

Electrolytes for high-energy lithium batteries

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Abstract From aqueous liquid electrolytes for lithium–air cells to ionic liquid electrolytes that permit continuous, high-rate cycling of secondary batteries comprising metallic lithium anodes, we show that many of the key impediments to progress in developing next-generation batteries with high specific energies can be overcome with clever designs of the electrolyte. When these designs are coupled with as cleverly engineered electrode configurations that control chemical interactions between the electrolyte and electrode or by simple additives-based schemes for manipulating physical contact between the electrolyte and electrode, we further show that rechargeable battery configurations can be readily designed to achieve desirable safety, energy density and cycling performance.

Keywords Electrolytes · Lithium ion battery · Ionic liquids · Nanoparticle organic hybrids · Lithium/air · Lithium dendrites

Introduction

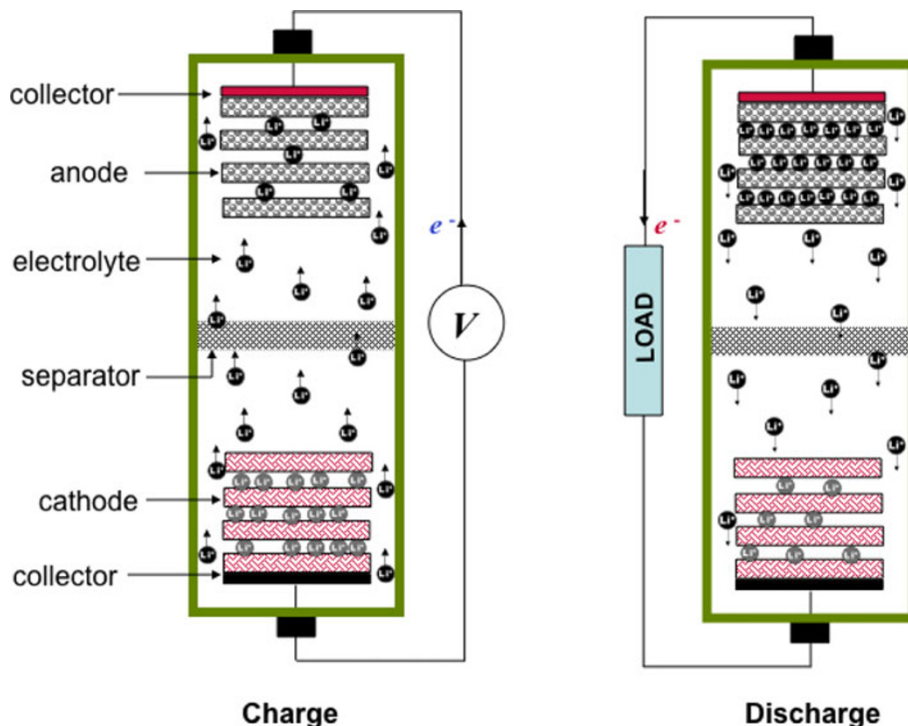
Most commercial secondary/rechargeable lithium batteries are based on the lithium ion cell depicted in Fig. 1. A carbonaceous material such as graphite serves as the anode and hosts lithium as LiC_6 in the charged state. A lithiated metal oxide (LiMO , e.g., LiCoO_2) cathode hosts the lithium in the discharged state. The anode and cathode are coupled internally by a lithium ion-conducting, aprotic

organic ester or ether doped with a lithium salt [e.g., lithium hexafluorophosphate (LiPF_6)]. Shuttling of lithium ions between the anode and cathode produces an electric current in an external circuit that drives a desired load. To prevent electrode/electrode contact and short circuits, a porous polyolefin film (separator) is typically inserted between the electrodes. Since the early 1990s, lithium ion batteries based on this design have been the subject of intense scientific and commercial interest for portable electronics applications. In recent years, the demand for secondary batteries with higher operating voltages, improved cycling stability, higher power densities, enhanced safety, and lower initial and life cycle costs has increased to meet new needs for smaller, lighter, more powerful electronic devices, as well as to accommodate a growing interest in hybrid electric vehicles (HEV) and plug-in hybrid electric vehicles (PHEVs).

As illustrated in Fig. 2, the $\text{LiC}_6/\text{LiCoO}_2$ cell delivers one of the lowest specific energies of possible secondary battery configurations. Yet it remains attractive because this cell configuration offers superior energy densities, attractive operating voltages, lower self-discharge rates and a performance/cost structure that is competitive with the nickel metal hydride (NiMH) and other rechargeable battery configurations already in commercial use for HEVs. Additionally, even after taking into account the substantially lower practical specific energies of the $\text{LiC}_6/\text{LiCoO}_2$ ion battery (typically, only about 1/3 of the maximum energy density is available in a fully packaged battery), this LIB configuration delivers a specific energy that exceeds the medium-term and comes close to the long-term goals set out by the US Advanced Battery Consortium (Miller 2009). Finally, all of the alternative cell configurations depicted in the figure, particularly those that offer exceptional specific energies, suffer from one or more

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Fig. 1 Schematic of a lithium ion battery during charge (*left*) and discharge (*right*)



debilitating limitations, most involving the electrolyte, which prevent their widespread use. This review focuses on the modern search for electrolytes suitable for large-scale deployment in secondary lithium-based battery technologies that offer significantly improved performance and safety relative to the $\text{LiC}_6/\text{LiCoO}_2$ -based platform.

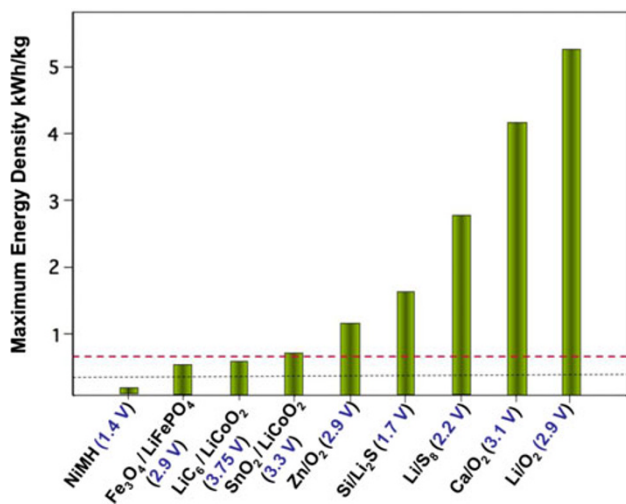


Fig. 2 Theoretical specific energy and open circuit potentials for various high-energy density secondary battery configurations. The specific energies for all of the metal/air battery configurations include the weight of oxygen. The horizontal lines are the USABC medium- (black) and long-term (red) targets escalated by a factor of 3 to account for the typical factor of three reductions in energy density that occur when inert cell components (packaging, electrolyte, conductivity aid and current collectors) are included

A successful electrolyte is required to play multiple, critical roles in an electrochemical cell. First, it should isolate the electron and ion transport pathways in the cell. Second, it should promote ion-pair dissociation and selectively facilitate transport of the active ionic species (e.g., Li^+ ions in a lithium battery). Third, it must penetrate and wet the porous, chemically heterogeneous hybrid materials that constitute the electrodes and separator. Fourth, it should not leak, combust or vaporize during cell storage or operation. Fifth, it should be chemically robust in the presence of the electrodes and their redox products. Finally, it must itself be stable in the normal operating voltage range for the electrochemical cell. Significantly, these features must be maintained over thousands, even tens of thousands of charge–discharge cycles spanning many years of cell operation. Because it is rare for all six requirements to be met in a single material, the search for a successful electrolyte typically requires years of trial-and-error experimentation, including independent searches for suitable additives that might correct one or more shortcomings of an attractive material.

Organic esters and ethers, which have polar groups, are attractive as LIB electrolytes because they possess good affinity for lithium ions, moderate dielectric constants and moderate to low viscosities at room temperature (Fig. 3). Small Bjerrum lengths,

$$l_B = \frac{e^2}{4\pi\epsilon kT},$$

and attractive Stokes ion mobilities,

$$u_i \approx \frac{z_i e}{6\pi a_i \eta},$$

are also typical of these electrolytes under normal LIB operation conditions. Here, e is the elementary charge; ϵ is the dielectric constant of the medium; k is Boltzmann's constant; T the absolute temperature; z_i and a_i are, respectively, the valency and radius of ionic species “ i ”; and η is the viscosity of the medium. Thus, even a moderately large counterion (radius: $a_- > l_B$) is sufficient to produce high levels of ion-pair dissociation from the compact lithium ions (radius: $a_+ = 0.076$ nm). The most common choices, ethylene carbonate (EC) coupled with a linear carbonate co-solvent—dimethyl carbonate (DMC), diethyl carbonate (DEC), ethylmethyl carbonate (EMC)—and doped with LiPF_6 , also offer superior ionic conductivities to all alternatives: ionic liquids, polymers and ceramics. However, these electrolytes are volatile, flammable, leaky, display poor thermal stability, possess high reduction potentials (Fig. 3), and have narrow electrochemical stability windows and poor mechanical stability, which present obvious challenges for their large-scale deployment in batteries. Additionally, electrolytes based on organic ethers dissolve lithium polysulfides LiS_x , which erodes the cathode in high-energy lithium/sulfur and silicon/ Li_2S secondary batteries, and do not dissolve Li_2O_2 , clogging the porous cathode in ultrahigh-energy density

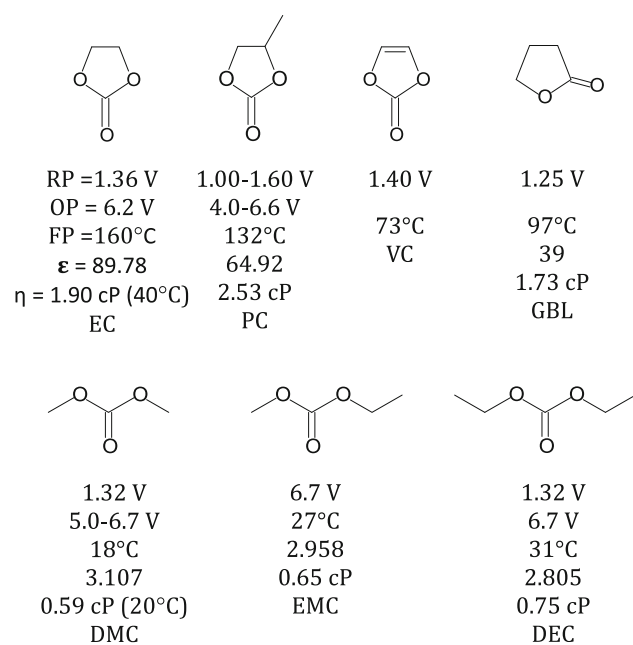


Fig. 3 Chemical structures of common liquid electrolyte components and their properties. *RP* reduction potentials [as reported by Yoshio et al. (2009)], *OP* oxidation potentials (as summarized from Xu³), *FP* flash point, ϵ dielectric constant at 25°C, η viscosity at 25°C unless otherwise noted

lithium–air batteries (Fig. 2), making them incompatible with the most energy-dense lithium battery platforms.

