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Synthesis of Li^+ Ion Conductive PEO-PSt Block Copolymer Electrolyte with Microphase Separation Structure

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A block copolymer consisting of a polyethylene oxide (PEO) and polystyrene (PSt) was applied to the preparation of a microphase separation of solid polymer electrolyte containing $LiClO_4$ with high ionic conductivity at room temperature (more than 10^{-4} S cm^{-1}). The polystyrene block provided the mechanical strength and the polyethylene oxide one allowed for fast ion conduction in the polymer electrolyte without any plasticizer. Using this new microphase separation solid polymer electrolyte, a $LiCoO_2$/polymer electrolyte/Li metal cell was constructed and tested. The prepared cell exhibited a discharge capacity of 100 mAh g^{-1} at 30°C.
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Solid polymer electrolytes have been extensively investigated to realize various kinds of electrochemical devices, such as rechargeable lithium batteries. Polyethylene oxides (PEOs) containing a lithium salt were first developed as an ion conductive solid polymer.[1] After this discovery, various kinds of ion conductive polymers have been studied and applied to lithium batteries.[2-15] However, their ion conductivity is decreased with increasing mechanical strength. Ion conduction in the solid polymer electrolyte depends on the movement of the polymer chain.[2] The mechanical strength of the polymer electrolyte is also related to the movement of the polymer chain. The high chain mobility results in high ion conductivity and low mechanical property of the solid polymer electrolyte. In this way, both properties are usually in conflict. So far, new solid polymer electrolytes have been prepared to improve not only ion conductivity, but also the mechanical strength of polymer electrolytes. One of the interesting solid polymer electrolytes is the polyethylene oxides with polyether branches. The main chain of this polymer keeps its mechanical strength, and the branch polymer provides high chain mobility. However, this kind of polymer with high ion conductivity does not have high mechanical strength. Recently, polymers with microphase separation structures have drawn much attention in various application fields. Polymer electrolytes with microphase separation structures have been proposed by several groups.[16-20] A Massachusetts Institute of Technology group has developed a Li^+-ion conductive polymer electrolyte based on a similar concept. They successfully fabricated a lithium polymer battery, and it worked at room temperature regardless of conductivities as low as 10^{-5} S cm^{-1}.[16]

In this study, BAB block copolymer was applied to prepare microphase separation structure with a high ion conductive phase. The prepared solid polymer electrolyte consisted of a polystyrene (PSt) block to improve mechanical properties and a polyethylene oxide (PEO) moiety to provide ionic conductivity. The ionic conductivity of a polymer electrolyte depends on the chain mobility. Therefore, a polymer with a short PEO chain was synthesized. Figure 1 shows a schematic illustration of a nanostructure-controlled solid polymer electrolyte. This polymer electrolyte exhibits a high ionic conductivity 10^{-4} S cm^{-1} without plasticizer at room temperature, and this is one of the highest ionic conductivities among reported values for PEO-based solid polymer electrolytes. This block copolymer was synthesized in Nippon Soda Company, and the electrochemical properties of the polymer as a Li^+ ion conductive electrolyte were characterized in collaboration with the Tokyo Metropolitan University group. Although the electrical conductivity of our solid polymer is not enough for the application to high power lithium batteries, this polymer electrolyte may be applicable to small lithium batteries which require high safety. Using this polymer, we fabricated a conventional composite cathode, and it was evaluated in an all solid-state rechargeable lithium battery.

Experimental

Figure 2 shows the synthesis process of nanostructure controlled BAB-block polymers. Here, BAB denotes a triblock copolymer which was synthesized by an active radical polymerization technique with ruthenium(II) complexes using a difunctional initiator.[21] In the first step, poly(ethylene glycol) methyl ether methacrylate (PME), $H_2C = C(CH_3)COO\text{-}(CH_2CH_2O)_yCH_3$ (PME-1000; $y = 23$, PME monomer was supplied from NOF Corporation), was polymerized in toluene at 80°C with $PhCOCHCl_2$, $RuCl_2(PPh_3)_3$, and dibuthyl amine. This polymer was used as the macroinitiator after the removal of both ruthenium complexes and residual monomers by silica column treatment. Block copolymerization with styrene (St) was carried out in toluene at 100°C with $Ru(Cp^*)Cl(PPh_3)_2$. The microphase separation structure of the polymer was observed by transmission electron microscopy (TEM, H-7100FA, Hitachi). In order to prepare samples for TEM observation, tetrahydrofuran/acetone (1:1 in volume) solution containing 10 wt % block polymer was cast on a polypropylene plate and dried at room temperature for 12 h. Then it was dried at 100°C under vacuum for 5 h. A cross section of the polymer film was prepared with a microtome (EM-ULTRACUT, LEICA). Os staining was performed to observe the microphase separation structure.

