ORIGINAL PAPER

Lithium-ion conduction in elastomeric binder in Li-ion batteries

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Abstract This paper describes two kinds of elastomeric binders which are styrene–butadiene (ST–BD) copolymer and 2-ethylhexyl acrylate–acrylonitrile (2EHA–AN) copolymer for electrode materials of rechargeable Li-ion batteries. These elastomeric binders were swollen by electrolyte solution (EC/DEC=1/2, 1 M LiPF$_6$), and 2EHA–AN copolymer retained larger amount of electrolyte solution than ST–BD copolymer. The Li-ionic conduction behavior was investigated for both copolymer films swollen by electrolyte solution. The Li-ion conductivity of ST–BD copolymer was 9.45×10^{-8} S·cm^{-1} and that of 2EHA–AN copolymer was 1.25×10^{-5} S·cm^{-1} at room temperature, and the corresponding amounts of activation energy were 0.31 and 0.26 eV, respectively. Because the observed activation energy in elastomeric binder was different from that in the bulk of electrolyte solution (0.09 eV), Li-ion conduction of the bulk of elastomeric binder swollen by electrolyte was affected by the polymer structure of binders. Electrochemical performance of cathode material, LiCoO$_2$, was investigated with three kinds of binders: ST–BD copolymer, 2EHA–AN copolymer, and poly(vinylidene fluoride). The initial charge–discharge capacity of the LiCoO$_2$ electrode with 2EHA–AN copolymer showed highest capacity, suggesting that Li$^+$-ion conduction inside of the elastomeric binder contributes to the enhancement of charging and discharging capacity. This result indicates that elastomeric binder with sufficient Li-ionic conductivity can be an attractive candidate for improving cathode of lithium-ion battery.

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Introduction

In lithium-ion battery (LIB), nonreactive polymer is blended into both cathode and anode electrode composites as a binder. This polymer binder unifies the nonadhesive particles of electrochemically reactive materials and conductive agents, realizing simultaneous ion and electron exchange during electrochemical reaction in the electrode. Poly(vinylidene fluoride) (PVdF) is a typical example of binder for LIB [1, 2] in which polymer spreads and links the nonadhesive particles. Recently, the elastomeric binder, styrene–butadiene (ST–BD) copolymer, has been widely used in commercial LIB for the anode instead of the PVdF binder [3–5]. Comparing with the PVdF binder, the elastomeric binder bonds the particles point to point [6, 7] that allows reducing the total amount of binder. As a result, the specific energy [capacity/the electrode weight (milliampere hour per gram)] is expected to increase by using the elastomeric binder. In addition, the use of water dispersion media in the case of elastomeric binders gives the environmental advantage compared with the PVdF binder, which based on toxic organic solvent such as N-methylpyrrolidine (NMP). This fact is especially important from the industrial-scale usage point of view.

It is assumed that the binder polymers have to have good mechanical adhesiveness, and they are considered as electrochemically nonreactive media. However, it is well known that gel–polymer electrolyte which is the polymer swollen by the electrolyte solution exhibits some of Li$^+$

conductivity [8–14]. Thus, it is expected that the binder polymer also absorbs the electrolyte solution and shows Li$^+$ ionic conductivity. Because the binder polymer is in direct contact with the active material particles in electrode, the ion exchange between the active material and the binder polymer would take place as well as between the active material and the electrolyte solution. Therefore, it is presumable that the ionic conductivity of the binder polymer gives significant impact to electrochemical performance for LIB. Despite of this, no systematic study on the clarification of the dependence of the electrochemical performance of battery on the ionic transport in binder has been done so far.

In this paper, the Li-ion transport mechanism in the elastomeric binder swollen by the electrolyte solution was presented. In addition, the electrochemical performance was investigated in terms of ionic conductivity of the elastomeric polymer binder.

