A Highly Conductive Star-Branched Organic−Inorganic Hybrid Electrolyte with Remarkable Swelling Properties Based on PPG−PEG−PPG Diamine, Cyanuric Chloride, and Alkoxysilane

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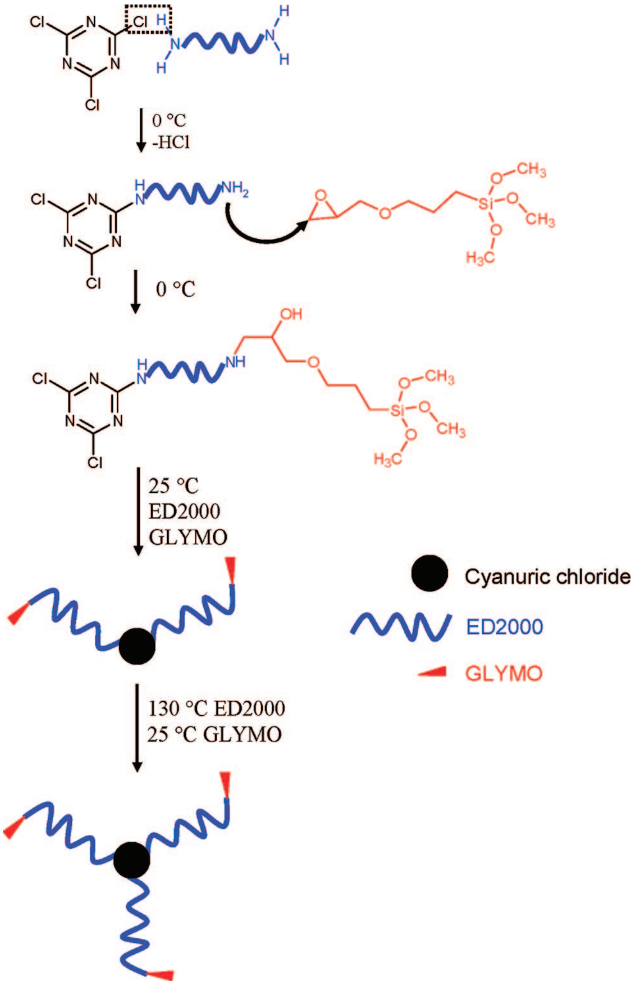
The development of solid polymer electrolytes (SPEs) with high ionic conductivity has received considerable attention because of their potential applications in many solid electrochemical devices such as high-energy density batteries, electrochromic windows, chemical sensors, and light-emitting devices.[1,2] The polymer electrolytes to be used in the devices have to satisfy several requirements, including high ionic conductivity, electrochemical stability, and good mechanical properties. Although poly(ethylene oxide) (PEO) and its derivatives have been widely used as matrix polymers in most of studies of the polymer electrolytes, PEO-based polymer electrolytes show comparatively low ionic conductivity ($\sim 10^{-7}$ S cm^{-1}) at ambient temperatures. An ionic conductivity of 10^{-3} S cm^{-1} at room temperature is generally required for an energy storage device. Moreover, PEO-based electrolytes often exhibit poor mechanical properties and are prone to crystallization, which interferes with the ion transport. The inherent limitations of ion transport in a solid PEO-based electrolyte system make it unlikely to reach this level of ionic conductivity for practical applications.

To provide SPEs with high ionic conductivity for Li-ion battery applications, attempts have been made to plasticize the polymers with low molecular weight solvents such as ethylene carbonate (EC) and propylene carbonate (PC).[3−7] However, plasticization of PEO-based electrolytes has been found to form soft solids with poor mechanical stability due to the solubility of PEO in organic solvents. Moreover, it may not be possible to avoid leakage problems in these systems. A polymer electrolyte works not only as an electrolyte but also as a separator film for lithium-ion batteries. The main challenge for the practical use of plasticized polymer electrolytes is to prepare a new material having good mechanical properties, high ionic conductivities, and good solvent retention. Hyperbranched polymer electrolytes have been considered recently as one of the most promising candidates because they are intrinsically resistant to crystallization, which is advantageous to improve their conductivities.[8−11] Another favorable strategy is to develop organic−inorganic hybrid electrolytes, so-called ormolytes (*or*ganically *mo*dified electro*lytes*) via in situ formation of inorganic component within the polymer matrix, which provides simultaneously an amorphous structure and good thermal, mechanical, and chemical stability.[12−15]

