Conducting Materials

An Organic–Inorganic Hybrid Electrolyte Derived from Self-Assembly of a Poly(Ethylene Oxide)–Poly(Propylene Oxide)–Poly(Ethylene Oxide) Triblock Copolymer**

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Intensive studies have focused on the development of new types of solid polymer electrolytes (SPEs) which combine high mechanical strength with high ionic conductivity, as needed for applications in, for example, solid-state lithium polymer batteries.[1,2] While poly(ethylene oxide) (PEO), chains act as solvents for lithium salts, practical use of PEO-based electrolytes is often hindered by their low conductivity at room temperature (ca. 10^{-7}–10^{-8} $\mathrm{S\,cm^{-1}}$) and poor mechanical properties. Moreover, PEO-based electrolytes are prone to crystallization. To alleviate these drawbacks of polyether-based electrolytes, considerable effort is being devoted to synthesizing new organic–inorganic hybrid materials by sol–gel routes, which usually involve hydrolysis and condensation of alkoxysilanes. A variety of organic–inorganic hybrids with covalent bonds or only weak physical bonds between the inorganic and organic phases have been proposed.[3–7] These solid polymer electrolytes, so-called ormolytes (organically modified electrolytes), combine the solvating power of the ether units with an inorganic network, which provides simultaneously an amorphous structure and good thermal, mechanical, and chemical stability. However, miscibility between the organic and inorganic entities is a major concern, but this can be overcome by the use of functionalized alkoxysilanes.

Block copolymers can be regarded as macromolecular analogues of low-molecular-weight surfactants, and they can self-assemble under certain conditions to give a variety of nanoscale morphologies.[8] In particular, PEO-PPO-PEO triblock copolymers (PPO = poly(propylene oxide)) consisting of two dissimilar moieties, that is, hydrophilic EO blocks and hydrophobic PO blocks, were recently used as structure-directing agents to prepare ordered mesoporous silica by self-assembly in acidic medium.[9] Herein we report the design and synthesis of a new organic–inorganic hybrid electrolyte derived from the self-assembly of a PEO-PPO-PEO triblock copolymer by co-condensation of (3-glydicyloxypropyl)trimethoxysilane (GLYMO) and tetraethoxysilane (TEOS). We

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used commercially available Pluronic F127 triblock copolymer ($EO_{106}PO_{70}EO_{106}$, $M_w = 12600$, BASF) both as the structure-directing amphiphilic surfactant and as the polymer matrix. Since the EO and PO units of F127 are relatively short, the mechanical properties of F127-based solid polymer electrolyte are a major concern for its practical applications. These properties can be greatly improved if the silica domain is incorporated within the polymer matrix. The F127 triblock copolymer was recently used for the self-assembly of ordered cubic mesoporous silica SBA-16 in acidic medium.[9] We therefore expected that F127 triblock copolymer would self-assemble on a functionalized silica network to generate a nanocomposite film. Moreover, the epoxide functionality of GLYMO can provide a cross-linking center for blending the triblock copolymer and thus improving the compatibility between organic and inorganic phases.

Figure 1 a shows the powder X-ray diffraction (XRD) patterns of the hybrids with various [O]/[Li] ratios. The appearance of peaks at $2\theta = 0.5°$ indicates that the hybrids exhibit mesoscopically ordered structures. The degree of ordering depends on the lithium content. The much sharper and more intense peak for the hybrid with [O]/[Li] = 16 indicates a higher degree of order than in the other two samples. The small-angle X-ray scattering (SAXS) profile of this hybrid (Figure 1 b) exhibits more and sharper peaks and thus also indicates superior ordering in this sample. For [O]/[Li] = 16, five scattering peaks with a spacing ratio of $1:\sqrt{3}:2:\sqrt{7}:3$ are observed. This spacing sequence is indicative of a hexagonal array of cylinders, with a cylinder spacing of 180 Å.[10a] The TEM images in Figure 2 also show a well-organized hexagonal mesophase with cylindrical assemblies in the hybrid with [O]/[Li] = 16. Unlike mesoporous silica materials, N_2 adsorption–desorption isotherms (Supporting Information) show that no significant adsorption is observed for the sample after calcination at 560 °C for 8 h, because the mesostructure collapses on removal of the copolymer. This effect is due to the relatively low inorganic fraction (silica) in these materials. Above its critical micellar concentration, F127 forms micelles in water, in which a hydrophobic core consisting of the PPO blocks is surrounded by an outer shell, or corona, of hydrated PEO blocks.[10b] Consequently, the silica species adopt the mesoscopic organization imposed by the block copolymer and are preferentially partitioned into the hydrophilic regions of the sample, where they form a rigid cross-linked network. A schematic representation of the mesophase formed by self-assembly of F127 is shown in Scheme 1.