Efforts to manage and/or ameliorate the most serious problems with aprotic organic electrolytes are extensive and nicely documented in several excellent reviews (Zhang 2006; Xu 2004; Verma et al. 2010; Aurbach et al. 2007; Yoshio et al. 2009; Scrosati and Garche 2010). It is now understood, for example, that because the potential at either LIB electrode decays over a distance of the order of the Debye length,

$$l_D = \left(\frac{\epsilon_0 \epsilon_r kT}{(n_+^2 + n_-^2 z_-^2) e^2} \right)^{1/2},$$

the high relative electrolyte permittivity, ϵ_r , and salt concentrations, ($n = n_+ + n_- : O(1M)$), typically employed to insure high ionic conductivities, also mean that the electrolyte in the vicinity of the electrode is subjected to large potential gradients; ϵ_0 is the permittivity of the vacuum and n_i is the molar concentration of the unassociated ionic species i in solution. Thus, even under moderate cell potentials where the pure electrolyte may be nominally stable, it will degrade continuously when in contact with either electrode. Several studies have shown that the degradation product is an electrically insulating but ionically conducting polymer, and that its thickness and porosity can be controlled (by introducing additives to the electrolyte and/or by initially cycling the cell at a low rate) to create a passivating coating that slows/stops subsequent electrolyte degradation (Aurbach et al. 2007; Yoshio et al. 2009; Scrosati and Garche 2010). This benefit is perhaps intuitive, since an electronically insulating polymer coating of any thickness reduces the magnitude of the potential gradients at the solid electrolyte interface (SEI). Numerous approaches for controlling the SEI in Li-ion batteries employing aprotic organic electrolytes have been reported; we will review the most recent methods at the end of “Liquid electrolytes for high-energy batteries” of the study.

The review is organized as follows. We report on the progress in development and characterization of novel liquid electrolyte systems for high-energy density lithium batteries in “Liquid electrolytes for high-energy batteries”. This is followed by “Solid-state electrolytes: ceramics, polymers, composites, and hybrids”, in which we review progress on solid-state electrolytes based on ceramics and polymers. Finally, in “mixed phase electrolytes”, we discuss mixed phase solid–liquid electrolytes.

Liquid electrolytes for high-energy batteries

Aqueous electrolytes for lithium batteries

Aqueous electrolytes preserve many of the advantages of aprotic liquid electrolytes, but provide an environmentally

friendly, non-flammable, low cost solution for some of their shortcomings. Until recently, the narrow electrochemical stability window of liquid water (1.23 V) and its reactivity with metallic electrodes prevented its successful implementation in lithium batteries. Lou et al. recently reported results from a detailed study of the reactivity of various electrode materials in aqueous electrolytes (Luo et al. 2010). These authors showed that by manipulating the pH of the electrolyte, it was possible to shift the electrochemical stability window. Further, they demonstrated that if dissolved oxygen was eliminated and carbon-coated electrodes employed, aqueous lithium ion batteries based on materials such as $\text{LiTi}_2(\text{PO}_4)_3/\text{LiFePO}_4$ could be cycled at a rate of 1C to yield a specific energy of 50 W h kg^{-1} based on the total weight of the electrode materials. This energy density is competitive with lead–acid and Ni–Cd batteries. However, the aqueous lithium ion battery offers a much higher power density, retaining 80% of the reversible capacity when the rate is increased to 10C. Furthermore, the battery manifested over 90% capacity retention over 1,000 charge/discharge cycles.

The benefits of aqueous electrolytes for lithium batteries are even more markedly evident for Li–air batteries (Zhou et al. 2010; Girishkumar et al. 2010). As illustrated in Fig. 2, the theoretical specific energy of the lithium/air battery (including the oxygen cathode) is 5.2 kWh/kg. Most designs utilize a porous/open carbon cathode configuration designed to facilitate continuous re-supply of oxygen from the surroundings and therefore potentially offer substantially higher specific energies, 11 kW h/kg. These values are comparable to typical energy densities for coal, 6.7 kW h/kg, and are only marginally lower than the specific energy of commercial-grade gasoline, 12 kW h/kg. Works on Li–air batteries employing aqueous electrolytes rely upon the high solubility of Li_2O_2 in water to avert problems with premature fouling of the porous cathode, but achieve this effect by employing decidedly different approaches for protecting the metallic lithium anode from water. The all-aqueous Li–air battery utilizes an inert ceramic solid-state electrolyte coating on the anode, which protects it from water, but is sufficiently conductive for Li^+ ions to facilitate the shuttling reaction. In the mixed electrolyte Li–air battery configuration proposed by Zhou et al. (2010), the anode and porous cathode are separated by a water-impermeable, lithium ion-conductive membrane (e.g., LISICON). The cathode is in contact with the aqueous electrolyte, and the metallic lithium anode is in contact with an aprotic liquid electrolyte. The primary advantage of these designs is that the cathode is submerged in water and the discharge reaction product is soluble in water, so this eliminates problems of cathode clogging, expansion and electrical conductivity that result from the use of an aprotic electrolyte. Wang and Zhou (2010) reported cathode capacities of 50,000 mAh/g (based

on the total mass of porous catalytic electrode) when the Li–air cells were cycled at a low rate (100 mAh/g).

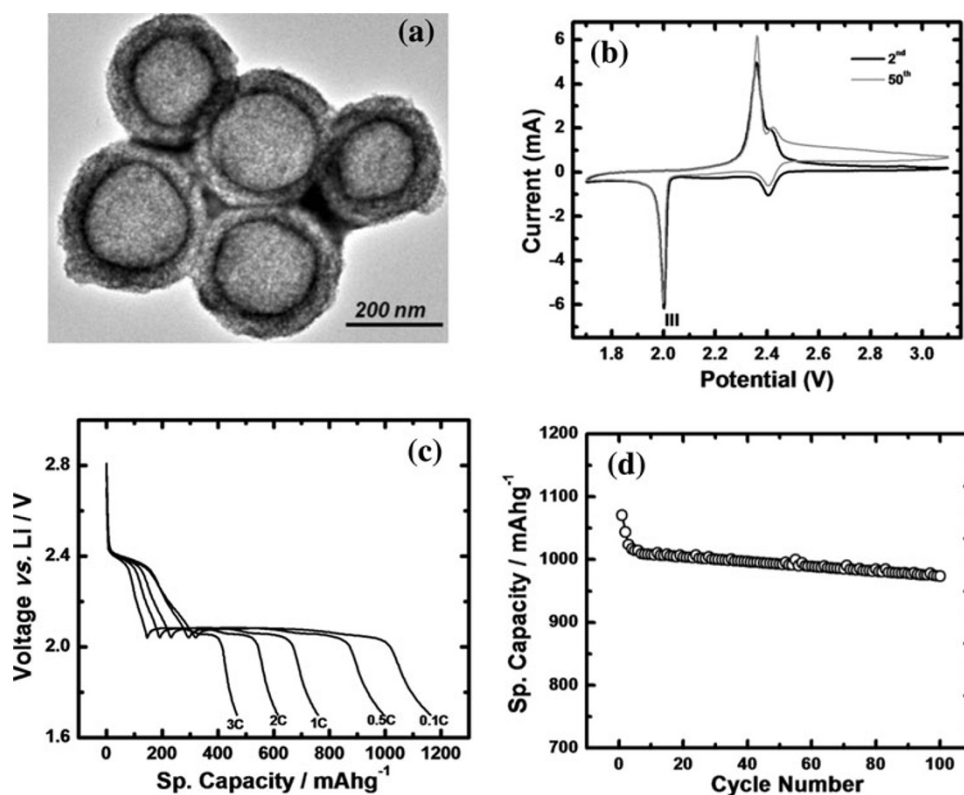
Electrolytes for secondary lithium–sulfur batteries

As illustrated in Fig. 2, the Li–S and Si– Li_2S secondary batteries provide among the highest specific energies of lithium-based cells. Sulfur, the active material used in both cathode configurations, is inexpensive, abundant and non-toxic. Early reports showed that Li/S cells with organic liquid electrolytes displayed poor cycle life and low Coulombic efficiencies. Cycling of a sulfur cathode results in the formation of various lithium polysulfides such as Li_2S , Li_2S_2 , Li_2S_3 and Li_2S_4 (Ryu et al. 2005; Chang et al. 2002; Yamin et al. 1988). These polysulfides are soluble in the typical aprotic carbonate liquid electrolytes, resulting in dissolution/erosion of the cathode by the electrolyte upon cycling. The resultant fall-off/fading of the cathode capacity presents a significant barrier for successful implementation of sulfur cathodes.

