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Cross-Linked Polybenzimidazole Membranes for Fuel Cells

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As an approach to high-temperature operation of proton-exchange membrane fuel cells,[1] phosphoric-acid-doped polybenzimidazole (PBI) membranes exhibit high proton conductivity under low water contents,[2−7] good mechanical properties,[8] and excellent thermal stability at temperatures up to 200 °C.[9] Operating features of the PBI-based fuel cells include little humidification,[10] high CO tolerance,[11] better heat utilization,[12,13] and possible integration with fuel processing units.[14] Issues for further development may include improved proton conductivity and mechancial strength, as well as stability, durability, and oxygen reduction kinetics, as recently reviewed.[15,16]

The conductivity of the acid−base polymer membranes depends on the protonation equilibrium, primarily of the acid. As a result, it is extremely important to build a network of $N-H^+ \cdots H_2PO_4^-$, $H_3PO_4 \cdots H_2PO_4^-$, and/or $N-H^+ \cdots H-OH$ chains in order to achieve a high conductivity.[7] In general, polybenzimidazole membranes can be protonated by doping in aqueous phosphoric acid solutions of concentrations up to 75% at room temperature, achieving an acid doping level of 5−6 mol phosphoric acid per repeat unit of the polymer.[17] At high acid concentrations or high doping temperatures, the obtained acid doping level and therefore proton conductivity are high; however, it is at the expense of deterioration in mechanical strength.[18]

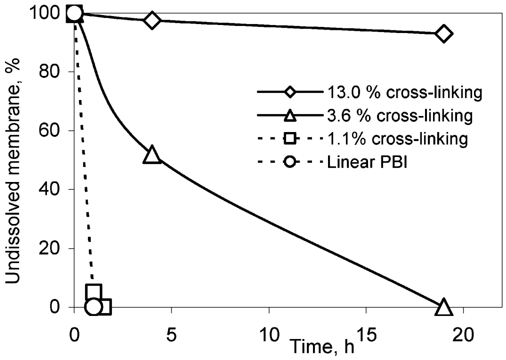

Figure 1. Solubility of PBI membranes in *N,N*-dimethylacetamide at 80 °C.

It is in fact a general issue for proton-conducting polymer membranes to have a compromised conductivity and mechanical strength. Different methods are being explored to improve the proton conductivity without sacrificing too much mechanical strength or vice versa. These include introduction of inorganic fillers or preparation of polymeric acid−base blend membranes.[19,20] The latter method is also referred to as ionic cross-linking.

Covalent cross-linking of polybenzimidazoles can be achieved by thermal treatment[21] or an amide-type linkage through imidazole groups of the polymer.[22] Very recently, Wang et al.[23] confirmed the chemical reaction between polybenzimidazole and the cross-linker *p*-xylene dichloride by FTIR spectra, elemental analysis, and solubility tests. In this communication, *p*-xylene dibromide is used as a cross-linking agent with contents of 0 (pure PBI), 1.0, 3.0, and 10.0 wt % in the prepared PBI membrane samples. Assuming a complete reaction for each mole of the cross-link agent with 2 equiv of polybenzimidazole amine hydrogen, these weight ratios correspond to a cross-linking degree of 0, 1.1, 3.6, and 13.0%, respectively, of the total amine hydrogen atoms in PBI.

For the membrane samples of low-molecular-weight PBI (21 500), 100% dissolution in *N,N*-dimethylacetamide (DMAc) at 80 °C was observed in 1 h for linear PBI membrane, 1.3 h for 1.1% cross-linked PBI membrane, and 19 h for 3.6% cross-linked PBI membrane, as shown in Figure 1. For the PBI membrane with 13% cross-linking, only 7 wt % of the sample is dissolved after 19 h of dissolution.

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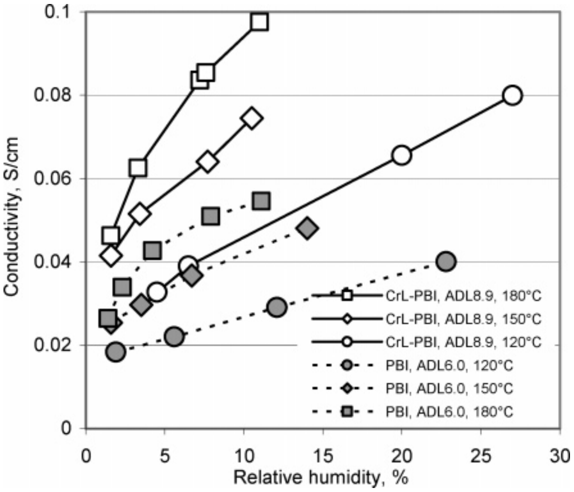

Figure 2. Proton conductivity of PBI membranes as a function of relative humidity. The acid doping level and temperatures are indicated in the figure.

Table 1. Tensile Properties of Linear and Cross-Linked (13%) PBI Membranes Undoped and Doped with Phosphoric Acid (PA in Mole Ratio).

