Significant effects of poly(3,4-ethylenedioxythiophene) additive on redox responses of poly(2,5-dihydroxy-1,4-benzoquinone-3,6-methylene) cathode for rechargeable Li batteries

Noboru Oyama [a,*], Tomoo Sarukawa [a,b], Yasumasa Mochizuki [a], Takeshi Shimomura [a], Shuichiro Yamaguchi [a]

[a] *Tokyo University of Agriculture and Technology, Graduate School of Science and Technology, Department of Applied Chemistry, 2-24-16 Naka-cho, Koganei, Tokyo 184-8588, Japan*
[b] *Subaru Technical Research Center, Fuji Heavy Industries Ltd., Japan*

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ABSTRACT

Redox behaviors of the poly(2,5-dihydroxy-1,4-benzoquinone-3,6-methylene) (PDBM)-coated electrodes composited with carbon black (CB) or poly(3,4-ethylenedioxy-thiophene) (PEDOT) are presented. Effects of PEDOT additive on the redox activity of PDBM were investigated to apply their composite materials as candidates of cathodes for rechargeable lithium batteries. The film having a PEDOT/PDBM with weight ratio of 1/1 shows a gravimetric capacity of 129 mAh g^{-1} (corresponding to 188 mAh g^{-1} for PDBM and 70 mAh g^{-1} for PEDOT). The highest energy density observed was 140 mAh g^{-1} (406 mWh g^{-1}) for the composite cathode. Good cycle-ability over 100 cycles was attained with a PEDOT/PDBM composite cathode.

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1. Introduction

Organic conducting polymers such as polyaniline, polythiophene and polypyrrole have attracted considerable attention for a lithium secondary battery system [1]. However, the redox activity of these films is recognized to be accompanied by anion movement but not cation [2]. Therefore, in such a case a lot of electrolyte solution is usually necessary to maintain the concentration of the electrolyte constant during the charging processes. Thus, it is impossible to construct a lightweight battery [3].

As a redox reaction example with lithium ion movement among organic compounds, a redox couple of benzoquinone is well known. This redox couple can be suitably used for the cathode material of lithium secondary batteries with high energy density [4–8]. Recently, Gall et al. [9] have reported that a poly(quinone) derivative of poly(2,5-dihydroxy-1,4-benzoquinone-3,6-methylene) (PDBM) composited with 40% acetylene black (AB) demonstrates reversible redox cycle-ability with a specific capacity of 120–130 mAh g$_{PDBM}^{-1}$. Here, addition of AB provides the electron hopping conduction to the redox centers of

quinone moieties but does not rise in the energy density. In addition, their described PDBM, even if that is a polymer, changes to be soluble essentially in organic solvents by the reduction to the semi-quinone of PDBM under the discharge state. Therefore, the reduced PDBM necessitates the depression of solubility to improve the cycle-ability of the responses. The PDBM electrode still requires the additives to improve the feature of energy density, conductivity and solubility.

We have recently reported that a poly(3,4-ethylenedioxy-thiophene) (PEDOT), which is one of polythiophene derivatives, has not only provided the electron conduction [10], but also the energy storage ability [11] and an acceleration effect of the redox reaction of organo-electroactive moieties such as a thiol function group [12–14]. Furthermore, it is well known that PEDOT shows the redox responses in the wide potential range (2.0–4.0 V vs. Li/Li$^+$) [5], where PEDOT is partially cationic and PDBM is anionic. Thus, an electrostatic interaction between the anionic state of PDBM and the cationic state of PEDOT expects to depress the solubility of the reduced-state of PDBM into the electrolyte solution during the charge–discharge process. Therefore, instead of AB, the usage of PEDOT as an electro-conduction additive expects to an improvement of the characteristics for the quinone polymer cathode as follows: (a) gravimetric energy density, (b) electronic conductivity and (c) cycle-ability of the responses. In the present research,

* Corresponding author. Tel.: +81 423 83 4719; fax: +81 423 83 4719.
E-mail address: oyama@cc.tuat.ac.jp (N. Oyama).

their composite materials composed of benzoquinone polymer and conducting polymer of PEDOT are investigated as a candidate of cathode materials for lithium ion battery [3–5].

2. Experimental

2.1. Synthesis of poly(2,5-dihydroxy-1,4-benzoquinone-3,6-methylene) (PDBM)

2,5-Dihydroxy-1,4-benzoquinone was dissolved in warm glacial acetic acid. In this solution, the aqueous formaldehyde solution was added and then the mixture was stirred for 24 h. The yellow precipitate was collected by filtration, washed sufficiently with water and methanol and dried under vacuum, as like the synthetic procedure of Bakelite [15]. The yield of this polymer product was 31.9% and the average molecular weight was more than 3500 estimated by GPC measurement. The measurements of IR spectra and ^{13}C solid state NMR were used to characterize the product, the results of which indicated essentially the same as the polymer structure reported previously [9].