Many investigations have focused on combinations of liquid electrolytes, as well as of electrolytes and additives, which display various levels of success in reducing polysulfide dissolution while still demonstrating sufficient ionic conductivity, safety and electrochemical stability. For example, tetrahydrofuran (THF) (Hamlen et al. 2001), 1,3-dioxolane (DOXL) (Chang et al. 2002; Wang et al. 2010a; Jin et al. 2003), dimethoxy ethane (DME), carbonates (Wang et al. 2003, 2004a) and polyethylene glycol dimethyl ethers (PEGDME) (Ryu et al. 2005; Wang et al. 2010a; Choi et al. 2008; Cheon et al. 2003a, b; Ryu et al. 2006a) have been investigated. Among these electrolytes, tetra(ethylene glycol)dimethyl ether (TEGDME), a dimethyl terminated polyethylene oxide oligomer, has been found to be particularly attractive. Without any efforts to modify the cathode, Li/S cells employing TEGDME-based electrolytes have been shown to provide specific capacities over 1,200 mAh/g during the first charge at room temperature (Chang et al. 2002; Hamlen et al. 2001; Ryu et al. 2006a, b). Choi et al. (2007, 2008) reported on the performance of TEGDME/1 M LiCF_3SO_3 electrolyte solution, which they compared with a variety of other electrolyte formulations. Significantly, a cell employing a solution of 5 vol.% toluene in TEGDME was reported to maintain a discharge capacity of 533 mAh/g following 50 cycles at a low rate (1/16C) and exhibited near stable impedance spectra on cycling.

Mikhaylik and Akridge (2003) and Ryu et al. (2006a) both show that the performance of TEGDME electrolytes in Li/S cells is markedly worse at low temperatures. By adding 1,3-dioxolane (DOXL) and methylacetate (MA) to the TEGDME electrolyte in the ratio of MA:DOXL:TEGDME—5:47.5:47.5, by volume—Ryu et al. observed that

Fig. 4 Li/S secondary battery based on S@C composite and PEGME/LiTFSI electrolyte. **a** Transmission electron micrograph of sulfur infused mesoporous, hollow carbon particles. **b** Cyclic voltammetry data for S@C at a scan rate of 0.2 mV/s. Results are for the 2nd and 50th cycle. **c** First discharge voltage profiles for Li/S at various discharge rates. **d** Specific discharge capacity versus cycle number for Li/S cell at a fixed discharge rate of 0.5C



the first discharge capacity could be significantly improved to 994 mAh g⁻¹ at -10°C from 357 mAh/g. Shin and Cairns (2008) showed that Li/S cells could be successfully cycled with an electrolyte mixture of PEGDME $M_n = 250$ and 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (C4mpyr TFSI) ionic liquid. The addition of PEGDME to the ionic liquid was found to reduce its viscosity and enhance ionic conductivity to 4.2×10^{-3} S/cm at 29°C. When cycled at room temperature and at low rates, the Li/S cell with C4mpyr TFSI–0.5 M LiTFSI–2 PEGDME electrolyte maintained a discharge capacity of 269 mAh/g after 100 cycles; however, the cells exhibited poor performance at lower temperatures. Cells containing pure C4mpyr–LiTFSI electrolyte, without PEGDME, exhibited poor cycling performance at all temperatures due to polysulfide dissolution.

Recently, several studies have reported that encapsulation of the sulfur into a porous carbon framework wetted by the electrolyte can significantly improve performance of Li/S batteries. Ji et al. (2009), for example, showed that Li/S cells based on a nanocomposite cathode, created by wicking molten sulfur into a conductive, mesoporous carbon framework and an electrolyte comprising 1.2 M LiPF₆ solution in ethyl methyl sulfone, could be cycled at moderate rates ($\sim 0.2C$) to yield specific capacities exceeding 800 mAh g⁻¹, with some capacity fade after 20 cycles. When a layer of polyethylene glycol was appended to the particles, the authors reported that the Li/S cell capacity

improved noticeably, to above 1,100 mAh/g, and that the cells showed no evidence of the capacity fade after 20 charge/discharge cycles. Figure 4 reports results from a more recent study by Jayaprakash et al. (2011), which employed a high-pressure method to infuse sulfur sublimate in the vapor phase into mesoporous, hollow carbon particles (Fig. 4a) synthesized by high-temperature calcination of petroleum pitch. Cyclic voltammetry measurements (Fig. 4b) of Li/S cells employing these S@C composite materials and an electrolyte comprising 1 M lithium bis (trifluoromethane sulfone) imide (LiTFSI) in TEGDME indicate stable electrochemical performance after 50 cycles. Figure 4c shows the first-cycle voltage profile of the material during galvanostatic cycling at low (0.1C) as well as high (3C) charge rates. Figure 4d reports the discharge capacity based on the active sulfur, which comprises 70 wt% of the S@C composite, measured at a rate of 0.5C. Although small levels of capacity fading is evident in Fig. 4d, these results attest to the electrochemical stability of the composite sulfur@carbon cathode material in the TEGDME-based electrolyte.

Electrolytes based on ionic liquids

One of the most straightforward changes that can be made within the current LIB framework (LiMO/LiC₆) to increase specific energies is to increase the Li ion insertion potential at the cathode. Cathodes based on LiM_{0.5}Mn_{1.5}O₄ or

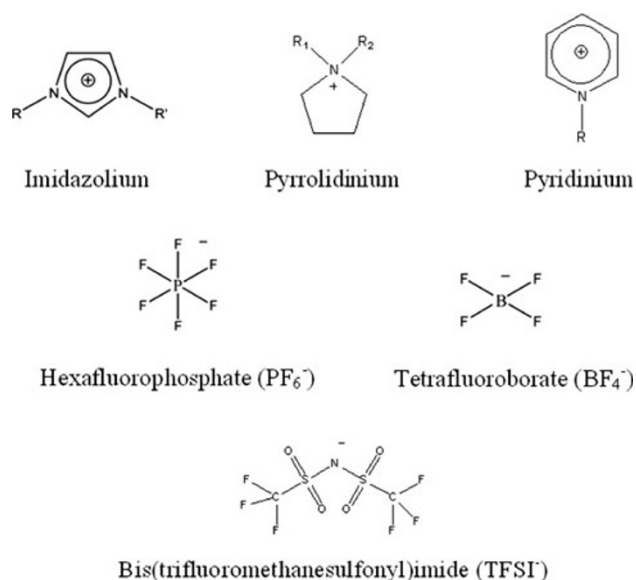


Fig. 5 Chemical structures of representative cations and ions used for ionic liquid electrolytes

LiMnO_4 spinels, where M is a divalent or trivalent metal (e.g., copper, nickel, iron, cobalt, chromium), can form the basis of LIBs with open circuit potentials close to, or even exceeding, 5 V (Todorov et al. 1999). Unfortunately, none of the currently used aprotic liquid electrolytes can be safely used at such high cell potentials. High-temperature molten salts (liquid oxides, silicates, etc.) have been studied for a long time (Terada et al. 2001) and have been speculated for some time as potential LIB electrolytes for high-voltage cells. Typical cation and anion structures that are suitable for creating ILs are depicted in Fig. 5. Unlike molten salts, room-temperature ionic liquids (ILs) are organic salts having melting points below 100°C (Benne- mann et al. 1982). The earliest IL, ethyl-ammonium nitrate, was synthesized in 1914 with a melting point of 12°C (Hussey 1983; Walden 1914). A few ionic liquids were later developed for electroplating (Zhao and Van der Noot 1997), catalysis (Welton 1999) and organic synthesis. Wilkes and Zaworotko (1992) developed air- and water-stable low melting point tetrafluoroborate ionic liquids.

ILs exhibit many interesting properties, including ultra low vapor pressure, good thermal stability, wide range of solubility of organic and inorganic compounds, high polarity and non-coordinating nature, hydrophilic and lipophilic nature, high ionic conductivity, wide electrochemical stability windows and tunability, which make them attractive as battery electrolytes (Wasserschied and Welton 2003; Davis 2004; Ohno 2005). Among the large number of possible IL configurations, imidazolium- and pyrrolidinium-based ILs are most widely studied for their potential as next-generation Li ion battery electrolytes. The inherent robustness of the cation and anion of IL plays a

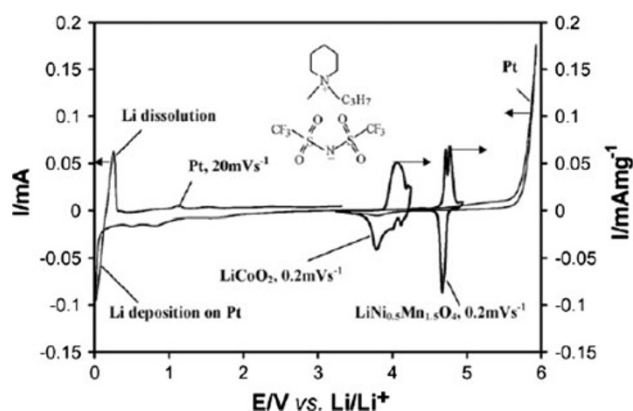


Fig. 6 The electrochemical stability window of 0.5 M LiTFSI in an *N*-methyl-*N*-propylpiperidinium bis(trifluoromethanesulfonyl)imide electrolyte solution measured on a Pt electrode and cyclic voltammograms of LiCoO_2 and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel electrodes as indicated in the reprint from Martha et al. (2009), with permission from Elsevier

vital role in dictating the overall redox stability of the IL (Moganty et al. 2009). Imidazolium-based ILs exhibit stability window of about 4 V and other cyclic amine-based ILs, pyrrolidinium and piperidinium cations, show stability limits of about 6 V (Fig. 6) (Martha et al. 2009; Lewandowski and Swiderska-Mocek 2009; Lewandowski and Swiderska-Mocek 2010). Imidazolium-based cations suffer from cathodic instabilities. Improvements in this area were demonstrated by Seki et al. (2006), whereas a ring substitution allowed for improved cycling efficiency against lithium metal. High stability windows have been reported for ILs containing TFSI anion (Borgel et al. 2009).