With the aim of developing highly conductive polymer electrolytes with sufficient mechanical strength and good solvent retention, we present herein a new star-branched organic−inorganic hybrid electrolyte based on the selectivity of the sequential triazine substitutions by using 2,4,6-trichloro-1,3,5-triazine (cyanuric chloride, CC) as the linking agent to couple with poly(propylene glycol)-*block*-poly(ethylene glycol)-*block*-poly(propylene glycol) bis(2-aminopropyl ether) triblock copolymer ($H_2N{-}PPG{-}PEG{-}PPG{-}NH_2$, Jeffamine ED2000, $M_w = 2000$), which is chemically cross-linked to the silicate network formed via condensation of (3-glycidyloxypropyl)trimethoxysilane (GLYMO), in a stepwise and selective manner, as illustrated in Scheme 1. Cyanuric chloride can serve as an excellent central core because of clear distinction of the relative reactivity among three chlorides at different temperatures.[16] This allows a possible synthetic methodology for tailoring the copolymer structure and composition by judiciously selecting the starting amines and reaction conditions. A star polymer, consisting of three linear polymer arms joined together by a central core, is made by a sequential reaction of the aryl chlorides of the central core CC

Scheme 1. Schematic Illustration for the Synthesis of 3ED-3G-CC



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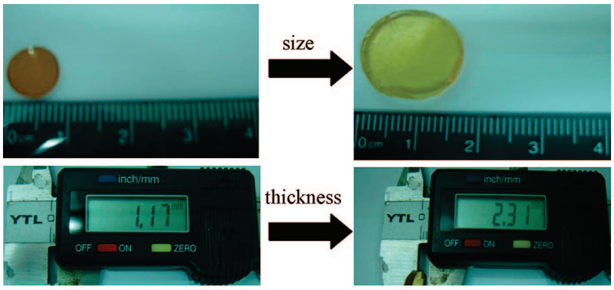

Pristine membrane (0 min) Swollen membrane (200 min)

Figure 1. Size and thickness variations of 3ED-3G-CC.

with the diaminoalkylene oxide. Further, GLYMO (denoted as G) provides a cross-linking unit with the polymer arms and forms an inorganic phase via a sol−gel process to increase the mechanical strength of the resulting free-standing membrane. The resulting hybrid was denoted as 3ED-3G-CC.

Solid-state ^{29}Si and ^{13}C NMR measurements were performed in order to determine the structure of the inorganic and organic part of the hybrid material, respectively. Two major ^{29}Si NMR peaks at −60 and −68 ppm were observed (Figure S1, Supporting Information) and can be assigned to silicon sites of T^2 ($\mathrm{R}\mathit{Si}(\mathrm{OSi})_2\mathrm{OH}$) and T^3 ($\mathrm{R}\mathit{Si}(\mathrm{OSi})_3$) groups, respectively, where R represents an alkyl group belonging to GLYMO. The ^{13}C one-pulse and CPMAS (cross-polarization magic angle spinning) spectra (Figure S2, Supporting Information) showed resonances from ED2000, GLYMO, and CC, assigned to −C−O− linkages (70 and 75 ppm, PEG and GLYMO), −C−N− (47 ppm, PPG), $-\mathrm{CH}_2-$ groups (22 ppm, GLYMO), $-\mathrm{CH}_3$ (18 ppm, PPG), −C−Si− (10 ppm, GLYMO), and $-\mathrm{C{=}N}-$ (165 ppm, CC). The ^{13}C signals (10 and 22 ppm) resulting from GLYMO were enhanced and became observable by use of the cross-polarization process, whereas the weak signal at 165 ppm due to the central core CC was observed by direct polarization in the one-pulse experiment. The ^{13}C peaks at 44 and 51 ppm expected for the carbon atoms in the epoxide ring of GLYMO were not observed, indicative of the completeness of the epoxide ring-opening.[17] The epoxide ring-opening resulted in the observations of new signals at 54 and 60 ppm (as a shoulder of 70 ppm). The NMR observations are consistent with the 3EG-3G-CC structure, as illustrated in Scheme 1.