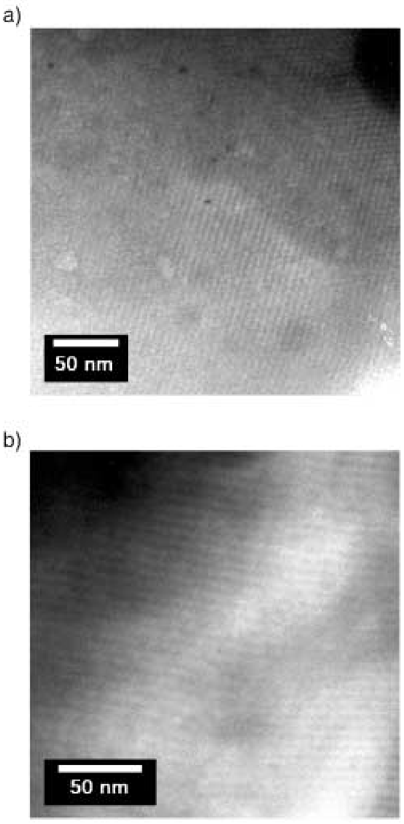


Figure 2. TEM images of the hybrid material with [O]/[Li] = 16 revealing a well-ordered hexagonal array of cylinders, viewed a) from above and b) from the side.

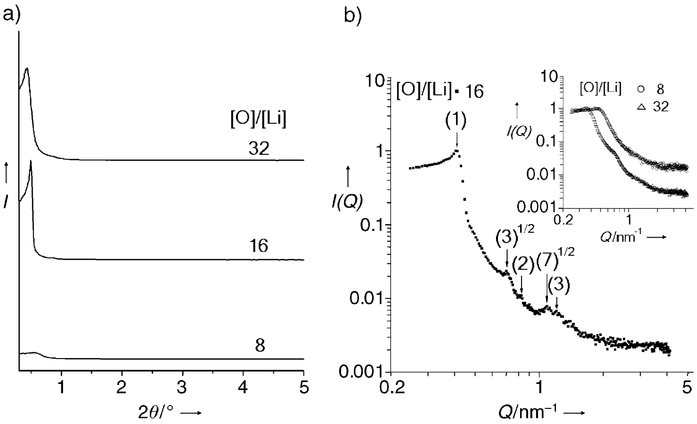
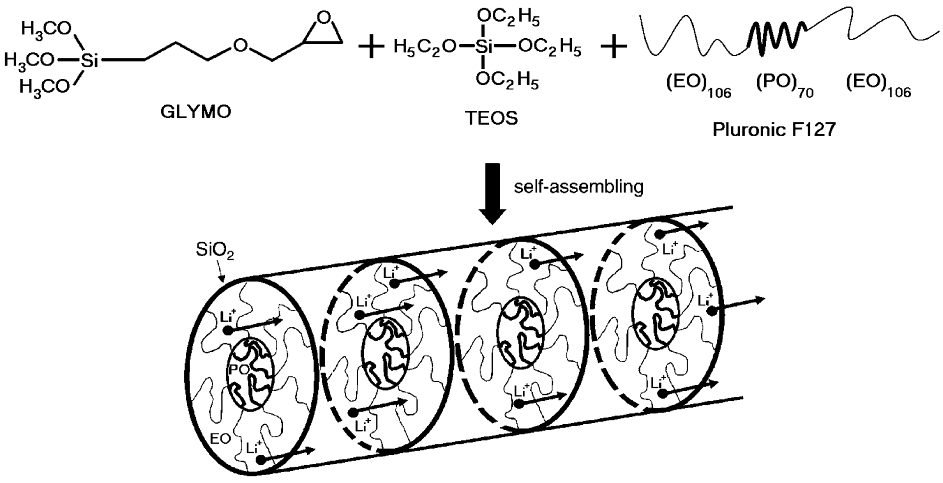


Figure 1. a) XRD and b) SAXS profiles of hybrids with various [O]/[Li] ratios. The scattering wave vector Q is given in terms of $Q = (4\pi/\lambda)\sin\theta$, where 2θ is the scattering angle and λ is the X-ray wavelength.