High lithium ion conductivity is a desirable characteristic for Li ion battery electrolytes. The total ionic conductivities of ILs range from 10^{-4} to 10^{-2} S/cm at room temperature (Moganty et al. 2009; Goodenough and Kim 2010). Imidazolium-based ILs show comparatively higher values of conductivities than pyrrolidinium-based ILs. Irrespective of the type of cation and anion, addition of Li salt to the IL decreases the overall ionic conductivity due to an increase in viscosity and the formation of ionic clusters with Li^+ . The effect of Li salt concentration on 1-2-dimethyl-3-propyl imidazolium bis(trifluoromethyl sulfonyl)imide IL electrochemical properties, such as ionic conductivity, viscosity and interfacial resistances at the LiCoO_2 and Li metal interfaces, was studied by Seki et al.; they found that an optimum Li salt concentration existed for high-rate performance batteries (Seki et al. 2007). Appetecchi et al. (2009) found that increase in alkyl chain length resulted in decrease in ionic conductivity of *N*-alkyl-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ILs. Tokuda et al. (2004) investigated the effect of anion on the physicochemical properties of 1-butyl-3-methylimidazolium cation-based ILs. They concluded that the molar

conductivity ratio has the following order in the IL anions studied: hexafluorophosphate (PF_6) > tetrafluoroborate (BF_4) > bis (pentafluoroethylsulfonyl) imide (BETI) > bis(trifluoromethylsulfonyl)imide (TFSI) > trifluoromethanesulfonate (TfO) > trifluoroacetate (TFA). The observed trend is related to the anionic characteristics such as charge delocalization and fluorine content, where a higher molar conductivity ratio is found for ILs that dissociate more readily. While ionic liquids display high total ionic conductivities, they exhibit low lithium transference numbers and thus lower lithium ion conductivity when compared with other liquid electrolytes. Addition of neutral molecules such as vinylene carbonate, tetrahydrofuran, ethylene carbonate and toluene have been reported by MacFarlane and coworkers to significantly change transport properties of *N*-ethyl-*N*-propylpyrrolidinium bis(trifluoromethane sulfonyl)imide (Bayley et al. 2009). The chemical identity and donor ability of diluents play a major role in enhancing the Li ion transport properties of LiTFSI solutions of IL.

Lee et al. (2006) reported synthesis and electrochemical characterization of a series of ILs with methyl acetate moiety. These ILs exhibited large redox stabilities and high ionic conductivities, with an increase in conductivity in the presence of Li salt due to the interaction between Li^+ and the ester group on the cation of the ILs. Similarly, Egashira showed the improved properties of the quaternary ammonium-based ILs containing cyano functional groups (Egashira et al. 2004). Most recently, Hussey and coworkers designed and synthesized a series of piperdinium cation-based ILs with a propylene carbonate (PC) moiety that showed favorable electrochemical characteristics for Li metal batteries (Tsuda et al. 2011).

Some ionic liquids, such as 1-butyl-1-methylpyrrolidinium bis (trifluoro methanesulfonyl) imide (C4mpyr TFSI) with LiTFSI (Howlett et al. 2004, 2006; Liu et al. 2010; Bhatt et al. 2010; Lane et al. 2010), have been shown to enhance uniform deposition on the lithium metal anode, thus reducing dendrite formation without additional additives. This opens up the way for the highest energy density lithium batteries of all: those employing metallic lithium as anode. The improved lithium plating behavior of (C4mpyr TFSI) doped with LiTFSI is thought to occur due to formation of crystalline-like liquid layers at the interface with the crystalline electrode (Valencia et al. 2002). This phenomenon is not understood, and varying effects are seen experimentally with chemical changes to the plating substrate or electrolyte.

The tunability of ILs evidently offers a spectrum of opportunities to modify the properties required for successful preparation of next-generation Li battery electrolytes that are non-volatile, non-flammable and thermally stable at high temperatures. Significant challenges exist in

developing ionic liquids with sufficiently high lithium ion conductivity that also function well with high-energy storage capacity electrodes, such as sulfur and lithium metal. However, the recent upsurge of broad-based interest in ILs leads us to the perhaps hopeful conclusion that in a matter of years, IL electrolyte configurations suitable for the most energy-dense batteries of all (metal-air cells) will be found.

Additives for aprotic liquid electrolytes

Easily polymerizable electrolyte additives, such as vinylene carbonate (VC) and catechol carbonate, have been shown to be particularly effective in producing stable SEI coatings on LiC_6 and LiCoO_2 (El Ouatani et al. 2009; Oesten et al. 2002). Their use results in very small irreversible capacity loss upon SEI creation without sacrifices in the stability of electrodes or ionic conductivity, thus extending the life cycle of lithium ion cells. The discharge capacity and cycling performance of PC-based electrolytes containing butyl sulfone (BS) have been studied by Xu et al. (2007). These authors showed that BS rapidly formed a protective film on the graphite electrode and improved room-temperature battery performance. Other sulfones, including 1, 3-propane sulfone (PS) (Park et al. 2009), have been used as additives in LIBs employing mixed carbonate electrolytes EC/DEC/DMC-1 M PF_6 electrolyte. Significantly, when paired with another SEI additive, succinic anhydride (SA), Lee et al. showed that PS additives were suitable for stabilizing a mixed 1:2 EC/EMC-1 M LiPF_6 electrolyte in $\text{LiNi}_{0.5} \text{Mn}_{1.5} \text{O}_4/\text{graphite}$ 5 V cells (Chen et al. 2007). Butylene sulfite has recently been shown to be a good SEI additive for PC-based electrolytes employed in both high-voltage, $\text{LiMn}_{1.99}\text{Ce}_{0.01}\text{O}_4/\text{graphite}$ and high-power, $\text{LiFePO}_4/\text{graphite}$ electrodes (Yao et al. 2009).

Another approach proposed by Menkin et al. (2009) employs a pre-formed, artificial SEI to stabilize the interface. These authors used electropainting and vacuum-insertion techniques to deposit a polymer based on poly(ethylene-co-acrylic acid) and carboxymethylcellulose on graphite as well as Sn–Cu composite anode. They showed that the artificial SEI produced close to a fivefold improvement in the cycling performance of the battery. Likewise, Song (Song and Baek 2009) employed Fourier transform infrared spectroscopy to show that trimethoxy methylsilane spontaneously polymerized on a metallic Si anode in an EC/DC (1:1) electrolyte. These authors reported capacities of 2,400 mAh/g for over 200 charge/discharge cycles. An even more dramatic illustration of this concept comes from the study by Lee et al. (2007), which investigated the effect of triacetoxymethylsilane (VS) on the surface morphology of a metallic lithium electrode cycled at 1.25 mA cm^{-2} (C/2) in 1:1 EC/DMC-1 M PF_6 with varying VS content. Remarkably, these authors showed

that an electrolyte containing 2 wt% VS minimized the formation of lithium dendrites and maintained 80% of the initial capacity after 200 cycles in the LiCoO₂/Li cell.

The flammability of aprotic liquid electrolytes represents another significant threat to their large-scale deployment, particularly in large secondary batteries (Balakrishnan et al. 2006). Flame retardant (FR) additives aim to reduce this threat while maintaining good ionic conductivity and cycling characteristics. Most FRs act by chemical radical scavenging, which terminates the radical chain combustion reaction (Wang et al. 2001). Ideally, the amount of FR should be kept below 20 vol.%, to minimize the deleterious effects on battery performance (Arai 2003); however, ignition under high pressure of oxygen or other kinds of abuse conditions is still possible with the highly flammable linear carbonate solvents in this range. Organic phosphates (alkyl phosphates and aryl phosphates) (Mandal et al. 2006), halogens, biphenyls, their combination or derivatives (Jow et al. 2005), and nitrogen-containing compounds are by far the most common FRs. Hyung et al. (2003) investigated a group of organic phosphate compounds, triphenylphosphate (TPP) and tributylphosphate (TBP) and found that they markedly improved the thermal stability of lithium-based cells. Shigematsu et al. (2009) found that in a C/VEC-VC-LiPF₆/Li_xCoO₂ cell, trimethyl phosphate (TMP) promotes thermal stability of both electrodes. Morita et al. (2005) showed that TMP perhaps achieves this benefit by preventing thermal decomposition of LiPF₆. Cresyl diphenyl phosphate (CDP) FRs have been studied by Shim et al. (2009), as well as by Zhou et al. (2008). Both groups showed that the thermal stability and non-flammability of aprotic liquid electrolytes can be markedly improved by adding only 5wt% CDP. Zhang et al. (2009) reported a new flame retardant called vinyl-tris-(methoxydiethoxy)silane (VTMS). Their combustion tests revealed that the addition of VTMS at 5–15 vol.% could dramatically reduce the flammability of a 1 M LiPF₆-EC/EMC/DMC (1:1:1, v/v/v) electrolyte. Recently, Fei and Allcock (2010) reported that a PC electrolyte containing methoxyethoxyethoxy phosphazene oligomers and the corresponding high molecular weight polymer simultaneously exhibited attractive flame retardance and good ionic conductivity.

Solid-state electrolytes: ceramics, polymers, composites and hybrids

All solid-state batteries have some inherent advantages over liquid electrolytes, namely no chance of electrolyte leakage and reduced flammability. They also allow for the implementation of advanced battery architectures and the possibility of safe implementation of rechargeable, high-energy density batteries employing lithium metal anodes

by mechanical inhibition of lithium dendrite formation that can cause cell short-circuiting. However, the ionic conductivity of dry cells is often less, especially at room temperature, than that of liquid cells. Current studies in the solid-state electrolyte field aim to mitigate losses in ionic conductivity, and therefore cell rate capability, while still improving safety and efficient cycling behavior.

