Lithium Ion Batteries

DOI: 10.1002/anie.201004551

Ionic-Liquid-Tethered Nanoparticles: Hybrid Electrolytes**

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Secondary batteries containing lithium (Li) metal as the anode provide one of the highest known energy densities for electrical energy storage.[1] Most currently used electrolytes are unsuitable for use with a Li metal anode because they are unstable at typical cell potentials and do nothing to mitigate Li dendrite growth during repeated charge–discharge cycles.[2] Because the latter is a fundamental problem that affects the safety and reliability of all secondary batteries containing metallic lithium as anode, a robust solution is a long sought-after goal in the field. Solid polymer electrolytes are effective in reducing dendrite growth and have been studied extensively for this purpose, either in pure form or as composites.[3,4] The widely used and intensely studied solid ionic conductor, polyethylene oxide (PEO), is crystalline and exhibits poor ionic conductivities at room temperature.[5] Several strategies have been proposed in the literature for improving the ionic conductivity and mechanical properties of PEO.[2,5–7]

The potential of ionic liquids (ILs) as electrolytes for energy storage devices has long been appreciated.[8–10] ILs offer a host of attractive properties, including ultralow vapor pressure, high thermal stability,[11] high ionic conductivity and wide redox stability,[12] which make them attractive as electrolytes. But, ILs suffer from low lithium ion transference numbers, poor mechanical performance, and are ineffective in arresting dendrite growth in Li metal batteries.[13] Tethering ILs to nanoparticles potentially offers a simple, versatile route towards simultaneously preserving their strengths and mitigating these deficiencies.

Recently, we reported a class of organic–inorganic hybrid materials created by covalently tethering an ammonium-type cation to a variety of inorganic nanoparticles.[14] By varying the counter ion from compact species, such as chloride, to bulky ions, such as isosterate, oleate and sulfonate, we discovered that physical properties of these materials can be facilely tuned to cover the spectrum from solids to solvent-free liquids. Liu et al.[15] recently showed that a similar methodology can be employed to synthesize luminescent ZnO nanocrystals stabilized by an ammonium-based IL with tunable photoluminescence. Most recently Nugent et al.[7] extended this concept to create a family of self-suspended polyethylene glycol(PEG)–SiO_2 hybrid electrolytes, by one-step covalent attachment of end-functionalized PEG oligomers to the surface of SiO_2.

Herein, we report a new family of solventless electrolytes created by tethering ILs to hard inorganic ZrO_2 nanostructures (Figure 1). Termed ionic liquid–nanoscale ionic materials (IL-NIMs), these fluids exhibit exceptional redox stability windows, excellent thermal stability, good Li transference numbers, long-term interfacial stability in the presence of a lithium anode, and, when doped with lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) salt, reasonable ionic conductivities. Additionally, mechanical characterization measurements indicate that the shear moduli of these IL-NIMs are many orders of magnitude larger than that of their ionic liquid precursors. These same measurements show that IL-NIMs electrolytes belong to a class of yield stress materials termed soft glasses, in which each nanoscale organic–inorganic hybrid building block is trapped in potential energy wells many times deeper than the mean thermal energy, kT. Thus, viewed from the vantage point of a diffusing Li ion or moving Li dendrite front, IL-NIMs electrolytes are analogous to porous solids with tunable pore chemistry, dimensions, tortuosities, and surface chemistry (e.g. by changing the core particle and/or IL ligand chemistry, size, and grafting density). By taking advantage of the already large libraries of available nanoparticle and ionic liquid chemistries, IL-NIMs open up a new

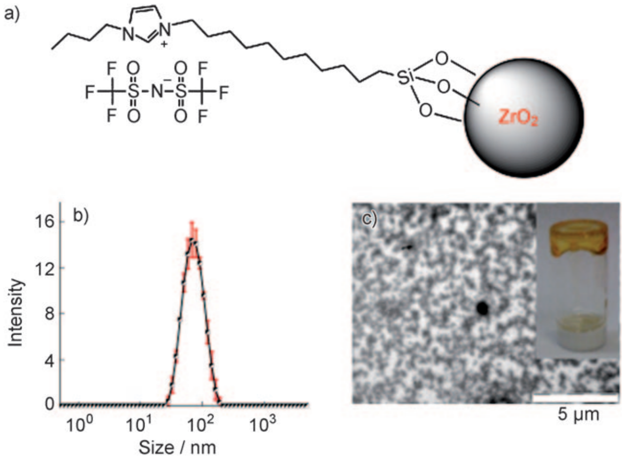

Figure 1. a) Ionic liquid tethered zirconia nanoparticle. b) Size distribution of ZrO_2-IL nanostructures from dynamic light scattering measurements in acetone. c) Transmission electron microscope image of ZrO_2-IL-NIMs containing LiTFSI; inset is a photograph of the ZrO_2-IL-NIMs electrolyte used for the subsequent electrochemical and mechanical characterization.

