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DEVELOPMENT OF HIGH PERFORMANCE PROTON-CONDUCTING SOLID ELECTROLYTES

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Abstract

This work seeks to improve the efficiency of fuel cell and electrolyzer operation by developing solid electrolytes that will function at higher temperatures. Two objectives were pursued: 1) determine the mechanism of hydrolytic decomposition of aromatic sulfonic acid ionomers, with the intent of identifying structural weaknesses that can be avoided in future materials; and 2) identify new directions in solid electrolyte development. After evaluating a number of aromatic sulfonates, it became apparent that no common mechanism was going to be found; instead, each polymer had its own sequence of degradation steps, involving some combination of de-sulfonation and/or chain scission. For electrochemical cell operation at temperatures > 200° C, it will be necessary to develop solid electrolytes that do not require sulfonic acids and do not require water to maintain its conductivity mechanism.

Background

Water electrolysis offers a means of making H_2 without consumption of hydrocarbon or biomass resources. Fuel cells offer a means of efficiently generating electricity from that hydrogen.

These devices have been found to operate more efficiently at higher temperature. The fundamental reason is that, like any other chemical process, the activation barriers associated with the electrode surface reactions are more easily surmounted at higher temperature. This makes for a faster rate of reaction, or higher current density, at the same overpotential. A further advantage for fuel cells is that if the cell operates at higher temperature than the boiling point of water, the electrolyte will spontaneously reject the product water resulting from the electrochemical reaction of H_2 and O_2, simplifying water management. An additional advantage for electrolyzers is that open circuit voltage, or the minimum thermodynamic voltage to drive the reaction, drops as temperature increases.

Solid electrolytes allow cell construction with much closer tolerances, especially with regard to the gap between anode and cathode. This reduces ohmic losses in the cell and alleviates containment problems. While hydroxide and lattice oxide conductors are known, most solid electrolytes employed in electrolytic H_2 technology are proton-conductors. The most common proton-conducting solid electrolytes are perfluoroalkyl sulfonic acid polymers, such as Nafion®.

It would be desirable to exploit both the ideas of solid polymer electrolytes and high temperature operation. However, most proton exchange membrane (PEM) devices operate at 80° C. At higher temperature, water management problems hurt performance, and ultimately the increasing applied pressure causes degradation of the membrane at ~150° C. We conducted a considerable effort at attempting to raise the decomposition temperature of the PEM polymer electrolyte. Toward this end, several aromatic sulfonic acid polymers were synthesized and characterized (Linkous 1997). These were polyetheretherketone (PEEK), polyethersulfone (PES), poly(phenylquinoxaline (PPQ), and poly(benzimidazole), PBI. Their base structures, along with that of Nafion, are shown in Figure 1.

Thermohydrolytic analysis on the polymers was performed and compared to conventional dry thermogravimetry. The susceptibility of theses polymers toward hydrolytic attack was certainly greater than for autoxidation (dry air combustion), especially for PPQ (Kopitzke 1998). The results of the hydrolytic degradation indicated that our aromatic PEM sulfonates could approach, but not exceed, the thermohydrolytic resilience demonstrated by Nafion. The remaining question to answer was, what is the hydrolytic degradation mechanism of aromatic sulfonic acids? Is there some weak link in the chain that can be removed in subsequent structures? Much of the work this year was directed at answering that question.

Results and Discussion

The original thermohydrolytic steam degradation studies involved 24 hr trials at saturating steam pressure in a batch reactor. Sometimes the extent of polymer degradation was very great, exceeding 30-40% of the original sample weight, representing a plethora of chemical reactions. In the present work, the idea was to just reach the onset of degradation, so as to identify the most vulnerable moiety to hydrolytic attack. Consequently, the present steam trials were run under a continuous flow of Ar carrier gas that went through a water bath before contacting the polymer, ensuring a 0.5 atm of steam pressure regardless of oven temperature. It was intended to hold oven temperature at a level corresponding to just a few percent weight loss, but that was difficult to control. Essentially, oven temperature was held at a value that resulted in some measurable level of weight loss over a few hours' time.

The effluent passed through a series of traps to condense the steam effluent and any volatile decomposition products. Acidity (pH), infrared spectroscopy, and gas chromatography/mass spectrometry were used to analyze the decomposition products. Results are shown in Table 1. Both sulfonated and plain aromatic polymer samples were examined. Nafion was included as a comparison. Percents in parentheses after the compound names refer to degree of sulfonation, i.e., one sulfonic acid group per repeating monomer unit is 100%.

Table 1. Hydrolytic Degradation Results for Aromatic Sulfonic Acid Polymers

Material	Temperature (° C)	% Weight Loss	Decomposition Products
Nafion	300	22.1	acid + "PTFE-like"
S-PEEK	350	26.1	acid + organics[1]
PEEK	350	0.40	none
PEEK	400	3.0	mild acid + organics[2]
S-PPQ (132%)	300	11.8	acid
S-PPQ (75%)	350	8.2	acid
S-PPQ (50%)	400	9.4	acid + organics[3]
S-PBI (100%)	300	17.1	acid + organics[3]

[1] 4-phenoxyphenol and 1,4-diphenoxybenzene

[2] phenol and 4-phenoxyphenol

[3] under analysis

The Nafion did not change its appearance to any extent, but a white ring formed at the reaction tube exit that was at least partially fluoroalkyl in nature. Sulfonation substantially weakened PEEK, as the underivatized material was quite resistant to attack. The predominate S-PEEK decomposition products were 4-phenoxyphenol and 1,4-diphenoxybenzene, suggesting that attack at the carbonyl linkage was most likely. Effluent from steam treatment of S-PPQ produced an acidic solution that tested positive for sulfate, but no indication of organic decomposition was evident, implying a clean de-sulfonation. While polyimides were examined early on, it was found that they could only be sulfonated as a Li salt; attempts to make the sulfonic acid via ion exchange failed, ostensibly because of hydrolytic attack on the imide linkage. Since this occurred at room temperature, there was no reason to treat them to conditions shown in Table 1 above. The PBI was susceptible to attack under comparatively mild conditions; product analysis is in progress.

