

Organic-Inorganic Nanocomposite Electrolyte Derived from Triblock Copolymers

Considerable efforts have been devoted to the development of new types of solid polymer electrolytes (SPEs), which possess both high mechanical strength and high ionic conductivity needed for applications in, for example, solid-state lithium polymer batteries. Although poly(ethylene oxide) (PEO) chains can act as solvents for lithium salts, the practical use for PEO-based electrolytes is often hindered due to the low conductivity at room temperature and the poor mechanical properties. Moreover, PEO-based electrolytes are prone to crystallization. For improving the performance of polyether-based electrolytes, new organic-inorganic nanocomposite materials produced by a sol-gel route have received much attention in recent years. Integrating the solvating power of ether units into inorganic networks, a variety of solid polymer electrolytes based on organic-inorganic hybrids, so-called ormolytes (organically modified electrolytes), provide amorphous structures with good thermal, mechanical, and chemical stability. However, the miscibility between organic and inorganic entities becomes a major concern, which, nevertheless, can be overcome by the use of functionalized alkoxysilanes

Block copolymers can be regarded as macromolecular analogs of low weight surfactants, and can self-assemble into a variety of nano-scale morphologies under certain conditions. In particular, poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) triblock copolymer, consisting of two dissimilar moieties, i.e., hydrophilic EO block and hydrophobic PO block, has been recently used as a structure-directing agent to make ordered mesoporous silica through self-assembling in acidic media. In this work, we present a new organic-inorganic nanocomposite electrolyte derived from the self-assembly of PEO-PPO-PEO triblock copolymer via co-condensation of (3-glycidyloxypropyl) trimeth-oxysilane (GLYMO) and tetraethoxysilane (TEOS). This study focuses on the use of commercially available Pluronic F127 and P123 triblock copolymers ($\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$ and $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, $M_w = 12600$ and 5800 , respectively, BASF) as the structural-directing amphiphilic surfactants and as the polymer matrices as well. Since the ethylene oxide and propylene oxide units of these polymers are relatively short, the mechanical property of the resulting solid polymer electrolytes is a main concern for their practical applications. Nevertheless, the mechanical strength can be largely improved if silica domains are incorporated into the polymer matrices. It is anticipated that these triblock copolymers can self-assemble into functionalized silica networks for nanocomposite films. Moreover, the functionality, epoxide ring, adopted in the GLYMO can provide a cross-linking center to blend the triblock copolymer, and thus improve the compatibility between organic and inorganic phases.

Figure 1 shows the XRD patterns of the F127- and P123-based nanocomposite electrolytes with various $[\text{O}]/[\text{Li}]$ ratios. The appearance of peaks at $2\theta = 0.5^\circ$ indicates that the F127-based nanocomposites exhibit ordered mesoscopic structures, especially at $[\text{O}]/[\text{Li}] = 16$. The degree of ordering depends on the lithium content. However, the structural ordering of P123-based nanocomposites is not as good as that of F127-based systems. For comparison, small-angle X-ray scattering (SAXS) analysis is attempted on these materials as an alternative method of investigation. The SAXS profile of the F127-based hybrid with $[\text{O}]/[\text{Li}] = 16$ (Fig. 2a), exhibiting more and sharper peaks, indicates a particularly better ordering than the other two samples. For the case of the F127-based material at $[\text{O}]/[\text{Li}] = 16$, five scattering peaks with

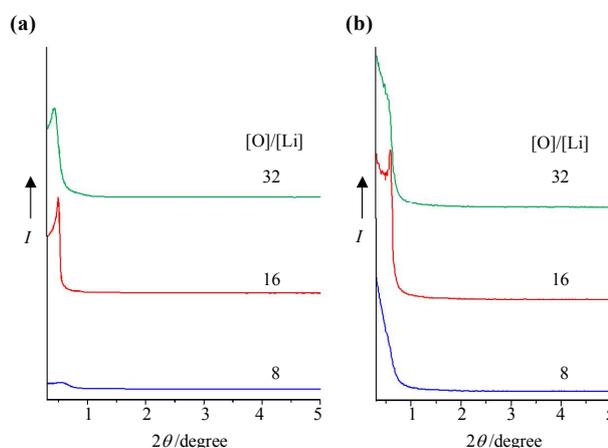


Fig. 1: XRD patterns of (a) F127- and (b) P123-based nanocomposite electrolytes with various $[\text{O}]/[\text{Li}]$ ratios.

