydroxyl conductivity significantly which is an encouraging result and the non-aqueous quaternization technique was used for our research.

Typically quaternary ammonium-tethered polymers are prepared from chloromethylated (or alkyl brominated) polymers and subsequent reaction with a tertiary amine to form the quaternary ammonium

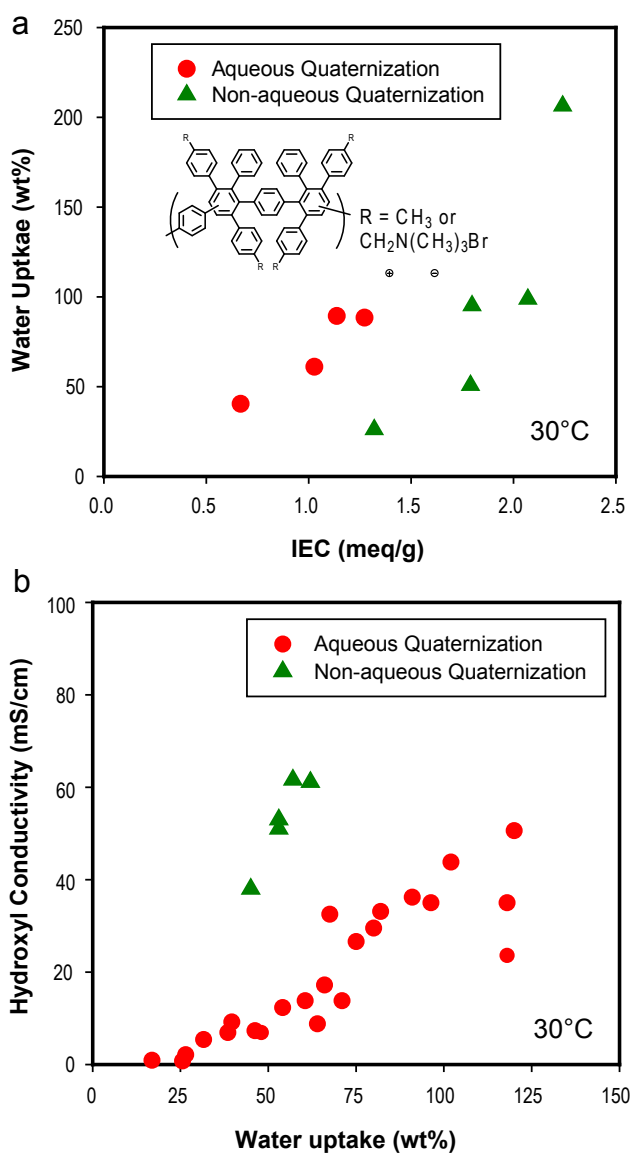


FIGURE 1. Comparison of aqueous and non-aqueous quaternization of aminated polyphenylene: (a) water uptake and (b) hydroxyl conductivity.

groups [5]. The amination step is typically performed by soaking a film of the halomethylated polymer in a solution of trimethylamine (TMA) such that the polymer remains in the solid state throughout the reaction (the heterogeneous method). Alternatively the amination can be done with the halomethylated polymer dissolved in a polar aprotic solvent such as *N,N*-dimethylacetamide (the homogeneous method). The heterogeneous method is somewhat simpler to perform in practice although it was our hypothesis that membranes prepared this way should have lower conductivities than their homogeneously-formed analogs due to lack of phase separation. Since the heterogeneous method involves casting films before the polymer has any attached ionic groups, the placement of those ionic groups should be random throughout the polymer matrix. By contrast,

in the homogeneous method the polymer is cast in its ionomeric form and the highly polar ammonium groups would have a chance to form highly-conductive microdomains within the membrane. We prepared anion exchange membranes from a halomethylated poly(phenylene) using both methods and were surprised to find that the membrane properties (particularly conductivity) were nearly independent from the amination method used. The presence or absence of water with the TMA (as discussed above) had a much greater impact on the membrane properties than the amination method did.