Considerations in Higher Temperature Proton Conductors

There are many attributes that a solid electrolyte should possess. Among these are:

- facile H^+-conduction (> 10^{-2} S/cm)
- electrically nonconductive
- resists chemical attack in oxidizing (O_2) atmospheres
- resists chemical attack in reducing (H_2) atmospheres
- dimensionally stable
- gas impermeable
- water insoluble
- reasonable cost

The need to go to higher temperature operation puts additional requisites on the system. A recurring problem is that waters of hydration or other means of association are lost, and with them the proton conductivity. The overwhelming majority of proton conductors contain some measure of water. Invariably, the water plays a major role in the proton-conducting mechanism. This was understood by Grotthus who early on defined a "bucket brigade" mechanism for proton transfer, as opposed to a conventional " vehicle" mechanism [Kreuer 1982]. The various solid oxide conductors, such as $H_3Mo_{12}PO_{40}\bullet 29H_2O$, $Zr(HPO_4)_2\bullet H_2O$, $H_3O^+\beta''Al_2O_3$, and $HUO_2PO_4\bullet 4H_2O$, all seem to lose their water between 100-200° C, with accompanying loss of conductivity. The Grotthus mechanism is apparently vital for good H^+ conductivity, but water is typically bonded so weakly that it cannot remain in the bulk of the electrolyte at high temperature.

Our criteria for making new higher temperature proton conductors are:

- maintain Grotthus proton transport mechanism
- avoid water as fundamental player in proton transport
- utilize tunnel or open planar structure.
- line conduction channels with strongly bonded basic species (-OH, $-NH_2$, -SH, etc.)
- possibly include acid and base functionalities

Conclusion

All sulfonic acid polymers are limited by the saturated steam requirement for maintaining good proton conductivity. As temperature rises, the absolute saturating steam pressure reaches a point where desulfonation is favored. Nevertheless, the various polymers each have their own peculiar hydrolytic decomposition characteristics. For S-PEEK, desulfonation appears to catalyze chain scission, thereby coupling the two reactions. For S-PPQ, clean desulfonation can occur, leaving the polymer chain intact. To increase operating temperature over 150-200° C, sulfonic acids will have to be set aside in favor of materials that do not contain water or otherwise require it to facilitate proton conduction.

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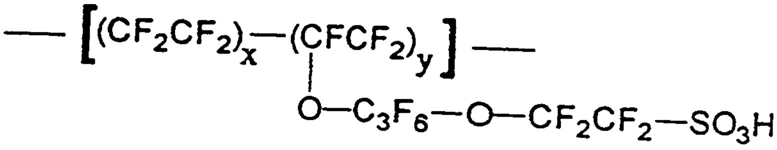
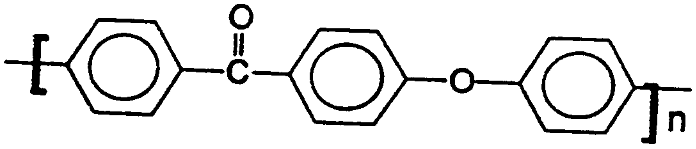
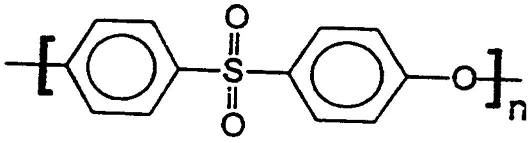


$$-\left[(CF_2CF_2)_x-(\underset{\displaystyle O-C_3F_6-O-CF_2CF_2-SO_3H}{\underset{|}{C}}FCF_2)_y\right]-$$

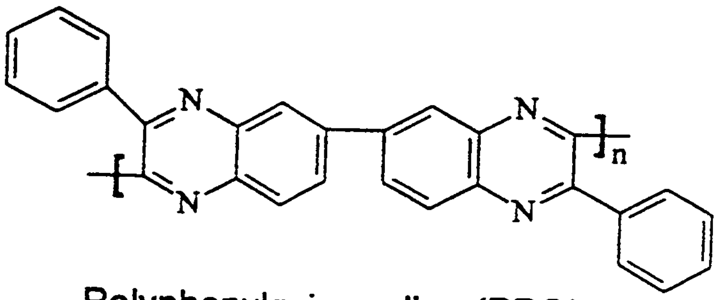
Nafion (TM)



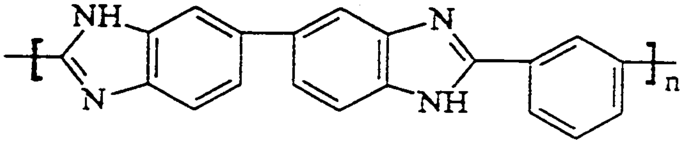
Polyetheretherketone (PEEK)



Polyethersulfone (PES)



Polyphenylquinoxaline (PPQ)



Polybenzimidazole (PBI)

Figure 1. Structures of Nafion® vs. Aromatic Sulfonic Acid Polymers.