

Abstract

Transport in polymer electrolyte membranes using
time-resolved FTIR-ATR spectroscopy

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Polymer electrolyte membranes (PEMs) hold potential to improve performance in fuel cells, electrochemical devices that can generate electricity efficiently. In particular, direct methanol fuel cells (DMFCs) are promising for powering portable electronic devices, however their performance diminishes significantly because of high methanol crossover (flux) in Nafion (the most frequently used PEM) at the desired stoichiometric methanol feed concentration. Hydrogen fuel cells are attractive alternative power sources for transportation; however, their performance degrades at the desired temperatures because Nafion dehydrates, reducing proton conductivity, which is a strong function of water equilibrium content and water dynamics. Therefore, understanding sorption and diffusion of methanol and water in Nafion is critical. In this work, the diffusion and sorption of methanol and water in Nafion were measured using time-resolved Fourier transform infrared – attenuated total reflectance (FTIR-ATR) spectroscopy. This technique is unique because of its ability to measure multicomponent diffusion and sorption within a polymer on a molecular level in real time as function of concentration. Both the effective mutual diffusion coefficients and concentrations of methanol and water in Nafion were determined with time-resolved FTIR-ATR spectroscopy as a function of methanol concentration and water activity. Methanol crossover (flux) was explicitly shown to increase with increasing methanol concentration. More importantly, the increase was found to be more strongly dependent on methanol sorption rather than

methanol diffusion. Therefore, an effective PEM for the DMFC must be chemically incompatible with methanol or minimize swelling by methanol while maintaining sufficient proton conductivity. To this end, crosslinked sulfonated block copolymers that minimized methanol swelling were investigated and found to have decreased methanol flux and similar conductivity as compared to Nafion. Critical assessment of water transport in Nafion identified vapor-phase mass transfer resistance, explaining some of the variation in diffusion coefficients reported in literature. Also, two non-Fickian regimes were identified and modeled, where a diffusion-reaction model accounted for hydrolysis in dry conditions and diffusion and polymer relaxation were measured simultaneously in wet conditions and subsequently modeled. Furthermore, multiple states of water were identified and their effect on proton conductivity determined. The results from this study provide new insights into the fundamental transport mechanisms in PEMs for the advancement of fuel cell technology.