When tetramethyl guanidine is used instead of TMA, two vicinal chloromethyl groups can react to form hexasubstituted guanidinium-containing polymers. Since two chloromethyl groups are involved in the reaction, the reaction ends up with gelation. In order to prevent the possible gelation, we synthesized guanidine functionalized polymers with TMG-fluorine reaction without the chloromethylation process. HCGB polymers were synthesized by reacting tetramethyl guanidine with polyarylene ether sulfone containing pendant 4-fluorophenyl sulfide groups and followed by

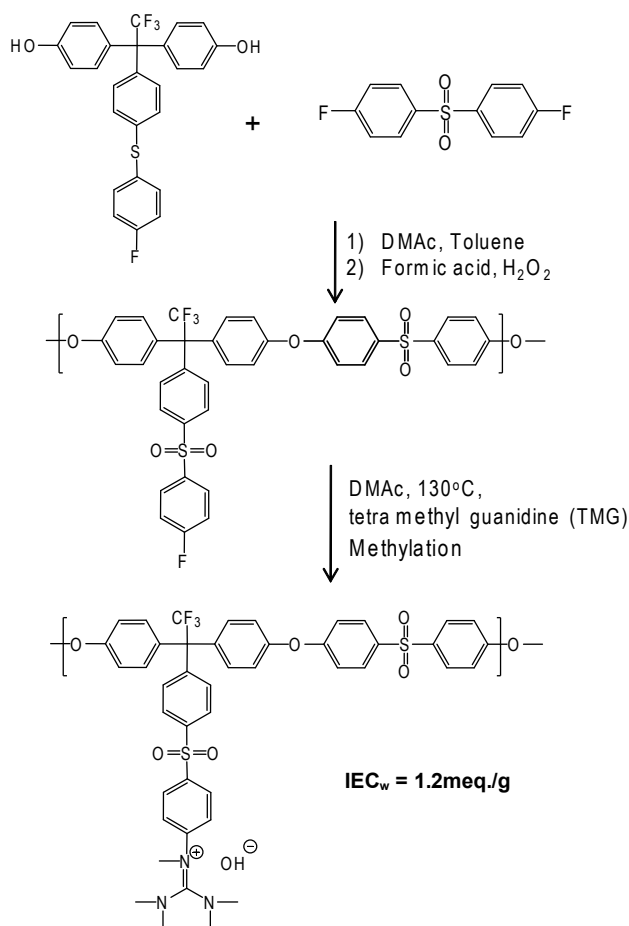


FIGURE 2. Synthesis of HCGB Base Polymer.

methylation (Figure 2). PFGB polymers were prepared from perfluorosulfonic acid precursor using similar fluorine-TMG reaction. Fourier transform infrared (FTIR) analysis showed that after the methylation reaction, the C=N form of tetramethyl guanidine was changed to a resonance hybridization structure CN₃ form.

Anionic conductivity of OH⁻ and CO₃⁻ form of HCGB and PFGB polymers was measured by an impedance analyzer. CO₃⁻ conductivity of both polymer electrolytes is about half of OH⁻ conductivity. HCGB and PFGB anion exchange polymer electrolytes exhibited excellent hydroxyl conductivity in the range of 0.01-0.08 S/cm, depending on molecular structure and temperature. The conductivity of PFGB (0.08 S/cm) exceeded our target conductivity (0.05 S/cm) at 80°C. Figure 3 compares conductivity of various anion exchange polymer electrolytes as a function of water uptake. Water uptake of guanidine base polymers is extremely small compared to previously developed anion exchange membranes so effective anion conduction can be achieved at relatively low water uptake [6,7]. The stability was evaluated by immersion of the membrane into 0.5 M NaOH solution at 80°C. While HCGB showed reasonably high stability (~40% conductivity decrease for over 380 h), PFGB showed rapid degradation. Based on FTIR and solid state nuclear magnetic resonance data, nucleophilic attack to the center carbon molecule of the guanidine base was proposed as a main degradation mechanism as shown in Figure 4. The degradation via nucleophilic substitution produced two neutral species to lower ion exchange capacity and conductivity. Significantly different degradation rates between HCGB and PFGB suggested that electron-withdrawing and donating characteristics