Experimental

The polymer films were made from ST–BD random copolymer (ST–BD=60/40), 2-ethylhexyl acrylate–acrylonitrile (2EHA–AN) random copolymer (2EHA–AN=85/15, 75/25), and PVdF. ST–BD copolymer and 2EHA–AN copolymer were dispersed in distilled water, while PVdF was dissolved in NMP. And then, the ST–BD and the 2EHA–AN polymer solutions were dried in the atmosphere at room temperature for 2 days, and uniform polymer film was formed. These films were dried in the vacuum oven for more than 5 h at 110 °C to remove solution agent. To confirm the residual water, these films were dried again for 72 h at 110 °C under the vacuum condition. No marked difference was observed in the mass before and after additional drying. Thus, it was confirmed that the water was removed by the first drying. The obtained polymer films were swollen by soaking into electrolyte solution for 24 h in Ar-filled glove box (dew point −76 °C). The electrolyte solution was 1 M LiPF$_6$ in the mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) with the volume ratio of EC/DEC=1/2. Hereunder, "dry binder"

and "binder electrolyte" refer to the polymer binder before and after soaking electrolyte solution, respectively.

The electrochemical stability of each binder was measured by cyclic voltammetry technique. Glassy carbon disk electrodes with a 3-mm diameter were used as working electrode. The electrode surface was polished with an alumina suspension (particle size, 100 nm) on a wool cloth. The electrode was cleaned and rinsed with water and acetone under a supersonic wave. Each binder was cast on the glassy carbon and dried for more than 1 h at 100 °C in the vacuum oven. The weight of binder cast on the electrode was about 10 mg. The counter electrode and reference electrode were Li metal on Ni wire. Cyclic voltammetry was carried out in the electrolyte solution (1 M LiPF$_6$ in the mixture of EC/DEC=1/2) at 25 °C with a computer-controlled potentiostat (HSV100, Hokuto Denko). The potential range was from 3.0 to 4.3 V, and the sweep rate was 0.1 mV/s.

The ionic conductivity of the binder-electrolyte film was measured by the AC impedance technique using a computer-controlled Hewlett-Packard 4192A LF impedance analyzer over the frequency range from 5 Hz to 13 MHz. The binder-electrolyte films were cut into disks of 8 mm in diameter, sandwiched between stainless-steel electrodes (SUS304), and subjected to the impedance analysis, which were performed by heating in the range of temperatures from 10 to 56 °C with intervals of 10 °C.

Thermal property of the obtained binder-electrolyte samples was examined by differential scanning calorimetry (DSC) using DSC6200 (Seiko Instruments). The samples in an aluminum pan was cooled at −120 °C and then heated at 100 °C. An empty aluminum pan was used as a reference.

The cathode electrodes consisted of LiCoO$_2$ as an active material, acetylene black as an electronically conductive additive, and ST–BD, 2EHA–AN copolymer, or PVdF as a binder. In the elastomeric polymers, carboxylmethyl cellulose was added, and the mixture was dispersed into slurry by distilled water. In PVdF, NMP was added to disperse. These slurries were cast onto Al foil. After drying, the sheets were pressed and used for measurements. Coin-type cells (CR2032) were assembled using Li metal as the counter electrode. The cell was galvanostatically cycled at

