

Liquid Polymer Nanocomposites PEGME–SnO₂ and PEGME–TiO₂ Prepared through Solvothermal Methods

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Received February 21, 2006. Revised Manuscript Received May 23, 2006

A large number of polyether groups are modified on SnO₂ and TiO₂ nanocrystals through sol–gel methods and solvothermal treatments to form the stable liquid nanocomposites poly(ethylene glycol) methyl ether (PEGME)–SnO₂ and PEGME–TiO₂. These transparent viscous liquids can be dissolved by organic solvents, and the resulting colloids are also very stable; these nanocomposites themselves are able to dissolve lithium salts to form liquid electrolytes which have good ionic conductivities for practical applications. The conductive mechanism for such liquid electrolytes is regarded as ion transfer under the assistance of the PEGME group motion, which is totally different from that for the typical ionic liquids and the traditional liquid electrolytes based on organic solvents and metal salts.

Introduction

The integration of organic and inorganic materials, especially polymers and nanoparticles, has led to revolution in materials science.^{1,2} Such integration is able to make the entire polymer nanocomposite material inherit merits of both polymers and nanoparticles and even exhibit unexpected properties. But polymer nanocomposites are usually solids at ambient temperature, and thus their applications are inhibited when liquids, for example, ferrofluids and electrolytes, are required. Only recently, some liquid inorganic–organic nanocomposites have been investigated as a new type of electrolyte.^{3–5} These nanocomposites are composed of transition-metal oxide nanoparticles or nanoclusters and organic ionic liquids (but not polymers) which coordinate with the metal atoms through metal–oxygen coordination bonds. Because of such special structures, the all of the composites are liquids at room temperature with high viscosity and zero vapor pressure. Their physical properties can be easily tailored by adjusting the ligand compositions, that is, they are ionic conductors when the ligands are liquid salts⁴ and they are protonic conductors when heteropolyacids are grafted onto the ligands.⁵ However, the ionic conductivities of these nanocomposites are usually below 10^{–6} S/cm at room temperature⁴ because the dissociation degrees of the liquid salts are low and the ion-modified nanoparticles have too large of a volume to move as carriers. This drawback negatively hinders the applications of such liquid inorganic–organic nanocomposites as electrolytes at room temperature.

Furthermore, the conventional preparation method for this type of nanocomposite is treating the pre-existing nanoparticles with liquid ligands⁶ so that plenty of uncoordinated sites will remain on nanoparticle surfaces, and the resulting particles are apt to aggregate, which weakens their physical properties and stabilities.

To prepare inorganic–organic nanocomposites with practical ionic conductivities, in our previous work,^{7–10} we modified poly(ethylene glycol) methyl ether (designated PEGME) onto SnO₂ and ZnO nanoparticles through chemical reactions. These nanocomposites were waxes or gels at room temperature because the liquid ligands (only 20–40 wt %) did not dominate the entire composition. These waxes or gels could dissolve lithium salts to form a series of solid electrolytes with ionic conductivities of about 10^{–5} S/cm at room temperature. Unfortunately, the resulting gel electrolytes could not be solely used as the practical electrolytes at room temperature or at moderate temperature (about 60 °C), because their conductivities were not sufficient in comparison with conventional liquid electrolytes at room temperature and their mechanical properties were poor in comparison with those typical solid polymer electrolytes at moderate temperature. Hence, these polyether-grafted nanoparticles were normally used as the dopants in the poly(ethylene oxide) (PEO)-based solid polymer electrolytes to enhance their ionic conductivities.^{7,10} To broaden their application as electrolytes, it is necessary to transform these nanocomposites into liquids with improved conductivity or solids with enhanced mechanical strength. As far as we know, liquid polymer

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nanocomposites, especially when used as electrolytes, have not been reported yet.

In this research, we improve the synthetic techniques so as to load more PEGME molecules onto SnO₂ nanoparticle surfaces successfully. Moreover, we design a new route, synthesizing TiO₂ nanoparticles with high crystallinity directly in the PEGME medium at 200 °C, to modify more than 80 wt % PEGME onto TiO₂ nanoparticles. The as-prepared PEGME–SnO₂ and PEGME–TiO₂ nanocomposites are transparent viscous liquids which can dissolve many salts to form electrolytes. After appropriate amounts of LiClO₄ are dissolved in them, the obtained liquids exhibit ionic conductivities above 10⁻⁴ S/cm at room temperature with almost zero vapor pressure.