The glass transition temperature T_g and melting temperature T_m of the hybrid samples were measured by differential scanning calorimetry (DSC; Table 1). The T_g of pure F127 copolymer is about −64 °C. The T_g value increases (becomes less negative) with increasing lithium content, and this suggests that the presence of lithium salts leads to the formation of transient cross-links between ether oxygen atoms and lithium cations. This cross-linking decreases segmental motion of the polymer chains and thus increases T_g. Except for the hybrid with [O]/[Li] = 32, no clear melting transitions were observable, that is, F127 crystallization is successfully suppressed by high levels of salt doping. Thermogravimetric analysis shows that the present hybrid electrolytes are thermally stable up to at least 200 °C.

Figure 3 shows the ionic conductivity σ as a function of temperature for hybrids with various [O]/[Li] ratios. The hybrid with [O]/[Li] = 16 has well-ordered mesophases and exhibits the highest ionic conductivity,



Scheme 1. Schematic illustration of the formation of a mesophase by self-assembly of Pluronic F127 triblock copolymer. For the sake of clarity, only the copolymer molecules and lithium cations at the cross-section of the cylinder assemblies are depicted, and the dissociated anions are not shown. TEOS = tetraethoxysilane.

Table 1: DSC and ionic conductivity of hybrids with various [O]/[Li] ratios.

[O]/[Li]	T_g [°C]	T_m [°C]	Conductivity [S cm^{-1}] at 30 °C	Conductivity [S cm^{-1}] at 80 °C
32	−44.1	45.7	1.20×10^{-6}	1.58×10^{-3}
16[a]	−38.2	–	3.17×10^{-5}	1.71×10^{-3}
8	−32.9	–	7.83×10^{-6}	7.24×10^{-4}

[a] The silica-free F127-based electrolyte at the same salt concentration exhibits a conductivity of only 2.30×10^{-7} S cm^{-1} at 30 °C.

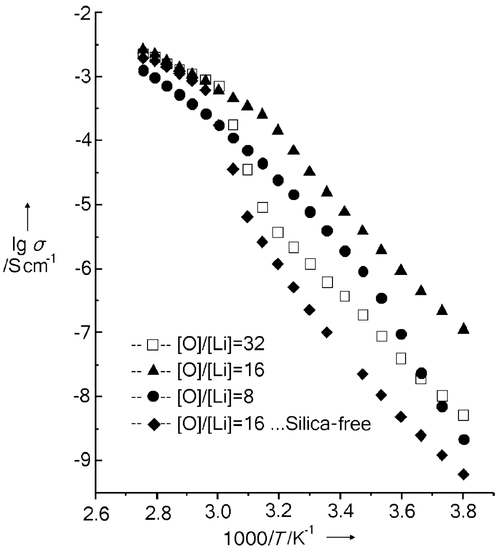


Figure 3. Temperature dependence of ionic conductivity of hybrids with various [O]/[Li] ratios. For comparison, the conductivity of silica-free F127-based electrolyte with [O]/[Li] = 16 is also shown.

especially in the temperature range from −10 to 45 °C. An optimal value of approximately 3×10^{-5} S cm^{-1} at 30 °C is obtained at [O]/[Li] = 16, which is comparable with the conductivity of PEO-based electrolytes containing nanoscale TiO_2 and Al_2O_3.[11] This conductivity is much better than those of composite polymer electrolytes containing other nanoscale ceramics, and it is at least two orders of magnitude higher than the conductivity of conventional PEO electrolytes. Interestingly, the conductivity of a silica-free F127-based electrolyte of the same [O]/[Li] ratio, which does not have a mesoscopically ordered structure, is only 2.30×10^{-7} S cm^{-1} at 30 °C. The conductivity of the silica-containing electrolytes increases with increasing temperature and reaches around 10^{-3} S cm^{-1}, the level needed for many practical applications, at about 80 °C. The hybrid electrolyte with [O]/[Li] = 8 shows Vogel–Tamman–Fulcher (VTF) behavior over the studied temperature range, that is, the ion mobility is coupled with the segmental motion of the polymer chain, while the other two hybrid electrolytes exhibit Arrhenius behavior between −10 and 40 °C. The hybrid with [O]/[Li] = 32 shows a conductivity jump at the temperature associated with its melting point and exhibits similar conductivity to the hybrid with [O]/[Li] = 16 at high temperatures. The hybrid with the largest amount of lithium salt (i.e., [O]/[Li] = 8), which has less ordered mesophases, exhibits the lowest ionic conductivity among the studied hybrid electrolytes.

