

Short communication

Enhancement of electrochemical performance of lithium dry polymer battery with LiFePO_4 /carbon composite cathode

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Abstract

LiFePO_4 /carbon composite electrode was prepared and applied to the dry polymer electrolyte. Enhanced low-temperature performance of LiFePO_4 was achieved by modifying the interface between LiFePO_4 and polymer electrolyte. The molecular weight of the polymer and the salt concentration as the Li/O ratio were optimized at 3×10^5 and 1/10, respectively. Impedance analysis revealed that a small resistive component occurred in the frequency range of the charge transfer process. The reversible capacity of the laminate cell was 140 mAh g^{-1} (C/20) and 110 mAh g^{-1} (C/2) at 40°C , which is comparable to the performance in the liquid electrolyte system.

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1. Introduction

The lithium ion battery can be considered to be a container holding a large amount of energy, and a number of studies have attempted to enhance the energy density of the lithium ion battery. However, at the same time, the remarkable advantages of the lithium ion battery can be a practical problem. If a device can contain higher energy, there is a higher risk of fire explosion. Therefore, safety is a key issue for future applications of the lithium ion battery such as large-scale batteries for electric vehicles and load leveling devices. In order to overcome this problem, the development of all-solid state batteries using a solid electrolyte may be one solution.

Inorganic and organic solid electrolytes have been examined for their potential application in a lithium ion battery. Li_3N [1], $\text{La}_{0.5}\text{Li}_{0.5}\text{TiO}_3$ [2], $\text{Li}_{3.6}\text{Si}_{0.6}\text{P}_{0.4}\text{O}_4$ [3], and LIPON [4] are inorganic lithium ionic conductors. Kanno et al. reported a series of sulfide-type lithium conductors called thio-LISICON, among which $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ shows the highest conductivity of $2.2 \times 10^{-3} \text{ S cm}^{-1}$ at 25°C [5]. On the other hand, as an organic solid electrolyte, polyethylene oxide (PEO)-based polymer has

been widely studied. The fire-resistant characteristics as well as the softness and flexibility of PEO will likely encourage new applications such as wearable devices and flexible displays. The construction of a cell using polymer electrolyte is simpler than that using ceramic electrolyte, because no special attention is necessary to maintain contact between ceramic powders inside the cell. Therefore, we have studied the dry polymer/electrode system for a safer lithium ion battery.

In using a polymer electrolyte, there is a voltage limitation in the positive electrode side. Conventional cathodes such as LiCoO_2 and LiMn_2O_4 , which operate at around 4.0 V, are difficult to use stably with PEO electrolyte [6]. Another reversible electrode material, LiFePO_4 is known to be safe at elevated temperatures [7,8]. In addition, this material shows a reversible electrode potential of around 3.5 V compared to lithium, which is appropriate for use with gel-type polymer electrolyte [9,10]. Note also that LiFePO_4 comprises abundant elemental iron, which is environmentally favorable. Among the cathodes, LiFePO_4 is considered as a candidate for the positive electrode of the dry polymer lithium ion battery [11–13].

However, polymer electrolyte has a significant drawback in that it has poor ionic conduction near room temperature. The study of the dry polymer battery using PEO as a host polymer has been usually performed above 60°C , which corresponds to the melting point of pure PEO. Not only the bulk of the elec-

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trolyte, but also the interface between electrolyte and electrode is the main constituent of the internal resistance. The reduction of this interface resistance is important because the charge transfer resistance becomes relatively larger when preparing a thin-film battery [14–16].

In the present study, the reduction of the operating temperature of LiFePO_4 electrode in the dry polymer electrolyte system has been attempted by optimizing the interface structure. In order to characterize the interface, the internal cell resistance was estimated and separated into individual processes by the impedance technique. The details of each process were discussed, and the enhanced electrochemical performances below 60°C were described.

