

## Extended Plenary Abstract for SSI-16, Shanghai, July 1-6, 2007

### On the relation of "dry" proton to "fast" $\text{Li}^+$ conductivity in crystalline, glassy, and polymer solid electrolytes

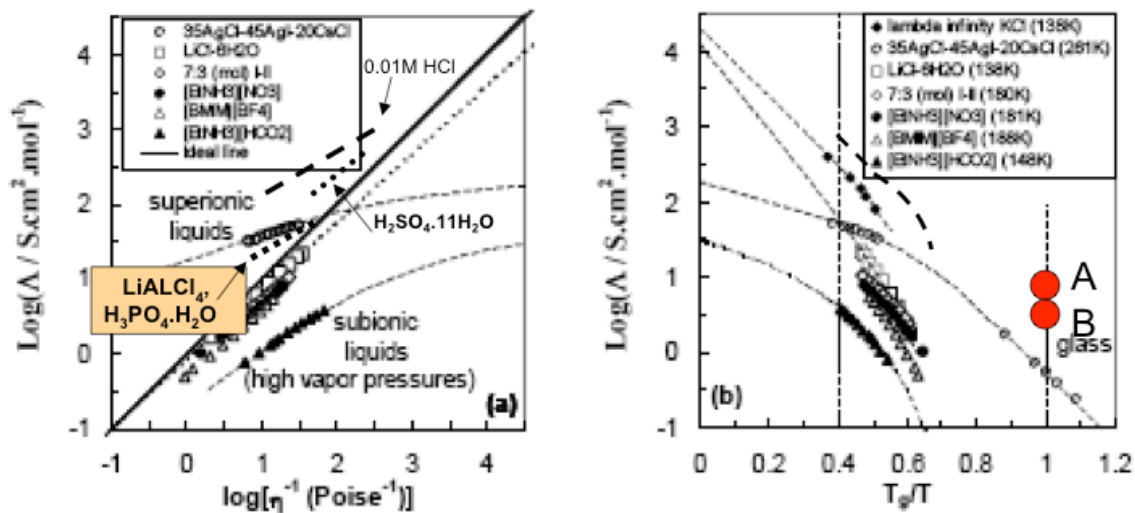
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Electrolyte requirements for lithium batteries and fuel cells have evolved in parallel, along essentially independent paths. This is a little surprising in view of the fact that both the proton and the  $\text{Li}^+$  cation are small, high charge intensity, entities each with Lewis acid properties. In this lecture we review the recent progress in harnessing each type of electrolyte for applications, and try to emphasize the points of overlap and the points of principal difference.

In each case there is, of course, great interest in finding conditions for maximum decoupling of the entities  $\text{H}^+$  and  $\text{Li}^+$  from their environments because of the advantages with respect to cell polarization that such "single ion conductors" must have. There are more examples of  $\text{Li}^+$  ion decoupling than there are of  $\text{H}^+$  ion decoupling, the term Grotthuss mechanism commonly being used to describe the phenomenon in the latter case.

To quantify the (favorable) decouplings and (unfavorable) couplings, we use either of two common diagrams, the Walden plot and the  $T_g$ -scaled Arrhenius plot [1], which provide a good visualizations of the degree to which the two small species can move independently of the motions of the majority species that determine the fluidity of the electrolyte. The first of these diagrams, shown in Fig. 1(a), is usually only employed



**Figure 1(a).** Walden classification plot exhibiting, ideal Walden behavior (diagonal), subionic behavior (below the diagonal) and superionic (or superprotonic) behavior (above the diagonal). The abscissa limiting value of 4.5 corresponds to the infinite temperature fluidity with shear relaxation time equal to the inverse lattice vibration frequency  $\{\chi\}$  (b)  $T_g$ -scaled Arrhenius representation of the same conductivity data, displaying the decoupling in the solid by the  $\Lambda$  value at  $T_g$  where the structural relaxation time is believed to be 100s. Points A and B are for the maximally decoupled glasses of Martin and coworkers [2] viz. A:  $0.3\text{AgI} + 0.7(\text{Ag}_2\text{S}_{50} \cdot [0.67\text{GeS}_2 : 0.33\text{B}_2\text{O}_3]_{50})$ , and B:  $0.7(\text{Li}_2\text{S})0.3(\text{B}_2\text{S}_3)$  at their respective  $T_g$ s.

to discuss the high conductivity end of the overall phenomenology, while the second is best suited for discussion of glasses and polymers. Neither is satisfactory for the discussion of plastic crystals [3-5], which do not have liquid-like viscosities. We discuss new cases of this sort of conductor. Also, care must be taken in use of the Walden plot in the case of polymer electrolytes because in these cases there is a built-in decoupling of the conductivity from fluidity due to the “polymer effect” on the viscosity [6]. But most polymers are very poor conductors at their  $T_g$ s, so Fig. 1(b) is not so useful either. We discuss polymer-in-salt and polymer-in-ionic liquid cases, which avoid such  $T_g$  control.

The decoupling of  $\text{Li}^+$  from the glass or polymer structure, is the equivalent of “dry” proton conductivity. It is a more common phenomenon. The decoupling can be quantified by the excess of equivalent conductivity over the Walden value, or by the ratio of conductivity relaxation time to the structural relaxation time. Data are shown for the case of  $\text{LiAlCl}_4$ , for which both conductivity and viscosity data are available. More common are conductivity data below  $T_g$  [2,7]. At  $T_g$ , the structural relaxation time has a standard value (100s) and the relaxation time ratio at  $T_g$  then becomes a material characterization property [7], the decoupling index.

In the subionic domain of Fig. 1(a), incomplete proton transfer causes ion pairing and hence diffusion without conductivity. What is the equivalent of this domain when it is the lithium ion that is in focus? In one instance it will be molecular salt cases like that of the fluoro-salt Li bisperfluoropinocolatoborate, which is low melting and distillable [8]. In others it will be systems in which the lithium ion is captured by Lewis base anions that convert it to a sort of complex anion, e.g.  $\text{LiCl}_2^-$  [8]. Then it cannot move freely towards the cathode, and in extreme cases could become like the cadmium ion in aqueous solutions of free chloride ion, i.e. it could acquire a negative transport number. This is a fundamental problem for current efforts to make lithium salt electrolytes using “ionic liquid” solutions (which are then incorporated into polymer hosts to make “solid electrolytes”), as was found in early work in this area [9].

All these factors will be incorporated into an overview of the field and a prospectus for future progress.

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