Solid-state ^{29}Si and ^{13}C NMR spectroscopy measurements were performed in order to determine the structure of the inorganic and organic parts of the hybrid, respectively. Three major ^{29}Si NMR signals at $\delta = -58$, -67, and -110 ppm are observed, and can be assigned to silicon sites of T^2 ($R\mathit{Si}(OSi)_2OH$), T^3 ($R\mathit{Si}(OSi)_3$), and Q^4 ($\mathit{Si}(OSi)_4$) groups, respectively, where R represents an alkyl group belonging to GLYMO. The ^{13}C cross-polarization/magic-angle spinning (CP/MAS) spectrum shows six major resonances, assigned to −C−O− linkages ($\delta = 71, 74$, and 76 ppm), $-CH_2-$ groups ($\delta = 24$ ppm), $-CH_3$ ($\delta = 18$ ppm, PPO), and −C−Si− ($\delta = 10$ ppm, GLYMO). The relative intensities of T and Q and ^{13}C signals are all as expected on the basis of the synthesis. The absence of the ^{13}C peaks at $\delta = 44$ and 51 ppm for the epoxide ring of GLYMO is indicative of complete epoxide ring opening. Variable-temperature $^7Li\{^1H\}$ MAS NMR measurements were performed to probe the local environments of the Li^+

cations. At 213 K, the ^{7}Li resonance at $\delta = -0.9$ ppm (site I) with a shoulder at about $\delta = -0.4$ ppm (site II) indicates that two distinct ^{7}Li local environments exist in the hybrid (Figure 4). On raising the temperature of the sample to 233 K, which is close to T_g, these two sites merge together into a signal at $\delta = -0.6$ ppm. Site I with the higher intensity peak is assigned to lithium cations in the polyether domain, whereas the site II possibly corresponds to the lithium cations in the polymer/silica interface or silica-rich domain. Thus variable-temperature ^{7}Li{^{1}H} MAS NMR spectroscopy is able to resolve the different lithium local environments in the hybrid system.

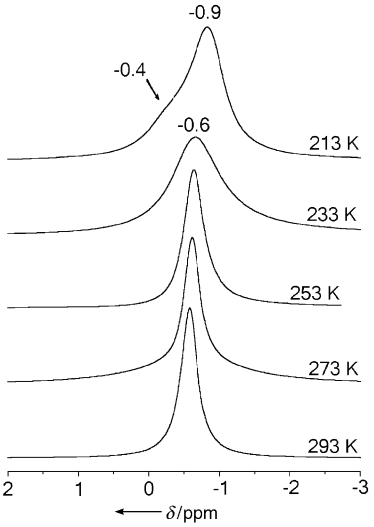


Figure 4. Variable-temperature ^{7}Li{^{1}H} MAS NMR spectra, acquired at a spinning speed of 3.4 kHz, of the hybrid with a [O]/[Li] ratio of 16.

Previous NMR spectroscopic investigations on similar hybrid materials showed that the hydrophilic PEO blocks are firmly anchored in the inorganic silica phase, which substantially restricts the molecular mobility, while the hydrophobic PPO blocks show a flexibility comparable to that observed for the bulk copolymer.[12] Therefore, the hybrid electrolyte is expected to exhibit low ionic conductivity, as the mobility of the lithium cations is associated with the segmental motion of the polymer chains. In contrast, the present hybrid electrolytes exhibit conductivity two orders-of-magnitude higher than that of silica-free F127-based polymer electrolyte. The resistive dynamics of polymer–salt electrolytes can be mediated by introducing nanoscale ceramics that function as solid plasticizers.[11] In the present system the surface interaction of the copolymer, cations, and anions with the nanoscale silica network is believed to play a key role in stabilizing the hybrid structure and facilitating motion of the Li^+ ions while retarding that of the anions. A possible explanation for the lower conductivity of the hybrid with [O]/[Li] = 8 relative to that with [O]/[Li] = 16 is increased ion-pair formation with increasing salt concentration. However, FTIR spectroscopy shows that the hybrids with [O]/[Li] = 16 and 8 exhibit similar degrees of salt dissociation. The conductivity data in combination with the structural characterization suggests that the drastically enhanced conductivity for the hybrid with [O]/[Li] = 16 is closely related to its well-ordered mesophase, which might improve the arrangement of Li^+-ion conducting pathways, as illustrated in Scheme 1. Both effects (i.e., surface interaction and formation of a well-ordered mesophase) are manifested as a substantial enhancement of the Li^+ ionic conductivity at room temperature. The ordered region of the mesophase and the amorphous region of the polyether moieties are possibly active simultaneously and work synergistically to yield favorable lithium-ion transport and thus contribute to the high ionic conductivity of the materials.