Fig. 1 The Li$^+$ ion transport mechanism in the binder film (1) ion transfer through the electrolyte, (2) ion transfer by the bulk structure of binder particle, and (3) ion transfer as a condenser
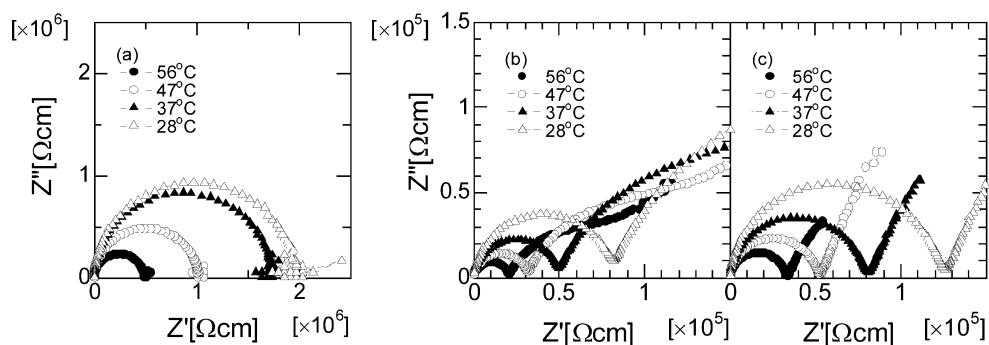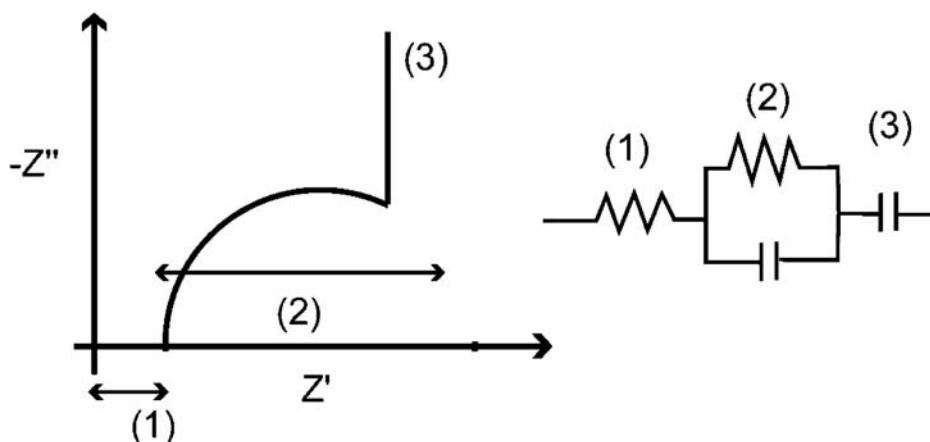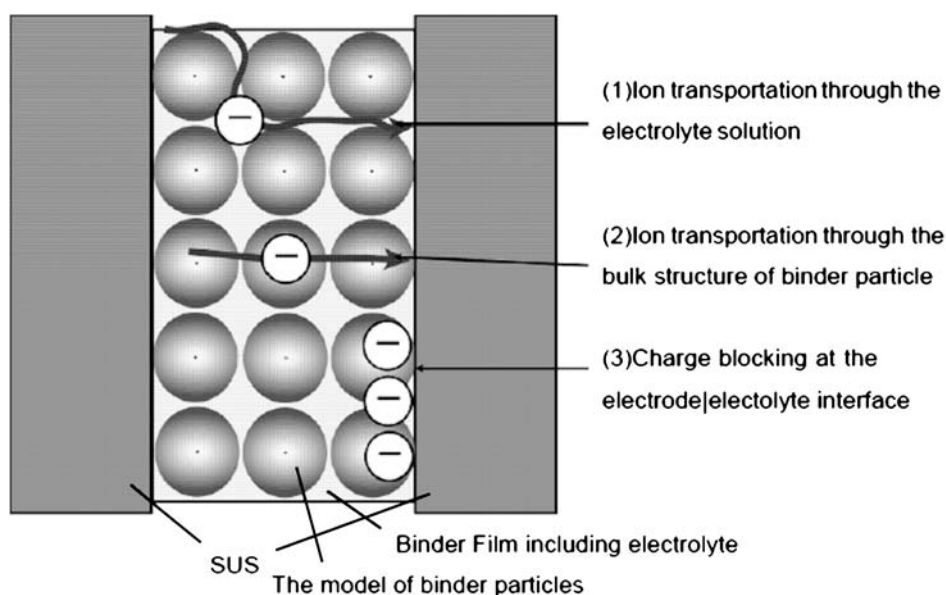
Fig. 2 Impedance plots of **a** ST–BD copolymer, **b** 2EHA–AN copolymer (2EHA–AN= 85/5), and **c** 2EHA–AN copolymer (2EHA–AN=75/25) in 1 mol dm^{-3} LiPF$_6$/EC+DEC

(1)Ion transportation through the electrolyte solution

(2)Ion transportation through the bulk structure of binder particle

(3)Charge blocking at the electrode|electolyte interface

Binder Film including electrolyte

SUS

The model of binder particles

room temperature with charge–discharge cut-off voltage of 4.3V/3V vs Li$^+$/Li electrode.