The BAB-block copolymer and $LiClO_4$ (in a ratio of $[Li]/[EO] = 0.03\text{-}0.08$, [EO], ethylene oxide unit) were dissolved in tetrahydrofuran/acetone solution, and the mixture was cast on an

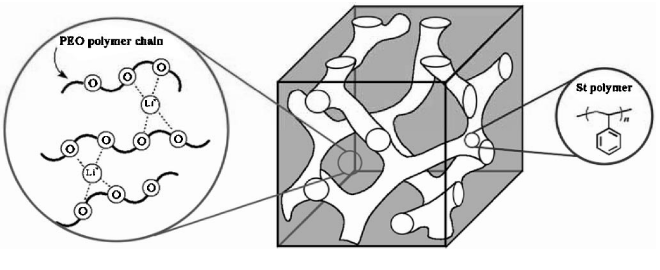

Figure 1. Schematic illustration of nanostructure-controlled polymer prepared from a block copolymer with PEO moiety and a PSt one by using self-organized microphase separation process.

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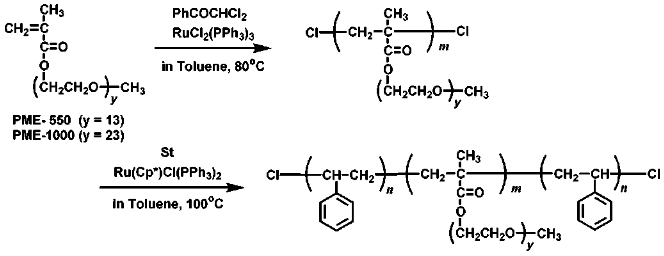

Figure 2. Preparation procedure for nanostructure-controlled polymer with lithium ion conductivity.

aluminum foil. The solvents were evaporated at room temperature in an argon filled glove box for overnight. The polymer was successively dried under high vacuum for 5 h at 120°C. The thickness of solid polymer electrolyte film was about 80 μm. This sample was supplied to follow the conductivity measurements. The ionic conductivity was measured in dry argon atmosphere in the temperature range from 20 to 60°C by the ac impedance method using an impedance analyzer (SI-1260, Solartron) over a frequency range from 0.1 Hz to 10 MHz. The polymer electrolyte was cast on a glassy carbon (GC) disk electrode, and the electrochemical stability of the electrolyte was evaluated by cyclic voltammetry with the two-electrode system using a potentiostat (HSV-100, Hokuto Denko). The counter electrode was a lithium metal foil.

Using the block copolymer electrolyte, $LiCoO_2$/polymer electrolyte/Li metal cell was constructed and tested. The composite cathode was prepared by casting *N*-methyl pyrrolidone slurry containing 70 wt % of $LiCoO_2$, 15 wt % of acetylene black, and 15 wt % of block copolymer- $LiClO_4$ ($[Li]/[EO] = 0.05$) on an aluminum foil using a doctor blade with successive high vacuum drying processes. The thickness of the composite was *ca.* 15 μm, and the mass of $LiCoO_2$ contained in the composite cathode was *ca.* 1.7 mg cm^{-2}. Then the block copolymer containing 5 mol % $LiClO_4$ dissolved in tetrahydrofuran/acetone solution was cast on the composite cathode as follows: the polymer solution was injected