Ceramic electrolytes

Ceramic electrolytes are non-flammable and thermally stable to high temperatures. They are also mechanically strong: nanoindentation measurements of lithium phosphonate oxide (LiPON) demonstrate elastic modulus of 77 GPa, (Herbert et al. 2011), which is well beyond the minimum value of 3.4 GPa predicted by Newman (Monroe and Newman 2009) that is required of an electrolyte to suppress metallic lithium dendrite formation. Despite their mechanical strength, many ceramic electrolytes demonstrate excellent room-temperature ionic conductivity (>10⁻³ S/cm) with lithium transference ~1. Fergus (2010) recently published a comprehensive review of ionic conductivity data for ceramic and polymer electrolytes, which provides an excellent comparison of the ionic conductivity of the three main classes of ceramic electrolytes—sulfides, oxides and phosphates. Another review by Patil et al. (2008) provides a comprehensive history of thin film battery development, including ceramic electrolytes, through 2008. It is important to note that while many ceramics exhibit ionic conductivity of the order of 10⁻³ S/cm at room temperature, it is LiPON with an ionic conductivity of only 2 × 10⁻⁶ S/cm that has had gained widespread use, suggesting that other properties play an important role in the success of the electrolyte. Vacuum-sputtered LiPON is an amorphous ceramic with a wide electrochemical stability window (5.5 V vs. Li), interfacial stability in contact with metallic lithium, thermal stability up to 300°C, and an ionic conductivity which is acceptable for use in a thin film battery with micron-scale (or thinner) electrolyte thickness (Yu et al. 1997).

Solid-state batteries utilizing ceramic electrolytes can exhibit high interfacial impedances, as some ceramics, including many sulfides, react with common anode and cathode chemistries such as LiCoO₂. Since reactivity of a pair of electrolyte–electrode materials is not always obvious, interfacial impedance characterization must be performed. For example, one report showed that a stable SEI formed between an alloy Li–Al anode and thio-LISICON type electrolytes with compositions Li_{3.4}Si_{0.4}P_{0.6}S₄ and Li_{3.25}Ge_{0.25}P_{0.75}S₄ and activation energies at the interface smaller or comparable to those reported for a lithium metal/composite polymer electrolyte interface (Kobayashi et al. 2008). However, Li₃PO₄-Li₂S-SiS₂ and thio-LISICON

$\text{Li}_{3.325}\text{P}_{0.935}\text{S}_4$ electrolytes reacted continuously with the Li–Al anode. Takahara has reported decomposition at the Li_3PO_4 – Li_2S – SiS_2 and Li metal interface (Takahara et al. 2004). Electronic conductivity of perovskite type of lithium lanthanum titanate oxide (LLT) is enhanced significantly by contact with metallic lithium due to Ti^{4+} reduction (Kotobuki et al. 2010a). Oxide impurities form at the interface of LLT and LiCoO_2 cathode with sintering, creating high interfacial resistance that dominates cell behavior, while LiMnO_4 was shown to form a low resistance interface with LLT. Similarly, the formation of the inert oxide layer increases the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ /LATSP interfacial resistance, blocking the Li ion diffusion through the interface (Xie et al. 2010). $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZ) was calcined to obtained garnet-like structure pellet that in a symmetric Li cell showed interfaced stability, reversible plating and de-plating with no reaction. However, Li/LLZ/ LiCoO_2 cell that was successfully cycled showed irreversible behavior between LLZ and LiCoO_2 (Kotobuki et al. 2010b).

To improve ceramic electrolyte–electrode compatibility and still maintain good overall cell capacity, nanoscale intermediary films were used to prevent interfacial reactions. LiCoO_2 cathodes were spray coated with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ to form a protective layer between the cathode and sulfide electrolyte thio-LiSICON, which prevented formation of a highly resistive space-charge layer (Ohta et al. 2006). In a more recent work, Li_2O – SiO_2 , a coating without a transition metal oxide, was shown to be effective in protecting LiCoO_2 for use with sulfide electrolyte Li_2S – P_2S_5 (Sakuda et al. 2008).

Ceramic electrolytes as a whole also have drawbacks that limit their implementation. They are brittle and can require more expensive processing conditions such as high-temperature sintering ($>1,300^\circ\text{C}$) and deposition by sputtering (Mei et al. 2009). The brittleness of the ceramic electrolyte can result in cracking, as the electrolyte is unable to accommodate volume changes in the electrodes due to lithium insertion/de-insertion. To mitigate this concern, a recent study investigated pairing the ceramic electrolyte against a polymer electrolyte that allowed for volume expansion (Tenhaeff et al. 2011). The brittleness of the ceramic electrolyte also limits the cell configurations it may be used in: traditionally, ceramic electrolytes were considered only for flat, thin film batteries. The growing field of micro electromechanical systems (MEMS) being developed requires a power source with maximum energy density and a minimized footprint; to meet this end, 3D battery configurations are being explored.

Ceramic electrolytes are ideal candidates for MEMS applications because not only are they immobile solids, but they are also thermally stable at the high temperatures present locally in microcircuits. Recently, conformal Li-PON films were successfully deposited by magnetron

sputtering in N_2 gas at 2.6 Pa on both off-axis planar substrates and 3D substrates with 10–100 μm features (Xu et al. 2010). While the deposition rate decreases for off-axis areas and the film composition varies, the electrolyte still provides a nearly uniform Li^+ ionic conductivity of $2 \pm 1 \times 10^{-6}$ S/cm throughout. In another study, 3D batteries were fabricated using a honeycomb, LLT electrolyte filled with oxide cathode particles and sol gel precursors (Kotobuki et al. 2010c). Good electrolyte–electrode contact was formed via this method, and a battery utilizing an LiMnO_4 cathode displayed low interfacial impedance. The batteries were successfully cycled, but suffered from very poor discharge capacities, attributed to the large size of the electrolyte honeycomb pores (180 μm).

Polymer electrolytes

Polymers have long been recognized as promising electrolyte candidates. Unlike brittle ceramic electrolytes, polymer-based electrolytes have the advantage of being lightweight and flexible, allowing for coiled cell configurations. Polymer electrolytes, unlike some ceramics, are unreactive with common oxide electrodes; they also perform better than liquid electrolytes in conjunction with sulfur cathodes and display wide electrochemical stability windows. The main drawback of polymer electrolytes is their low ionic conductivity, especially at room temperature.

In 1973, polyethylene oxide (PEO) was found to be conductive when complexed with an alkali metal salt (Fenton et al. 1973). In 1979, the first battery using a solid polymer electrolyte (SPE), PEO complexed with a lithium salt, was produced (Armand et al. 1979). Remarkably, the majority of work in this field is still dedicated to PEO due to its relatively high ionic conductivity when compared with other polymers. PEO-based electrolytes have traditionally been plagued with poor room-temperature conductivity due to crystallization of the matrix, so efforts have been made to extend amorphicity into the room-temperature range. Large organic salts such as LiTFSI aid in this regard, as the anions act as a plasticizer, allowing the polymer chains to move more freely.

While improvements in conductivity are desirable, studies have shown that among electrolytes with similar lithium ion conductivity, those with high total ionic conductivity and low lithium transference numbers exhibit poorer electrochemical properties (Doyle et al. 1994). In addition, theoretical predictions by Rosso et al. (2001) suggest that the onset time for dendritic lithium growth, and subsequent short circuit time, has an inversely squared dependence on the anion transference number. Thus it is desirable to make single ion polymer conductors, or ionomers—polymer backbones with tethered anions that associate with free Li^+ . Colby et al. have shown that ions

in these environments tend to aggregate into pairs, trimers or quadrapoles, with few free lithium ions (Klein et al. 2006; Fragiadakis et al. 2008, 2009; Wang et al. 2010b). Therefore, conduction is governed by the trimer, which moves by segmental motion of the backbone, dissociating and reforming as it travels. This mechanism leads to impractically low conductivities in these systems, though lithium transference is unity. Recently, mixed polymer systems of PEO and poly(lithium acrylate) salts were shown to have improved conductivity (10^{-6} S/cm at room temperature and 10^{-4} S/cm at elevated temperatures) in the presence of the additive BF_3OEt_2 , which coordinates with the tethered carboxylate anion and promotes ion-pair dissociation (Itoh et al. 2009). This study suggests that single ion-conducting conductors with high conductivity may be possible with improvements in anion coordinating additives.

Amorphous polymer electrolytes typically soften with improvements in ionic conductivity; this loss of mechanical integrity makes them less desirable for application in lithium metal-based batteries. Improvements in mechanical properties of solid-state polymer-based electrolytes have been demonstrated via cross-linked polymer, block co-polymer and small molecule polymer crystalline electrolytes, as well as polymer–ceramic composite and polymer–ceramic hybrid electrolytes, discussed in later sections.

Cross-linked polymer electrolyte films have been synthesized by a number of methods, including chemical cross-linking (Borghini et al. 1996; Matoba et al. 2002; Fogeling et al. 2010), photochemically cross-linking (Rupp et al. 2008), UV-cross-linking (Choi and Park 2009) and electron-beam cross-linking (Uchiyama et al. 2009). Solid cross-linked electrolytes based on PEO, without added solvent, generally exhibit ionic conductivities around 10^{-5} S/cm at room temperature as the cross-linking inhibits chain crystallization, though it slows chain mobility. Cross-linking also increases the tensile strength of the films to the MPa range.