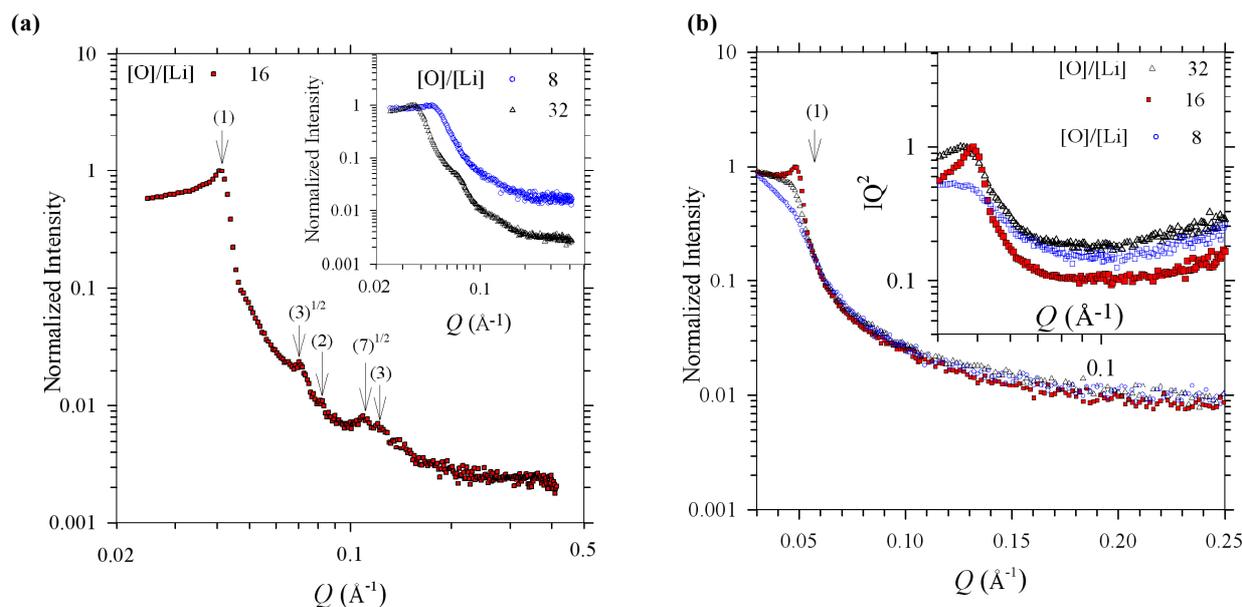


Fig. 2: SAXS profiles of (a) F127- and (b) P123-based nanocomposite electrolytes with various $[O]/[Li]$ ratios. The scattering wave vector Q is given in terms of $Q = (4\pi/\lambda) \sin(\theta)$, where 2θ is the scattering angle and λ is the X-ray wavelength.