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[**] This work was supported by Award No. KUS-C1-018-02, made by King Abdullah University of Science and Technology (KAUST). Facilities available through the Cornell Center for Materials Research (CCMR), a Materials Research Science and Engineering Center of the National Science Foundation (DMR-0079992) were used for this study.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201004551.

vista for engineering novel hybrid electrolytes with exceptional electrochemical, mechanical, and thermal stability for applications in secondary lithium metal and lithium ion batteries.

The IL-NIMs reported here were formed by covalently tethering imidazolium-based ILs to zirconia (ZrO_2) nanoparticles in a single-pot synthesis. The IL precursor was synthesized using a previously reported procedure[21] and the ZrO_2 cores created using a modified Stober scheme. A similar approach can be used to create IL-NIMs based on most other metal oxide core particle chemistries. Results from light scattering measurements (Figure 1 b) show that the average particle size is 86 ± 2 nm and that the particle size distribution is narrow. The inset to Figure 1 c shows that IL-NIMs electrolytes containing 1 M LiTFSI are gel-like fluids at room temperature. Transmission electron microscope (TEM) images (Figure 1 c) of these electrolytes show that they are hybrids comprised of a dense collection of nanostructures.

Thermal properties of the materials were characterized by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). TGA data (Supporting Information Figure S1) shows that the IL-NIMs electrolytes are stable against thermal degradation up to temperatures exceeding 400 °C. DSC results (Figure S2) indicate that the glass transition temperature (T_g) of the IL-NIMs (−50 °C) is substantially higher than that of the precursor IL (−80 °C), implying that the constraints provided by the nanoparticle cores propagate down to the IL segments. It also means that covalent tethering of the IL to the ZrO_2 nanoparticle core lowers the overall mobility of IL constituents. Addition of LiTFSI salt to the IL-NIMs further increased the T_g, an effect similar to what has been reported in PEO systems.[7]

Ionic conductivities of the IL and IL-NIMs with and without 1 M LiTFSI were measured using dielectric spectroscopy at different temperatures. Figure 2 compares the measured ionic conductivities as a function of temperature. The addition of LiTFSI to the IL increases its viscosity, which results in a lower ionic conductivity. However, in the case of the IL-NIMs, addition of LiTFSI salt produces a measurable increase in ionic conductivity. At room temperature, ionic conductivity values for both the LiTFSI doped IL-NIMs and IL-NIMs are comparable to that of a PEO-based polymer electrolytes.[2] Figure 2 also shows that the temperature dependence is of the Vogel–Fulcher–Tammann (VFT) type, characteristic of a typical glass-forming system. The VFT parameters are provided in the Supporting Information (Table S1).

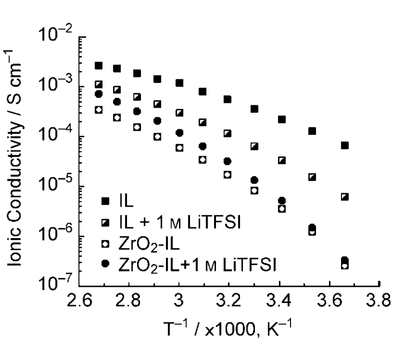

Figure 2. Ionic conductivity of IL and IL-NIMs as a function of reciprocal temperature.

An ideal Li battery electrolyte should be permeable only to Li ions. However, in practical situations contributions from counterions can be appreciable. The Li ion transference number (T_{Li^+}), that is, the Li ion contribution to ionic conduction, of IL-NIMs was measured by imposing a step dc polarization as proposed by Bruce et al.[16] (Figure S3). This approach yields $T_{Li^+} = 0.35 \pm 0.04$, which is close to seven times larger than the value for the pure IL electrolytes (0.05).[18] The improvement in T_{Li^+} is believed to reflect immobilization of the IL cations by the ZrO_2 nanoparticle core, which substantially reduces their contribution in ionic conduction.