	L-PBI (dry)	L-PBI 4.5 PA	L-PBI 6.8 PA	L-PBI 13.0 PA	CrL-PBI 8.5 PA
strength (MPa)	100−120	30−36	20−23	7.8−8.2	21−23
elongation (%)	2−3	75−94	130−160	80−96	20−28
modulus (GPa)	5.6	0.47	0.21	0.05	0.29

By immersing the membrane samples in 85% phosphoric acid at 150 °C for 20 h, as an example, the linear PBI membranes was doped with 15.5 mol phosphoric acid per PBI repeat unit, which, in turn, results in a volume swelling of the membrane by 160%. As a comparison, the cross-linked PBI membranes have acid doping levels of 8.5, 14.1, and 15.1 mol phosphoric acid, respectively, corresponding to volume swellings of 62, 143, and 160% for cross-linking degrees of 13.0, 3.6, and 1.1%, respectively. Different acid doping levels can be achieved with different acid concentrations at different tempeartures.

Linear PBI membranes showed an engineering tensile strength at break of 100−120 MPa at a strain of 2−3% when dry and 120−160 MPa at a strain of 5−10% when saturated with water. The tensile properties of the linear and cross-linked PBI membranes are listed in Table 1 for different phosphoric acid doping levels. As recently reported, an increase in the molecular weight of the polymer gives better mechanical strength of the membrane.[24] When cross-linked, the PBI membranes show much improved mechanical strength, especially after being acid-doped. As seen from Table 1, cross-linked (13.0%) PBI membranes that are doped with 8.5 mol phosphoric acid exhibit similar tensile strength and young modulus as those for linear PBI at an acid doping level of 6.8.

For membranes of cross-linked PBI at an acid doping level of 8.9 and linear PBI at an acid doping level of 6.0, which might be assumed to have similar mechanical properties, the measured conductivity is very different, as shown in Figure 2. Under the same relative humidity at different temperatures studied, a significantly higher conductivity is observed for the cross-linked membranes with an acid doping level of 8.9. As expected, of course, higher acid doping levels are effective in achieving higher conductivity. The cross-linked PBI membranes make this possible to some extent without deteriorating the mechanical strength.

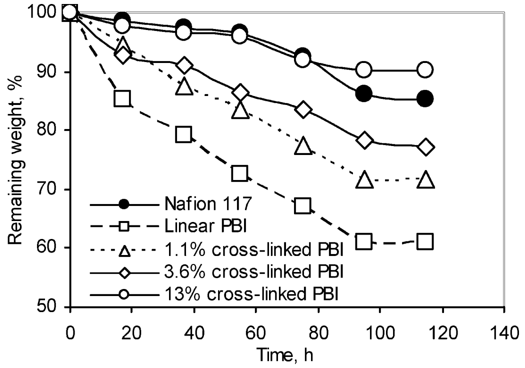

Figure 3. Membrane degradation in 3% H_2O_2 containing 4 ppm Fe^{2+} at 68 °C. Solid lines indicate that the samples remained in a whole membrane form, whereas dashed lines indicate that samples were broken into small pieces.

Chemical stability of membranes is of much concern to the lifetime of PEMFC. The formation of H_2O_2, and $^{\bullet}$OH or $^{\bullet}$OOH radicals from its decomposition, is believed to attack the hydrogen-containing bonds in polymer membranes. This is assumed to be the principal degradation mechanism of PEMFC membranes. Experimentally, the generation of these radicals can be achieved by Fe^{2+}-catalyzed H_2O_2 decomposition. On the basis of this method, the so-called Fenton test is widely used for the stability evaluation of PEMFC membranes.[25] It seems that membranes based on perfluorinated sulfonic acid, e.g., Nafion, exhibit better chemical stability than those based on polyaromatic hydrocarbons. And this peroxy radical attack would be much more aggressive at temperatures exceeding 100 °C.

By exposed the membrane to a 3% hydrogen peroxide solution containing 4 ppm Fe^{2+} at 68 °C, we can evaluate its degradation by the weight loss and visual observation. The linear polybenzimidazole was broken into small pieces after 30 min (indicated with the dashed lines in Figure 3), whereas the cross-linked polybenzimidazole membranes (with a cross-linking degree of above 3.6%) remained in a good membrane form even after 118 h (indicated with solid lines).

As a comparison, Nafion 117 membranes were also included in the study. After the first 20 h, about 1% weight loss was observed for the Nafion membrane. For the linear PBI membrane, the weight loss was about 15% during the same period of time, whereas the weight loss was 7 and 2% for PBI membranes with cross-linking degrees of 3.6 and 13%, respectively. After a longer testing period, the effect is more significant for the membrane of 13% cross-linking degree, even better than Nafion 117 membranes after 100 h.

As shown by Gaudiana et al.,[26] the initial stages of oxidative attack to benzimidazoles occur preferentially on

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the benzenoid rings bearing the nitrogen function and subsequently the amine portion of the molecules. That is to say, the weak link is the nitrogen-containing heterocyclic and adjacent benzenoid rings. Fortunately, the covalent cross-linking of polybenzimidazoles occurs by an amide-type linkage through imidazole groups. As a consequence, the covalent cross-linking dramatically improves the oxidative stability of the aromatic heterocyclic polymers.

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Supporting Information Available: Experimental procedures, figure of dogbone samples used, and schematic representation of the four-probe conductivity cell. This material is available free of charge via the Internet at http://pubs.acs.org.

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