2. Experimental

LiFePO_4 as a positive electrode was prepared in the form of a composite with carbon material. Li_2CO_3 , $(\text{NH}_4)_2\text{HPO}_4$, and $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ were mixed in a 1:2:2 molar ratio, and 6.0 g of the mixture and 0.6 g of polyvinyl chloride (PVC) as a carbon precursor were mixed in tetrahydrofuran (THF). The suspension was dried and pressed into tablet form. The tablet was heated in two steps. The first calcination was performed at 350°C for 6 h under a nitrogen atmosphere. At this temperature, PVC decomposes and becomes a carbonaceous material. The product was then crushed and ground well with new PVC powder at a weight ratio of 8:2. The mixture was annealed again at 700°C for 16 h under a nitrogen atmosphere to obtain the final composite product of LiFePO_4/C . The formation of crystalline LiFePO_4 was identified by X-ray diffraction (XRD) analysis.

LiFePO_4/C and polyvinylidene fluoride (PVDF) at a 9:1 weight ratio were mixed in *N*-methyl-2-pyrrolidone (NMP) and then spread on aluminum foil. The film was dried in air at 80°C for 1 h, pressed, and dried under a vacuum at 120°C for 1 h. The film thickness after the drying process reached approximately 40–70 μm , and the active electrode area was 2.25 cm^2 ($1.5\text{ cm} \times 1.5\text{ cm}$).

The PEO-based polymer was prepared as a separating electrolyte. PEO (Aldrich, average molecular weight: 3×10^5 , 6×10^5 , or 9×10^5) and $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ (LITFSI, Fluka) were dissolved in acetonitrile (AN) with Li/O at a molar ratio of 1/18 or 1/10. A polymer electrolyte solution was cast in a PTFE dish under an argon atmosphere. After the evaporation of AN at room temperature, the film was dried at 100°C for 12 h under a vacuum. The resulting film thickness was approximately 100 μm .

The porous LiFePO_4/C film electrode was impregnated with PEO electrolyte by casting an acetonitrile solution of the electrolyte under a depressurized condition. The impregnated electrode was dried under an argon stream at room temperature and then under a vacuum at 100°C overnight. After that, the polymer electrolyte sheet was placed onto the positive electrode mixture, and a lithium metal sheet was placed on the other side as a negative electrode. The entire system, Al/ $\text{LiFePO}_4/\text{PEO}$ sheet/ Li/Cu , was sealed into a laminate cell for the electrochemical test.

A two-electrode laminate cell was galvanostatically charged and discharged under a current density of $25\ \mu\text{A cm}^{-2}$ (approx-

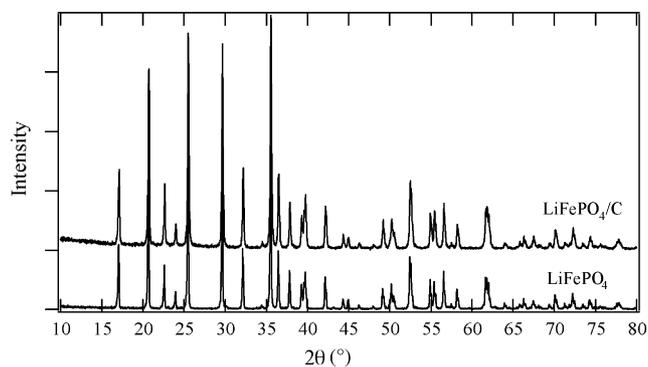


Fig. 1. X-ray diffraction patterns of composite material of $\text{LiFePO}_4/\text{carbon}$ and single-phase LiFePO_4 . Cu $\text{K}\alpha$ line generated under 40 kV and 150 mA. Continuous scanning was performed at a speed of 1° min^{-1} .

imately 6 mA g^{-1} and C/20 rate), a cut-off voltage range of 4.1–2.5 V, and at a temperature of 40 or 50°C . The impedance measurement was used to estimate the interface resistance. An ac perturbation of 10 mV was applied in the frequency range from 1×10^6 to 0.5 Hz by a Solartron 1260 frequency response analyzer. The temperatures were controlled from 20 to 60°C in order to obtain the Arrhenius plots.