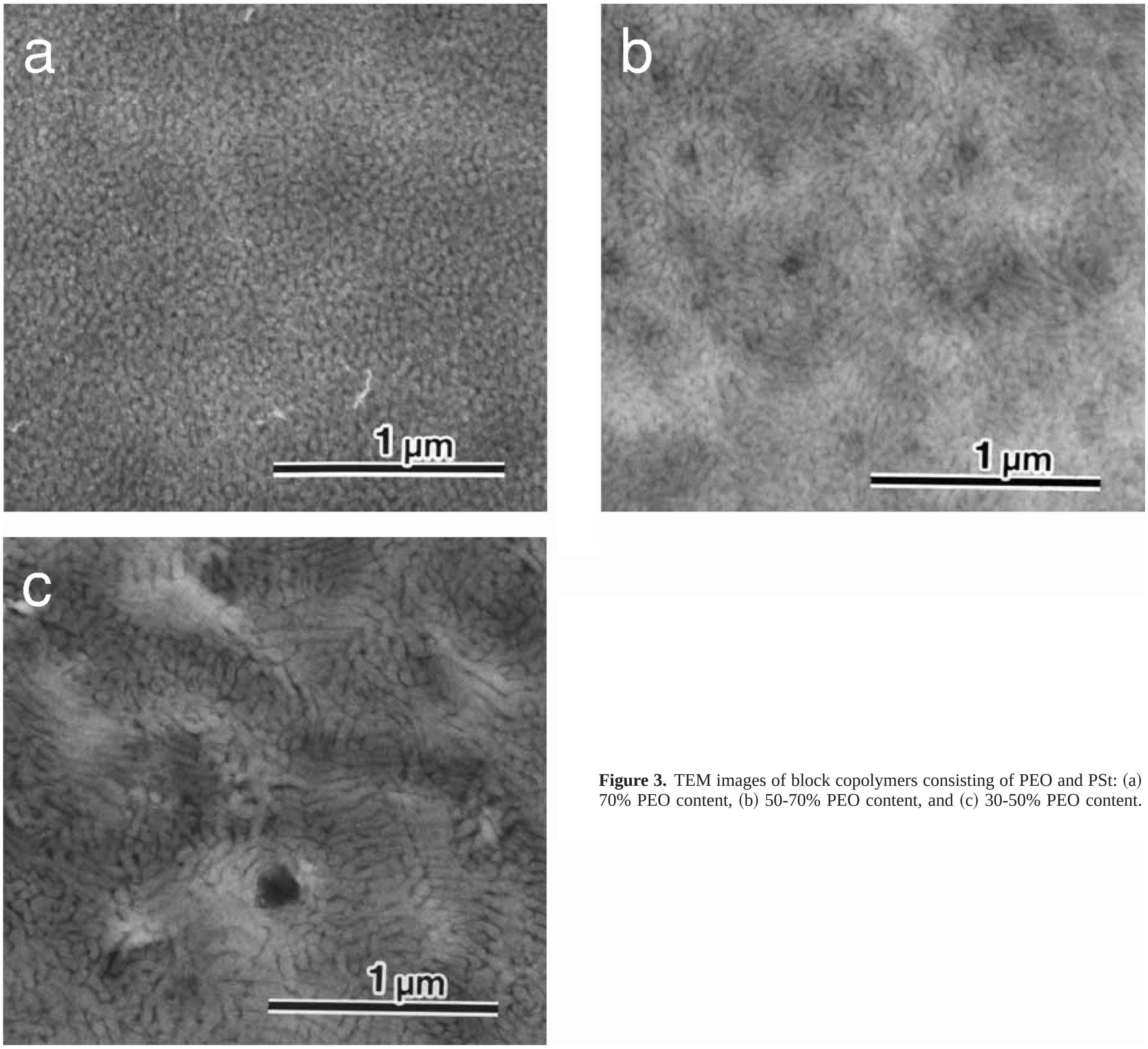

Figure 3. TEM images of block copolymers consisting of PEO and PSt: (a) 70% PEO content, (b) 50-70% PEO content, and (c) 30-50% PEO content.