The majority of studies in the block copolymer electrolyte field has centered on materials with continuous, majority PEO blocks and minority blocks of a stiffer, typically non-conducting polymer to enhance mechanical properties. We will highlight two recent works. Ghosh et al. (2010 and Ghosh and Kofinas (2008) synthesized a PEO-*b*-(PMMA-*ran*-PMMALi) diblock copolymer with a minority random copolymer block of methyl methacrylate (MMA) and lithium salt of methacrylic acid (MMALi) to provide an additional lithium source. When doped with LiBC_4O_8 (LiBOB), the copolymer electrolyte is a transparent, flexible film with an ionic conductivity of 1×10^{-5} S/cm, lithium transference of 0.9 and electrochemical stability above 5 V at room temperature. Niitani et al. (2009) reported a polystyrene (PS)-block-polyethylene glycol methyl ethyl

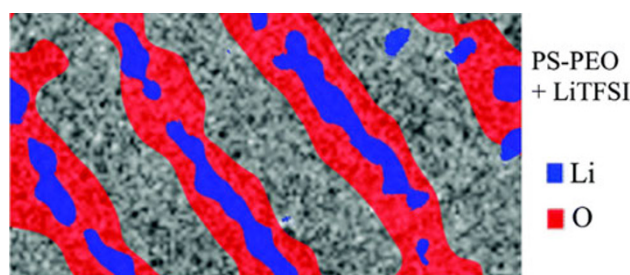


Fig. 7 Distribution of lithium in a PS-PEO block copolymer electrolyte doped with LiTFSI as determined by energy-filtered transmission electron microscopy (reprinted with permission from Gomez et al. 2009, Copyright (2009) American Chemical Society)

methacrylate (PPEGMA)₂ star-shaped copolymer with a PS core and PPEGMA arms. When doped with LiBETI, the star copolymer electrolyte is a flexible film with a total ionic conductivity in the order of 10^{-4} S/cm at room temperature. The notable enhanced total ionic conductivity of this electrolyte may be attributed to the geometric configuration of the block copolymer, where many short ethylene oxide chains are employed instead of one long chain, which inhibits crystallization of the conducting phase.

Decoupling of mechanical and conduction properties in a block copolymer electrolyte has been demonstrated by Singh et al. (2007) and Gomez et al. (2009) using a material with a continuous non-conducting phase (Fig. 7). The PS-block-PEO lamellar electrolytes, doped with LiTFSI, manifested ionic conductivities in the range 10^{-4} – 10^{-5} S/cm from 90 to 120°C and dynamic storage moduli of 10^7 – 10^8 Pa. The lamellar block copolymer electrolyte exhibited significant improvement in mechanical properties with little change in conductivity, thereby demonstrating that independent control of these properties is possible. Energy-filtered TEM showed that ions were accumulating, increasingly localized, at the center of the PEO lamellae as the chain molecular weight increased. Stress calculations indicate that local stress interferes with the ability of the PEO near the phase boundaries to interact with the salt, thus decreasing ion concentration in wall regions that have lower mobility. Overall, the properties of the lamellar block copolymer electrolyte are quite attractive at elevated temperatures ($\sim 100^\circ\text{C}$); improvement in conductivity at lower temperatures appears necessary for use of the system in a room-temperature secondary battery.

Decoupling of mechanical and conduction properties in polymers has also been demonstrated by a relatively new class of materials, crystalline polymer–salt complexes or small molecule electrolytes (Gadjourova et al. 2001; Christie et al. 2005; Bruce 2008; Bruce et al. 2008). These complexes of short PEO chains (glymes) and lithium salt form crystals with varying structures depending on the EO/ Li^+ ratio and glyme length. In most cases, the glyme chain

forms a helix around the lithium ions, and anions are free outside of the helix. The lithium ions are then able to conduct through the helix tunnel and along the glyme backbone. Increasing order, and therefore decreasing defects between tunnels, improves the ionic conductivity. Dopants of lithium salts with a different ion (i.e., addition of a small amount of LiTFSI to an LiAsF₆-doped electrolyte) have been shown to improve conductivity, as have increasing the number of chain ends per crystallite and having chains with –OC₂H₅ ends. The ionic conductivity of crystalline electrolytes is still low, 10^{–8} to 10^{–6} S/cm at room temperature, but this field is relatively new. Like all polymer electrolytes, they are easily processable—an advantage over their ceramic electrolyte counterparts.

Polymer–ceramic composite electrolytes

The addition of ceramic nanoparticles, such as TiO₂ (Croce et al. 1998, 1999; Jeon et al. 2006), SiO₂ (Raghaven et al. 2008; Capiglia et al. 1999), Al₂O₃, (Bruce 2008; Krawiec et al. 1995; Jayathilaka et al. 2002) Fe₃O₄ (Reddy et al. 2006) and S-ZrO₂ (Croce et al. 2006; Panero et al. 2007) to polymer electrolytes has been shown to improve ionic conductivity, and mechanical and electrochemical properties of the polymer electrolyte. The increase in ionic conductivity in composite electrolytes (CPEs) with inert fillers has been attributed to the nanoparticles acting as solid plasticizers, disturbing polymer crystallization. Comparative studies of nanofillers with varying chemistries and surface functionalized nanofillers reveal that the electrostatic environment near the particle surface can promote conduction of one species over another. It is understood that Lewis acid–base surface groups interact with ions and PEO segments to create additional conduction pathways along the particle surfaces for lithium cations and/or interfere with anion transport.

Inadequate movement of polymer chains next to an electrode surface leads to a decline in salt transport and thus an increase in a salt concentration gradient (Kerr et al. 2004). The addition of ceramic additives increases polymer amorphicity and chain mobility. Ceramic fillers also can scavenge impurities from the electrolyte, which may have undesirable reactions with the electrode (Mazor et al. 2008). These combined effects reduce the interfacial resistance at the lithium electrode (Bruce 2008; Jeon et al. 2006). Reduction in the SEI improves the interface stability and reduces dendrite formation on lithium metal anodes. CPEs also have enhanced mechanical properties, with an increase in the Young's modulus and yield strength. Still, even with the use of additives such as calix(6)pyrrole (Jayathilaka et al. 2002; Croce et al. 2006), solid-state composite polymer systems based on high molecular weight PEO suffer from low ionic conductivity at room

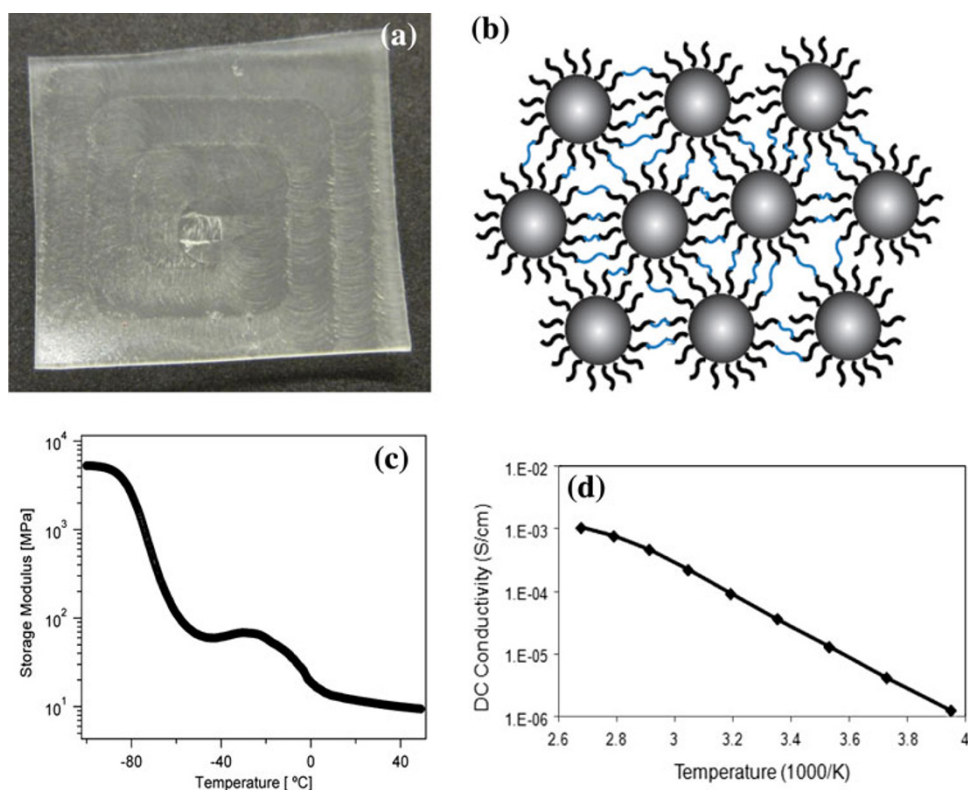
temperature and below, which limits their practical application.

Polymer–ceramic hybrid electrolytes

Polymer–ceramic hybrid electrolytes are studied for their potential to improve mechanical properties and prevent crystallization of polymer-based electrolytes. Miscibility between the organic and inorganic constituents of these materials is a concern that can be alleviated by appropriate chemistry. The majority of these hybrid materials have molecular-scale inorganic regions cross-linked by an organic component. They are often synthesized by a sol–gel technique, polycondensation reactions of alkoxysilanes and end-functionalized homopolymers or copolymers (Popall et al. 1998; Kao et al. 2006; Jeyapandian et al. 2010). Hybrid materials of similar form but varying chemistry were recently demonstrated by the reaction of polyethylene glycol with organometallic precursor methylaluminumoxane, an oxaluminum cluster that contains up to 12 active reaction sites (Piszcz et al. 2010). A deviation from this form was reported by Kao and Chen (2004) who synthesized a mesoscopically ordered electrolyte with hexagonal arrays of inorganic cylinders by co-condensation of glycidicyloxypropyl trimethoxysilane (GLYMO) and tetraethoxysilane (TEOS) and self-assembly of PEO–PPO–PEO triblock copolymer. Ionic conductivities in the range of 10^{–6}–10^{–4} S/cm at room temperature are typical of these hybrids; the framework is typically successful in preventing polymer crystallization above room temperature. Notably, all of these studies fail to characterize the mechanical properties of the electrolyte and it is not clear how their strength compares to that of pure polymer and composite polymer electrolytes.