3. Results and discussion

The X-ray diffraction pattern of the prepared LiFePO_4/C composite is shown in Fig. 1. Comparison with the reference pattern reveals that all of the peaks are assigned to genuine LiFePO_4 and no peaks of other phases are observed. It is confirmed that the LiFePO_4 and carbon composite was prepared without any residual side reactions. The carbon content in LiFePO_4/C composite was estimated to be approximately 10 wt% by elemental analysis using a CHN CORDER MT-5 (Yanaco). A TEM photograph of the composite product is shown in Fig. 2. A single particle of LiFePO_4 shows a clear lattice image. On the surface, there is an amorphous layer showing a degraded image, which is considered to be a carbonaceous material. This photo shows the composite structure of crystal LiFePO_4 and amorphous car-

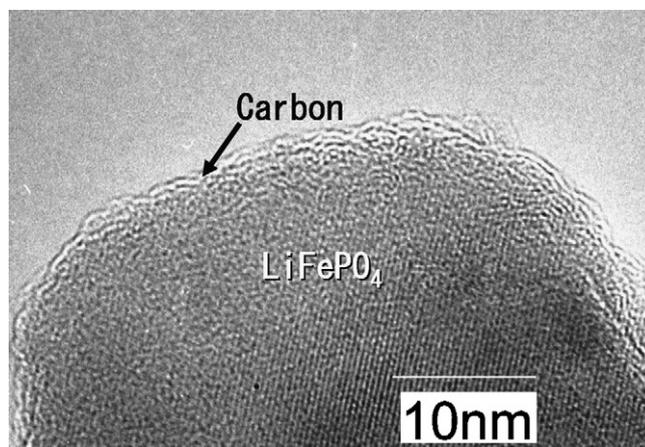


Fig. 2. TEM photograph of the product prepared from Li_2CO_3 , $(\text{NH}_4)_2\text{HPO}_4$, FeC_2O_4 , and polyvinyl chloride. The photograph was captured using a Hitachi H-9000 at an accelerating voltage of 300 kV.

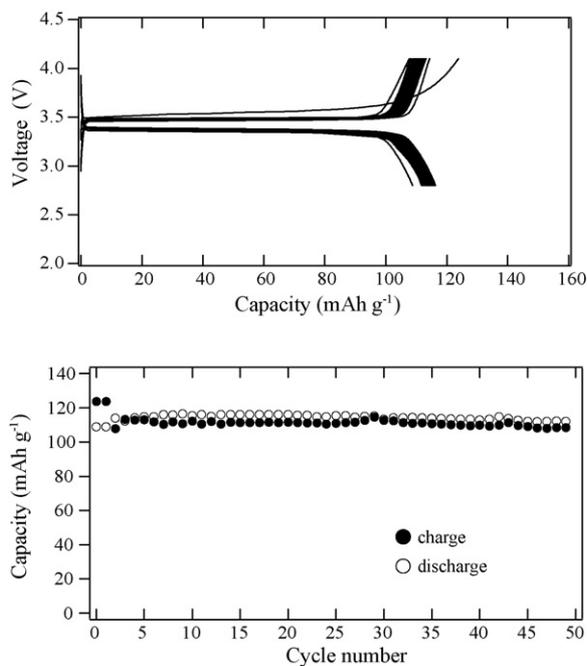


Fig. 3. Charge and discharge curves (above) and cycling behaviour (below) of the LiFePO₄/C composite electrode in 1 M LiClO₄ in an EC-DEC liquid electrolyte system. The current density was C/10 (approximately 50 μA cm⁻²), and a two-electrode laminate cell was used as the test cell.

bon. The electrochemical characterization of the composite was examined using 1 M LiClO₄ dissolved in ethylene carbonate and diethyl carbonate (50:50 vol%) as the liquid electrolyte, which was purchased from Kishida Chemical Co. Ltd. Fig. 3 shows the charge and discharge curves measured at room temperature and the change in capacity in the first 50 cycles. The capacity was calculated for 1 g of the composite. The LiFePO₄/C electrode shows a good capacity retention of over 99.9% per cycle in this liquid electrolyte system. The excellent reversibility of the composite electrode suggests that the carbon around the LiFePO₄ particles provides a good electronic network and compensates for the poor electronic conductivity of the active material. The theoretical capacity of the composite is calculated to be 153 mAh g⁻¹, assuming that the carbon content is 10 wt%. The observed capacity is still smaller than this calculated value. The small capacity of the composite can be accounted for by the occurrence of Fe³⁺ without changing the crystal structure [17].

