

MAR05-2004-002769

Abstract for an Invited Paper  
for the MAR05 Meeting of  
the American Physical Society

### **Lithium and proton conducting membranes: Two sets of challenges for the polymer physicist**

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Advanced energy conversion systems are sought actively for chemical to electric transformation, as storage (batteries) or production (fuel cells). Solid-state systems mean higher energy density and safety. Polymers add the extra advantages of mechanical and design flexibility, ease of processing. Lithium is now synonymous for high energy density batteries, while proton-conducting membrane is the motto in fuel cells. Though the two species are kin in the first row of the elements, the requirements for moving the corresponding ions differ considerably in concept and practice.

- $H^+$  does not exist formally and is always borne by a guest molecule. Its coordination is one, or two when H bonds are present. Proton motion is either that of the guest (vehicular) or from translocation (Grotthuss) through a chain of hydrogen bonded relays (tenfold increase in mobility). Water is the ubiquitous guest/relay ( $H_3O^+$ ), as it is the by-product of the electrochemical reaction. In terms of polymer membranes, the need for a chemically robust backbone (fluorinated, electron-depleted aromatics...) incompatible with the aqueous proton environment leads to bi-continuous phase-separated systems. The fraction of vehicular process that leads to co-transport of water and the lack of selectivity between water and methanol—the most practical fuel—, remain the main challenges. Other guests (imidazole,  $pK_a = 7$ ) are also considered.

$Li^+$  ( $6.5 \times 10^{-2}$  nm radius) requires a 4 to 6-fold coordination in a water-free environment. When the ligand shell is the polymer [e.g. poly(ethylene oxide)], the motion of  $Li^+$  is allowed by a solvation/desolvation process. This “immobile solvent” conductivity, assisted by the segmental motion, requires ( $T_g + \approx 100$  °K), i.e. @ 60 °C. Adding plasticizing discrete molecules lowers  $T_g$  and ultimately they replace the  $Li^+$  close environment (gels with liquid-like conductivity). Safety is still an incentive to get a solvent-free electrolyte working at (sub)ambient temperature. Most recent progresses come from establishing some order [(liquid)crystal, chain orientation, chirality...]. The conductivity in this case decouples from  $T_g$ , initially thought to be an inevitable barrier.