Results and discussion

Li concentration in each binder film was measured by the inductive coupled plasma (ICP) technique. The results showed that Li content in the ST–BD copolymer was 810 mg/g (per binder film), whereas that in the 2EHA–AN copolymer was 3,000–3,300 mg/g (per binder film). Thus, lithium salts can reside in both ST–BD and 2EHA–AN copolymers swollen by electrolyte solution, suggesting that these binder electrolytes offer additional pathway of ionic conduction. The electrochemical stability of each binder was almost the same as the stability in the potential range between 3.0 and 4.3 V (vs Li/Li$^+$). The current density at 4.3 V of without binder was less than 1.4×10^{-4} A/cm^2, and
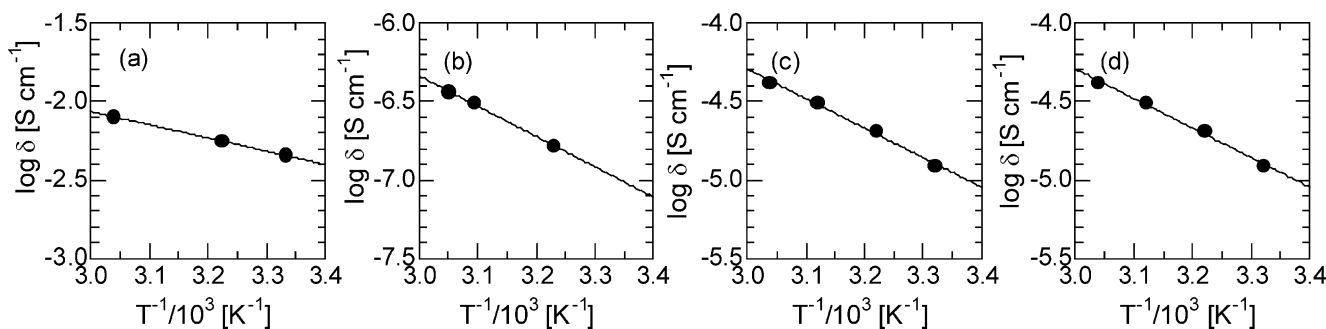

Fig. 3 Arrhenius plots of ionic conductivity for each binder polymer

Table 1 The ionic conductivity at 30 °C and Arrhenius parameters of ionic conduction for (a) electrolyte (EC/DEC=1/2, 1 M LiPF$_6$), (b) ST–BD copolymer, (c) 2EHA–AN copolymer (2EHA–AN=85/15), and (d) 2EHA–AN copolymer (2EHA–AN=75/25)

		Li concentration [μg/g]	σ [S/cm]	E_a [eV]
(a) Electrolyte			7.90E-03	0.093
(b) ST–BD copolymer	ST–BD= 60/40	810	9.40E-08	0.319
(c) 2EHA–AN copolymer	2EHA–AN= 85/15	3,300	1.20E-05	0.256
(d) 2EHA–AN copolymer	2EHA–AN= 75/25	3,000	8.00E-06	0.272

that of each binder was from 8.8×10^{-5} to 2.9×10^{-4} A/cm^2. These data indicate that these binders were electrochemical stabile in the range of 3.0 to 4.3 V at 25 °C.

