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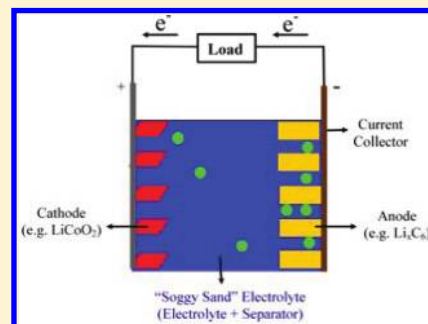
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# Ion Transport in Liquid Salt Solutions with Oxide Dispersions: “Soggy Sand” Electrolytes

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**ABSTRACT:** “Soggy sand” electrolyte, which essentially consists of oxide dispersions in nonaqueous liquid salt solutions, comprises an important class of soft matter electrolytes. The ion transport mechanism of soggy sand electrolyte is complex. The configuration of particles in the liquid solution has been observed to depend in a nontrivial manner on various parameters related to the oxide (concentration, size, surface chemistry) and solvent (dielectric constant, viscosity) as well as time. The state of the particles in solution not only affects ionic conductivity but also effectively the mechanical and electrochemical properties of the solid–liquid composite. Apart from comprehensive understanding of the underlying phenomena that govern ion transport, which will benefit design of better electrolytes, the problem has far-reaching implications in diverse fields such as catalysis, colloid chemistry, and biotechnology.



The electrolyte along with the two electrodes plays a very important role in determining the yield and efficiency of an electrochemical reaction occurring inside of an electrochemical cell(s)<sup>1</sup> such as lithium batteries.<sup>2–5</sup> Electrolytes perform the important task of transferring ions between the positive and negative electrodes during cell operation and, jointly with the electrodes, shoulder the durability of an electrochemical cell. The chemical constitution and physical state of the electrolyte completely determine the extent of electrochemical compatibility with the electrodes. Nonaqueous liquid electrolytes have always been the preferred electrolyte for lithium ion batteries. Nonaqueous liquid electrolytes<sup>6,7</sup> possess high ambient temperature ionic conductivity and a wide electrochemical voltage window, sometimes as high as ~5 V (~1 V for aqueous electrolytes), making them suitable for operation with a wide range of lithium battery electrode materials. However, poor mechanical properties introduce several constraints on cell safety and design. These detrimental issues along with the diverse demands of lithium-based technologies for high energy and power applications have led research to focus on alternatives to liquid electrolytes. Despite the early promise, the vast majority of crystalline solid electrolytes<sup>8–13</sup> have so far been found to be unsuitable for commercial lithium cells. Solid crystalline electrolytes involve complex synthesis optimization procedures at high temperatures and possess special structural arrangements in the crystal lattice that provide specific (fast) ion conduction pathways. Presence of disorder of any kind would result in detrimental decrease in conductivity and electrochemical performance. With the advent of nanostructured electrodes for high energy and power applications,<sup>3,14,15</sup> it is envisaged that employment of solid electrolytes in an electrochemical cell is going to be even more challenging. However, there have been exceptions such as LIPON (lithium phosphorus oxynitride)<sup>10,11,13</sup> and

Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub>,<sup>12</sup> which hold some promise in niche applications such as thin film or miniature batteries.

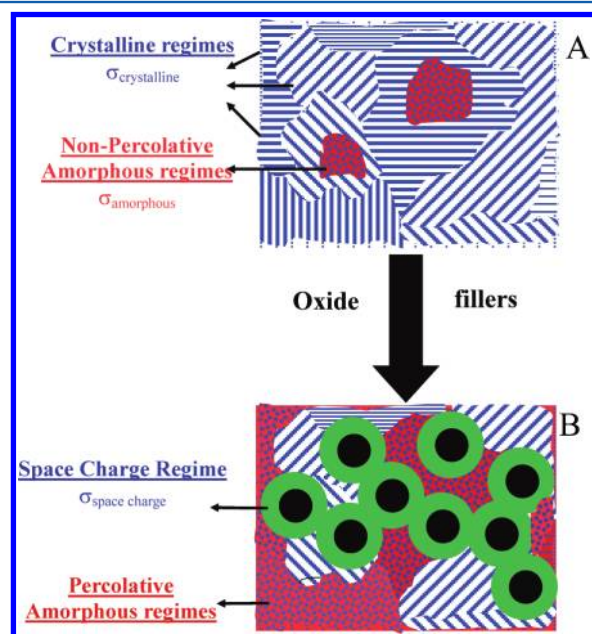
“Soggy sand” electrolytes are a unique class of solid-like electrolytes.