Experimental Section

The preparation method for PEGME–SnO₂ nanoparticles is improved on the basis of our previous work.⁷ The fresh SnO₂ nanoparticles, obtained by hydrolyzing a 0.5 M SnCl₄ aqueous solution in a poly(tetrafluoroethylene) (PTFE)-lined autoclave at 160 °C for 2 h, were centrifuged, and then the white precipitates were dispersed supersonically in liquid PEGME (Aldrich, MW = 350 g mol⁻¹). The obtained sols were precipitated and washed by absolute ethanol as a nonsolvent¹¹ and then re-dispersed in PEGME to form a transparent colloid. The colloid was heated at 100 °C for 30 min to remove ethanol thoroughly and then heated in an autoclave at 180 °C for 1 h. The PEGME–SnO₂ nanoparticles were also precipitated from the so-treated colloid by adding excess ethanol and washing with absolute ethanol, and then they were dissolved in acetonitrile to form a transparent colorless colloid. Such a liquid colloid was stable for months at room temperature. Moreover, the PEGME–SnO₂ nanoparticles can be precipitated from their concentrated acetonitrile solution by adding excess absolute ethanol, centrifuging, and then dissolving in acetonitrile again. Such a “precipitation–redispersion” procedure can be conducted repeatedly, and thus the product can be purified in this way.

To prepare PEGME–TiO₂ nanocomposites, 10 mL of tetrabutyl titanate was added into 40 mL of PEGME dropwise under strong sonication. A titanium horn was immersed into the resulting transparent colloid for further sonication at 100 W/cm² for 90 min. Then the colloid was sealed in a PTFE-lined autoclave under the protection of argon and heated at 200 °C for 24 h. After cooling to room temperature, the PEGME–TiO₂ nanoparticles were also precipitated, washed by absolute ethanol, and then dissolved in acetonitrile to be a transparent yellow solution. This solution could also be dealt with using the “precipitation–redispersion” procedure.

The diluted acetonitrile solutions of PEGME–SnO₂ and PEGME–TiO₂ were dropped on copper meshes respectively and dried for taking high-resolution transmission electron microscope (HRTEM) images and electronic diffraction (ED) patterns on a JEOL JEM-2010 transmission electron microscope operated at 200 kV. Both solutions were dropped on KBr pellets and dried under vacuum at 100 °C to prepare samples for infrared measurements on a Nicolet Impact 360 FTIR spectrometer. To avoid the water influence from air, these KBr pellets were put in a small cell with CaF₂ windows for further treatment under 0.01 Pa at 100 °C for 10 h. Then the IR spectra within the wavenumber range 4000–1000 cm⁻¹ were recorded in situ under vacuum. The purified PEGME–SnO₂ and PEGME–TiO₂ liquids were analyzed by a thermogravimetric technique on a Perkin-Elmer TGA 7 thermal analyzer in air with the

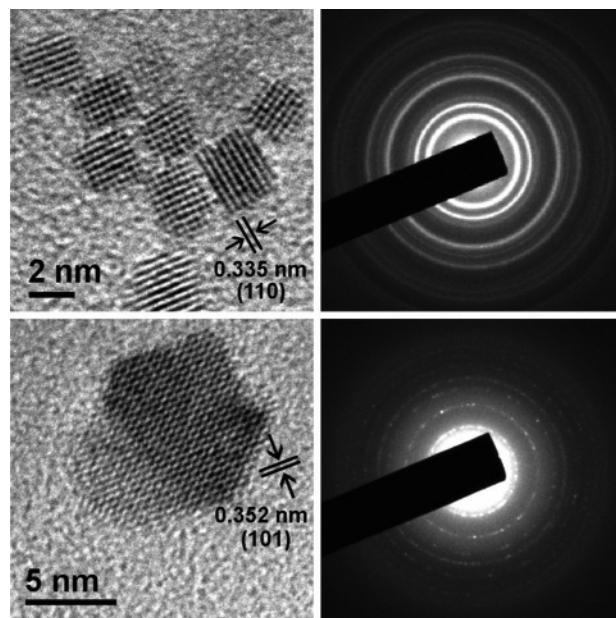


Figure 1. HRTEM images and ED patterns for PEGME–SnO₂ (upper) and PEGME–TiO₂ (lower) nanocomposites.