Fig. 4 shows the charge/discharge behaviours of the LiFePO₄/C composite electrode with PEO polymer electrolyte at 50 °C. The capacity of 100 mAh g⁻¹ is approximately equivalent to that of the liquid electrolyte system. This performance depends greatly on the dimensions of the electrode with approximately 3 mg of active material per 2.25 cm², provides rather thin film morphology. However, our preliminary results [18] indicate that insertion materials such as graphite or silicon show much less capacity at 50 °C. The behaviour shown in the figure is considered to be specific to LiFePO₄. The capacity change with the cycle number indicates that stable charge and discharge behaviour can be maintained during the first 50 cycles. After the second cycle, the capacity retention was calculated to be greater than 99.8% per cycle, and little capacity fading was observed.

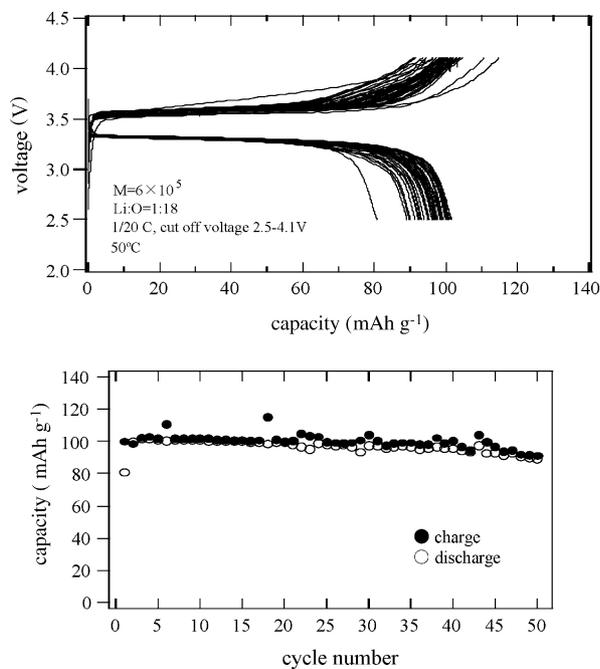


Fig. 4. Charge and discharge curves (above) and cycling behaviour (below) of LiFePO₄/C composite electrode in a solid polymer electrolyte system at 50 °C. The current density was C/20 (approximately 25 μA cm⁻²), and a two-electrode laminate cell was used as the test cell.

This performance is attributed to the interfacial contact between LiFePO₄ and PEO polymer. The surface of LiFePO₄ is considered to have good wettability by PEO polymer or good chemical affinity to the polymer. The fact that LiFePO₄ is not charged beyond the electrochemical window of PEO electrolyte also works to maintain stable cycling.

Next, the influence of the different molecular weights of PEO is examined. Fig. 5 shows the first voltage curves with different polymers at 40 °C. The capacity strongly depends on the molecular weight of PEO, and the electrolyte with lower molecular weight has better charge–discharge properties. This behaviour is interpreted as being caused by a combination of several factors. One is the structure of the solid–solid interface. The interface between the electrode and the hard electrolyte with Mw = 9 × 10⁵ consists mainly of a point contact, while the soft

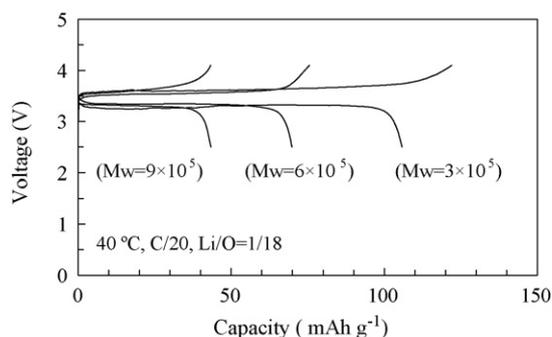


Fig. 5. Charge and discharge curves of LiFePO₄/C in the polymer electrolyte system. Comparison among molecular weights of PEO polymer of 3 × 10⁵, 6 × 10⁵, and 9 × 10⁵. The Li/O ratio was fixed at 1/18, and the temperature was adjusted to 40 °C.