Other major efforts toward replacement of liquid electrolytes have been via development of room-temperature ionic liquids (RTILs)<sup>3,16–18</sup> and soft matter electrolytes.<sup>19–27</sup> Exceptional physicochemical properties of RTILs have made them frontrunners to replace molecular solvent liquid electrolytes in future lithium ion batteries.<sup>3,18</sup> However, their electrochemical performance especially at lower voltages (i.e., with anodes) is still not promising and is a long way from realization in a commercial lithium cell. Further, similar to molecular solvent liquid electrolytes, RTILs too would require separators for mechanical stability of the cell, thus significantly decreasing the gravimetric capacity. On the other hand, soft matter electrolytes such as polymer electrolytes (i.e., a polymer–salt complex)<sup>19,20</sup> do not require any additional separator for mechanical stability of the cell. The mechanical strength of the polymer (~10 MPa) keeps the cell electrodes at an optimum distance during battery operation and also suitably solvates the ionic salt, providing ionic conductivity. Though polymer electrolyte is not the main emphasis of this Perspective, we still discuss it in some more detail. This will considerably help in elucidating the need for “soggy sand” electrolytes, the main theme of this Perspective. The main concern for polymer

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electrolyte has been their low ambient temperature ionic conductivity due to low amorphous phase content (Figure 1A)

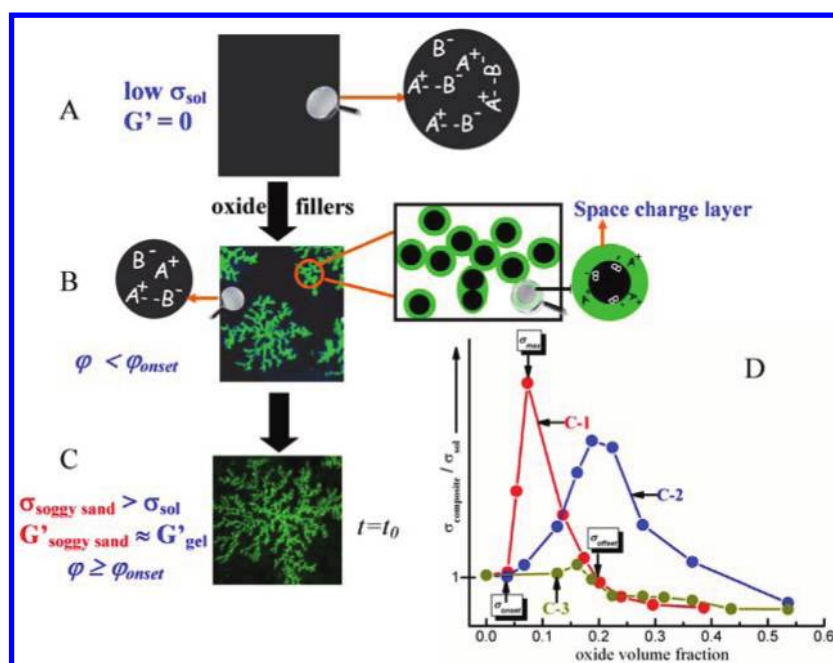


**Figure 1.** Transformation of solid polymer electrolyte from low to high conducting state following addition of fine oxide dispersants. The effective overall composite polymer electrolyte conductivity is comprised of three distinct contributions, (a) a crystalline polymer–salt complex regime (blue stripes,  $\sigma_{\text{crystalline}}$ ), (b) an amorphous polymer–salt complex regime (red dotted/red with blue dotted regions;  $\sigma_{\text{amorphous}}$ ), and (c) the space charge regime (rich in cations with anions adsorbed on the oxide surface or vice versa) at the interface of oxide and polymer host ( $\sigma_{\text{space charge}}$ ). Depending on the oxide type and extent of its interaction with the polymer host, the conductivity in the interface may be high, much higher than that in the (percolative) amorphous regimes, and completely dominate the effective overall composite ionic conductivity for oxide concentrations,  $\varphi \geq \varphi_{\text{onset}}$  ( $\varphi_{\text{onset}}$ : oxide concentration at which  $\sigma_{\text{composite}} > \sigma_{\text{polymer electrolyte}}$  for the first time — the percolation threshold).

as well as the low ion transference number,  $t_i$  ( $t_i \approx 0.3$ ). As already known, ion transport in polymer electrolyte is due to segmental motion of polymer chains, which are significantly higher in the amorphous regions compared to crystalline counterparts.<sup>19,20</sup> The majority of the strategies have aimed at ambient temperature stabilization of the volume fraction of the liquid-like amorphous phase typically present at  $T \geq T_m$  ( $T_m$  is the polymer melting temperature). This would ensure percolation in ionic conductivity even at room temperature. In this regard, two of the most widely employed approaches have been (a) addition of fine oxide (e.g.,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ) particles<sup>21–23</sup> (Figure 1B) and (b) incorporation of liquid (e.g., dimethyl carbonate)<sup>24</sup> or semisolid (e.g., succinonitrile) solvents in the polymer matrix.<sup>25–27</sup> Both methods (a) and (b) have, however, not been successful in delivering polymer electrolytes for large-scale commercial applications. Method (b) is theoretically trivial as high ambient temperature ionic conductivity ( $\sim 10^{-2} \Omega^{-1} \text{ cm}^{-1}$ ) can be achieved only at polymer to liquid ratios corresponding to the “gelled” state. On the other hand, ion transport in polymer–oxide composite electrolytes offers several formidable challenges. A vast majority in the polymer community interprets the role of the oxide merely as a “solid plasticizer” that enhances the ambient