Figure 1 demonstrates the size and thickness variations of 3ED-3G-CC after different intervals of soaking time in an electrolyte solution of 1 M $\mathrm{LiClO_4}$ in EC/PC (1:1, w/w). After 200 min of soaking time, almost 9 times in volume enhancement was observed, indicating a large electrolyte uptake capacity of the present star-branched hybrid material. The swelling behavior of 3ED-3G-CC as a function of soaking time is displayed in Figure 2a. The percentage of swelling, determined by $(W - W_0)/W_0 \times 100\%$, where W and W_0 are the weights of the wet and dry hybrid membranes, respectively, reached the maximum value of about 1180%. The high value of swelling ratio suggested a high electrolyte uptake capacity of the three-armed polymeric structure of 3ED-3G-CC. No apparent degradation of the mechanical properties was observed upon dipping in the electrolytic solution. The remarkably high swelling ratio of 3ED-3G-CC also favored a faster movement of lithium ions and thus a significant enhancement of the ionic conductivity. Figure 2b shows the temperature dependence of ionic conductivity of the saturated 3ED-3G-CC hybrid electrolyte. The electrolyte showed a Vogel−Tamman−Fulcher (VTF)-like enhancement of the conductivity when the temperature was increased, implying a diffusion mechanism for transport of the charge carriers where the charge carriers were coupled with the segmental motion of the polymer chain. The 3ED-3G-CC hybrid electrolyte exhibited the highest ionic conductivity with a value of 1.11×10^{-2} S cm^{-1} at 30 °C, an exceptionally high value for plasticized polymer electrolytes. These important characteristics, namely high ionic conductivity and remarkable swelling properties, of 3ED-3G-CC make it a promising candidate for use in Li-ion batteries.

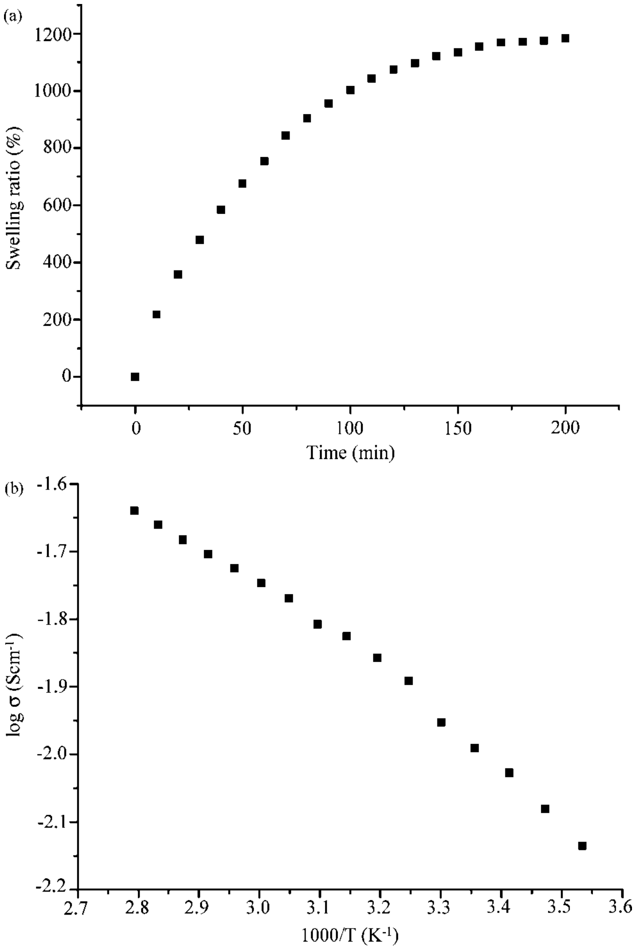

Figure 2. (a) Swelling behaviors of 3ED-3G-CC as a function of soaking time and (b) temperature dependence of ionic conductivity of 3ED-3G-CC, saturated with an electrolyte solution of 1 M $\mathrm{LiClO_4}$ in EC/PC (1:1, w/w).