2.2. Synthesis of poly(3,4-ethylenedioxythiophene) (PEDOT)

The reactant of 3,4-ethylenedioxythiophene (EDOT) was dissolved in acetonitrile (AN). The transition metal salt ($Cu(BF_4)_2$) of an oxidant reagent was added in the solution and the mixture was stirred for 8 h. The brown precipitate was collected by filtration, washed thoroughly with AN and dried under vacuum. The yield of polymer product was 95.0%. The product was not dissolved in any organic solvents.

2.3. Electrochemical measurements

Cyclic voltammetry (CV) was carried out with a Hokuto Denko model HZ-3000 or HZ-5000 potentiostat/galvanostat. The voltammetric measurements were performed in a three-electrode cell configuration using a glassy carbon disk electrode (GCE) (BAS, diameter: 3.0 mm), a Pt coil counter electrode, and an Ag/Ag$^+$ (inner solution of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:2 vol. ratio) containing a 0.05 M AgClO$_4$ and 1.0 M LiPF$_6$) reference electrode. To characterize the redox behavior of PDBM, which was prepared at Section 2.1, experiments regarding the PDBM-coated GCE were carried out at room temperature (25 °C) in an electrolyte of EC and DMC (1:2 vol. ratio) containing 1.0 M LiPF$_6$, which was thoroughly deaerated using argon gas. Preparation of the polymer-coated electrodes was performed as follows: slurries were prepared by mixing PDBM, PEDOT, PVdF, and carbon black (CB) in 1-methyl-2-pyroridinone (NMP), where CB is #3230B produced by Mitsubishi Chemical Co., having specific surface area of 220 m^2 g^{-1} and averaged diameter of 23 nm. The resulting slurry was coated on a GCE, followed by vacuum drying at 100 °C for 2 h. The thickness of the coating film was about 2–4 μm. Here, the PEDOT employed for the preparation of the PEDOT-coated and the PEDOT/PDBM-coated GCEs was chemically synthesized as shown in Section 2.2.

To prove the generation of electron exchange reactions between PDBM and PEDOT, the ultraviolet and visible (UV/vis) spectroelectrochemical studies were performed at room temperature under an argon gas atmosphere, using a Shimadzu model UV-1650PC spectroscopy. A three-electrode cell configuration, in which a quartz cell is connected to the main compartment, was employed with an indium tin oxide (ITO)-coated glass electrode as the working electrode. In this experiment, the PEDOT film coated on the ITO was prepared by electrochemical polymerization of EDOT monomer described below, but was not done with the PEDOT synthesized

in Section 2.2, where the CB and PVdF are not contained within the PEDOT film to eliminate interference for the UV/vis transparency. The experiments were carried out in a 0.1 M LiClO$_4$/AN solution, which was purged using a pure argon gas. The potential of the ITO electrode was controlled with the potentiostat/galvanostat mentioned above. To obtain in situ UV/vis spectra for a PEDOT film, the potential of the PEDOT film-coated ITO electrode was held at a prescribed value for 2 min, and then in situ UV/vis spectrum was taken at that potential. Here, the films of PEDOT on ITOs for UV/vis studies were prepared by anodic electrochemical polymerization of EDOT monomer at a concentration of 25 mM in a 0.1 M LiClO$_4$/AN solution via potential cycling at 20 mV s^{-1} over the potential range between −0.60 and +0.90 V versus an Ag/Ag$^+$ reference electrode. After polymerization, the films were thoroughly rinsed with an AN solution and subsequently used for the characterization of electron-transfer reaction with PDBM. The thickness of the film was controlled with the potential cycling times. To ascertain qualitatively an electron exchange reaction between the PDBM dissolved in a solution and a reduced film of PEDOT, a film of PEDOT was held at −1.50 V for 2 min in a three-electrode cell containing a 0.1 M LiClO$_4$/AN solution, subsequently immersed in a NMP solution containing 15 mM concentration (with quinone monomer unit) of PDBM during 2–60 min with the different immersing time under a pure argon gas and then removed from NMP solution, and the UV/vis spectra were taken at open circuit.

As a solvent, an Ag/Ag$^+$ reference electrode was used EC/DMC(1/2) solution for the CV measurement and AN solution for the UV/vis spectroelectrochemical study, respectively, while a Li foil pseudo-reference or a Li foil anode was used in EC/DMC(1/2) solution for the measurement of the charge–discharge performance in the test cell. Therefore, the potential was measured and quoted with respect to the Ag/Ag$^+$ or Li/Li$^+$ reference electrode, according to the measurement method and object.