electrolyte with $M_w = 3 \times 10^5$ should have a larger contact area. The difference in the actual interfacial areas leads to the different current densities and polarizations. The ionic conductivities of each polymer were measured in order to discuss the influence of ionic conductivity on performance. The conductivities of electrolytes at 40 °C with $M_w = 9, 6, 3 \times 10^5$ were 5.24×10^{-5} , 4.04×10^{-5} , and $4.89 \times 10^{-5} \text{ S cm}^{-1}$, respectively. Since the values are similar, ionic conductivity is assumed not to be the main reason for the different capacities. It is thought that the intercalation is not controlled by the mass transfer process under the present experimental condition. Uchimoto et al. reported that the charge transfer resistance is dependent on the relaxation of the electrolyte solvent using polyethylene glycol dimethyl ether [19]. Although the polymers used in the present study have molecular weights that are several orders of magnitude higher than those examined by Uchimoto et al., their theory may explain our results.

Fig. 6 shows the influence of salt concentration in the same host polymer ($M_w = 9 \times 10^5$) at 40 °C. The electrolyte with a Li/O molar ratio of 1/10 shows a higher performance in that the discharge capacity becomes approximately 1.5 times larger than the standard 1/18 electrolyte. According to our conductivity measurement, PEO with Li/O at 1/10 shows a higher ionic conductivity than 1/18 at 40 °C, which suggests that the higher ionic conductivity results in lower interface resistance. It is also possible to apply the same explanation as in the case of the discussion on molecular weight. The electrolyte with Li/O = 1/10 has a soft nature because it contains more plasticizing imide salt. The effects of molecular weight and salt concentration in Figs. 5 and 6 only appear at low temperatures. At temperatures above 60 °C, these effects may be cancelled by strong segmental motion of polymer chains.

The interface resistance was analyzed by measuring impedance spectra. Since it is difficult to set a reference electrode in a polymer cell, the symmetrical cell $\text{LiFePO}_4/\text{PEO}$ electrolyte/ LiFePO_4 was constructed to remove the contribution of lithium electrode. The molecular weight of the PEO used herein is 6×10^5 and the Li/O ratio is fixed at 1/10. In this cell, the detectable components should be an interface between PEO and LiFePO_4 , a bulk of PEO, and another bulk of LiFePO_4 . The typical spectrum is shown in Fig. 7, in which there are four major components. These components are simple ohmic resistance

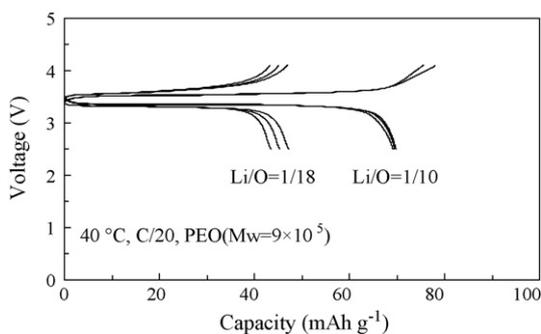


Fig. 6. Charge and discharge curves of LiFePO_4/C in the polymer electrolyte system with salt concentrations of 1/18 and 1/10. The polymer molecular weight was fixed at 9×10^5 , and the temperature was adjusted to 40 °C.

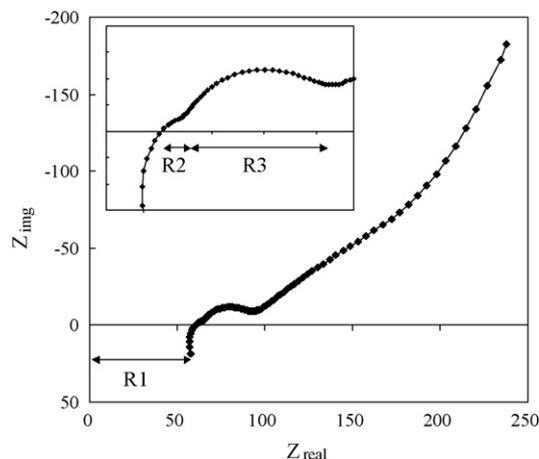


Fig. 7. Complex impedance plot (Cole–Cole plot) of the symmetrical cell, $\text{LiFePO}_4/\text{PEO}$ electrolyte/ LiFePO_4 . The inset shows the enlarged spectrum of the high-frequency region. There are three components, which are designated R1, R2, and R3 (see text). The low-frequency area showing a slope and capacitive behaviour is considered to be caused by ionic diffusion in the polymer inside the electrode.