Two other important requirements for a successful Li battery electrolyte are electrochemical stability over the voltage range of interest in applications and good interfacial stability towards the Li metal electrode. The electrochemical stability window (EW) of IL-NIMs was determined against a Li metal electrode using linear sweep voltammetry (Figure 3, see also Figure S7). The voltage region demarking the onset of anion oxidation and cation reduction is about 4.5 V vs Li for the IL liquid and 4.3 V for the IL-NIMs indicating that the improvement in T_{Li^+} for the IL-NIM electrolyte is achieved without loss of electrochemical robustness of the IL corona.

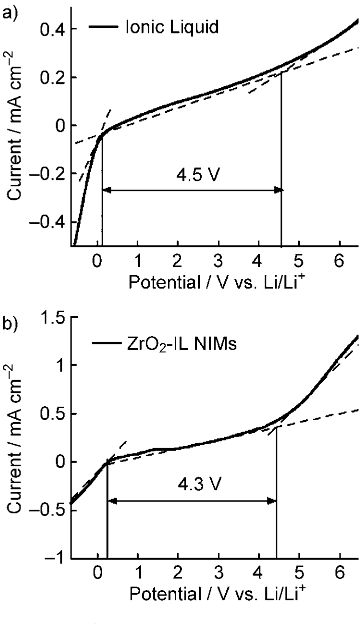

Figure 3. Linear sweep voltammetry using a) Li/IL + 1 M LiTFSI/Li and b) Li/IL-NIMs + 1 M LiTFSI/Li cells at room temperature and 1 mV s^{-1} scan rate. The electrochemical window against Li metal electrode is indicated by the voltage range where Faradaic currents from redox processes are negligible.

To evaluate the stability of the Li/IL-NIMs interface, the interfacial resistance of the Li metal electrode and IL-NIMs electrolyte was monitored over a one-month period using electrochemical impedance spectroscopy. Figure 4 shows the

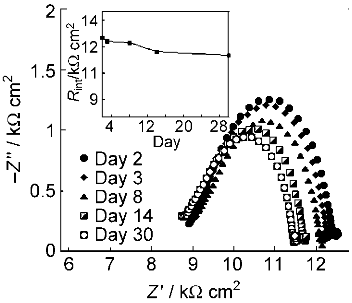

Figure 4. Nyquist/Cole–Cole plots for a Li/IL-NIMs + 1 M LiTFSI/Li symmetric cell. The time-dependent interfacial resistance (R_{int}) between IL-NIMs electrolyte and the Li metal electrode is shown in the inset.

evolution of impedance spectra, collected at open circuit potential of a Li/electrolyte + Li salt/Li cell, as a function of time. The time evolution of the Li interfacial resistance was estimated by fitting an appropriate equivalent electrical circuit to the impedance spectra. As shown in Figure 4 (inset), the interfacial resistance exhibits little, if any, changes with time, confirming the stability of NIMs electrolyte towards Li metal. Additionally, the interface stability and reversibility of the IL-NIMs electrolytes were evaluated using lithium stripping–platting experiments. For these experiments, a current flux of 1 μA cm^{-2} was applied to a Li/electrolyte + Li salt/Li symmetric cell for 5 min before reversing the polarity. The resulting voltage profiles due to lithium platting/stripping are provided in the Supporting Information (Figure S8). It is clearly evident that the voltage profiles stabilize after five cycles and exhibit time-invariant characteristics for 100 cycles similar to the impedance studies. This result nicely confirms the interfacial stability and reversibility of ZrO_2-IL-NIMs electrolytes towards Li metal.