The cathode properties of the synthesized PDBM powder were studied in a two-electrode cell configuration using a separator between the anode and cathode. Charge–discharge tests were carried out using BLS2500 (Keisokuki Center Co. Ltd.). The cathode examined was coated with the composite of the PDBM (chemically synthesized at Section 2.1), CB, PEDOT (chemically synthesized at Section 2.2), and PVdF (10 wt%) in selected weight ratio. A slurry of the composite containing NMP, was spread out over a carbon-coated Al foil as the current collector by using a bar-coating apparatus and kept for vacuum-drying in an oven at 80 °C for 24 h. The resulting sheet electrode was pressed under the constant pressure of 98 MPa, and then the loading amount of the electro-active materials on the current collector was measured after the sheet electrode was cut by the size of 20 mm × 20 mm. The thickness of the electro-active materials is about 20–30 μm. Test cells consist of the composite cathode (described above), lithium metal foil anode, polyolefin separator (Asahi Kasei Co.) and an electrolyte of EC and DMC (1:2 vol. ratio) containing 1.0 M LiPF$_6$. The cathode, separator, and anode were stacked each other to make the battery core, and then the core was set into a aluminum-plastic laminated film packaging box. The electrolyte solution was injected into it. The packaging box was sealed with a heat-sealing machine. The packaged test cell was put between two stainless-steel plates so as the both sides of the battery core in the package was stacked under a constant pressure of 2.7 MPa. The AC impedance measurements were applied for the test cells described above to examine the conductivity change and the capacity retention of the cell built with the cathode using the present synthesized PDBM. A two-electrode cell is used instead of a three-electrode cell, since the evaluation of AC impedance spectra under the real cell is to be interested in the present research [16].

The AC measurements were conducted at AC amplitude of 10 mV, with frequency from 65 kHz to 0.01 Hz by using a Solartron 1250 frequency response analyzer.

2.4. Apparatus for characterization of PDBM and PEDOT

Infrared (IR) spectra measurements were performed on FT-IR 8400 (Shimadzu) with KBr pellet method. Elemental analysis was performed on VarioELIII (Elementar). Thermal gravimetric analysis was performed on TG/DTA 320 (Seiko Instruments Inc.) under N_2 gas at 10 °C min^{-1}. XPS spectra were recorded with 250 scan cycles in ESCA 3400 (Shimadzu). ^{13}C NMR spectra were performed on CMX-300 (Chemagnetics). Powder X-ray diffraction (XRD) was carried out using Ultima III (Rigaku Corporation) with Cu Kα (1.542 Å) radiation.

3. Results and discussion

3.1. Electrochemistry of PDBM and its composite with PEDOT

It is interesting to compare the redox behavior of the PEDOT/PDBM film with those of the pure PEDOT film, the pure CB film and the CB/PDBM film. Typical cyclic voltammograms (CVs) of these films coated on GCEs are shown in Fig. 1. With a CB/PDBM film-coated electrode, a few of oxidation peaks and one reduction peak at the first and second potential scans were observed in the range of potential −0.55 to +0.40 V vs. Ag/Ag$^+$ and then the peaks of oxidation alter a single one after the following potential cycling. The responses decay out as the potential cycling, though not shown here, because of a part of dissolution of these reduced species of PDBM from the GCE into the electrolyte solution. At the potential between −0.55 and −0.20 V in the range of potential −0.55 to +0.40 V vs. Ag/Ag$^+$, the negatively charged semi-quinone form of PDBM is produced mainly and thus becomes soluble, since this form of PDBM likes as a polyelectrolyte, contrary to insolubility for the non-charged quinone form of PDBM. It was found that the CV responses obtained with the first and the second potential scans were very sensitive to the portion of carbon additive and the preparation method of the composition, being probably due to the electronic conductivity and the reconstruction of the film structure by the redox reaction accompanied with Li$^+$ ion and solvent movements, as mentioned by Gall et al. [9]. The potential cycles after the first and the second show a much better defined pair of the quinone-alkoxide
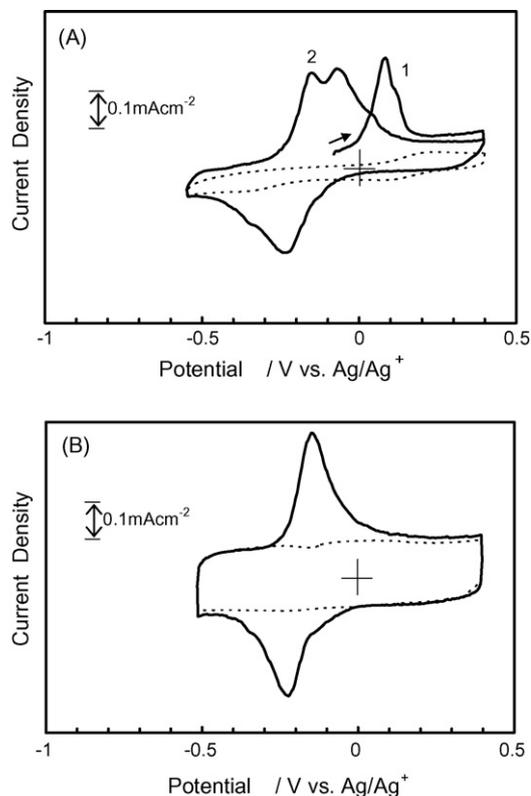
Fig. 1. Cyclic voltammograms (CVs) of the film-coated glassy carbon electrodes (GCEs); (A) CB/PDBM of 1/1 weight ratio (solid curve) and CB (dotted curve), and (B) PEDOT/PDBM of 1/1 weight ratio (solid curve) and PEDOT (dotted curve) in EC/DMC (1/2) containing 1.0 M LiPF$_6$ at the rate of 10 mV s^{-1}. Notations 1 and 2 in (A) denote the first and the steady-state potential-sweep cycle. CVs of (B) are the steady-state. All films coated on GCEs contained PVdF binder of 10 weight %.