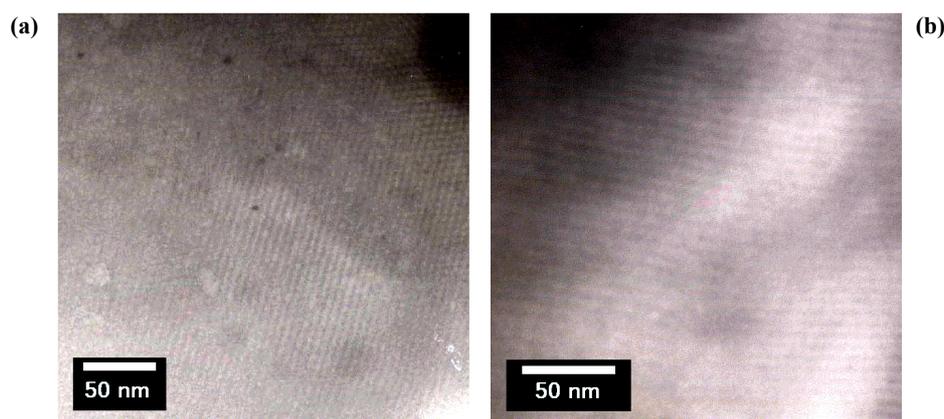


Fig. 3: TEM micrographs of the F127-based nanocomposite electrolyte with $[O]/[Li] = 16$ revealing a well-ordered hexagonal arrays of cylinders viewed (a) from the top and (b) from the side.

a Q -spacing ratio of $1:\sqrt{3}:2:\sqrt{7}:3$ are observed, where Q is the vector transfer of the scattered photons. This Q -spacing sequence is indicative of a hexagonal array of cylinders, with a cylinder spacing of 180 Å. Again, the SAXS results of P123-based nanocomposites did not show any structural ordering, as displayed in Fig. 2b.

The TEM micrographs in Fig. 3 also show a well-organized hexagonal mesophase with cylindrical assemblies in the F127-based nanocomposite material with $[O]/[Li] = 16$. Above critical micellar concentration, F127 is known to form micelles in water, which possess a hydrophobic PPO core-shelled by hydrated PEO corona. The silica species

can adapt the mesoscopic morphology of the block copolymer matrix, and deposit preferentially into the hydrophilic regions of PEO corona, which leads to a rigid cross-linked network. The schematic representation of the composite, of a hexagonal mesophase, formed by the self-assembly of F127 is shown in Fig. 4.

The glass transition temperature (T_g) of pure F127 copolymer is around -64°C . The T_g value of nanocomposites increases with increasing lithium contents to the range of -33 to -44°C , suggesting that the presence of lithium salts induces the formation of transient crosslinking between ether oxygens and lithium cations. This effect decreases

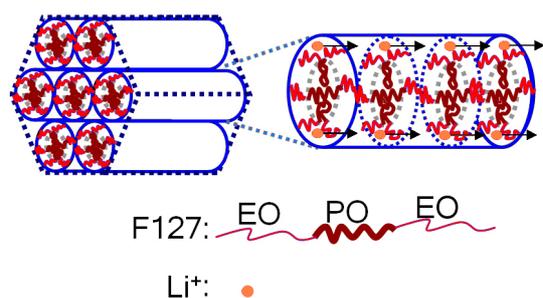


Fig. 4: Schematic illustration for the formation of hexagonal mesostructure derived from the self-assembly of Pluronic F127 triblock copolymer. For the sake of clarity, only the copolymer molecules and lithium cations at the cross-section of the cylinder assemblies are depicted, and the dissociated anions are not shown.

segmental motions of the polymer chains, and thus increases the T_g . Except for the hybrid with $[O]/[Li] = 32$, no clear melting transitions are observable for other compositions, showing that the F127 crystallization has been successfully suppressed due to the high level of salt doping.

Figure 5a illustrates the ionic conductivity (σ) as a function of temperature for the F127-based nanocomposites with various $[O]/[Li]$ ratios. The nanocomposite with $[O]/[Li] = 16$ exhibits the highest ionic conductivity, especially at the tem-

