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234th National Meeting of the American
Chemical Society

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August 2007

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Introduction

Development of long-lived high-energy lithium-water batteries hinges upon developing solid polymer electrolytes (SPEs) with the appropriate properties. These polymer membranes paradoxically must allow lithium atoms to pass from the metallic surface, oxidize to the ionic form, and then pass through the membrane to the water outside. At the same time, the membrane must exclude all water, tramp ions, and deleterious gases such as oxygen and carbon dioxide. Current non-membrane approaches being pursued by other research groups suffer from two insurmountable problems. First, shelf-life and any type of storage prior to deployment are extremely problematic as there is no protecting membrane surrounding the lithium metal anode. This is both a service problem as well as a more serious safety issue. Second, while the cell is in use, battery lifetimes depend upon the non-energy productive consumption of a portion of the lithium metal anode to form the primary electrolyte barrier/interface between the anode and the water. Employing SPE-based technology provides the benefits of enhanced safety, increased battery lifetimes and energy efficiency while avoiding the problems inherent in the “classical” devices as noted above.

Previous INL research has developed deliberately modified polymer electrolytes based upon phosphazene polymers that address the above paradoxical situation. The approach that we have employed builds upon the concept for ion transport within solid polyphosphazene matrices, the backbone-centered ion-channel mechanism. (BIM) Parts of this work have been fully investigated and are the subject of peer-reviewed papers and patent disclosures.^{1,2} This work has progressed for application to the challenges presented in developing a SPE for lithium water batteries. One of the key discoveries was the importance of the molecular architecture of these membrane formulations.³ This work led to the conclusion that in order to simultaneously maximize lithium ion transport while minimizing the undesired back-transport of water, retention of the transporting species, in this work repeat ethyleneoxy units, proximate to the phosphazene backbone was required, leaving the hydrophobic portions remote from the phosphazene core.

Even with this understanding of the mechanism of ionic transport through phosphazene polymers, this concept still requires additional research to complete the understanding of the interplay between the BIM transport mechanism, dominating cation transport, and more typical solution-diffusion transport mechanism(s) governing the transport of both neutral species – namely permanent gasses and water. A more complete understanding of this mechanistic interplay will allow us to realize the full potential possible with polyphosphazene solid polymer electrolytes for lithium/water batteries. In this paper, a series of suitable polyphosphazenes with the BIM molecular architecture have been synthesized and the transport of an indicating gas (carbon dioxide) and water quantified.

Experimental

Polymer Synthesis. The dichlorophosphazene polymer was made by ring-opening polymerization of phosphonitrilic chloride trimer (Strem) using previously described methods.^{4,5} An average of 40-45% conversion to the linear polymer, $(\text{PNCl}_2)_n$ was achieved.

The organophosphazenes (T-1 – T-7) were made using standard literature procedures. A typical synthetic scheme is given here. A solution of dichlorophosphazene polymer was made with anhydrous toluene at room temperature under a purge of dry Nitrogen. To this was added to a solution of the appropriate phenoxide (or alkoxide) formed from the reaction of the appropriate surfactant and sodium hydride in dry THF. Once added, the mixture was stirred at a gentle reflux until the reaction was complete as indicated by ³¹P NMR. (singlet at approximately -7ppm) The nucleophilic substitution was rapid in all cases, with typical reaction times being on the order of 3-6 hours. Once substitution was complete, the polymer was precipitated into a water/alcohol solution (approximately 40:60 water:reagent alcohol) followed by precipitation into hexane and then again into alcohol/water twice sequentially from THF to obtain white to tan-colored gums.

Water Permeation Measurements. This measurement technique was developed at the INL to specifically support electrolyte research of this nature.⁶ A typical procedure is as follows. The polymer membranes were cast directly on porous supports with an average thickness of 50 μm . These supported membranes were loaded into cells obtained from Millipore and modified for pervaporation experiments. Modification to the Millipore cells consisted of a pumping system to flow feed solution over the membrane at approximately 50 mL/min. A diaphragm vacuum pump capable of providing a transmembrane pressure differential of 550 mmHg was installed on the system with a cryo-trap between the pump and the cell. Permeates were collected for six to eight hours and quantified gravimetrically. Transmembrane fluxes are reported in terms of $\text{L}/\text{m}^2\text{h}$, where L = volume of permeate, m^2 = membrane area (0.0017 m^2), and h = experimental time.