(semi-quinone) transformation with Li$^+$ movement, as shown in Fig. 1(A).

As shown in Fig. 1(B), the PEDOT film electrode gave a stable CV response (dotted curve) with the capacity response having no redox peaks, as well-known [11]. At the potential of −0.50 to +0.40 V vs. Ag/Ag$^+$, where the positively charged thienyl moiety of PEDOT exists, the insolubility of PEDOT persists during the potential cycling [17]. The solid curve in Fig. 1(B) presents a typical
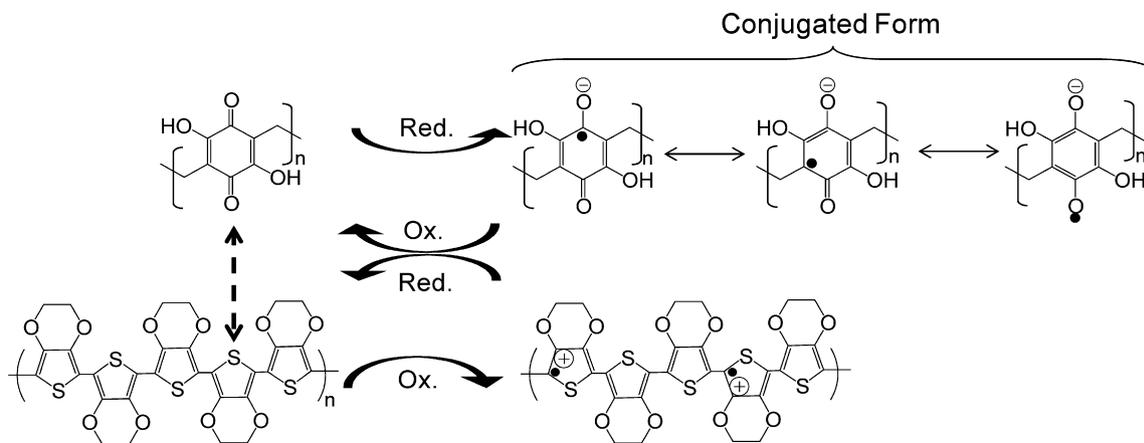
Scheme 1. Coupling reaction scheme between oxygen of PDBM moieties and sulfur of PEDOT moieties in the film composed of PEDOT/PDBM.

steady-state CV of the PEDOT/PDBM film. A couple of oxidation and reduction wave was observed in the range of potential −0.50 to +0.40 V, where the peak separation between their peak-potentials decreased, compared with the CV in Fig. 1(A). The corresponding redox peak currents were almost proportional to the scan rate from 0.2 to 250 mV s^{-1}. The obtained result shows clearly that the promoting effect of PEDOT on the redox reaction of PDBM can be produced in a composite electrode, where PEDOT and PDBM powder are dispersed in the film containing 10 wt% PVdF binder. This observation can be explained in terms of the conductivity and the high catalytic activity of PEDOT. In the potential between −0.50 and +0.40 V, as shown with the dotted curve in Fig. 1(B), thiophene moieties of PEDOT is partially oxidized to be conductive, hence it facilitates electronic conduction to some extent [18]. Some chemical interactions between PDBM and PEDOT may be responsible for the charge-transfer reaction. As shown in Scheme 1, we propose chemical interactions (1) between the cationic thienyl group of PEDOT and anionic semi-quinone group of PBDM, and (2) the neutral quinone group of PDBM and the neutral thiophene group of PEDOT, at present. Indeed mixing PDBM with PEDOT as suspension state in organic solvent gave some new IR peaks, one of which is an intense, sharp band at 1550 cm^{-1} in the near-IR for a semi-quinone anion radical [19,20], although not described at the present paper.