Figure 1 presents the impedance plots for each binder electrolyte. Single semicircle was observed in the frequency range of 10~100 kHz being ascribed to the ionic conduction in bulk of binder electrolyte. In the following low-frequency region, a spike was observed and would be due to the capacitance of electric double layer formed at the electrode | electrolyte interface. It can be seen that the 2EHA–AN-based polymer electrolyte exhibited the room temperature conductivity in the range of 10^{-4}~ 10^{-5} S·cm^{-1} that is three to four times higher than that

of ST–BD copolymer-based electrolyte. This is in good agreement with ICP measurement that indicated the three to four times higher lithium concentration in the 2EHA– AN copolymer compared with the ST–BD one, i.e., the higher charge carrier content results in the higher ionic conductivity. Therefore, it is suggested that the two conceivable ion transport mechanisms, where ionic conductivity is proportional to the salt concentration, are as follows: (1) ion migrates through the cavity among binder polymers, and/or (2) ion migrates through the binder polymer bulk via interaction with the polymer chains (see Fig. 2).

To ascertain the above transport mechanisms, the activation energy of ionic conduction was evaluated from the Arrhenius plots of conductivity (Fig. 3). Table 1 summarizes the Li$^+$ concentration, ionic conductivity, and activation energy for each binder electrolyte. The Li-ion conductivity and the activation energy closely relate to the Li$^+$ content in binder-electrolyte film as mentioned above. The activation energy of the samples was different in each case, so that the assumption (2), where ion migrates through the bulk of polymer, could be verified. In the case of assumption (1), the ion transports through the liquid electrolyte in the micropores of the polymer matrix and the same range activation energy may be expected due to the use of the same electrolyte solution. Furthermore, this implies the picture that the polymer chains capture the liquid electrolyte, resulting in the plasticizing or hardening of their framework structure.

Fig. 4 DSC curves of ST–BD copolymers **a** without electrolyte, **b** with electrolyte (0.5 mol dm^{-3} LiPF$_6$, EC/DEC=1/2), and **c** with electrolyte (1.0 mol dm^{-3} LiPF$_6$, EC/DEC=1/2)
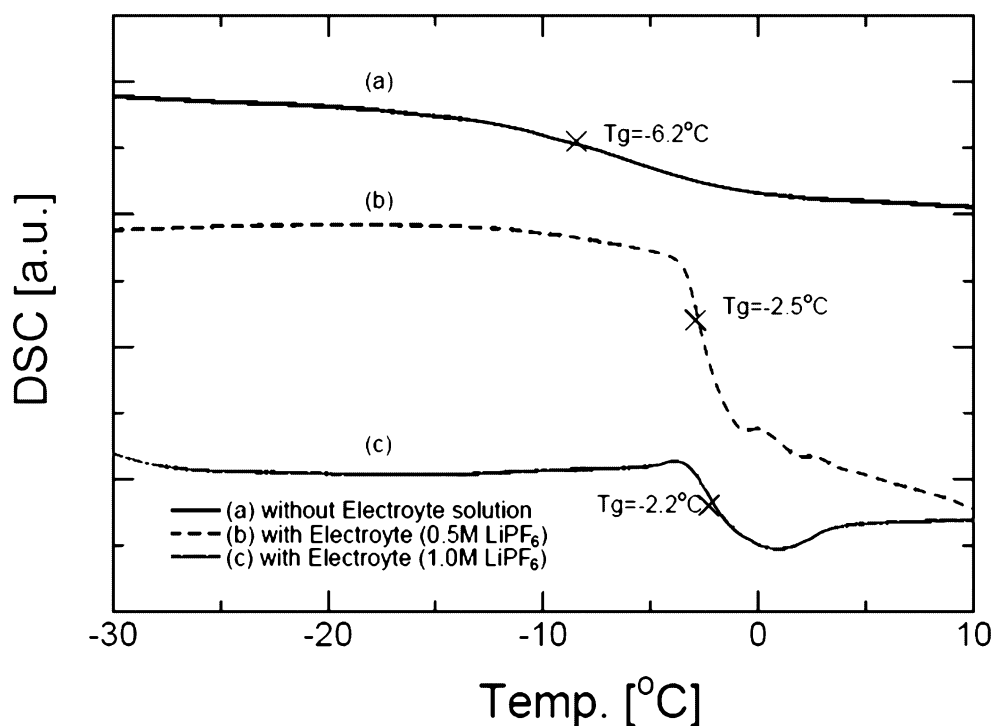
Table 2 The glass transition temperatures of ST–BD copolymers (a) without electrolyte, (b) with electrolyte (0.5 M LiPF$_6$, EC/DEC=1/2), and (c) with electrolyte (1 M LiPF$_6$, EC/DEC=1/2)