temperature amorphous content and the ionic conductivity of the polymer electrolyte. This is of course true (Figure 1B) but not sufficient enough to account for all of issues observed for polymer electrolyte ionic conductivity as a function various parameters, especially the filler concentration. The oxide inclusion is not a chemically passive component in the polymer electrolyte. Substantial interaction exists between the oxide surface and polymer, leading to considerable changes in the ion mobility as well as concentration at the interface of the oxide and polymer electrolyte. Under certain conditions of the oxide, such as the concentration, surface chemistry, and morphology, these changes in charge concentration completely dominate the overall effective conductivity (Figure 1B). Very few published reports<sup>23,24</sup> have attempted to interpret the composite ionic conductivity in terms of the interface effect, which forms the core of the concept of heterogeneous doping (vide infra<sup>28</sup>), which convincingly accounts for the ionic conductivity of the crystalline compound ionic conductor such as  $\text{LiI}-\text{Al}_2\text{O}_3$  or  $\text{PbF}_2-\text{SiO}_2$ . The heterogeneous doping concept along with consideration of polymer and oxide functionalities should in principle also account for the ion transport mechanism in polymer electrolyte. What complicates matter in polymer electrolytes and also limits direct application of the heterogeneous doping concept is the existence of phase heterogeneity in polymers. Due to inconclusiveness over the understanding of the roles of solvation and solvent dynamics on ion transport, very few polymer electrolytes have materialized as being worthy of applications. In an attempt to understand better the ion transport in polymer electrolytes and similar soft matter electrolytic systems (such as polyelectrolyte<sup>20</sup>), an effective strategy would be to replace the heterogeneous polymer solvent by a homogeneous host such as liquid. We devote now our discussions in this Perspective to a new type of soft matter electrolyte comprised of solid oxide dispersions in molecular-solvent-based liquid solutions. While the liquid on one hand facilitates elimination of the structural heterogeneities of the polymer and aids in generation of an electrolyte having potential electrochemical applications, several other nontrivial matters of fundamental interests crop up. The Perspective discusses these issues in detail in the following paragraphs.

The idea of having a soft matter electrolyte starting from a conventional liquid medium was first realized and demonstrated by Bhattacharyya and Maier<sup>29</sup> (Figure 2A–D). In this work, addition of optimum amounts of fine oxide particles of  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , and  $\text{TiO}_2$  in nonaqueous lithium salt solutions (low dielectric constant  $\epsilon_r$ ,  $\epsilon_r < \epsilon_{\text{water}} = 80$ ) led to remarkable increase in the ionic conductivity compared to that in the pure liquid electrolyte. Additionally, in the regime of oxide concentration (10–30%) where high ionic conductivity was observed, the liquid salt solution transformed to the soft matter state, resembling soggy sand.<sup>29</sup> Since the initial report by Bhattacharyya and Maier,<sup>29</sup> which employed submicrometer particles ( $\sim 300$  nm), successive reports have demonstrated similar changes in the mechanical strength and ionic conductivity of the nonaqueous solutions using nanometer-sized particles (5–10 nm). The visible appearance of the composite electrolyte with nanometer-sized particles resembled more semitransparent gels rather than soggy sand. Nevertheless, the nomenclature of soggy sand has been retained independent of the nature of the dispersant and appearance. Apart from the differences in macroscopic appearance, high ionic conductivities were observed in an oxide concentration regime of  $\varphi \leq 1\%$ . All work done in this regard essentially