In addition, we investigated the electron exchange reactions between the neutral quinone group and the neutral thiophene group, following the procedures described previously [14]. The electron exchange reactions can be studied by monitoring changes in the absorption spectra of PEDOT films since neither quinone nor semi-quinone show any absorption spectra within the wavelengths of interest. All experiments about the present spectroelectrochemistry were carried out in acetonitrile (AN) solution, which was thoroughly purged using argon gas.

The PEDOT film used for this spectroelectrochemistry were one prepared with electropolymerization but not chemical synthesis. Fig. 2 demonstrates UV/vis spectra of PEDOT film, being held at −1.50 V, before and after immersing it into an NMP solution containing the neutral quinone group of PDBM. Following immersion into the PDBM solution, the absorption peak at 591 nm decreased in intensity, concomitantly there was an increase in absorption over the range from 714 to 1100 nm. Thus, it is obvious that the electron exchange reaction occurs in one direction between the neutral (oxidized) quinone and the neutral (reduced) thiophene [19,20]. Since the changing speed of the absorption peak at 591 nm was fast, it means that the electron exchange reaction was fast. 90% change against the steady-state absorption spectrum observed with the 60 min immersion was attained, even after 2 min immersing the PEDOT-coated ITO into the NMP solution containing PDBM. This steady-state absorption spectrum resembles the shape to one when observed with the PEDOT-coated ITO electrode, the potential of which was held at −0.30 V vs. an Ag/Ag$^+$ reference electrode in a 0.1 M LiClO$_4$/AN solution. As seen in Fig. 2(A), the PEDOT film on ITO is partly oxidized at −0.30 V. Therefore it is said that the same degree of oxidation for the reduced form of the PEDOT film as one electrochemically oxidized at −0.30 V proceeds by immersing the PEDOT-coated ITO into the NMP solution containing PDBM.

Furthermore, we found that the decay of the CV responses for the PEDOT/PDBM film was within 5% even after the potential cycling was continued for a week, as is distinct from the CB/PDBM film. This can be understood in terms of that the negatively charged semi-quinone moiety of PDBM probably combines electrostatically with a positively charged thienyl group on PEDOT, as a described structure at the left-hand side of Scheme 2, and thus the resulted
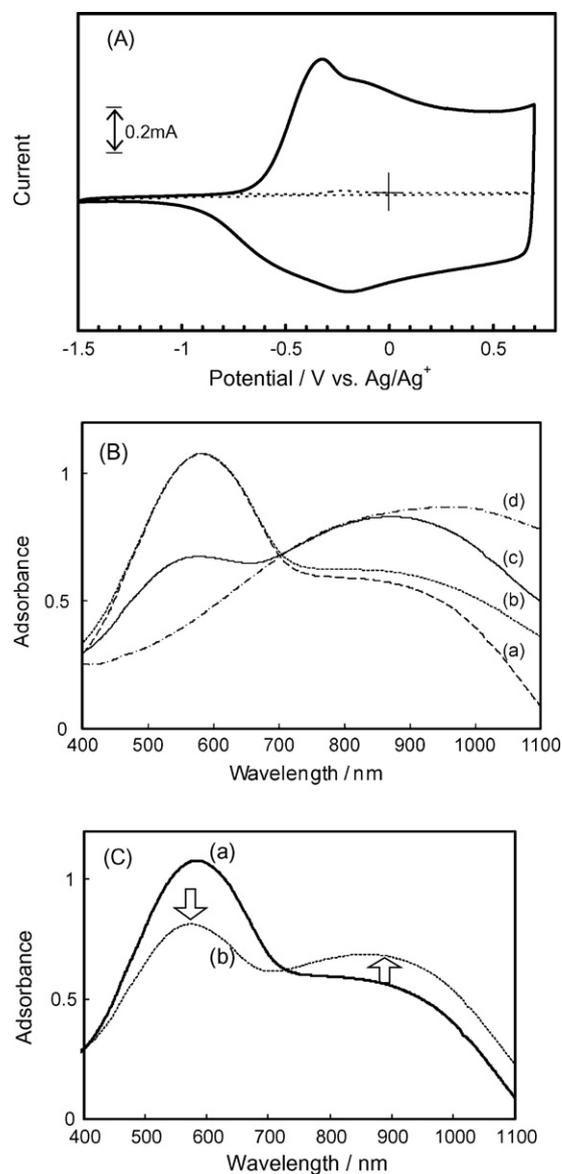
Fig. 2. (A) Cyclic voltammogram (solid curve) for a electropolymerized PEDOT film-coated ITO electrode in a 0.1 M LiClO$_4$/AN solution (dotted curve: for bare ITO electrode). Scan rate of potential was 20 mV s^{-1}. (B) UV/vis spectra of a PEDOT film-coated ITO electrode obtained at different applied potentials in a 0.1 M LiClO$_4$/AN solution. Potentials were applied at (a) −1.50, (b) −0.70, (c) −0.30, and (d) 0.00 V vs. Ag/Ag$^+$. (C) UV spectra of a PEDOT film, being held at −1.50 V vs. Ag/Ag$^+$, before (a) and after (b) 2 min immersing into a NMP solution containing 5.0 mM quinone monomer unit of PDBM.

