ENHANCED PROTON CONDUCTIVITY THROUGH POLYMER MEMBRANES VIA A PHASE-SEPARATED NETWORK OF IONIC NANO-STRUCTURES.

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The length of graft chains in graft polymers is controlled in order to dictate the formation of a nanochannel network of ions in a non-ionic matrix. Model graft polymers were prepared by copolymerization of styrene with poly(sodiumstyrene sulfonate) macromonomers (*mac*PSSNa). The latter were prepared with controlled molecular weight and narrow polydispersity by stable free radical polymerization. Phase separation of ionic aggregates occurs to a greater extent in films prepared from amphiphilic polymers possessing longer graft chains. Films prepared from polymers containing low ion content comprise of isolated ionic domains and exhibit low ionic conductivity. Increasing the ion content of the membrane, by increasing the number density of ionic graft chains in the polymer, results in ionic domains that coalesce into a network of nanochannels (Figure 1), and a dramatic increase in ion conductivity is observed. Polymer membranes possessing ions dispersed randomly along the polymer backbone (PS-*r*-SSA) were found to yield lower ionic conductivity (Figure 2). The ionic network is developed to a greater extent for films based on longer ionic graft chain polymers; an observation explained on the basis of phase separation.

Since kinetic and mass transport parameters at the electrocatalyst/polymer electrolyte interface play an important role in fuel cell operation, the effects of nano-phase separation and membrane composition on the electrochemical reduction of oxygen at platinum/solid polymer electrolyte interfaces was investigated under conditions of controlled humidity and temperature using microelectrodes. Proton conductivity is also measured under conditions of controlled humidity and temperature using a.c. impedance spectroscopy (up to 1 GHz). These results will be put into context with the electrochemical properties of various other proton conducting membranes possessing a series of equivalent weights. These include membranes based on sulfonated polystyrene-*block*-hydrogenated butadiene, polystyrenesulfonic acid grafted onto ethylenetetrafluoroethylene, sulfonated trifluorostyrene- copolymers. Important attributes of proton exchange membranes will be discussed in relation to fuel cell applications.
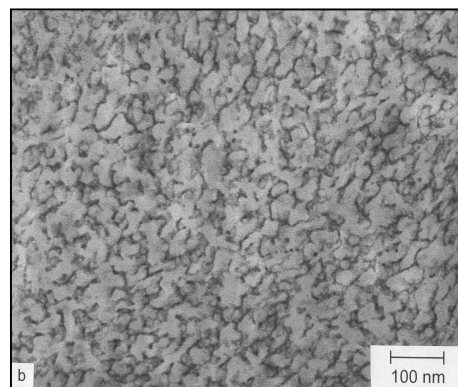

Figure 1. TEM micrograph of Pb^{2+}-stained PS-*g*-*mac*PSSA graft polymer membrane.
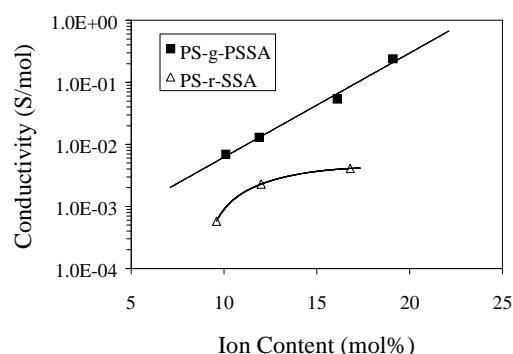

Figure 2. Proton conductivity of PS-*g*-*mac*PSSA (square) and PS-*r*-SSA (triangle) copolymer membranes as a function of ion content (mol% styrenesulfonate).