For applications in lithium-ion batteries, it is necessary for the polymer electrolyte to have high electrochemical stability. Electrochemical window is one of the important parameters to evaluate the stability of the polymer electrolyte. The electrochemical window of 3ED-3G-CC was measured by the linear sweep voltammetry (LSV) experiment to endure the operating voltage of the battery system. Figure 3 shows the current response of the working electrode. A very low background current was measured in a potential region between 0 and 6 V. This small current might be attributed to the change of the stainless steel surface.[18] The small hump between 1 and 2 V was ascribed to the oxidation of some trace species such as water and oxygen.[19] Upon reaching 6 V, a considerable current began to flow, indicating the onset of the electrolyte decomposition process. The linear sweep voltammogram in Figure 3 displays that the onset decomposition voltage of the hybrid electrolyte is around 6.0 V vs Li. This value is particularly high as compared to the common values of around 4−5 V reported for other polymer electrolytes. It is sufficiently high for the lithium

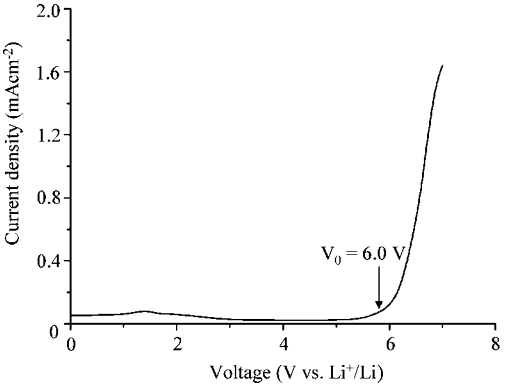

Figure 3. Linear sweep voltammogram of the cell prepared by using the 3ED-3G-CC membrane.

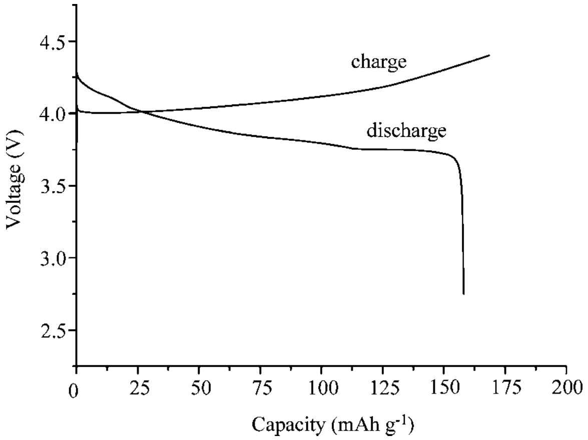

Figure 4. Galvanostatic charge−discharge curves for the Li/3ED-3G-CC/$LiCoO_2$ cell.

oxide cathodes such as $LiCoO_2$ and should ensure its acceptable performance for rechargeable batteries of high energy density.

$LiCoO_2$ is the most widely used commercial cathode material for lithium-ion batteries, although it suffers from severe limitations in cell capacity and safety due to overcharge problems, which occur when the cutoff charge potential exceeds 4.3 V. To verify the overcharge performance of the 3EG-3G-CC hybrid electrolyte, a coin cell of Li/3ED-3G-CC-based separator/$LiCoO_2$ was assembled. The 3ED-3G-CC hybrid electrolyte was first soaked in an electrolyte solution of 1 M $LiPF_6$ in ethylene carbonate:diethyl carbonate (EC/DEC, 1:1, v/v) and reached saturation after soaking for 3 h. Figure 4 presents the first-cycle charge−discharge voltage profiles for the hybrid electrolyte, which showed a sloping curve in the 3.8−4.4 V range, indicating the one-phase redox process and a flat voltage plateau in the 3.7−3.8 V range due to the two-phase nature of lithium intercalation and deintercalation between the hexagonal and monoclinic phase.[20] It is evident that cycle stability and initial capacity declined drastically, which could be attributed to the formation of a solid electrolyte interface (SEI) film that resulted in significant impedance growth.