(R1), semicircles of two different sizes (R2, R3), and a straight line with a 45° slope indicating diffusion. The component that appears at the highest frequencies corresponds to the sum of the ionic resistance of PEO and the electronic resistance of LiFePO_4 . On the other hand, the slope appearing in the lowest frequency region can be attributed to the lithium diffusion in the infiltrated PEO electrolyte inside the micro-pores of the electrode. In some cases, the spectrum shows a clear capacitive character following the slope. This is due to the finite diffusion length being limited by the thickness of the cast electrode layer. One of the two semicircles appears in the frequency range from 10^4 to 10^3 Hz. In general, the charge transfer reaction of the electrode has a time constant in this frequency range. Thus, the resistance of lithium intercalation at the interface between LiFePO_4 and PEO is assigned to this larger semicircle (R3). Another small semicircle is located around 10^5 Hz. The frequency range shows a fairly fast charge transfer with a small relaxation time. This component R2 is thought to be part of a series of interfacial ionic transfer processes, such as ionic adsorption and surface diffusion. However, no experimental evidence for identification was obtained in the present study.

The resistance values of R1, R2, and R3 were obtained by fitting the experimental data to the equivalent circuit, which is composed of a serial combination of R1 and two RC pairs consisting of a resistor connected in parallel with a capacitor. Arrhenius plots of these resistances are shown as a function of temperature in Fig. 8. The resistance R1, which consists mainly of the polymer electrolyte, shows a slightly bent line, which is characteristic when the salt concentration Li/O is fixed at 1/10. The bending point is located around 35 °C, which corresponds to the crystallization (melting) temperature of polymer bulk. R3 is considered to be the charge transfer resistance of LiFePO_4 , and the small R2 resistance results in the sharp bend in the plot at approximately 40 °C. This change is also considered to stem from the crystallization of the polymer. The magnitude of the charge transfer resistance of R3 is controlled by the nature of the

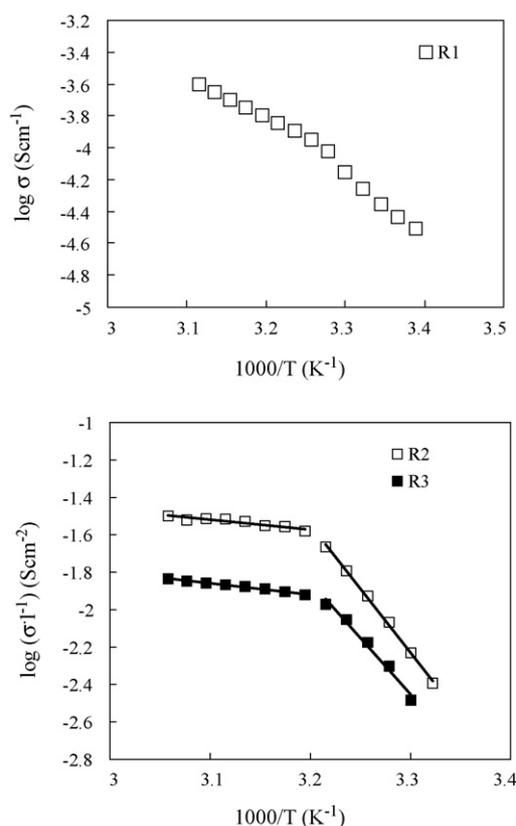


Fig. 8. Arrhenius plots of R1, R2, and R3. Data were recorded every 2 °C between 20 and 60 °C in the direction of heating. The conductivity values of the R2 and R3 component are expressed in the unit of $S\text{ cm}^{-2}$, because they refer to the interface.

