

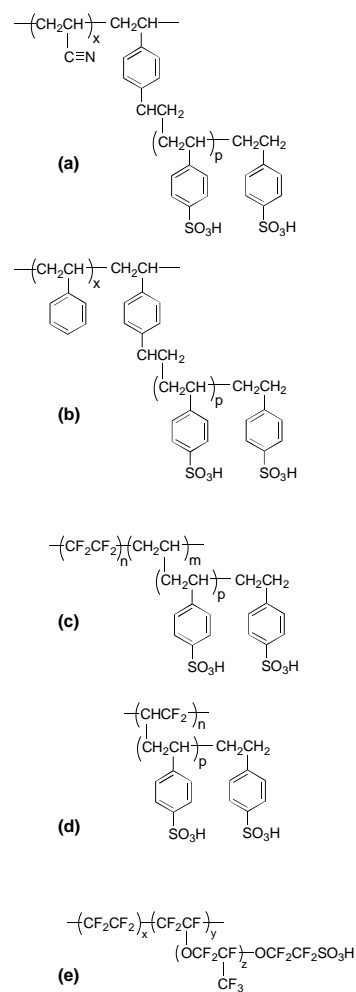
**CONDUCTIVITY AND ELECTROCHEMICAL ORR  
MASS TRANSPORT PROPERTIES OF NOVEL SOLID  
POLYMER ELECTROLYTES**

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In order to assess the applicability of proton exchange membranes in fuel cells, it is necessary to undertake fundamental studies on different solid polymer electrolytes. Research on the conductivity of different proton exchange membranes has shown that proton conductivity is correlated to the membrane's water content, ratio of water molecules to ionic sites ( $\lambda$ ), and the overall proton concentration. These factors are determined by the composition and chemical structure of the membrane. In addition to Ohmic losses caused by membrane resistance, fuel cell performance is also dependent on the electrochemical kinetics and oxygen mass transport properties at the electrode|membrane interface. As a result, ORR kinetics in several polymer electrolyte membranes has been actively studied using microelectrode techniques under conditions that mimic the environment of PEM fuel cells.

Recently, we reported the synthesis of graft polymers of styrene and styrene sulfonic acid. Films of these polymers phase separate into hydrophilic and hydrophobic domains. By varying the length and number density of the ionic graft chains on the polymer, the degree of phase separation can be modified. The extent of phase separation has been shown to affect the membrane's water content and proton conductivity. In this work, we report the synthesis and characterization of a series of graft polymers prepared with poly(styrene sulfonic acid) (PSSA) graft chains attached to a polyacrylonitrile (PAN) main chain. Polyacrylonitrile is more hydrophilic than polystyrene but in the solid state it is more crystalline because of its relatively polar nature. Membranes prepared from these polymers are protonated and characterized in terms of their morphology, water content, conductivity, and electrochemical ORR mass transport properties. These membranes are compared to other poly(styrenesulfonic acid) graft membranes prepared by different routes. The structure of the various graft polymers used in this study are shown in Scheme 1. Comparisons of these membranes in terms of their conductivity (Figure 1) and electrochemistry provide a means to evaluate the role of polymer structure and morphology on the electrochemical properties of solid polymers electrolytes.



Scheme 1. Polymer structures of membranes employed in this work

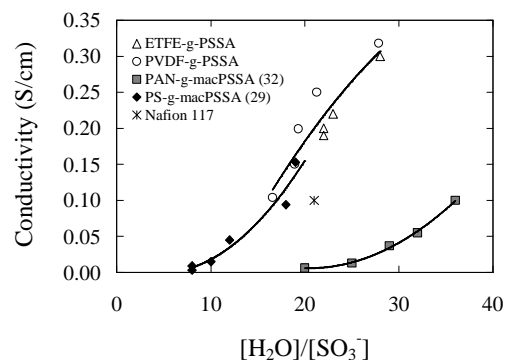


Figure 1. Conductivity versus H<sub>2</sub>O/SO<sub>3</sub><sup>-</sup> ratio for various membranes.