polymer complex formation depressed the solubility of the reduced form of PDBM.

3.2. Impedance changes in the test cells built with the composited cathodes

The conductivity of the film electrode after the charge–discharge cycling twice was studied by observing the impedance response of Li metal/electrolyte/the cathode (prepared in this work) cell. Fig. 3(A)–(D) displays the typical Nyquist AC impedance results for the test cells composed of the CB/PDBM (with the weight ratio of 1/1) + PVdF (10 wt%) film, the PEDOT/PDBM (1/1) + PVdF (10 wt%) film, CB + PVdF (10 wt%), and PEDOT + PVdF (10 wt%) cathodes, respectively, as the function of the dc bias cited potentials
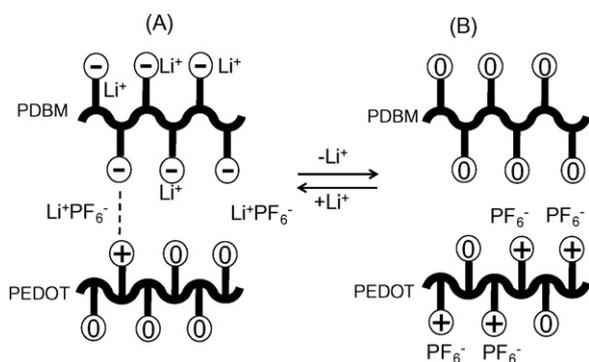
Scheme 2. Distribution profile of charges for polymers and ions within the PEDOT/PDBM composited film under (A) discharging state (+2.0 V vs. Li/Li+) and (B) charging state (+4.0 V vs. Li/Li+).

versus a Li/Li+ electrode; (a) 2.5 V, (b) 3.0 V, (c) 3.4 V, (d) 3.8 V and (e) 4.0 V. In this experiment a sinusoidal perturbation signal with the amplitude of 10 mV was superimposed onto the described dc potential, in which the oxidation state of the cathode composite materials is altered.

Nyquist plots described at the upper column of Fig. 3(A) and (B) show the loops in each case for the both cells with the CB/PDBM and the PEDOT/PDBM (1/1) cathodes in the frequency range of 0.01–65 kHz. Here, the difference in the diameter of these described semicircles represents the change of the electrical parameters characterizing the cathode and the interface between the cathode and electrolyte, because the interface between lithium anode and electrolyte is in common with the cells in Fig. 3(A) and (B) and thus the electrical parameters at its interface are identical. In general, the diameter of a semicircle is defined as electron-transfer resistance (R). The values of R obtained for the PEDOT/PDBM film decreased by a factor of 2–5, in comparison to the CB/PDBM film. The result means that the PEDOT is a favorable additive, which provides higher electro-conductivity and catalytic activity for the electron-transfer reaction of PDBM than those of the CB additive. Furthermore, it is also considered that the difference of polydispersity in CB and PEDOT dispersed in a NMP solution of PDBM, which was used to prepare the redox-active materials of cathode, seems to produce the difference of inhomogeneous distinction of electronic conductive pass [21,22], and indicates the superiority of PEDOT over CB. The variation of R as a function of the dc potential was shown at the lower column in Fig. 3(E), where the data observed with the cells using the pure CB, the pure PEDOT, and the PEDOT/PDBM (1/1) cathodes were also plotted. In the case of the pure PEDOT and the pure CB cathodes, the values of R for PEDOT and CB were smaller by 10 to100 times as compared with the values obtained with the CB/PDBM and the PEDOT/PDBM (1/1) cathodes. Thus, we found that the contribution of the pure PEDOT and the pure CB cathodes and the Li anode for the values of R was negligibly small, compared to the CB/PDBM and the PEDOT/PDBM cathodes. However, even if the values of R obtained with the pure PEDOT and the pure CB cathodes were small, the values decreased by 30–40% with increasing the applied dc potential step by step from 2.50 to 4.00 V. It can be concluded that the electrochemical oxidation for the PEDOT brought about the high-conductivity [10] and the redox reaction of the PEDOT was accelerated at the cathode with increasing the applied potential. In the case of the CB film, with increasing the applied potential for the CB surfaces the quantity of anion adsorption to the CB surfaces increases to neutralize the surface charge of the CB, as known as the principle of electrochemical capacitor, and thus the ionic conductivity of the CB increases. However, no faradic reaction process on the CB electrode occurs. Therefore, we

would imagine that the decrease in R with increasing the applied potential would result in a capacitive behavior.