perature ranging from -10 to 45°C . An optimal value of 3×10^{-5} S/cm at 30°C is obtained at $[O]/[Li] = 16$, which is comparable to the conductivity of PEO-based electrolytes containing nano-scale TiO_2 and Al_2O_3 . This conductivity value is much better than the conductivity of composite polymer electrolytes containing other nano-scale ceramics, and is at least two orders of magnitude higher than that of conventional PEO electrolytes. Interestingly, the conductivity of silica free F127-based electrolyte of the same $[O]/[Li]$ ratio, of no ordered mesoscopic structure, is only 2.3×10^{-7} S/cm at 30°C . The nanocomposite with $[O]/[Li] = 32$ shows a conductivity jump at the temperature associating with its melting point, and exhibits similar conductivity to the nanocomposite with $[O]/[Li] = 16$ at high temperatures. The nanocomposite with the largest amount of lithium salt (i.e., $[O]/[Li] = 8$), possessing less ordered mesophases, exhibits the lowest ionic conductivity among the studied hybrid electrolytes.

Solid-state ^{29}Si and ^{13}C MAS NMR measurements are performed in order to determine the structure of the inorganic and organic parts of the nanocomposites, respectively. Three major ^{29}Si NMR peaks at -58 , -67 , and -110 ppm are observed, and can be assigned to silicon sites of T^2 ($\text{RSi}(\text{OSi})_2\text{OH}$), T^3 ($\text{RSi}(\text{OSi})_3$), and Q^4 ($\text{Si}(\text{OSi})_4$)

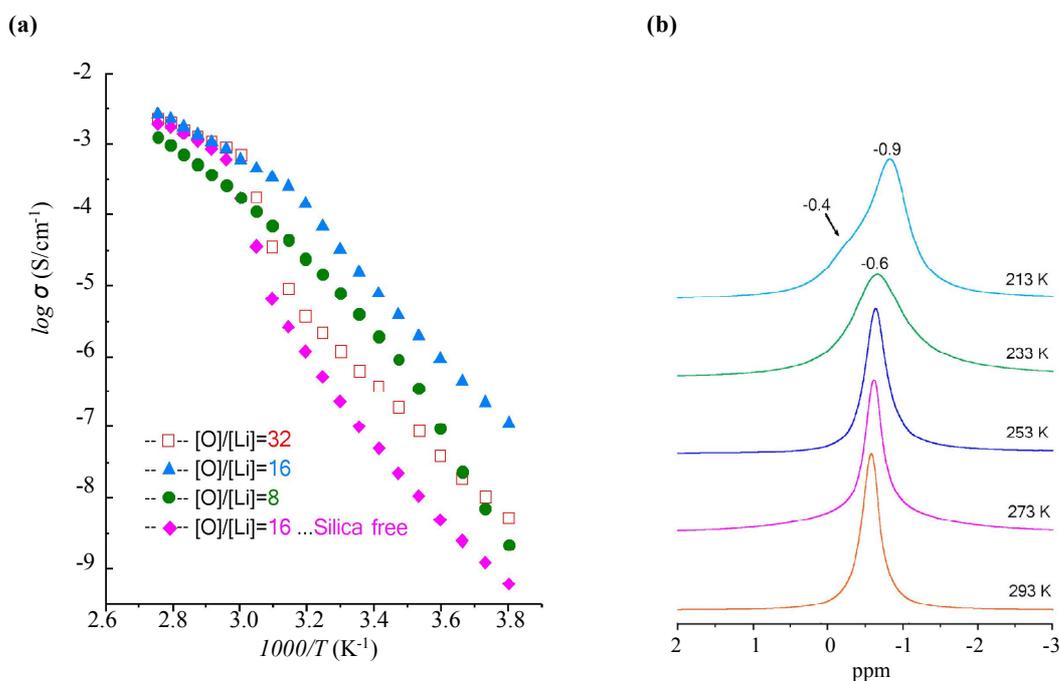


Fig. 5: (a) Temperature dependence of ionic conductivity of F127-based nanocomposite electrolytes with various $[O]/[Li]$ ratios. For comparison, the conductivity of silica free F127-based electrolyte with $[O]/[Li] = 16$ is also shown. (b) Variable temperature proton decoupled ^7Li MAS NMR spectra, acquired at a spinning speed of 3.4 kHz, of the F127-based nanocomposite electrolytes with a $[O]/[Li]$ ratio of 16.