heating rate 10 °C/min. Appropriate amounts of LiClO₄ were dissolved into PEGME–SnO₂ and PEGME–TiO₂ liquids, which were dried in a vacuum oven at 100 °C for 10 h and then put into a small cell (1 cm in diameter, 2 cm in height) with two stainless steel electrodes for alternating current impedance measurements, using a Solartron Instrument model 1287 electrochemical interface and a 1255B frequency response analyzer controlled by a computer. The frequency limits were typically set between 10⁶ and 1 Hz, and the data were analyzed by the Zplot software. A Brookfield DV-III ultra-programmable rheometer was used to measure the viscosities of the PEGME–LiClO₄, PEGME–SnO₂–LiClO₄, and PEGME–TiO₂–LiClO₄ electrolytes at room temperature when the LiClO₄ content varied from 0 to 20 wt %. For comparison, the LiClO₄ contents of different electrolyte samples for conductivity and viscosity measurements were set at 0, 1, 2, 5, 10, 15, and 20 wt %, respectively.

Results and Discussion

Figure 1 shows the HRTEM images and ED patterns of PEGME–SnO₂ and PEGME–TiO₂ nanoparticles. The PEGME–SnO₂ nanoparticles are monodispersed cubic single crystals with average diameter of 2.2 nm. Their ED data and crystal lattice distances prove that these PEGME–SnO₂ nanoparticles have cassiterite structure. The PEGME–TiO₂ nanoparticles are monodispersed polyhedral single crystals with average diameter of about 8 nm. Their ED patterns and crystal lattice distances prove that these PEGME–TiO₂ nanoparticles have anatase structure. These results indicate that our methods are able to produce small nanoparticles with high crystallinity. It should be mentioned that the traditional routes to synthesize TiO₂ nanocrystals through calcination,¹² milling,¹³ or hydrothermal reaction¹⁴ usually produce large agglomerates, and these TiO₂ aggregates cannot be dispersed into

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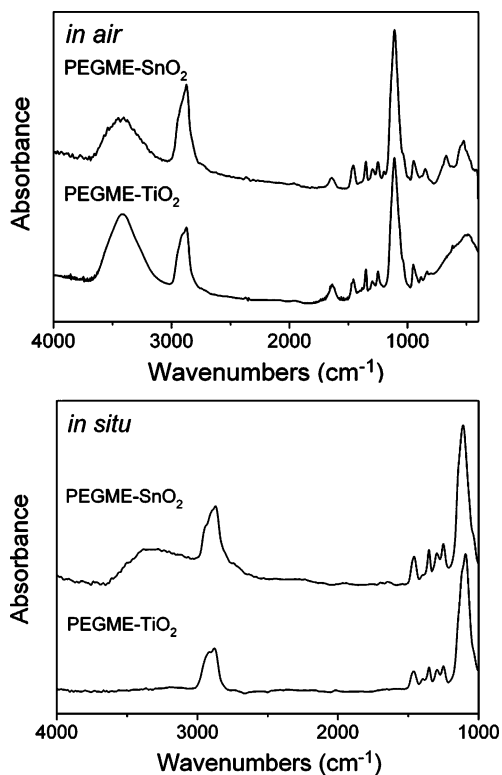


Figure 2. IR spectra recorded in air and in situ (after removing water thoroughly) for PEGME-SnO₂ and PEGME-TiO₂ nanocomposites.

organic solvents to form stable colloids. Our method excludes water influence and produces TiO₂ nanocrystals directly in the polymer medium so that the nanoparticles are prevented from aggregation by the polymers. Furthermore, the solvothermal treatment renders the nanoparticles highly crystalline only at 200 °C so as to avoid TiO₂ aggregation effectively. To our knowledge, this is the first report of liquid polymer nanocomposites for SnO₂ and TiO₂, which further inspires the prospective applications of SnO₂ and TiO₂ nanocrystals.

In Figure 2, the IR spectra of pure PEGME-SnO₂ and PEGME-TiO₂ nanocomposites are shown. Because the samples are apt to absorb water from air, the measurements were carried out in air and in situ (using CaF₂ windows after evacuation), respectively. In the air, the IR spectra exhibit strong OH group vibrations at 3420 cm⁻¹ and 1640 cm⁻¹. These IR absorptions are not ascribed to the residual PEGME molecules because the unreacted PEGME molecules have been removed by washing the product with absolute ethanol. Meanwhile, the absorption bands at 2875, 1460, 1350, 1295, 1250, and 950 cm⁻¹ are typical vibrations of C-H bonds, and the strong absorption at 1110 cm⁻¹ is typical for C-O-C stretching in polyether.⁷ Therefore, PEGME groups have been modified on the nanoparticles undoubtedly. In addition, the vibrations at 530 and 675 cm⁻¹ for PEGME-SnO₂ are ascribed to the Sn-O-Sn symmetric stretching inside SnO₂ nanoparticles and the Sn-O antisymmetric stretching on SnO₂ surfaces, respectively,¹⁵ while the broad IR band near 495 cm⁻¹ might be ascribed to Ti-O vibrations. The IR absorptions for Sn-O vibrations appear much weaker relatively than those in our previous paper⁷ because more PEGME molecules have been coated on SnO₂ nanoparticles in the present work. After evacuation at 100 °C, the in situ IR spectra for PEGME-SnO₂ and PEGME-TiO₂ nanocom-