The content of lithium salt [M]	T_g (°C)
(a) 0	−6.2
(b) 0.5	−2.5
(c) 1.0	−2.2

It is known that the glass transition temperature T_g of polymer is affected by the degree of plasticizing or hardening, or the changes in the framework of polymer can be clarified by measuring T_g. The thermal properties of the polymer were investigated using DSC, and the results are shown in Fig. 4. T_g was taken at the center of the slope of heat flow, which appeared at around −5 °C, and the estimated T_g of the polymer electrolytes are summarized in Table 2. The T_g increased by swelling in electrolyte solution, indicating that a hardening occurred. The T_g

Fig. 5 a The first charge–discharge curves of the LiCoO$_2$ electrode using different binders. **b** Magnification of the charge curves (initial part): *1* ST–BD copolymer, *2* 2EHA–AN copolymer (2EHA–AN=85/15), *3* 2EHA–AN copolymer (2EHA–AN=75/25), and *4* PVdF
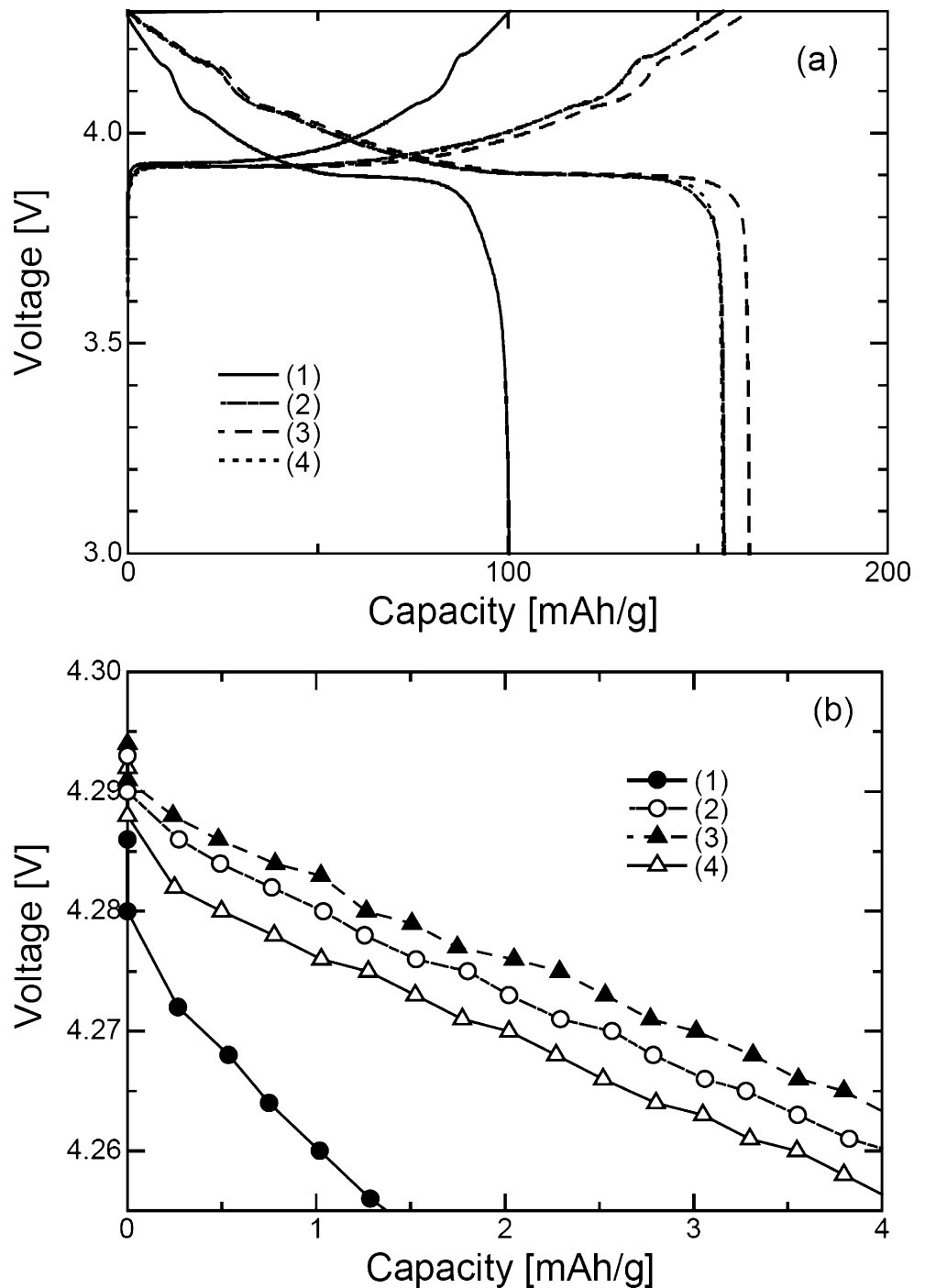
seems to be independent of the salt concentration, so that the hardening mainly arises from the liquid molecules of solvent (EC/DEC). The hardening indicates suppression of polymer mobility by the interaction between the liquid molecules of solvent and polymer.