Figure 5 shows the capacity and cyclability of the cell using 3ED-3G-CC electrolyte as a separator between 2.75 and 4.40 V. Additionally, another coin cell using a commercial polypropylene (PP) membrane with 40% porosity and 25 μm thickness as a separator was measured for comparison purposes. The cutoff capacity was fixed at 80% of the first-cycle discharge capacity for both samples. As evidenced in Figure 5, the hybrid electrolyte sample exhibited enhanced cycling stability of 72 cycles compared to 34 cycles for the polypropylene separator sample, which represents a remarkable 2-fold increase in cyclability during overcharge at 4.40 V. This clearly shows that the present hybrid electrolyte is a promising candidate for use in Li-ion batteries with an excellent overcharge capacity.

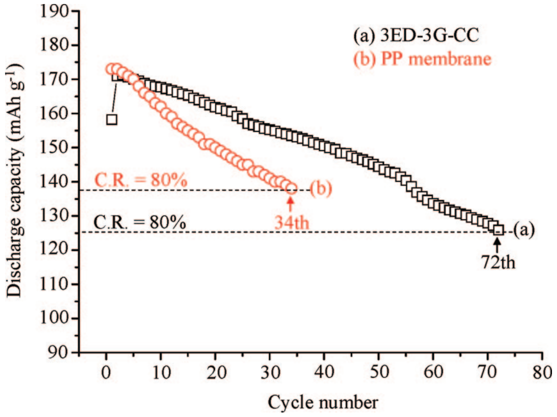

Figure 5. Cycling behaviors of (a) the Li/3ED-3G-CC/$LiCoO_2$ cell and (b) the conventional PP membrane cell. The charge−discharge process was performed between 2.75 and 4.40 V at a scan rate of 0.2 C.

In summary, we have synthesized a new star-branched organic−inorganic hybrid electrolyte based on the use of cyanuric chloride as the central core to couple with triblock copolymers PPG−PEG−PPG diamine, followed by cross-linking with epoxy alkoxysilanes via a sol−gel process. The resulting hybrid exhibits not only a remarkably high value of swelling ratio and conductivity about 10^{-2} S cm^{-1} at room temperature but also has an electrochemical stability window of at least 6.0 V, which makes it very promising for Li-ion battery applications.

Experimental Section. To prepare the 3ED-3G-CC membrane, 1.5 g (0.75 mmol) of $H_2N-PPG-PEG-PPG-NH_2$ triblock copolymer (Aldrich, commercially designated by Jeffamine ED2000, with M_w = 2000 g/mol containing about 40.5 PEG units) and 0.138 g (0.75 mmol) of cyanuric chloride were dissolved in 40 and 10 mL of tetrahydrofuran (THF), respectively. The reaction temperature of both the solutions was lowered to 0 °C in ice bath. The cyanuric chloride solution was then added to the diamine-capped poly(alkylene oxide) (ED2000) solution and stirred for 2 h at 0 °C. With this solution, 0.177 g (0.75 mmol) of GLYMO was added and stirred for 6 h at 0 °C. The hydrogen chloride generated from the reaction between CC and ED2000 serves as a catalyst for condensation of GLYMO. The reaction temperature was slowly increased to room temperature (25 °C), and ED2000 (0.75 mmol) was added followed by stirring for 24 h. Then GLYMO (0.75 mmol) was added into the above solution and stirred for another 24 h. No gel formation was observed during the reaction, which gave evidence that the polymer was not cross-linking prematurely via reaction of the third reactive site on cyanuric chloride. Once the linear polymer was made, the third site was reacted at 130 °C to provide cross-linked network. For that, the reaction temperature of the solution was raised to 130 °C, and ED2000 (0.75 mmol) was added to the solution and stirred and refluxed for 24 h. Then solution temperature was reduced to room temperature and GLYMO (0.75 mmol) was added to the solution and stirred for another 24 h. The resulting viscous solution was then cast onto Teflon dishes and air-dried for 2 days to remove solvent. After being vacuum-dried at 80 °C for 2 days, the final arm-branched hybrid was obtained.