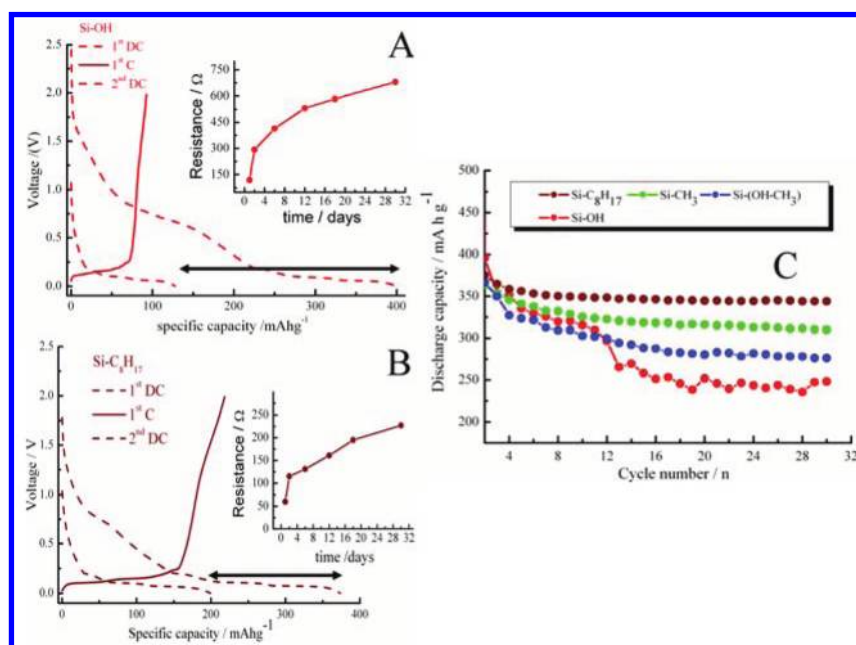
**Figure 2.** Conversion of liquid salt solution (A) using functional fine oxide particles (such as silica,  $\text{SiO}_2$ ) to a soft matter electrolyte (B and C). Addition of oxide leads to dissociation of ion pairs (present in copious amounts as in (A)) and trapping of ionic species of one kind ( $B^-$  as in (B)) on the oxide surface (heterogeneous doping,<sup>28</sup> (B)). As a consequence, the space charge region at the interface of the liquid and electrolyte becomes rich in counterion concentration ( $A^+$  as in (B)), and this condition is necessary for electrolyte function. The concentration of ion pairs in the solid–liquid is much lower compared to that of the starting liquid electrolyte (B). The aggregation of oxide particles in solution forms fractal structures (B and C) and grows in number and size with an increase in the oxide volume fraction,  $\phi$ . At  $\phi = \phi_{\text{onset}}$ , an infinite particle cluster is formed, which leads to an increase in the ionic conductivity (C). The stability of fractal structures is time-dependent, and coarsening leads to local breaking of the network and decrease in the ionic conductivity (D). Not all combinations of oxide and solvent result in nonmonotonic variation in the ionic conductivity, such as oxides C-1 and C-2. For C-3 oxide, the ionic conductivity is independent of  $\phi$  for  $\phi \leq \phi_{\text{offset}}$  (cf. text for details).

exemplifies achievement of “solid-like” electrolytes with improved physical properties via manipulations of liquid macroscopic (viscosity) and microscopic parameters (solvation). Particle aggregation subdues the normal temporal fluctuation in the liquid and may induce local ordering in the liquid.<sup>30</sup> The ordering may result in preferred pathways for the mobile species. However, as discussed later,<sup>31–36</sup> the configuration of particles in solution is nontrivial. It is dependent on several parameters of oxide and solvent as well as on time. Recently, the configuration of oxide particles as a function of time and oxide concentration has been demonstrated to form of diffusion-limited aggregate fractal structures<sup>34–36</sup> (Figure 2B,C). The attractive physical properties of the soggy sand electrolyte was soon realized to be of potential interest for electrochemical devices, especially lithium batteries. The soft matter texture of the electrolyte may make the electrochemically passive separators redundant and lead to lithium ion batteries with high gravimetric/volumetric energies. This was amply demonstrated in refs 33, 37, and 38 where soggy sand electrolytes were cycled in a half-cell assembly without any conventional separator material. The Swagelok cell comprised of  $\text{LiLiFePO}_4/\text{graphite}$  and soggy sand electrolyte ( $\text{LiPF}_6\text{-EC/DMC}$ ) did not exhibit any detrimental effect on the cyclability. Excellent performance against lithium suggests a multifunctional role of the soggy sand electrolyte both as an electrolyte as well as a mechanical separator. Recently, it was vividly demonstrated that the surface chemistry of the oxide particles also plays a major role in cyclability.<sup>33</sup> It was shown that Stöber silica particles grafted with hydrophobic groups showed better interface stability (interface resistance,  $R_{\text{interface}} < 5 \text{ } \Omega/\text{day}$  (obtained using ac impedance spectroscopy; Figure 3B) and

cyclability compared (Figure 3C) to silica particles with hydrophilic groups (interface resistance,  $R_{\text{interface}} \approx 20 \text{ } \Omega/\text{day}$ ; Figure 3A). Silica particles with both hydrophobic and hydrophilic groups, that is, “Janus” particles, displayed cyclability intermediate to the hydrophobic and hydrophilic cases. The varying battery performance was intrinsically correlated with the characteristics of the spanning particle network (vide infra).