groups, respectively, where R represents an alkyl group belonging to GLYMO. The ^{13}C CP/MAS spectrum shows six major resonances, assigned to $-\text{C}-\text{O}-$ linkages (71, 74, and 76 ppm), $-\text{CH}_2-$ groups (24 ppm), $-\text{CH}_3$ (18 ppm, PPO), and $-\text{C}-\text{Si}-$ (10 ppm, GLYMO). The relative intensities of T and Q groups and ^{13}C groups are as expected on the basis of the synthesis. The absence of ^{13}C peaks at 44 and 51 ppm for the carbon atoms in the epoxide ring of GLYMO indicates the completeness of the epoxide ring opening. Variable temperature $^7\text{Li}-\{^1\text{H}\}$ (i.e., proton decoupled) MAS NMR measurements are performed to probe the local environment of Li^+ cations. At 213 K, the ^7Li resonance at -0.9 ppm (site I), associating with a shoulder at about -0.4 ppm (site II), are observed (Fig. 5b), which indicates the existence of two distinct ^7Li local environments in the nanocomposite. Upon raising the sample temperature to 233 K, which is close to its T_g , these two sites merge together into a peak at -0.6 ppm. The site I with larger intensity is assigned to the lithium cations in the polyether domains, whereas the site II is possibly due to the lithium cations in the polymer-silica interfaces or silica rich domains. This NMR observation shows that variable temperature $^7\text{Li}-\{^1\text{H}\}$ MAS NMR technique is able to resolve the different lithium local environments existing in the nanocomposite system.

Previous NMR investigation showed that the hydrophilic PEO blocks are firmly anchored in the inorganic silica phase, giving rise to substantial restriction of the molecular mobility for the copolymer. Therefore, it is expected that the nanocomposite electrolyte should exhibit low ionic conductivity, if the mobility of lithium cations associates with the segmental motions of the polymer chains. In contrast, the present F127-based nanocomposite electrolytes exhibit conductivity two orders of magnitude greater than that of silica free F127-based polymer electrolyte. The surface interactions of the cations, copolymer, and anions with the nano-scale silica network, is believed to play a key role in stabilizing the nanocomposite

structure and facilitating the motions of the Li^+ ions. The conductivity results together with the structural characterization suggest that the drastically enhanced conductivity of the nanocomposite of $[\text{O}]/[\text{Li}] = 16$ relates closely to the well-ordered mesophase, which might improve the arrangement of Li^+ conducting pathways, as illustrated in Fig. 4. Both effects, i.e., the surface interactions and the formation of well-ordered mesophase, are necessary for the substantial enhancement of the ionic conductivity.

In summary, we demonstrate that the complexation of Pluronic F127 triblock copolymer with LiClO_4 , via a sol-gel route involving the co-condensation of alkoxy-silanes, can give rise to a well-ordered hexagonal mesostructure, especially at a $[\text{O}]/[\text{Li}]$ ratio of 16. The present self-organized nanocomposite provides a novel architecture for ion conductive materials with several advantages in simple preparation from commercially available components, substantial suppression of polymer crystallization, high ion conductivity, and potential for nanostructural patterning. The present nanocomposite electrolyte shows promising potentials in the very important field of lithium battery technology.

BEAMLINE

17A W20 X-ray Diffraction beamline

EXPERIMENTAL STATION

Powder X-ray Diffraction end station

AUTHORSH. M. Kao and C. L. Chen
Department of Chemistry, National Central University, Chung-Li, TaiwanU. S. Jeng
National Synchrotron Radiation Research Center, Hsinchu, Taiwan**PUBLICATION**• H. M. Kao and C. L. Chen, *Angew. Chem., Int. Ed.* **43**, 980 (2004).**CONTACT E-MAIL**

hmkao@cc.ncu.edu.tw