As mentioned above, the binder polymers showed an ionic conduction due to swelling by electrolyte solution although the contribution of the bulk ionic conductivity of the binder is generally unregarded. Because the binder connected directly to the active materials of electrodes, it is presumable that the Li^+ ion exchange takes place in the interface of electrode | binder polymer as well as that of the electrode|liquid electrolytes. If so, the higher the ionic conductivity in binder electrolyte, the better electrochemical performance is expected.

To clarify the above suggestion, the electrochemical performance of the cathode material, $LiCoO_2$, consisting of various binders, ST–BD copolymer, 2EHA–AN copolymer, and PVdF, was investigated. Typical charge–discharge curves of Li/$LiCoO_2$ electrodes are shown in Fig. 5a. Again, one to one correspondence was observed between charge–discharge capacity and Li ionic conductivity, where initial charge–discharge capacity of the $LiCoO_2$ electrode with 2EHA–AN copolymer showed highest capacity.

The variation of the cell voltage at the initial part of the first charging were shown in Fig. 5b. The difference of cell voltage was observed with respect to the binder. The results showed that the larger the cell voltage at the same state of charge was, the lower ionic conductivity of lithium was presented in binder electrolyte. Therefore, the lower polarization would be attainable by using the binder with high lithium ionic conductivity. Maybe, high Li^+ conductivity made the Li ions concentrated at the interface of binder | electrolyte, leading to decrease the polarization.

Conclusions

The Li ion transport mechanism in the binder electrolyte films has been evaluated. Based on the values of activation energy of the ionic conduction, it is suggested that Li-ion transport takes place through the bulk polymer structure. One to one correspondence was obtained that the larger the amount of swollen solvent in the binder was, the higher ionic conductivity of lithium showed. The same relationship was found for the electrochemical performances: the higher the ionic conductivity of lithium in binder electrolyte, the larger the charge–discharge capacity. Accordingly, the present study showed the availability of designing the elastomeric binder with high lithium ionic conductivity.

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