The nonmonotonic variation in ionic conductivity as a function of the oxide volume fraction is now discussed in detail (Figures 2D and 4). The ionic conductivity may be enhanced by a few times to an order in magnitude compared to that of the nonaqueous liquid solutions.<sup>29,31–36,38,39</sup> The variation and degree of enhancement in the ionic conductivity depends considerably on the choice of solvent (dielectric constant,<sup>29,31–33</sup> viscosity) and oxide (content, size, morphology, surface chemical functionality<sup>31–33</sup>). For oxide concentration  $\phi \geq \phi_{\text{onset}}$  (number of infinite clusters = 1), the ionic conductivity increases with an increase in the oxide volume fraction until the appearance of a maximum in conductivity at a particular oxide volume fraction,  $\phi_{\text{max}}$  (such as C-1 and C-2 in Figure 2D and several results of Figure 4). The increase in the ionic conductivity with the oxide volume fraction is attributed to the formation of a percolative particle network spanning the sample dimensions (Figure 2C).<sup>40</sup> It is envisaged that the number of possible percolative pathways for  $\text{Li}^+$  ion conduction increases with an increase in the oxide concentration, with the number being maximum at  $\phi = \phi_{\text{max}}$ . For  $\phi > \phi_{\text{max}}$ , the ionic conductivity decreases, and at  $\phi \geq \phi_{\text{offset}}$ , the composite conductivity becomes lower than that of the nonaqueous solution (Figure 2D, C-1, C-2, and C-3). The decrease in



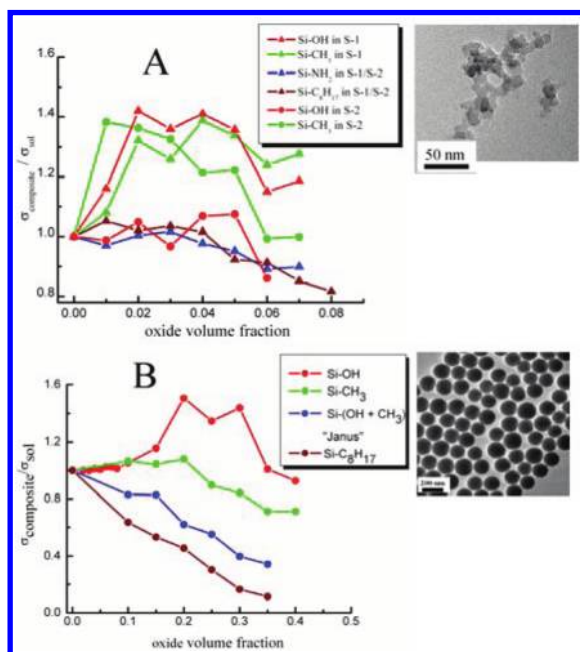


**Figure 3.** Room-temperature ( $\approx 23^\circ\text{C}$ ) galvanostatic charge-discharge curves for the Lilsoggy sand electrolyte/graphite cell at current density =  $60\text{ mA g}^{-1}$ . Soggy sand electrolytes are comprised of dispersion of (A)  $\text{SiO}_2$  [Si-OH] and (B) O-SiO<sub>2</sub> [Si-C<sub>8</sub>H<sub>17</sub>] in 1 M LiPF<sub>6</sub> in EC-DMC/SiO<sub>2</sub>/O-SiO<sub>2</sub>. The approximate silica particle size is  $\sim 150\text{ nm}$ , irrespective of the type of surface chemical functional groups. (C) Despite the lower ionic conductivity compared to that of hydrophilic particles, oxide surfaces with hydrophobic groups show better battery performance (lower irreversible capacity loss from the first discharge-DC to the first charge-C and higher interface stability (lower interface resistance,  $R_{\text{interface}}$ ; Insets of (A) and (B)). (C) Variation of the discharge capacity versus the cycle numbers for different oxide particles. In addition to [Si-OH] and [Si-C<sub>8</sub>H<sub>17</sub>], the plot in (C) also shows the capacity versus cycle number for [Si-CH<sub>3</sub>] (methyltrimethoxysilane group on surface) and [Si-(OH+CH<sub>3</sub>)] (both silanol and methyltrimethoxysilane on the surface, “Janus” particle).