As already mentioned, another important characteristic of a good electrolyte for Li metal cells is its mechanical strength.[6,7] Dynamic shear moduli of IL-NIMs were measured as a function of shear strain. In a typical measurement, an oscillatory shear strain is imposed with a fixed frequency ($\omega = 10$ rad s^{-1}) and the dynamic storage (G') and loss (G'') moduli measured as a function of applied strain. Figure 5 a depicts the strain-dependent moduli and shear stress for our materials. At low strains, G' and G'' are seen to be independent of the applied strain and $G' \gg G''$, both characteristics of a solid-like elastic material. The elastic modulus in the limit of zero strain is found to be 4.5 MPa, that is more than five orders of magnitude higher than that of the untethered ionic liquid. With progressive increase in shear strain, G'' rapidly increases, exhibits a pronounced maximum, and subsequently dominates G', indicative of a strain-induced transition to a fluid-like state. All of these observations are generic behaviors seen in a class of materials, termed as "soft glasses".[7,19] In the soft glass framework, the maximum in G'' and the transition from solid- to liquid-like behavior are predicted to be accompanied by a change in slope of the shear stress τ, which is evidently also observed in our material (Figure 5 a), and is a macroscopic consequences of yielding of the nanoscale cages that constrain each IL-NIMs building block. Figure 5 b clearly shows that the loss modulus maximum increases as temperature is increased and the yield strain, that is, strain at which the loss maximum occurs, is nearly independent of temperature. Neither feature can be explained in the soft glassy rheology framework,[19,20] but imply that the IL-NIMs become mechanically stronger as temperature is increased in this range.

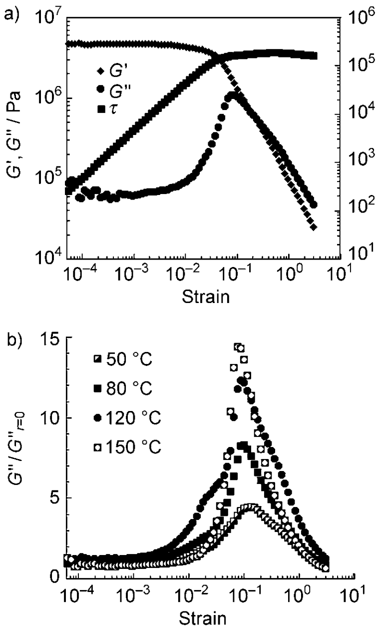

Figure 5. a) Mechanical properties of IL-NIMs electrolytes measured in oscillatory shear at 150 °C. The dynamic moduli (G', G'') and shear stress (τ) are plotted as a function of applied shear strain. b) Loss moduli (G'') divided by its strain-independent value at low strains plotted as a function of strain at different temperatures.

In summary, we have shown that by densely tethering ionic liquids to nanoparticles it is possible to create a new family of electrolytes that possess multiple attractive attributes for Li battery applications. Specifically, we show that IL-NIMs based on ZrO_2 cores spontaneously form porous media with tunable mechanical properties, exhibit excellent thermal stability, wide redox stability windows, good Li ion transference numbers, and moderate ionic conductivities. Additionally, we have shown that these electrolytes exhibited excellent time-invariant interfacial stability against Li metal.

Experimental Section

The ionic liquid precursor, 1-undecyltrimethoxysilane-3-butyl imidazolium bis(trifluoromethylsulfonyl) imide was synthesized using a literature procedure.[21] Purity of the IL was verified using NMR spectroscopy (Figure S6). The as-prepared IL was tethered to ZrO_2 nanoparticles in a single-pot synthesis using a modified Stober-type sol–gel method.[22] In a typical reaction, 0.4 mL of zirconium iso-(butoxide) and 0.4 mL of 0.1 M KCl were mixed in 100 mL of ethanol. After 20 min, when the solution becomes hazy indicating the formation of ZrO_2 nanoparticles, 3 g of IL was added and the contents stirred for at least 48 h. IL tethered ZrO_2 nanoparticles were collected by centrifugation and washing with anhydrous ethyl ether.

TGA and DSC measurements were conducted using TA instruments model Q5000 and Q2000 thermal gravimetric analyzer and differential scanning calorimeter, respectively. TEM images were taken at 120 kV using TECNAI F12 TEM. Ionic conductivity was measured with a Novacontrol Dielectric spectrometer fitted with a Quatro temperature control system. Electrochemical measurements were performed using a Solartron CellTest model potentiostat. Impedance measurements were conducted using a Solartron Frequency Response Analyser (Model 1252) at frequencies ranging from 100 kHz to 100 mHz and at 25 mV. Lithium symmetric coin cells were prepared in a Mbraun glovebox. Rheology measurements were obtained using an Anton Parr MCR 501 mechanical Rheometer.

Received: July 25, 2010
Revised: September 15, 2010

Keywords: ionic liquids · lithium dendrites · lithium ion batteries · nonaqueous electrolytes · soft glasses

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