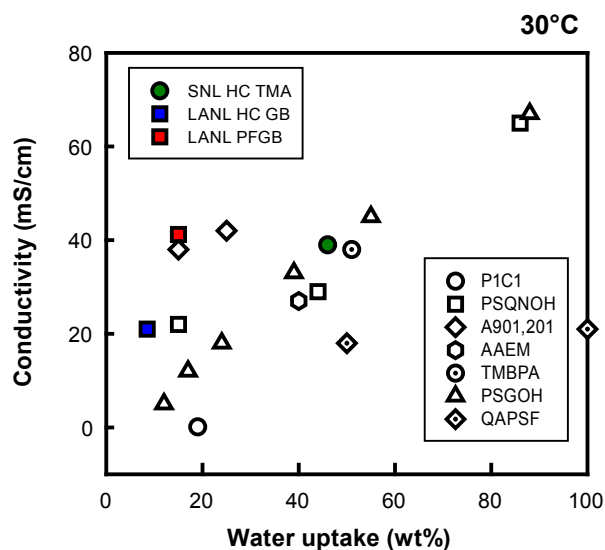


FIGURE 3. Hydroxyl conductivity of anion exchange polymer electrolytes as a function of water uptake.

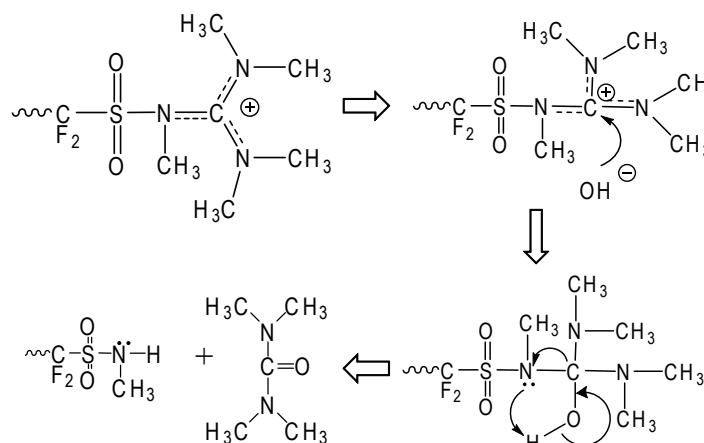


FIGURE 4. Proposed Degradation Mechanism of PFGB by Nucleophilic Attack of the Hydroxyl Ion

of the cation adjacent group is critically important and affects the nucleophilicity of the central carbon. We have therefore proposed to modify the polymer structure in order to mitigate cation degradation to achieve our stability target, which is our ongoing study.

Conclusions and Future Directions

- New highly conductive guanidine-based anion exchange polymer electrolytes were prepared using non-aqueous quaternization.
- Conductivity of anion exchange polymer electrolytes met or exceeded our internal target.
- Stability of anion exchange polymer electrolytes is strongly influenced by electron density of the adjacent cation group. Currently we are changing polymer structures to improve cation stability.
- We are planning to synthesize binary and ternary late-transition-metal (LTM) alloys based on Ni, Co, and Fe; and these LTM elements alloyed with the valve metals (Ti, Zr), in order to determine their performance for use as electrode materials in alkaline electrolytes.
- We are planning to fabricate a membrane electrode assembly for fuel cell performance evaluation as component materials are prepared.

Special Recognitions & Awards/Patents Issued

1. Anion exchange polymer electrolytes, Patent Pending (2009).

FY 2010 Publications/Presentations

1. Dae-Sik Kim and Yu Seung Kim, Anion conducting Polyaromatics having Guanidine Base, Submitted to 2010 ECS Transactions.

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