conductivity after the maximum is attributed to blocking of percolating pathways, which may result from direct contact of the oxide particles. The blocking effects may also result from local disruption of the network connectivity. All threshold values, namely,  $\varphi_{\text{onset}}$ ,  $\varphi_{\text{max}}$ , and  $\varphi_{\text{offset}}$  have been observed to depend heavily on the type of solvent and inclusion employed for preparation of the electrolyte. The  $\varphi_{\text{offset}}$  however, may not be observed for every composite sample. This depends on the inclusion type as high concentration may result in a sample with a considerable amount of heterogeneities. Similarly, in certain other situations, such as for oxides grafted with strong hydrophilic chemical groups (e.g., (aminopropyl)-trimethoxysilane, abbreviated Si-NH<sub>2</sub>) or with a large hydrophobic group (e.g., octyltrimethoxysilane; abbreviated Si-C<sub>8</sub>H<sub>17</sub>) dispersed in low ( $\epsilon < 10$ ) to intermediate ( $\epsilon \leq 40$ ) solvents,  $\varphi_{\text{max}}$  and  $\varphi_{\text{onset}}$  may not be observed at all. Ionic conductivity is nearly independent of  $\varphi$  until  $\varphi = \varphi_{\text{offset}}$  and decreases for  $\varphi > \varphi_{\text{offset}}$  (Figure 2D, C-3 and Figure 4).

Initially, heterogeneous doping was suggested to be the sole mechanism for accounting for ion transport in soggy sand electrolytes. Heterogeneous doping<sup>28</sup> was introduced by J. Maier (Max Planck Institute, Stuttgart) for the prediction and quantification of the beneficial effects of insulator dispersions in weak crystalline electrolytes. In the classic example of Al<sub>2</sub>O<sub>3</sub> dispersion in solid LiI, the enhancement in the composite (LiI-Al<sub>2</sub>O<sub>3</sub>) ionic conductivity was interpreted via Li<sup>+</sup> adsorption at the oxide's surface, resulting in an increased vacancy concentration in the lithium sublattice at the oxide LiI interface. In the case of PbF<sub>2</sub>-SiO<sub>2</sub>, it is rather the anion F<sup>-</sup> that is adsorbed, leading to formation of fluoride vacancies. Therefore, the dispersion of oxide breaks up the undissociated ground state, and the counter charge carrier (in this case, the

vacancy) is set free. Following this example of insulator conversion to conductor, heterogeneous doping was also successfully applied to account for other interesting cases such as transformation from anion to cation conductors (TiCl-Al<sub>2</sub>O<sub>3</sub>) and interstitial to vacancy conductors. Coming back to the case of nonaqueous Li salt liquid electrolytes, the undissociated ion pair does not contribute to Li<sup>+</sup> conductivity. Therefore, for increasing Li<sup>+</sup> conductivity and transference number, the path would be to adsorb the anion at the surface, leading to the dissociation of the LiX ion pair (Figure 2B). This can be achieved via dispersion of acidic oxides, for example, silica (SiO<sub>2</sub>) or oxides having the ability to trap anions out of liquid Li salt solutions. The trapping of anions on the silica surface was confirmed by X-ray absorption studies (EXAFS and XANES)<sup>41</sup> and  $\zeta$ -potential measurements (negative values of the surface potential)<sup>29,31–33,35–37</sup> in several LiX-solvent-SiO<sub>2</sub> complexes (X: ClO<sub>4</sub>, PF<sub>6</sub>; solvent: tetrahydrofuran, EG, polyglycols). Ionic conductivity and  $\zeta$ -potential measurements also revealed that acidic oxides such as SiO<sub>2</sub> were more efficient in trapping anions at the surface (and hence more free Li<sup>+</sup> ions) compared to the basic oxides (e.g., Al<sub>2</sub>O<sub>3</sub>).<sup>29</sup> While the ionic conductivity enhancement was higher in the case of acidic silica than that for basic alumina,  $\zeta$ -potential measurements revealed a more negative potential (higher anion trapping) for silica than alumina. Similar trends can be observed by varying the surface chemistry of the fillers.<sup>31–33</sup> At an optimum volume fraction of silica  $\varphi = \varphi_{\text{onset}}$ , a particle network<sup>29,31–33</sup> spanning the dimensions of sample size is formed. The Li<sup>+</sup>-rich space charge layers (typically a few nanometers in the case of grains of a few tens of nanometers in size) formed at the interface of the oxide filler and salt solution overlap and lead to the percolation state for ionic conductivity. This in a way is analogous to the