Carbon Dioxide Permeation Measurements. This measurement technique was also developed at the INL employing a custom pure gas permeation test apparatus.⁷ Permeabilities were determined using literature barometric methods (time-lag) where the permeate volume was 1021.5 mL, the membrane area was 3.2 cm^2 , and the initial feed gas pressure $206.8 \times 10^3 \text{ Pa}$ (30 psi)

Results and Discussion

As the goal of these investigations was to begin to probe the interplay between the simultaneous transport of both water and lithium ions within a given molecular architecture, it was deemed most appropriate to have a series of closely related phosphazene formulations that varied each of the major components of a hydrophobic SPE. These two components are 1) the size of the ion channel; and 2) the nature and size of the hydrophobic capping groups. Given that the synthesis of polyphosphazenes proceeds most readily when the starting pendant groups are alcohols, a search of available chemical sources revealed that there were several non-ionic surfactants that possessed all of the desired chemical properties, a hydrophilic tail comprised of a varying number of repeat ethyleneoxy units as well as closely structurally related hydrophobic capping head groups. The surfactants Triton and Brij series were obtained through Aldrich and the Igepal series was received as a gift from Rhodia, all used as received. (See Table 1) As these were technical grade reagents, the number of ethyleneoxy repeat units was non-integral, as surveyed by ¹H NMR, indicating that a mixture of repeat units was present in each formulation, see Table 2. The same was found to be true for the isomerization of the alkyl groups in the hydrophobic head groups. However, the average number of carbons was found to be accurate as described by the product literature (for example, Igepal CO430 does average out to be a C₉ substituted phenol) and the average structure, correct in carbon count but expressed as a single linear isomer is what is given in the Table.

Table 1. Structure of the Hydrophobic Capping Group for Each Polymer Formulation

Polymer	Head group
T-1	
T-2	
T-3	
T-4	
T-5	
T-6	
T-7	

Table 2. Surfactant Brand Name used to Synthesize Each Polymer Formulation with Corresponding Ion Channel Size

Polymer	Ion Channel Size [(OEt) _n]	Starting Surfactant
T-1	8	Triton X114
T-2	1.5	Igepal CA210
T-3	1.5	Igepal CO210
T-4	4	Brij - 30
T-5	4	Igepal CO430
T-6	9.6	Igepal DM530
T-7	2	Brij - 72

In order to better understand the influence of the BIM on transport of the nonionic species in polymers of this molecular architecture, careful measurement of the transport of both water and the indicating gas carbon dioxide were made for each of these polymer formulations. It has been reported in the recent polyphosphazene literature⁷ that the transport of carbon dioxide closely mirrors the molecular flexibility in formulations of differing molecular architecture. Deviation from this prior observation could

prove valuable in the assessment of the transport behavior in these polymers as well. The data collected for the transport behavior is presented in Table 3. In some cases, the water permeability of the formulations was too great to quantify with our equipment, and those data are simply represented as a lower bound for permeability. For the aromatic containing polymers, a clear trend is seen that does correlate polymer backbone flexibility with both carbon dioxide and water transport, with polymer that have the highest glass transition temperature exhibiting the poorest transport. However, the aliphatic polymers (T-4 & T-7) exhibit a different behavior. Permeability of both water and carbon dioxide are much lower than expected given the trend observed for the aromatic polymers. This is attributed to an enhanced self-association of the long aliphatic chains over their aromatic-containing counterparts. This creates regions within the polymer matrix that are completely non-polar that provide for little transport of the highly polar water and CO₂ molecules. This region is displaced from the more polar environment of the polymer backbone, though, so it retains its flexibility and low T_g.

Table 3. Water and Carbon Dioxide Permeability Correlated to Thermal Properties of Each Polymer Formulation

Polymer	T _g (°C)	CO ₂ Perm. ^a	H ₂ O Perm. ^b
T-1	-39	157	>1000
T-2	11	12	50
T-3	-11	45	100
T-4	-45	386	425
T-5	-33	131	>1000
T-6	-41	275	>1000
T-7	-39	9	183

a. Barrers; b. g · μm/hr/m² (static measurement)

Conclusions

The results of these studies lead the authors to two important conclusions. First, the transport of the neutral species, both gas and liquid is facilitated by an increase in molecular flexibility in the phosphazene backbone as primarily evidenced by the glass transition temperature. This indicates that, as in the case of the lithium ion transport, permeation occurs through the ion channel region of the polymer membrane. Second, hydrophobic capping groups that lack an aromatic functionality yield a polymer that has better self-association of the hydrophobic regions leading to water transport rates that are depressed over expectations, given their thermal behavior.

Acknowledgement. This work was supported by the U.S. Department of Energy, Office of Nuclear Energy, Science, and Technology, and the INL Laboratory Directed Research & Development (LDRD) Program under DOE-NE Idaho Operations Office Contract DE-AC07-05ID14517.

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