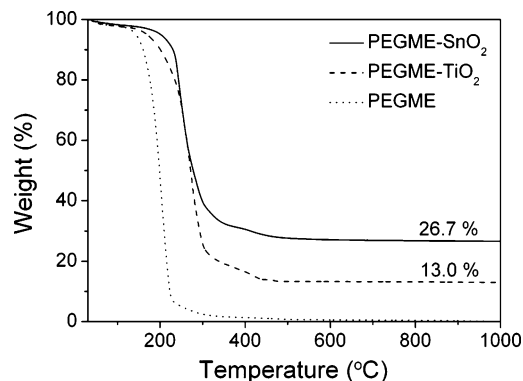
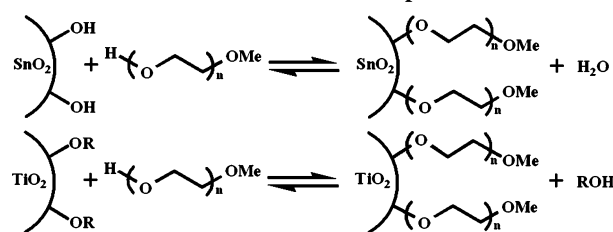


Figure 3. Thermogravimetric data for PEGME-SnO₂ and PEGME-TiO₂ nanocomposites, in comparison with the PEGME raw material.

Scheme 1. Exchange Reaction Mechanisms for the Solvothermal Preparations of PEGME-SnO₂ and PEGME-TiO₂ Nanocomposites^a



^a Here, "R" is a butyl group.

posites are different. PEGME-SnO₂ still has strong OH absorption at about 3300 cm⁻¹, indicating that there remain plenty of OH groups on the SnO₂ surface. Comparatively, there are no OH absorption bands in the IR spectra for PEGME-TiO₂ because this nanocomposite is synthesized under anhydrous conditions. This result further proves that there are no free PEGME molecules in the purified PEGME-SnO₂ and PEGME-TiO₂ liquids. Hence, the ionic conductivity for PEGME-SnO₂ and PEGME-TiO₂ liquids after they dissolve lithium salts cannot be ascribed to the residual organic solvents or water.

Thermogravimetric analyses were used to determine the compositions of the nanocomposites, and the results are shown in Figure 3. The PEGME vaporizes or decomposes at about 200 °C while both nanocomposites decompose at around 300 °C, indicating that the composites have better thermal stability than PEGME. It is obvious that the PEGME content reaches 70 wt % in the present PEGME-SnO₂ nanocomposites, which is much higher than that (about 20 wt %) for our previous PEGME-SnO₂ samples.⁷ Hence, more PEGME loading on SnO₂ nanoparticles makes the whole composites change from solid to liquid. Such change results from the additional solvothermal treatment on PEGME-SnO₂ nanoparticles in the PEGME medium which makes PEGME exchange more OH groups on the SnO₂ surface. We have proved this exchange reaction mechanism for PEGME-SnO₂ nanocomposites in our previous report,⁷ so it can be inferred that TiO₂ nanoclusters also undergo similar exchange reactions as shown in Scheme 1. Interestingly, the SnO₂ nanocrystals are smaller than TiO₂ nanoc-

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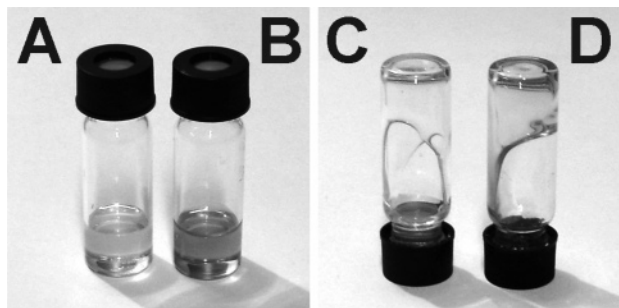