Recently, we reported on the synthesis of organic–inorganic hybrids created by dense functionalization of nanoscale ceramic particles with short polymer chains (Nugent et al. 2010). Physical properties of these materials are facilely tuned by changing the polymer chain (corona) length, grafting density, as well as the particle size and inorganic content of the hybrids. The systems exist as jammed, self-suspended suspensions of nanoparticles (Nugent et al. 2010; Agarwal et al. 2010, 2011), which manifest a yield stress and, depending on the corona molecular weight, exhibit room-temperature ionic conductivities from 10^{–3} to 10^{–6} S/cm. Hybrids based on corona chains with terminal, reactive functional groups allow the nanoparticle cores to be cross-linked to yield homogeneous organic–inorganic hybrid films with tensile moduli exceeding 0.1 GPa at room temperature (Agarwal et al. 2010, 2011). Doping these films with a 1 M solution of LiTFSI in TEGDME produces a tenfold reduction in the modulus to ~10 MPa (Fig. 8) and room-temperature ionic conductivities of 2 × 10^{–5} S/cm.

Fig. 8 Cross-linked, nanoporous SiO₂-PEG film. **a** Photograph and **b** schematic of PEG hybrid's highlighting cross-linked chains; **c** dynamic elastic modulus; and **d** ionic conductivity of cross-linked hybrid film as a function of temperature, after swelling with 1 M LiTFSI in TEGDME



Mixed phase electrolytes

Mixed phase electrolytes, containing both solid and liquid components, offer a compromise in material properties, whereas the liquid aids in conduction and the solid enhances mechanical properties. The majority of work in this field has previously been devoted to gel polymer electrolytes and soggy sand electrolytes.

Polymer–liquid electrolytes

Gel polymer electrolytes comprise a polymer matrix swollen with a liquid electrolyte, with or without a ceramic particle additive. The gel polymer is a free-standing film that eliminates the problem of leakage as with a traditional liquid electrolyte and thus the need for a separator, but still has nearly the same ionic conductivity and electrochemical properties of the imbibing fluid. The polymer matrix may be cross-linked or uncross-linked.

In the 1990s, Bellcore commercially produced the first plastic Li ion battery. It utilized a poly(vinylidene fluoride)-hexafluoropropylene (PVdF-HFP) matrix with an EC-DMC-LiPF₆ liquid electrolyte and SiO₂ filler in an LiMn₂O₄/C cell (Tarascon et al. 1996). PVdF-HFP is a copolymer with good mechanical integrity, chemical stability and miscibility with carbonate-based electrolytes, unlike PEO. Still, the Bellcore electrolyte suffers from the other problems associated with aprotic liquid electrolytes:

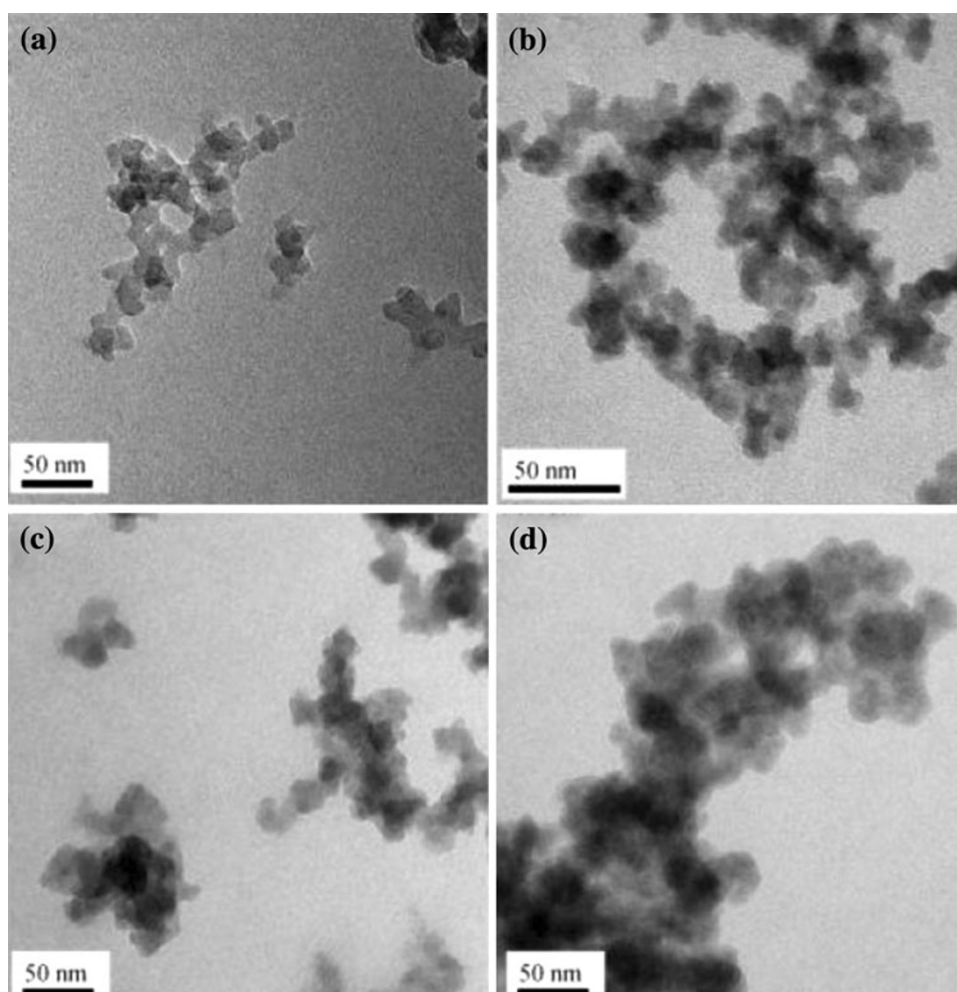
low thermal stability, low cathodic stability, volatility, flammability and insufficient moduli to prevent dendritic lithium growth. Ionic liquid-based gel polymer electrolytes are now widely studied as a possible solution to some of these issues (Rupp et al. 2008; Fuller et al. 1998; Nakagawa et al. 2003; Cheng et al. 2007; Liao et al. 2010); PEO-based gel polymer electrolytes have also been explored, by swelling a high molecular weight PEO matrix with PEG oligomers (Borghini et al. 1996).

Ceramic–liquid electrolytes

“Soggy sand” electrolytes are created by doping a liquid electrolyte with ceramic nanoparticles (Bhattacharyya et al. 2004; Das and Bhattacharyya 2009, 2010; Walls et al. 2003). At a given particle volume fraction $\phi_{\text{onset}} \ll 0.01$, a percolating particle network forms in the system (Fig. 9) and the physical nature of the bulk material may become gel-like. This gel state, similar to that achieved in polymer–liquid gel electrolytes, may render the separator in Li ion cells unnecessary. The onset percolation threshold ϕ_{onset} is a function of the chemical moieties on the particle surface for a given particle size, and the network is formed by hydrogen bonding and/or Van der Waals interactions between surface groups.

Certain dopants, such as unmodified aerosol silica (Bhattacharyya et al. 2004), methyl-capped aerosol silica (Bhattacharyya et al. 2004) or Li-exchanged hectorite

Fig. 9 Transmission electron micrographs showing the intrinsic morphology of nonfunctionalized and functionalized aerosil silica particles used in the preparation of soggy sand electrolytes: **a** as received; **b** methyl capped; **c** amine capped; and **d** octyl capped. (reprinted with permission from Das and Bhattacharyya (2009), Copyright (2009) American Chemical Society)



nanoclay (Das and Bhattacharyya 2010), may increase ionic conductivity of the electrolyte up to half an order of magnitude at low $\phi > \phi_{\text{onset}}$ by attracting the anion, thus breaking up an ion pair and freeing Li^+ for conduction. Beyond a threshold volume fraction ϕ_{max} , the ionic conductivity then declines due to blocking of the ionic conduction pathways. A soggy sand electrolyte of lithium perchlorate-ethylene glycol solution doped with unmodified aerosil silica at $\phi = 0.07$ has a storage modulus $G' = 5 \times 10^{-4}$ Pa and ionic conductivity of 7×10^{-4} S/cm at room temperature, a 30% increase in conductivity compared with the pure electrolyte solution (Bhattacharyya et al. 2004). However, a change in the liquid to lithium perchlorate-methoxy polyethylene glycol solution resulted in a gel with $G' = 1 \times 10^{-6}$ Pa and ionic conductivity of 1×10^{-4} S/cm, with no improvement in conductivity over the undoped solution (Das and Bhattacharyya 2009). The effect of bonding structure and surface chemistry on conductivity in soggy sand electrolytes is still under investigation.