As seen from Fig. 3(E), in the case of the composite cathodes for the PEDOT/PDBM film and CB/PDBM film, the resistance decreases as increasing the potential and becomes minimum value around 3.0 V vs. Li/Li+, and again increases. The change of the resistance by potential was substantial compared to these observed for the pure PEDOT and the pure CB cathodes. With increasing the applied potential above 3.0 V, the negatively charged semi-quinone structure of quinone-function group of PDBM transforms into the non-charged quinoid one, which is insulator. Therefore, these charge-transfer resistance changes of PDBM in PEDOT and in CB electrodes are consistent with the transformation of the benzenoid structure into quinoid one occurring upon oxidation, since in this case the change of the charge-transfer resistance of PDBM seems to reflect the degree of the transformation. Effectiveness of PEDOT usage as a composite substrate was established obviously by comparison of PEDOT and CB composition, when the applied potential is above 3.0 V vs. Li/Li+. The AC impedance measurements for the test cells built with four kind of composite cathodes which were PEDOT/PDBM weight ratios of 1/2, 2/3, 1/1, and 2/1 have been also performed. As PEDOT/PDBM weight ratio increased, the value of R markedly reduced and finally closed to one observed with the pure PEDOT film, although not shown here.

3.3. Charge–discharge performance of the PEDOT/PDBM film

As described above, since the PDBM has two-redox active sites in its monomer unit, the PDBM is expected to apply for a cathode material for energy storage. Therefore, charge–discharge cycling tests for the lithium cell using the composite cathode of the PEDOT/PDBM film were performed to estimate its capacity and cycle-ability, compared with those of the pure PEDOT film and CB/PDBM film.

Figs. 4–6 demonstrate the rate capability of the composite cathodes in the test cells built with the CB/PDBM having weight ratio of 1/1, the PEDOT/PDBM having weight ratio of 1/1 and the pure PEDOT, respectively. As being expected from the CV measurement in Fig. 1, smooth discharge curves in the range of potential 4.0 to 2.0 V vs. Li/Li+ were obtained with the CB/PDBM film and the PEDOT/PDBM film. The results of discharge performance of the test cells shown in Fig. 4 provide undoubted evidence of the promoting effect of PEDOT. The cell having PEDOT/PDBM cathode has the same output potential as compared with the cell having the CB/PDBM cathode at the low-rate discharge with 0.05–0.10 C. However, at the high-rate of 1.0–5.0 C, the cell of the PEDOT/PDBM cathode has by 0.10–0.50 V higher output potential than the cell of the CB/PDBM cathode. In addition, we notice that the slope of the discharge curves of the cell of PEDOT/PDBM cathode changes more moderately with increasing the discharge rate as compared with the cell of CB/PDBM cathode. This tendency supported facts that PEDOT worked to promote the redox reaction of PDBM, *i.e.* to provide smaller polarization and raise the electro-conductivity of the composite cathode film. We consider that the promoting effect can be explained by considering the reaction intermediate between free-sulfur sites in PEDOT moieties and free-oxygen sites in PDBM moieties, as shown in Scheme 1.