In summary, we have demonstrated that the complexation of Pluronic F127 triblock copolymer with $LiClO_4$ by a sol–gel route involving the co-condensation of alkoxysilanes can give rise to a well-ordered mesophase that is dependent on the salt concentration. The SAXS and TEM results confirm the formation of stabilized and well-ordered hexagonal mesophase by self-assembly of F127 and lithium salts, especially at a [O]/[Li] ratio of 16. The present self-organized nanocomposite network provides a novel architecture for ionically conductive materials with a combination of several advantageous properties, for example, simple preparation from commercially available components, substantial suppression of polymer crystallization, reasonably high ionic conductivity with copolymers of relatively low molecular weight, excellent mechanical strength, and potential for nanostructurablility. The present work can be extended to other similar triblock copolymers which are capable of self-assembling on a silica network, to make electrolytes with high ionic conductivity for use in the field of lithium-battery technology.

Experimental Section

The organic–inorganic hybrid electrolyte based on F127 was synthesized by a sol–gel route. In a typical synthesis (3-glydicyloxypropyl)-trimethoxysilane (1.5 g; GLYMO, Fluka) and tetraethoxysilane (0.3 g; TEOS) were mixed and hydrolyzed with 0.01 N HCl (30 mL) at room temperature for 5–6 h. A solution of F127 (5.0 g) in acetonitrile (30 mL) was mixed with $LiClO_4$ to give the desired [O]/[Li] ratio, and the mixture was stirred for 5–6 h. Then the two solutions were mixed and stirred at room temperature for 2 days. The resulting gels were dried at room temperature for 2 days and then heated at 95 °C under vacuum for 2–5 days to give a piece of transparent and crack-free material. Samples prepared with other ratios of GLYMO/TEOS tended to be structurally unstable after drying. They exhibited nonuniform shrinkage or had a constantly wet surface. The salt concentrations were expressed as the ratio of the total concentration of EO and PO ether oxygen atoms to the lithium-ion concentration (i.e., [O]/[Li] ratio).

Powder XRD and SAXS data were collected on BL17A Wiggler-A beamline ($\lambda = 0.1326$ nm) at National Synchrotron Radiation Research Center of Taiwan. TEM images were taken with a Hitachi H-7100 instrument operated at 75 keV. The samples were embedded in Spur resin and cured at 60 °C overnight. Ultrathin sections (ca. 60–90 nm) were cut from the embedded specimen with a diamond knife. DSC studies were performed in the range of −60 to 125 °C by using a Mettler Toledo DSC system at a heating rate of 5 °C min^{-1}. Alternating-current impedance measurements on the polymer electrolytes were performed with a CH Instrument Model 604A Electrochemical Analyzer over a frequency range of 10 Hz to 100 kHz with an amplitude of 10 mV. All solid-state NMR experiments were performed on a Bruker AVANCE-400 spectrometer, equipped with a

Bruker double-tuned 7 mm probe. The Larmor frequencies for ^{7}Li, ^{13}C, and ^{29}Si nuclei were 155.45, 100.58, and 79.46 MHz, respectively. A repetition time of 5 s was used for ^{13}C CP/MAS NMR experiments. A pulse length of 2 μs (π/6 pulse) and a repetition time of 50 s were used to obtain ^{29}Si MAS NMR spectra. Both ^{13}C and ^{29}Si chemical shifts were referenced to external TMS at 0 ppm. To remove the heteronuclear ^{7}Li–^{1}H dipolar interactions from the ^{7}Li resonance, high-power proton decoupling (^{7}Li{^{1}H} NMR) was used. ^{7}Li chemical shifts were referenced to external 1 M aqueous LiCl at 0 ppm.

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