All solid-state NMR experiments were performed on a Varian Infinityplus-500 NMR spectrometer, equipped with a 5 or 4 mm

Chemagnetics probe. The Larmor frequencies for ^{13}C and ^{29}Si nuclei are 125.7 and 99.3 MHz, respectively. ^{13}C one-pulse and CPMAS NMR spectra were recorded by using a contact time of 1 ms and a recycle delay of 5 s. A $\pi/6$ pulse of 2 μs and a recycle delay of 200 s were used to acquire the quantitative ^{29}Si MAS NMR spectra. Both ^{13}C and ^{29}Si chemical shifts were externally referenced to tetramethylsilane (TMS) at 0.0 ppm.

The 3ED-3G-CC film was dipped in an electrolyte solution of 1 M $LiClO_4$ in EC/PC (1:1, w/w) for measurements of the extent of swelling. The preweighed films were kept immersed in electrolyte solution at room temperature for different time periods after which the films were withdrawn. The surface electrolytes were removed by soaking with a filter paper and then reweighed.

Alternate current (AC) impedance measurements of the hybrid electrolyte were performed using a frequency response analyzer Autolab/PGSTAT 30 electrochemical instrument over a frequency range of 10 Hz to 1 MHz with an amplitude of 10 mV. All the samples were sandwiched between two stainless steel (SS) blocking electrodes for conductivity tests. The conductivity values (σ) were obtained from the equation $\sigma = t/R_bA$, where R_b, t, and A were the bulk resistance, thickness, and area of the sample, respectively. The electrochemical stability of the hybrid electrolytes was determined by LSV using stainless steel as a working electrode and lithium as counter and reference electrodes for a Li/3ED-3G-CC/SS cell at a scan rate of 1 mV s^{-1} from 0 to 7 V.

The 3ED-3G-CC membrane (255 μm thick) was dried overnight at 60 °C in an oven and placed into an argon-filled glovebox (VAC, MO 40-1) that contained <2 ppm oxygen and moisture, to soak in the electrolyte solution of 1 M $LiPF_6$ in EC:DEC (1:1, v/v) for 12 h, and then was cut into small circular disks of 2.98 cm^2 (diameter = 1.95 cm) for cell assembly and use. Charge−discharge studies were carried out with coin cells assembled in standard 2032 coin-cell hardware. Lithium metal was used as the anode, and the 1 M solution described above was used as the electrolyte. The cathode used commercially available FMC cathode powder of $LiCoO_2$ by blade-coating a slurry of 85 wt % active material with 10 wt % conductive carbon black and 5 wt % poly(vinylidene fluoride) (PVDF) binder in *N*-methyl-2-pyrrolidone (NMP) on aluminum foil, drying overnight at 120 °C in an oven, roller-pressing the dried coated foil, and punching out circular disks. A commercial polypropylene membrane (Celgard 3501, Celanese Separation Products) with 40% porosity and 25 μm thickness was used for comparison. The cycle tests of normal charge were carried out at a 0.2 C rate between 2.75 and 4.20 V, but between 2.75 and 4.40 V for overcharge, in a multichannel battery tester (Maccor 4000).

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Supporting Information Available: ^{29}Si MAS NMR spectrum of 3ED-3G-CC (Figure S1) and one-pulse (with proton decoupling) and CPMAS ^{13}C NMR spectra of 3ED-3G-CC (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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