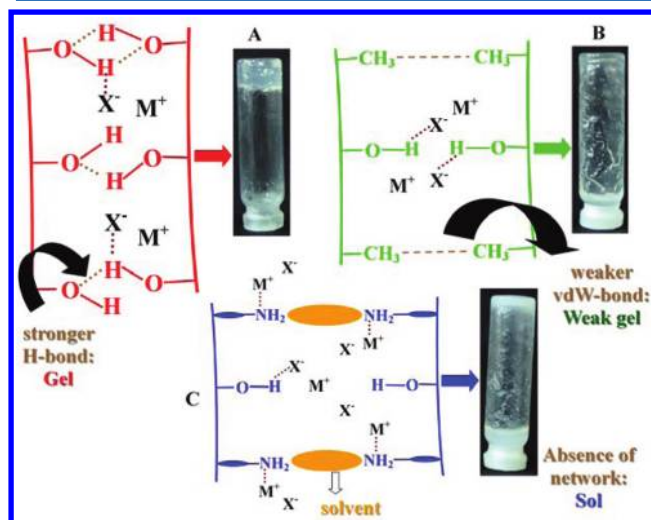


**Figure 4.** (A) Variation of the effective overall composite ionic conductivity (calculated from ac impedance spectroscopy) as a function of the aerosil silica volume at 25 °C. The waiting times prior to each measurement are  $\sim 15$ – $30$  min. S-1: 0.1 M LiClO<sub>4</sub>–ethylene glycol (EG;  $\epsilon = 37.7$ ); S-2: 0.1 M LiClO<sub>4</sub>–methoxypolyethylene glycol (m-PEG,  $\epsilon = 10.9$ ). (Inset) The general morphology of the silica remains the same irrespective of the type of surface chemical functional groups. The particle size for various silica types is  $\sim 10$ – $25$  nm. (B) Variation of the effective overall composite ionic conductivity as a function of the Stoiber silica volume dispersed in 1 M LiPF<sub>6</sub>/EC-DMC at 25 °C. (Inset) General morphology of the Stoiber silica. The particle size for various silica types is  $\sim 150$  nm (Si–OH: as received aerosil silica with silanol [OH]; Si–CH<sub>3</sub>: methyltrimethoxysilane; Si–C<sub>8</sub>H<sub>17</sub>: octyltrimethoxysilane; Si–NH<sub>2</sub>: (3-aminopropyl)-trimethoxysilane).

proton-conducting polymeric systems such as Nafion.<sup>42</sup> Unlike soggy sand, the counterions in Nafion are covalently bonded to the backbone present from the very beginning. The protons dissociate from the sulfonic groups in the presence of water and contribute to the conductivity.

Recently, several systematic studies have been independently carried on by the groups of Bhattacharyya (IISc Bangalore)<sup>31–33</sup> and Maier (MPI-Stuttgart).<sup>34–36</sup> These studies conclude that heterogeneous doping mainly accounts for the local effect that is necessary for the electrolyte function. Das et al.<sup>31–33</sup> showed that the parameters related to oxide inclusions are highly critical in determining not only the ion transport and mechanical strength but also the electrochemical properties of the soggy sand electrolytes. References 31–33 vividly and systematically demonstrate the influence of oxide surface chemistry on ion transport in soggy sand electrolytes. A soggy sand electrolytic system comprised of aerosil silica functionalized with various hydrophilic and hydrophobic silanes dispersed in lithium perchlorate (LiClO<sub>4</sub>) EG/m-PEG solution were used for the studies (Figure 4). Static (viscosity versus shear rate) and dynamic (storage and loss moduli versus frequency) rheology studies confirmed formation of an attractive particle network in the case of composites having oxides decorated with moderate hydrophilic groups (e.g., silanol [OH]). In general, the macroscopic appearance was that of a gel for composites having oxides decorated with moderate hydrophilic and hydrophobic

groups. This was also supported by static and dynamic rheology experiments, which showed, respectively, shear thinning and  $G' > G''$  ( $G'$ : storage modulus;  $G''$ : loss modulus). The formation of an attractive particle network in liquids with oxides having a moderate hydrophilic group was attributed to strong hydrogen-bonding forces between particles in the network (Figure 5A).



**Figure 5.** Schematic representation of various interactions prevailing in soggy sand electrolytes at room temperature. The scheme typically signifies a prototype soggy sand system comprised of oxide dispersions in a Li salt solution of intermediate dielectric constant ( $\epsilon \leq 40$ ).

This along with a higher concentration of charge in the space charge layer (than that in the bulk liquid) resulted in percolation and nonmonotonic variation in the ionic conductivity as a function of  $\phi$ . While dispersion of Aerosil silica with silanol groups in lithium perchlorate EG ( $\epsilon = 37.7$ ) solution resulted in enhancement of the ionic conductivity, dispersion of the same in lithium perchlorate m-PEG (m-PEG–LiClO<sub>4</sub>;  $\epsilon = 10.9$ ) did not result in any significant enhancement. Despite both being gels (due to a particle network held together via hydrogen bonds), the measured ionic conductivities were quite different. The difference in ionic conductivity is attributed to the solvent dielectric constant. High dielectric constant in the case of EG ( $\epsilon = 37.7$ ) aided in better screening of the interparticle forces and thus retention of the excess Li<sup>+</sup> ions as well as the bulk liquid. This results in percolation in the ionic conductivity in the regime of  $\phi_{\text{onset}} \leq \phi \leq \phi_{\text{max}}$ . A low dielectric constant medium such as m-PEG ( $\epsilon = 10.9$ ) is ineffective in screening the strong interparticle attraction, and as a result, the particles may lie very close to each other, leading probably to expulsion of all conducting species from the interface regime.<sup>31</sup> Hence, no enhancement in ionic conductivity is observed. No spanning attractive particle network is formed interestingly for aerosil particles with surfaces modified with stronger hydrophilic groups ((aminopropyl)trimethoxysilane). Nonflocculation of particles occurs due to short-range repulsion forces between particles arising from the solvation layer comprised of the polar solvent molecules arranged near the oxide surface (Figure 5C). In this context, it is also important to discuss the recent results from the group of Maier.<sup>34–36</sup> Their systematic studies show considerable dependence of ionic conductivity on time. At low concentration ( $\phi \leq 0.15\%$ ) of silica particles ( $\sim 300$  nm) in lithium trifluoromethanesulfonate (LiOTf)–tetrahydrofuran (THF) solution, an increase in the ionic conductivity was observed over a period of