Figure 4. Photos for (A and C) PEGME-SnO₂ and (B and D) PEGME-TiO₂ liquids.

crystals, that is, SnO₂ species have larger surface areas and more coordination sites for ligands, but the PEGME content in the PEGME-TiO₂ nanocomposite is more than that in the PEGME-SnO₂ species, even above 80 wt %. This result can be explained by the difference between the synthetic methods for the two nanocomposites. As illustrated by the IR spectra in Figure 2, there remain many OH groups on the SnO₂ surface after exchange reactions. Therefore, the way to prepare the PEGME-TiO₂ nanocomposite that is more effective is to load polyether groups onto the nanoparticle surface, which involves direct reactions in the PEGME medium, solvothermal treatment for a long time, and wholly anhydrous conditions.

The compositions and structures of the nanocomposites determine their physical states. Both PEGME-SnO₂ and PEGME-TiO₂ are much more viscous than the PEGME liquid. In Figure 4, when the bottles are upside down for a few seconds, the liquids in the bottles flow down slowly. Although the PEGME-TiO₂ has more PEGME content than its counterpart, it is even more viscous. This situation can be ascribed to the larger size of TiO₂ nanocrystals, because PEGME-TiO₂, like a “super molecule”, moves more difficultly than PEGME-SnO₂. It is well-known that many nanocrystals protected by organic ligands cannot be re-dispersed into solvents when they are dried from colloid forms, because their aggregation processes during evaporation are irreversible. But our nanocomposites are able to dissolve in organic solvents spontaneously to form stable colloids, and they can be obtained again by drying the colloids. Such “dissolve-dry” processes can be operated repeatedly with the original compositions of the solutes remaining. Hence, our nanocomposites are more stable than many ligand-protected nanoparticles, which is due to covalent bonds between nanoparticles and PEGME groups. As a matter of fact, pure PEGME liquid can be distilled under about 1 Pa at 100 °C, but the PEGME-SnO₂ and PEGME-TiO₂ have almost zero vapor pressure. When the purified PEGME-SnO₂ and PEGME-TiO₂ nanocomposites are heated under even 0.01 Pa at 100 °C, no distillate is observed, which confirms that there are no residual PEGME molecules in the composites after ethanol washing and purification.

Like those amorphous polymer electrolytes based on PEO,^{16–19} that is, cations that move through the electrolytes assisted by PEO chain motion, our nanocomposites exhibit

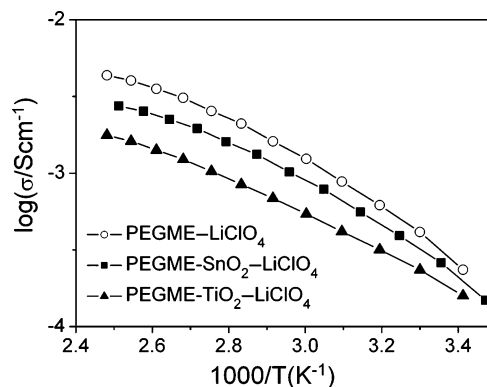


Figure 5. Ionic conductivities for PEGME-LiClO₄, PEGME-SnO₂-LiClO₄, and PEGME-TiO₂-LiClO₄ electrolytes during a heating scan. The LiClO₄ content in each sample is 10 wt %.

ionic conductivity when metal salts are dissolved by the PEGME surface groups. In Figure 5, the conductivity curves for PEGME-LiClO₄, PEGME-SnO₂-LiClO₄, and PEGME-TiO₂-LiClO₄ during heating scan are compared. These curves obey the Vogel-Tamman-Fulcher (VTF) model just like the classical liquid electrolytes composed of organic solvents and metal salts.²⁰ However, in the classical liquid electrolytes, ions move along with small solvent molecules while in the present composite electrolyte, ions transfer under the assistance of PEGME chain thermal motion. Moreover, the conductive mechanism for our composite electrolytes is also different from that for ionic liquids in which the large molecules disassociate to be charge carriers. The conductivities of the PEGME-TiO₂-LiClO₄ samples are generally lower than those for PEGME-SnO₂-LiClO₄ electrolytes under the same LiClO₄ concentration probably because the former is more viscous so that the segmental motions of the PEGME chains are more difficult. It is found that the higher viscosity the electrolyte has, the more difficult the PEGME segment motion is, resulting in the lower conductivity.