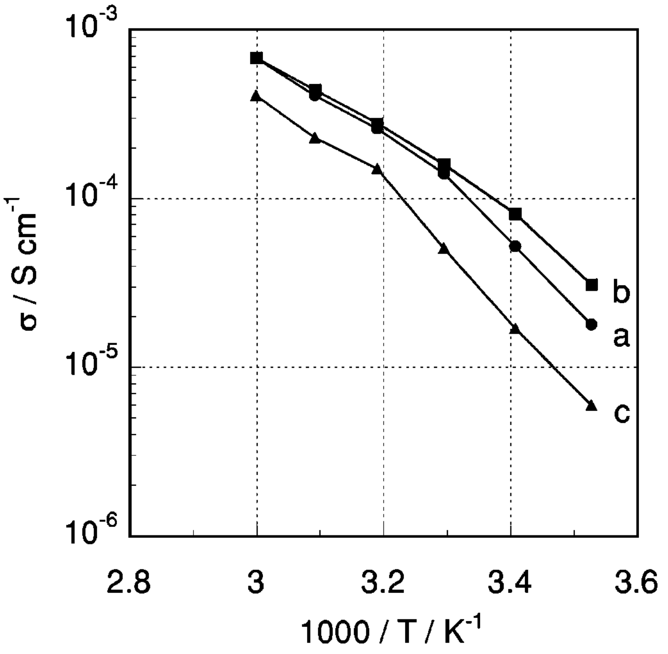

Figure 4. Temperature dependence of ionic conductivity of polymer electrolyte (*m*, *n*, and *y* were 210, 190, and 23, respectively) containing various concentrations of $LiClO_4$. [Li]/[EO] ratios were (a) 0.03, (b) 0.05, and (c) 0.08.

into the composite cathode, and the polymer solution was filtered into the cathode matrix by holding it for 10 min under weak reduced pressure (−30 kPa). This process was repeated several times, which was very useful for the construction of an all solid-state cell with porous electrodes. After it was dried at 120°C under vacuum for 12 h, the anode (pure lithium metal foil) was put on the electrolyte film. This cell assembly was placed between two polypropylene plates, and they were pressed together by a clip. Electrochemical properties of this solid polymer electrolyte cell were measured in a dry argon atmosphere at 30°C. Charge and discharge tests were measured by using a dc power supply (HJ1001SM8, Hokuto Denko). Cutoff voltages for charge and discharge tests were 3.0 V on discharge and 4.3 V on charge. The current of 0.1 C rate for $LiCoO_2$ active material was 14 mA g^{-1}, which corresponded to a current density of 25 μA cm^{-2}.

Results and Discussion

As mentioned above, the polymer prepared in this study consisted of both continuous PSt and PEO parts. This polymer can be dissolved into tetrahydrofuran or other organic solvents, so that lithium salts can be easily injected into the PEO part of the polymer. Electrolyte salts, such as $LiClO_4$ or $LiPF_6$, could be dissolved into the PEO matrix to provide high ion conductivity. In addition, the polymer membrane can be easily prepared by the casting method. The microstructure of the polymer depends on the ratio between PEO and PSt parts. The structure as shown in Fig. 1 can be obtained when the ratio between PEO and PSt is higher than 1. This polymer did not show any formation of a crystalline phase. As stated above, the ionic conductivity of a polymer electrolyte depends on the chain mobility, so that PME monomer with a low molecular weight PEO ($y = 23$) was used. The mechanical strength depends on the number of *n*, and the ionic conductivity depends on the number of *m*, where *n* and *m* are lengths of the polystyrene polymer chain and polyethylene polymer chain, respectively, as shown in Fig. 2. Thus, numbers of *n* and *m* are very important for controlling the properties of the solid polymer electrolyte. In other words, the ratio between PEO and PSt determines the microphase separation structure, ionic conductivity, and mechanical strength of the prepared polymer. Figure 3 shows TEM images of the prepared solid polymer electrolytes with different weight ratios of PEO and PSt. From these TEM images, it can be seen that the microphase separation structure depends on the ratio between PEO and PSt. The domain size of PSt or PEO was less than 100 nm and decreased with increasing PEO content. The tensile strengths of these polymers were measured to be higher than 3 MPa,[22] which were high enough for their utilization in battery applications.