polymer, whether in liquid or solid form. The activation energies are estimated, and they summarized in Table 1. The energy of charge transfer is only approximately 10 kJ mol^{-1} above 40 °C, which is surprisingly small, and this value is comparable to the values measured in the liquid electrolyte system. This data explains the good charge–discharge performance shown in Fig. 4 and indicates that the $\text{LiFePO}_4/\text{PEO}$ system can operate at temperatures down to 40 °C. The activation process in the charge transfer in the liquid electrolyte system is considered to be caused by the desolvation of lithium ions at the interface, and the activation energy of the process is calculated to be approximately 50 kJ mol^{-1} [20]. The small activation energies in Table 1 suggest that the lithium ion phase transfer proceeds without complete desolvation. Note also that the Arrhenius plot of R2 has the same profile as R3, which supports the idea that R2 is a process at the electrode/electrolyte interface.

Table 1
Activation energies of the component R2 and R3 are calculated based on the plots shown in Fig. 8

	Activation energy (40–54 °C) (kJ mol^{-1})	Activation energy (28–38 °C) (kJ mol^{-1})
R2	10.2	130.5
R3	11.6	115.2

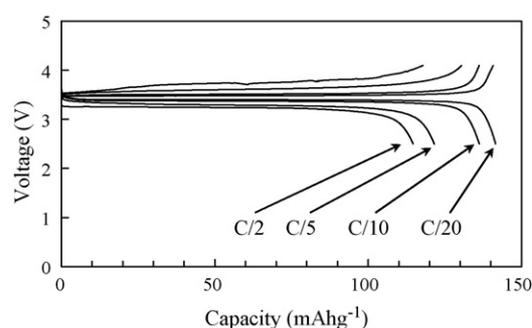


Fig. 9. Rate performance of the optimized positive electrode system measured at 40 °C. The LiFePO_4/C composite electrode was combined with the polymer electrolyte in which the molecular weight of PEO was 3×10^5 and the Li/O ratio was fixed at 1/10. VGCF was used as a conducting agent.

The high-rate performance at 40 °C was examined for the composite cell system after optimization such that the molecular weight of PEO was chosen at 3×10^5 and the Li/O ratio was set to be 1/10. For the electrode preparation, another new procedure was adopted whereby LiFePO_4/C , vapor-grown carbon fiber (VGCF; Showa Denko), and polymer electrolyte were mixed at 4:1:5 wt%. VGCF as a conducting agent is a graphitized carbon having a diameter of 150 nm and a length of 10–20 μm . The one-dimensional fiber morphology can act as a good current conductor, even in the thicker electrode. No polymeric binders were included because the PEO electrolyte can work to hold the film in a solid shape. The mixture in AN was cast on the aluminum foil and then dried at room temperature in the argon-filled glove box. After being cut into the desired dimensions, the mixture was dried at 120 °C under a vacuum for 12 h in order to remove AN completely. Other components of the laminate cell are subjected to the same conditions.

The charge–discharge performances of the optimized electrode at 40 °C are shown in Fig. 9. The capacity at C/20 is 140 mAh g^{-1} , which is comparable to the maximum capacity in the liquid electrolyte system. At C/2, the reversible capacity is greater than 100 mAh g^{-1} . Such high capacity under the high rate with a dry polymer electrolyte at 40 °C is remarkable. These performances show the potential possibility of an all-solid lithium ion battery containing the LiFePO_4 positive electrode and polymer electrolyte. Furthermore, the optimization of the interface is expected to lead to the enhancement of low-temperature performance.

4. Conclusion

As the positive electrode of a dry polymer lithium ion battery, LiFePO_4 and carbon composite material was revealed to provide promising performance. This is attributed to the particularly low activation energy between LiFePO_4 and PEO electrolyte in the liquid phase. This unique interface allows considerable opportunity for modification, and a consequent improvement in the charge transfer rate. If the crystallization temperature of the component R3 is further reduced, an all-solid state polymer battery, which operates practically at room temperature, can be realized. However, softening of the polymer electrolyte results in a safety

problem. It is important to develop a total cell system to reconcile the good compatibility of electrode/electrolyte and adequate safety at the same time.

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