100 h. Beyond this time, the conductivity saturated to a value depending on the silica concentration. For  $\phi \geq 0.3\%$ , the ionic conductivity was observed to decrease continuously with time. The temporal dependences were interpreted in terms of the kinetics of particle (fractal) network formation (Figure 2B,C) and coarsening. While network formation kinetics scales with  $\phi$  and contributes to an increase in conductivity, coarsening, which is independent of  $\phi$  (time constant  $\approx 1 \text{ h}^{34}$ ), leads to a decrease in the ionic conductivity. At low  $\phi$ , the kinetics of network formation dominates and leads to an effective increase in the ionic conductivity. At high filler concentration, the kinetics of network formation is fast (due to the very close proximity of the neighboring particles) compared to that of coarsening. Therefore, on the time scale of the ionic conductivity measurements, one observes only a continuous decrease in the ionic conductivity with time. We suppose that the findings of the dependence of the particle network on time are also very relevant with regard to the observations as reported in refs 31–33. In the case of strongly hydrophilic groups, the network formation might occur on a very fast time scale compared to the time scale of measurements, and hence, the conductivity either remains constant or continuously decreases with an increase in the silica volume fraction. The other important issue that reflects the influence of time on the network stability is with regard to the waiting times prior to an actual conductivity measurement. All reported ionic conductivity measurements of Das et al. were recorded following a waiting time varying from 15 to 30 min. We suppose, based on the observations as in refs 34 and 35 that the reported values in refs 31–33 are lower compared to values at  $t \rightarrow 0$ . Attractive particle networks were also demonstrated to form in composites with aerosil particles grafted with hydrophobic groups (Figure 5B). However, they are weaker in strength (particles are held via van der Waals forces; Hamaker constant,  $A_{\text{eff}} \approx 10^{-21} \text{ J}^{43}$ ) compared to the network of hydrophilic silica particles. The percolation in ionic conductivity in addition was dependent on the size of the hydrophobic moiety. Due to higher steric hindrance in the case of larger hydrophobic groups, no enhancement in ionic conductivity was observed. In general, composites with hydrophobic particles show lower ionic conductivity compared to hydrophilic particles. However, electrochemical stability and battery cyclability for hydrophobic particles were much superior to hydrophilic particles. It is supposed that a hydrophobic surface is a better deterrent for water adsorption leading to prevention of electrolyte deterioration, leading to a stable electrolyte–electrode interface.

Soggy sand electrolytes are multifunctional electrolytic systems acting as both electrolyte and separator between electrodes of the cell.

Therefore, despite the potential of soggy sand electrolytes in technological application, the mechanism of ion transport continues to be a challenging basic research problem. As described above, the complexity arises due to the dependence of ionic conductivity on several parameters of the chemical components comprising the electrolyte as well as the temporal dependence of the particle microstructure. Comprehensive understanding would necessarily require invoking principles

related to statistical phenomena and solid- and liquid-state chemistries. First principles based theoretical modeling will be a formidable task at this stage. Prior to the availability of a comprehensive theoretical model, more numerical experimentation such as that demonstrated in ref 34 needs to be attempted and accomplished. Realistic computer simulation studies might be sufficient in providing vital information on the mechanisms of particle network formation and hence ionic conductivity of soggy sand electrolytes. This would not only help in the design of better electrolytes for potential electrochemical applications but would also be useful for understanding fundamental phenomena attached to fields of catalysis, colloids, and drug delivery.<sup>44,45</sup> Porous inorganic hosts such as  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  have been demonstrated as biocompatible model hosts for targeted delivery of pharmaceutical drugs. The amounts of drug loading and release severely depend on the host characteristics and the strength of the chemical host–guest interaction. The release kinetics not only depends on the nature of the host but also on the configuration of the carrier host particles and physiological surroundings around the target site. Optimized network formation leads to faster access of the aqueous buffer to the interior of the nanostructured host, resulting in drug dosages within the beneficial pharmaceutical action window for the drug.

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