

## Polyimides for Solid Polymer Electrolyte Membranes

Jennifer A. Irvin\*<sup>1</sup>, Daniel Stasko,<sup>2</sup> Cynthia K. Webber<sup>1</sup>,  
Andrew J. Guenther<sup>1</sup>, Stephen Fallis<sup>1</sup>,  
and John Blackwell<sup>3</sup>

(1) Chemistry and Materials Division, Naval Air Systems  
Command, China Lake, CA, (2) Department of  
Chemistry, University of Toledo,  
Toledo, OH (3) Macromolecular Science & Engineering,  
Case Western Reserve University, Cleveland, OH

Solid polymer electrolyte membranes are crucial components of both lithium ion batteries (LIBs) and fuel cells (PEMFCs). However, performance of these devices is currently materials-limited, and many groups are working on alternative materials to improve performance.

We have investigated a variety of polyimides (Figure 1, Table 1) for use as solid polymer electrolytes. Crown ethers have been incorporated to form channels for lithium ion transport in low temperature LIBs and to improve hydrophilicity for use in high temperature PEMFCs. Six-membered imide rings have been incorporated for improved hydrolytic stability<sup>1</sup> for PEMFCs. Hexafluoroisopropylidene (HFIP) groups have been incorporated to improve solubility without detracting from thermal stability.<sup>2</sup>

Polyimides were prepared using standard thermal polymerization techniques in *m*-cresol. 1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTDA) and/or 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) were heated with diamines to form polyimides. Diamines used were 2,2-bis(4-aminophenyl)hexafluoropropane (Bis-A-AF), *anti*-4,4'-diamino-dibenzo-18-crown-6 (C18), 4,4'-diaminodibenzo-24-crown-8 (C24), and/or 2,5-diaminobenzenesulfonic acid (DABS).

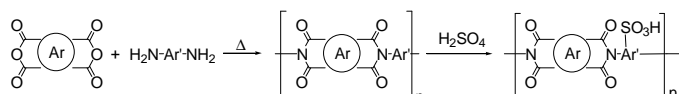
For use in PEMFCs, several polymers have been sulfonated according to a literature procedure.<sup>3</sup> Degree of sulfonation (Table 2) was determined by titration; up to three sulfonic acid groups were introduced per repeat unit. Proton conductivity of sulfonated polymers was determined from AC impedance measurements (Table 2); conductivity reached 0.01S/cm in fully hydrated polymer.

Polymers exhibit good thermal stability, with decomposition in air typically occurring above 300°C. Two different forms of order were detected in crown ether-containing polyimides via cryogenic differential scanning calorimetry (DSC, Figure 2) and X-ray diffraction (XRD). Polymers 1 and 2 are semi-crystalline, with melting points at or above the thermal decomposition temperatures of the polymers. First-order transitions akin to crystallization occur below room temperature in both polymers; these transitions are likely due to a conformational change in the crown ether rings. Molecular models based on the XRD data suggest structures in which the chain axes are in the plane of the film, with the crown ethers stacked perpendicular to the surface. This type of structure may facilitate Li<sup>+</sup> transport.

Several polyimides have been prepared; incorporation of HFIP groups improves solubility without detracting from thermal stability. Sulfonation of several of these polymers yielded room temperature proton conductivities reaching 0.01S/cm. Some evidence of crown ether channel formation has been seen, suggesting that some of these polymers may be useful as battery electrolytes.

## References

- Genies, C.; Mercier, R.; Sillion, B.; Petiaud, R.; Cornet, N.; Gebel, G.; Pineri M., *Polymer* **2001**, *42*, 5097-5105.
- P. E. Cassidy, *J. Macromol. Sci.-Rev. Macromol. Chem. Phys.*, **1994**, C34, 1.
- Zaidi, S. M. J.; Mikhailenko, S. D.; Robertson, G. P.; Guiver, M. D.; Kaliaguine, S., *J. Membr. Sci.*, **2000**, *173*, 17-34.
- a) Togano, T.; Takiguchi, T.; Takao, H.; Hanyu, Y.; Asaoka, M.; Iwaki, T., *Eur. Pat. Appl.* EP499,159, August 19, 1992. b) Russanov, A. L.; Bulycheva, E. G.; Elshina, L. B.; Askadskiy, A. A.; Vlasov, U. M.; Rogozhnikova, O. Yu., *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1998**, *39* (2), 853-854.
- Pethrick, R. A.; Wilson, M. J.; Affrossman, S.; Holmes, D.; Lee, W. M., *Polymer* **2000**, *41*, 7111-7121.



**Figure 1.** General synthesis and sulfonation of polyimides

**Table 1:** Summary of Polymer Formulations

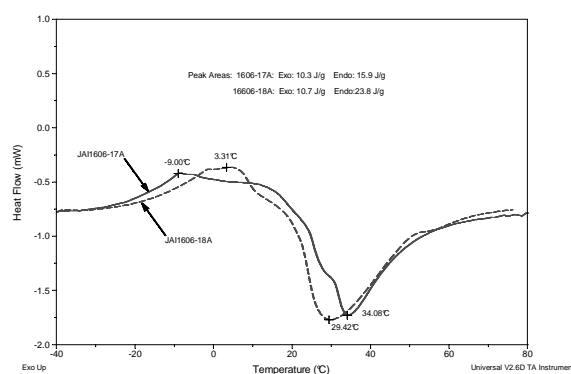
Polymer*	Monomers					
	Ar =		Ar' =			
	NTDA	6FDA	Bis-A-AF	C18	C24	DABS
1/1s	x			x		
2/2s	x				x	
3	x		x		x	
4s	x					x
5 <sup>4</sup>	x		x			
6s	x			x		x
7	x	x			x	
8	x	x		x		
9 <sup>5</sup>		x			x	

\*Sulfonated polymers are denoted by an s following the polymer number

**Table 2:** Proton Conductivity Measurements of Polymer Systems

Polymer	Wt % SO <sub>3</sub> H	Approx. # SO <sub>3</sub> H per repeat	σ of dry films*	σ at 10% water*	σ saturated w/ water*
1s	32 %	3	1x10 <sup>-6</sup>	-	1x10 <sup>-2</sup>
4s	12 %	1	1x10 <sup>-7</sup>	5x10 <sup>-7</sup>	1x10 <sup>-4</sup>
6s	6 %	1	7x 10 <sup>-8</sup>	-	2x10 <sup>-5</sup>

\*All conductivity measurements performed at room temperature and presented in units of S/cm



**Figure 2.** DSC thermograms of polymer 1 (solid line) and polymer 2 (dashed line)