Sulfonated Polyphosphazene-Polybenzimidazole Membranes for Direct Methanol Fuel Cells

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One of the biggest obstacles in commercializing direct methanol fuel cells is the lack of a proton conductive membrane material with good stability and low methanol crossover.

Polyphosphazenes were proposed as potential fuel cell membrane polymers by Pintauro and coworkers, who showed that sulfonated poly[(alkylphenoxy) phosphazenes] offer good proton conductivity, crosslinkability and low methanol permeability. In a parallel study, Allcock and coworkers at Penn State University developed polyphosphazene fuel membranes with phosphonic or sulfonamide groups.

The focus of this presentation is on a series of membranes prepared from newly-formulated blends of sulfonated poly[bis(phenoxy)phosphazene] and polybenzimidazole (Fig.1), where the latter was used as a crosslinking component.

Films were tested in a direct methanol fuel cell operating at 60°C with a 1M aqueous methanol solution and air as the oxidant. Two types of membrane-electrode assemblies (MEA) were investigated. For the first type, a polyphosphazene membrane was physically sandwiched between two half-MEAs prepared from Nafion 112. The second set of MEAs was prepared by hot-pressing electrodes directly onto a polyphosphazene membrane. Comparable current-voltage characteristics were obtained by the two methods, and it was postulated that the sandwich type MEA could be universally used for preliminary screening of new membrane materials without the need to optimize the electrode formulation (i.e., catalyst and polymeric binder) and hot-pressing conditions.

The resultant maximum power density of the fuel cell, with MEAs prepared by direct hot-pressing of electrodes, ranged from 23 to 89 mW/cm2 (as compared to 96 mW/cm2 with Nafion 117), while methanol crossover was significantly lower than that in Nafion ($0.6\text{-}3.9\times10^{-6}$ mol/cm^2-min vs. 1.0×10^{-5} mol/cm^2-min with Nafion 117), for membranes containing the sulfonated polyphosphazene and 3-12% polybenzimidazole (Fig.2).

It can be seen, that the current density-voltage curve with the SPOP (IEC=1.2 mmol/g) - 3 wt% PBI membrane was essentially identical to that of Nafion 117, but the methanol crossover was 2.5 times lower than with Nafion.

DMFC performance, at 60°C, with methanol aqueous solution feeds of different concentration, ranging from 0.25 to 5 M was tested. It was found (Fig.3) that the maximum DMFC power density with the SPOP12-PBI03 membrane (SPOP of IEC=1.2 mmol/g, 3 wt% PBI) was less dependent on methanol feed concentration than Nafion, and the maximum power output was greater than that with Nafion for feed concentrations smaller than 1 M and greater than 3 M.

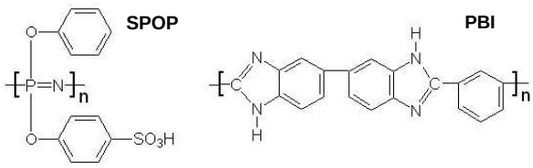

Figure 1.Chemical structures of the sulfonated polyphosphazene (SPOP) and polybenzimidazole (PBI) used in the work.

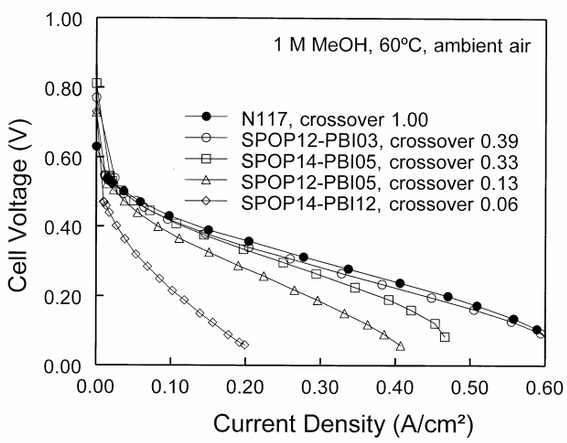

Figure 2.DMFC performance with the MEAs prepared by direct hotpressing of the electrodes onto the SPOP-PBI membranes. Measurements were taken at 60°C with 1M methanol as the feed and ambient air as the oxidant.

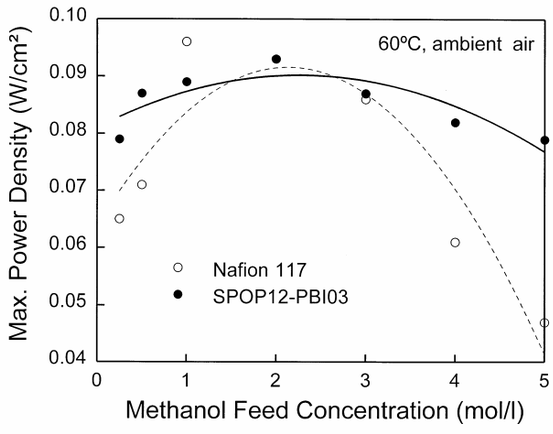

Figure 3.Dependence of the maximum power density on methanol concentration in the feed. Measurements were taken at 60°C with ambient air as the oxidant.

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