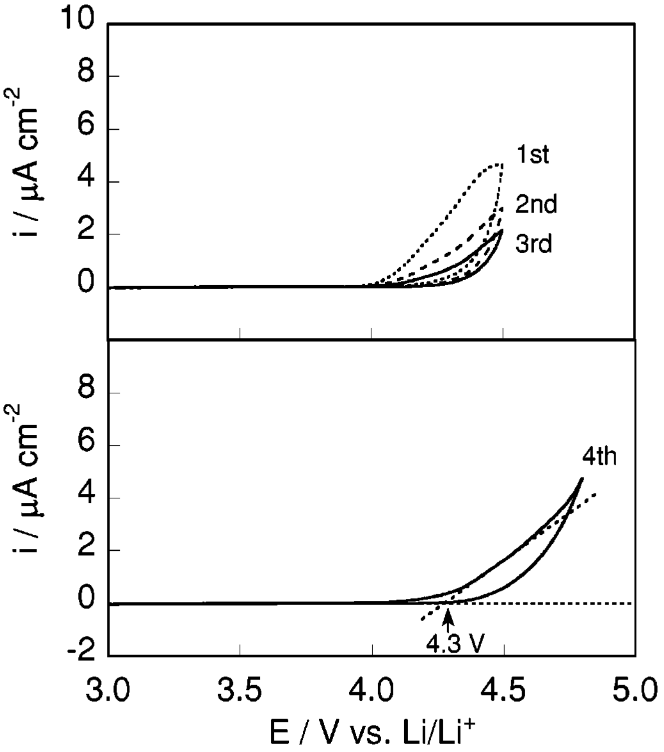

Figure 5. Cyclic voltammograms of a GC disk electrode in solid polymer electrolyte measured at 30°C. Potential sweep rate was 1 mV s^{-1}.

Figure 4 shows the temperature dependence of ionic conductivity of microphase separation polymer with $LiClO_4$ electrolyte salt ([Li]/[EO] = 0.03-0.08). This polymer contained 92 wt % of PME-1000 and 8 wt % of St (*m*, *n*, and *y* were 210, 190, and 23, respectively). The highest ionic conductivity of 2×10^{-4} S cm^{-1} (30°C) was realized at 5 mol % ([Li]/[EO] = 0.05) concentration of lithium salt. The conductivity decreased at higher lithium salt concentration than 8 mol %, meaning that the ion dissociation of $LiClO_4$ in this polymer was gradually suppressed with increasing concentration of $LiClO_4$ in the PEO phase. This tendency has been observed for other ion conductive polymers.[2] The obtained ionic conductivity was relatively high compared with reported values for solid polymer electrolytes based on polyethylene oxide without plasticizer.[2] As stated above, this polymer did not show any formation of a crystalline phase at room temperature. Moreover, the ionic conductivity of a polymer electrolyte depends on the chain mobility. Therefore, a polymer with a short PEO chain ($y = 23$) was synthesized in this study. Indeed, the ionic conductivity of the polymer changed depending on the EO length (number of *y*) as reported in our previous paper.[22] The formation of the continuous phase of PEO gives the high ionic conductivity. The ionic conductivity was increased with increasing PEO content; however, this led to low mechanical strength of the polymer electrolyte.[22] The optimized PEO content was 80-90% to achieve both high ionic conductivity (higher than 10^{-4} S cm^{-1}) and good mechanical strength.

Figure 5 shows cyclic voltammograms of the GC electrode with the polymer electrolyte (*m*, *n*, and *y* were 210, 190, and 23, respectively) containing $LiClO_4$ ([Li]/[EO] ratio was 0.05) measured at

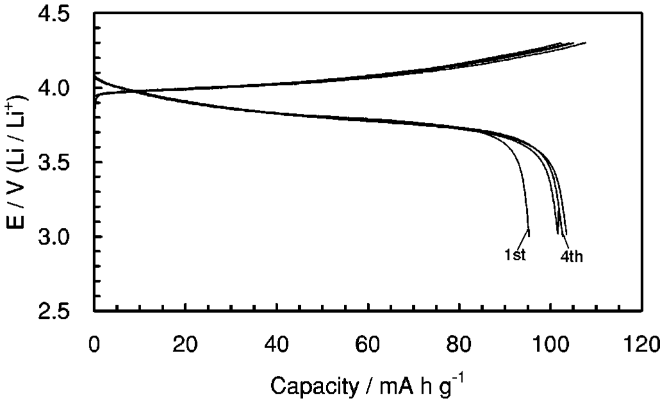

Figure 6. Charge and discharge curves of $LiCoO_2$/solid polymer electrolyte/Li cell at 0.1 C rate (30°C).