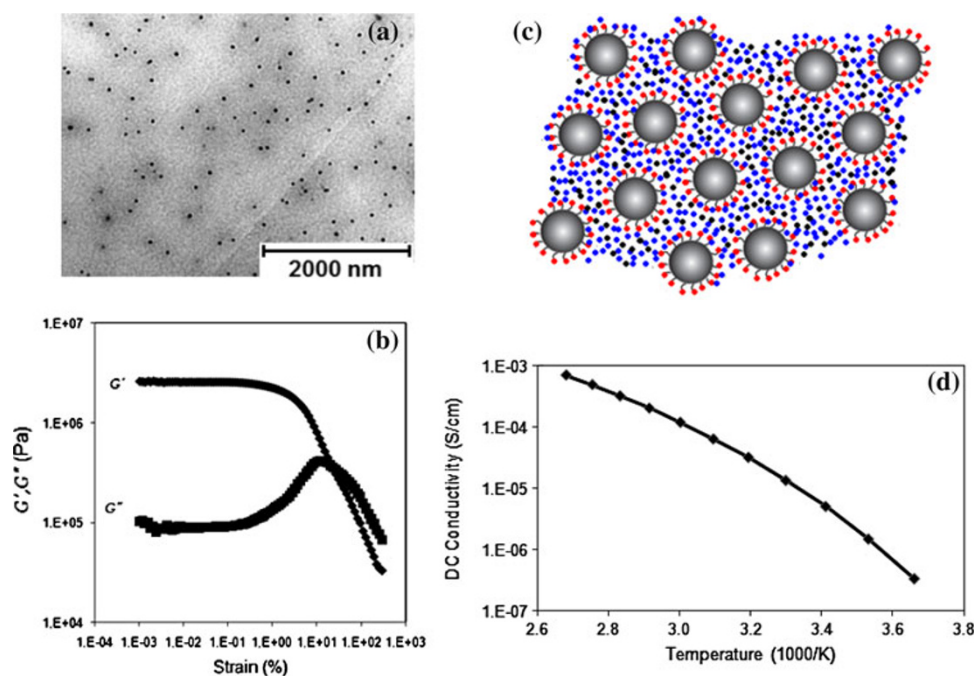
Ceramic-IL nanocomposites ILs have been investigated as electrolytes for dye-sensitized solar cells. Wang et al. (2004b) and Katakabe et al. (2007) have both noted improved properties by doping an IL electrolyte with silica.

Recently, Syzdek et al. (2009) reported on a liquid-in-ceramic composite, where the ceramic provides a continuous supporting phase and is soaked with a liquid electrolyte. The porous ceramic matrix was formed by a tape-casting method, uni-axial pressing and grain sintering of a slurry of $\gamma\text{-Al}_2\text{O}_3$ particles. Electrolytes were prepared by soaking the ceramic matrix in various PEGDME/ LiClO_4 liquids. The electrochemical properties of the resulting electrolyte were found to depend on the liquid component and porosity of the support matrix.

Nanoporous hybrid electrolytes

Recently, we reported on a new class of mixed phase electrolytes, nanoporous hybrid electrolytes, of zirconia-imidazolium based ionic liquid hybrid ($\text{ZrO}_2\text{-IL}$) doped

Fig. 10 ZrO₂-IL hybrid electrolyte with a tethered imidazolium-based cation and free TFSI anion, doped with 1 M LiTFSI: **a** transmission electron micrograph of ZrO₂-IL particles; **b** dynamic shear moduli as a function of shear strain at 50°C; **c** schematic, where *red* indicates imidazolium cation, *black* Li⁺ and *blue* TFSI⁻; **d** ionic conductivity



with LiTFSI (Fig. 10) (Moganty et al. 2010) and silica-polyethylene glycol (SiO₂-PEG) hybrids suspended in PEGDME/LiTFSI (Fig. 11) (Schaefer et al. 2011). Like the solvent-free, cross-linked electrolytes introduced in “Polymer–ceramic hybrid electrolytes”, both of these systems have uniformly dispersed, non-agglomerated ceramic nanocores surrounded by a percolating, organic ionic conduction pathway. This percolating conduction pathway allows for good ionic conductivities even at high particle loadings. A SiO₂-PEG suspension electrolyte with $\phi = 0.38$ displays a storage modulus close to 1 MPa and an ionic conductivity of 3.5×10^{-4} S/cm at 35°C, as well as a practical conductivity of 1.0×10^{-4} S/cm at 10°C. In comparison, the ZrO₂-IL electrolyte displayed an ionic conductivity of 7×10^{-4} S/cm at 100°C and 2×10^{-5} S/cm at 25°C with a storage modulus of 5 MPa at 150°C. Significantly, the ZrO₂-IL electrolyte has a lithium transference number $T_{Li^+} = 0.35 \pm 0.04$, seven times larger than the value for the pure IL electrolytes (0.05) (Hayamizu et al. 2004). This improvement in lithium transference is attributed to the tethering of the IL imidazolium cation, leaving Li⁺ as the only mobile cation in the system. Both of these systems display wide electrochemical stability windows and stable interfacial impedances against lithium metal.

Unlike previously studied electrolytes, these nanoporous hybrids behave mechanically as soft glasses when $\phi > \phi^*$, the threshold value for particle jamming. At ceramic fractions above ϕ^* and at rest or under low strain (γ), the electrolyte is jammed and behaves as a solid. When the applied strain exceeds the yield strain γ_y , the electrolyte flows as a liquid; this property is significant because it means that the electrolyte behaves as a solid in static

conditions, such as inside a battery, yet can be readily processed during normal cell assembly.

Conclusions

From aqueous liquid electrolytes for lithium–air cells to ionic liquid electrolytes that permit continuous, high-rate cycling of secondary batteries comprising metallic lithium anodes, we show that many of the key impediments to progress in developing next-generation batteries with high specific energies can be overcome with clever designs of the electrolyte. When these designs are coupled with cleverly engineered electrode configurations that control chemical interactions between the electrolyte and electrode (e.g., in Li/sulfur cells that employ encapsulation/physorption strategies for limiting dissolution of redox products in the electrolyte) or by simple additives-based schemes for manipulating physical contact between the electrolyte and electrode (e.g., through sacrificial additives that spontaneously form a stabilizing SEI layer), we further show that rechargeable battery configurations can be readily designed to maximize performance and cycling stability. Judging from the large number of degrees of freedom inherent in synthesizing organic–inorganic hybrid materials systems with explicit desired properties, and the recent upsurge in interest in synthesizing ionic liquids with tunable solvation and ion transport properties, while preserving their desirable thermal and electrochemical stability, we are optimistic that in a matter of few years commercially viable electrolytes will begin to appear that are suitable for safe deployment in the most energy-dense battery configurations of all, those based on the metal–air cell.

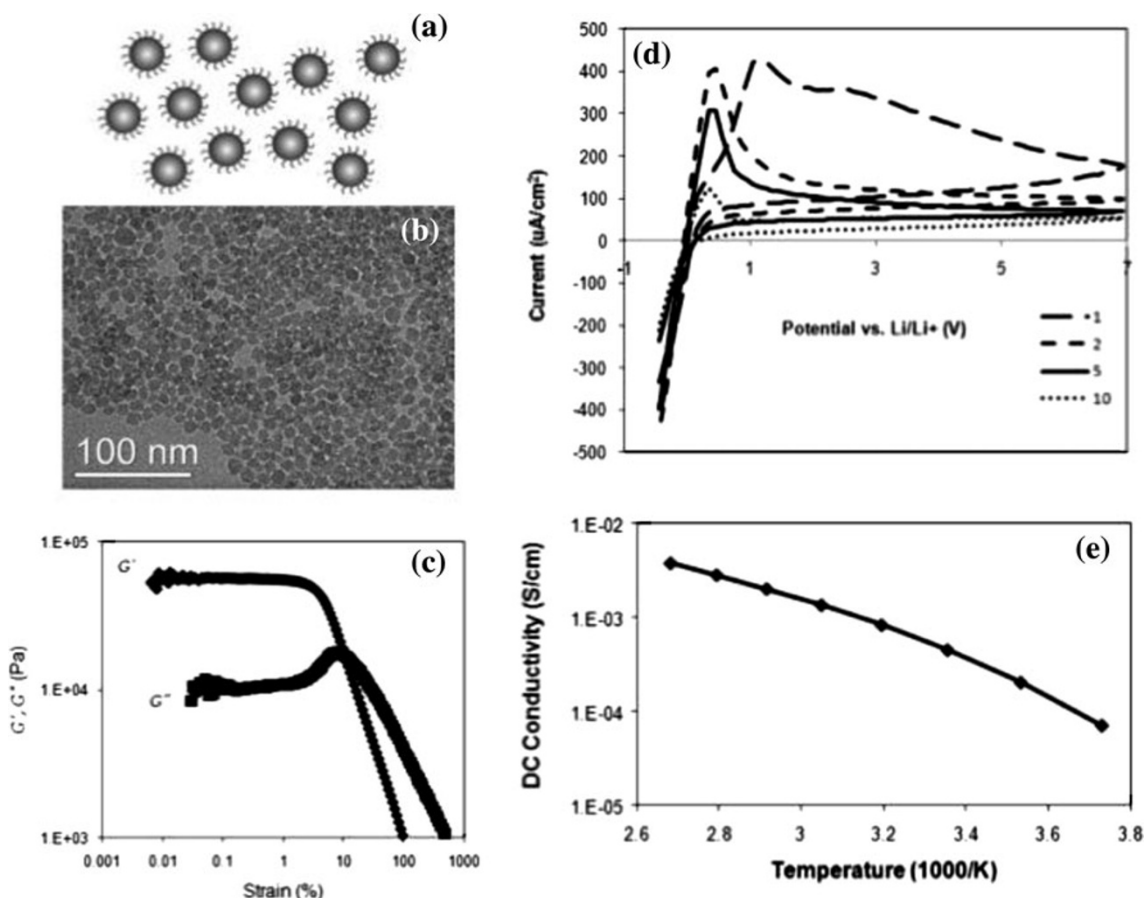


Fig. 11 SiO₂-PEG hybrid suspended in PEGDME and doped with 1 M LiTFSI in the organic phase, $\phi = 0.3$: **a** schematic of hybrid suspensions; **b** transmission electron micrograph of SiO₂-PEG/PEGDME; **c** dynamic shear moduli as a function of strain at 35°C;

d cyclic voltammety of a Li/electrolyte/Li cell at a scan rate of 1 mV/s for ten cycles from -0.5 to 7.0 V versus Li/Li⁺; **e** ionic conductivity of SiO₂-PEG/PEGDME suspension with $\phi = 0.3$

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