To study the relationships among conductivity, viscosity, and concentration of the electrolyte samples, different amounts of LiClO₄ were dissolved in the PEGME, PEGME-SnO₂ and PEGME-TiO₂ liquids, and then the conductivities and viscosities of the obtained electrolytes were measured. It is clear in Figure 6A that conductivities for all three samples increase as the lithium salt concentration increases within the range 0–10 wt % and decrease when more LiClO₄ is dissolved into the electrolytes. Because the ionic conductivity depends on the free ion (carrier) concentration in the sample, while the carrier concentrations are determined by the salt concentration and salt disassociation degree in the meantime, it can be inferred that LiClO₄ disassociation degrees in these electrolytes are poor when the LiClO₄ concentration reaches 20 wt %. Hence, the optimal LiClO₄ concentrations for all three electrolytes are near 10 wt % with regard to their conductivities. At this concentration, our composite electrolytes exhibit conductivity above 10⁻⁴ S/cm at ambient temperature, indicating their potential applications

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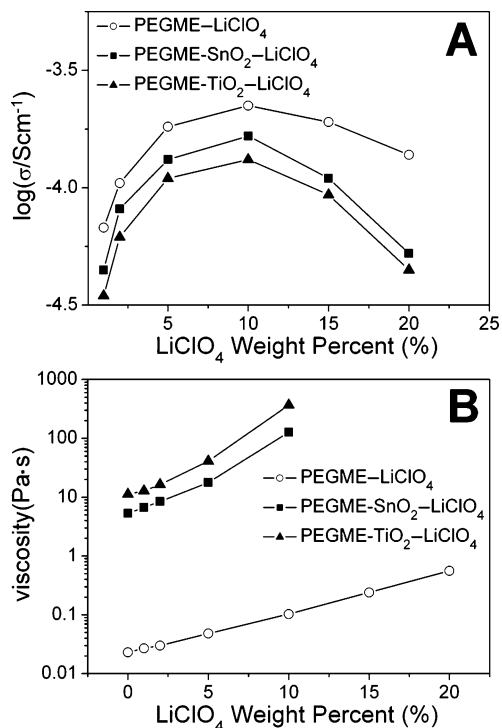


Figure 6. Ionic conductivities (A) and viscosities (B) for PEGME-LiClO₄, PEGME-SnO₂-LiClO₄, and PEGME-TiO₂-LiClO₄ electrolytes at 28 °C.

in practical devices such as lithium batteries and supercapacitors. It is interesting that although our composite electrolytes are much more viscous than the prototypical PEGME-LiClO₄ species, their conductivities are only slightly lower than those of the latter. In Figure 6B, viscosities of these samples are compared at different LiClO₄ concentrations. The viscosity of the PEGME-LiClO₄ electrolyte increases linearly when the LiClO₄ concentration increases, but the viscosities of our composite electrolytes increase much faster at the same time. Furthermore, the viscosities of both composite electrolytes exceed the measurement range of the rheometer when the LiClO₄ concentra-

tion is up to 20 wt %. This phenomenon is ascribed to the ion-nanoparticle interactions which finally cross-link all of the electrolytes into gel-like samples. Such interactions are probably Lewis acid-base interactions because SnO₂ and TiO₂ nanoparticles are Lewis acids while ClO₄⁻ ions are Lewis bases. Such interactions could help to release more free lithium ions so that our composite electrolytes exhibit considerable conductivities in comparison with the PEGME-LiClO₄.

Conclusion

A great number of polyether groups have been successfully modified onto SnO₂ and TiO₂ nanocrystals through sol-gel routes and solvothermal treatments. The as-prepared nanocomposites are transparent viscous liquids which can dissolve lithium salts so as to exhibit good ionic conductivities for practical uses at room temperature. Such composite electrolytes overcome some drawbacks of the classical solvent-based electrolytes and the ionic liquids: In comparison with the traditional liquid electrolytes, the present electrolytes have better thermal stability and almost zero vapor pressure. Compared with ionic liquids, the composition and conductivity of our electrolytes are easy to control just by changing the salts and their concentration, and our electrolytes can be easily purified by the nonsolvent method while the purification for ionic liquids remains a crux. Moreover, our electrolytes exhibit much higher conductivity and stability than the prototypical PEO-based solid polymer electrolytes, although their conductive mechanisms are similar. Therefore, our present work opens an attractive vista in the field of electrolytes, as well as in the synthetic techniques for metal oxide nanoparticles.

Acknowledgment. This work was supported by National Natural Science Foundation of China (Grant 20503007) and Shanghai Natural Science Foundation (Grant 05ZR14016).

CM060432U