

Controlling Protonic Conductivity in Layer-by-Layer
Assembled Thin Films Through the Use of Multivalent
Salts for Fuel Cell Applications

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There is an ever increasing need for clean, portable energy devices, such as fuel cells and high energy batteries to replace or reduce the world's dependence on fossil fuels. The continued development of thin-film solid polymer electrolytes with improved mechanical and ion transport properties is critical for the further advancement of such electrochemical energy devices. For hydrogen and methanol fuel cells, the proton exchange membrane (PEM) has to have high protonic conductivity, low fuel crossover, and be mechanically and chemically stable. There has been considerable interest in finding an alternative to Nafion and other similar fluorinated polymers, which, while being chemically stable and highly conductive, are also expensive to produce and have low dimensional stability particularly when hydrated above 100° C.

LbL assembly allows for the controlled deposition of alternating polyelectrolytes at the nanometer scale. An LbL system composed of poly(diallyl dimethyl ammonium chloride) (PDAC) and sulfonated poly(2,6-dimethyl 1,4-phenylene oxide) (sPPO) has shown to have proton conductivity comparable to that of Nafion®, the industry standard, but with methanol permeability two orders of magnitude less than Nafion's. While this system by itself is mechanically deficient when hydrated, the mechanical properties can be greatly improved if the film is spray-coated on an electrospun fiber mat to form a composite membrane, with swelling reduced by four times and about an order of magnitude less than Nafion. Such composite membranes have been shown with methanol permeability twenty times lower than Nafion and through-plane proton selectivity five times greater than Nafion.

In addition, the LbL assembly allows for the control of the composition and transport properties of the film by use of monovalent and divalent salts in the polyelectrolyte solution, allowing for further tuning and improving of the LbL system. The use of divalent salts in the polymer solution shields the polyelectrolyte more so than with monovalent salts, allowing more of the sulfonated polymer to be added to the PEM, increasing the film's proton conductivity. The use of the different charged ions also affects the film's proton mobility, its energy of activation, and its water transport properties. By careful choice of the type of salt and its concentration, the existing PDAC/sPPO LbL system increased its protonic conductivities (from 15 mS/cm to 70 mS/cm), and retained more of its conductivity at 50% RH than before.