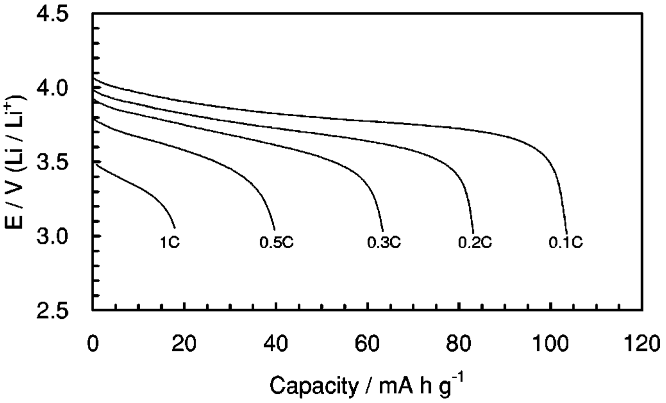

Figure 7. Discharge curves of $LiCoO_2$/solid polymer electrolyte/Li cell measured at various rates (30°C). The cell was charged up to 4.3 V at 0.1 C prior to each discharge.

30°C. The anodic current was observed to be higher than 4.1 V in the first cycle due to oxidation of the polymer, however, the current decreased in the second and third cycles. The decrease of the current was considered to be due to the formation of some kind of passivation film on the electrode. In the fourth cycle, the electrode potential was swept up to 4.8 V, and the anodic potential window of the electrolyte was estimated to be 4.3 V at 30°C. It has been reported that polyethylene oxide decomposes at 4.0 V *vs.* Li/Li^+ at elevated temperatures such as 70°C.[23] The potential window of this polymer electrolyte at room temperature may be wider compared to the case in which the temperature is elevated. In addition, both PSt and PEO groups are in contact with the electrode to form an interface. The microphase separation solid polymer electrolyte may provide high electrochemical stability.

An all solid-state rechargeable lithium cell of $LiCoO_2$/polymer electrolyte/Li was prepared successfully, and its electrochemical characteristic was investigated. The block copolymer used in this experiment contained 92 wt % of PME-1000 and 8 wt % of St (m, n, and y were 210, 190, and 23, respectively), and $LiClO_4$ was dissolved into the polymer ([Li]/[EO] ratio was 0.05). Figure 6 shows the charge and discharge curves of the $LiCoO_2$/polymer electrolyte/Li cell cycled at 30°C. The solid polymer electrolyte cell showed the discharge capacity of 100 mAh g^{-1} (normalized by the mass of $LiCoO_2$) at 0.1 C rate. The coulombic efficiency of the first charge-discharge cycle was 93%, and it increased up to 99% at the fourth cycle. This high coulombic efficiency was attributed to the electrochemical stability of the polymer electrolyte, and it could be applicable to the 4 V class lithium batteries. The high reversibility suggested that a stable contact between the $LiCoO_2$ particle and the polymer electrolyte during charge and discharge. Figure 7 shows the rate capability of the $LiCoO_2$/polymer electrolyte/Li cell. The cell was charged at 0.1 C rate and discharged at various rates. As the current density increased the discharge capacity decreased rapidly. The decrease of discharge capacity at higher rates was considered to be due to the low ionic conductivity and low transport number of Li^+ ion in the electrolyte. Other lithium salts such as $LiPF_6$ and $LiN(SO_2CF_3)_2$ may be useful for increasing the transport number. In addition, the microstructure of the composite cathode should be optimized in order to improve the rate capability of the polymer battery. Efforts are under way to optimize the fabrication process of the composite cathode and test charge-discharge cycle life of the polymer battery.

Conclusions

A BAB-block copolymer consisting of polyethylene oxide and polystyrene was synthesized by an active radical polymerization technique. The prepared polymer electrolyte containing $LiClO_4$ (in a ratio of [Li]/[EO] = 0.05) exhibited a high ionic conductivity of 2×10^{-4} S cm^{-1} at room temperature. An all solid-state electrochemical cell $LiCoO_2$/polymer electrolyte/Li was successfully fabricated. The electrochemical cell showed a discharge capacity of 100 mAh g^{-1} at 0.1 C rate at 30°C, and the reversibility of the charge and discharge was good. This solid polymer electrolyte was electrochemically stable up to 4.3 V *vs.* Li/Li^+.

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