Here, the gravimetric discharge capacity obtained for the cell with the composite cathode of the CB/PDBM having weight ratio of 1.0 was less than 70 mAh g^{-1} as shown in Fig. 4 and recalculated as the contribution of PDBM in Table 1 , since the CB is electro-inactive. Whereas the gravimetric discharge capacity obtained for the composite cathode of the PEDOT/PDBM having weight ratio of 1/1 was 129 mAh g^{-1}, as shown in Fig. 5. In this figure, both PEDOT and PDBM contribute to the observed capacity. The contribution
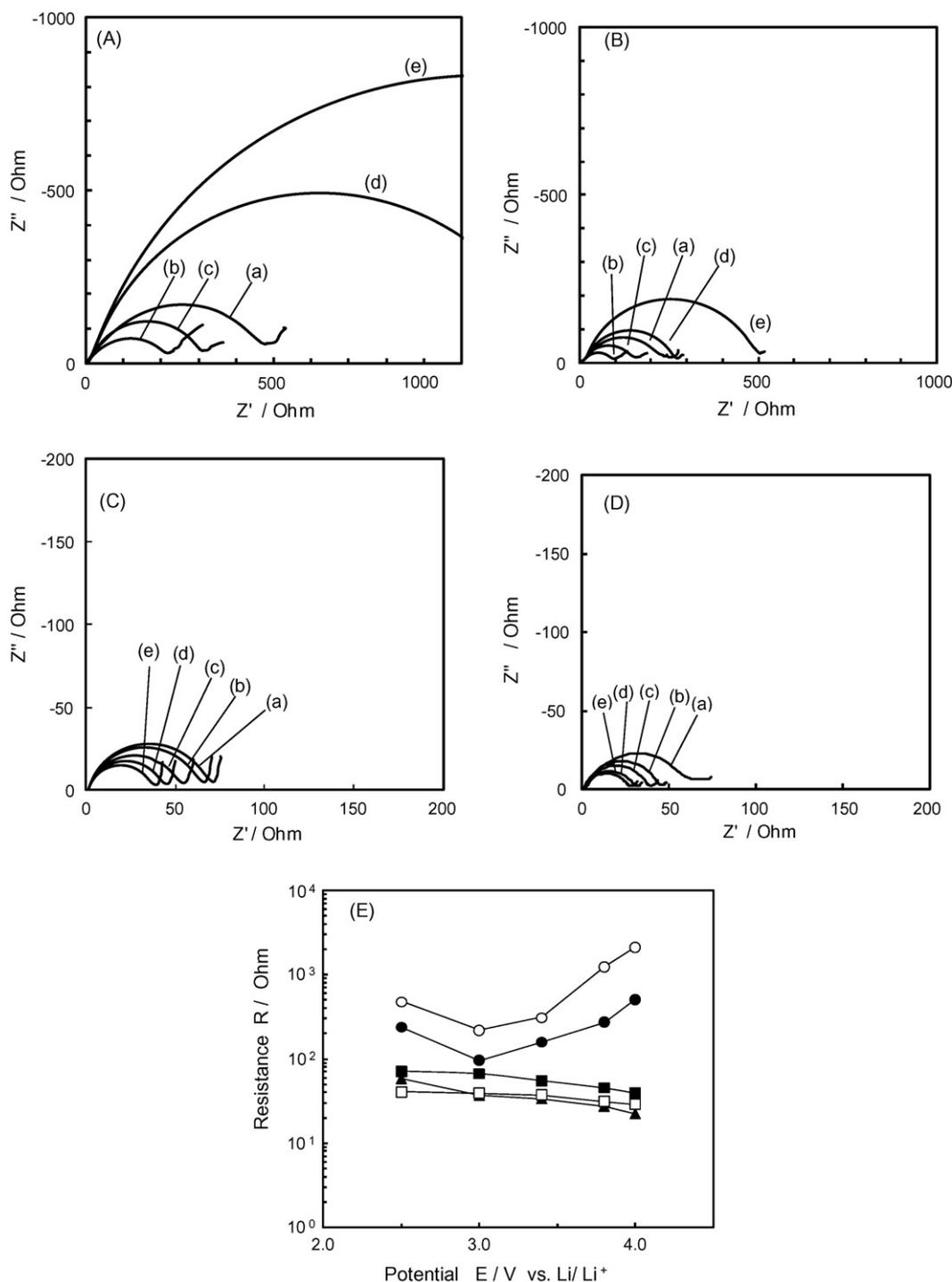
Fig. 3. Nyquist plots for the test cells composed of (A) the CB/PDBM (1/1) + PVdF (10 wt%) film and (B) the PEDOT/PDBM (1/1) + PVdF (10 wt%) film, (C) CB + PVdF (10 wt%) and (D) PEDOT + PVdF (10 wt%) cathodes as the function of the dc bias cited potentials versus a Li/Li$^+$ electrode; (a) 2.5 V, (b) 3.0 V, (c) 3.4 V, (d) 3.8 V and (e) 4.0 V. A sinusoidal perturbation signal with amplitude of 10.0 mV was superimposed onto the dc potential. (E) Changes in the resistance (R) obtained from Nyquist plots as the function of the dc bias potential for the test cells composed of (A) (○), (B) (●), (C) (■), (D) (▲) and PEDOT/CB (1/1) + PVdF (10 wt%) (□). Electrolyte solution of EC and DMC (1:2 vol. ratio) containing 1.0 M LiPF$_6$ was used for the test cells.

of PEDOT and CB was independently examined by the discharge capacity shown in Fig. 6(A) and (B), respectively. The cell with the pure PEDOT cathode provides a constant capacity of 70 mAh g^{-1} in the potential range 4.0–2.0 V vs. Li/Li$^+$, in spite of changes of the discharge rate from 0.20 to 5.0 C. The discharge response of PEDOT was the characteristics of a capacitor, which shows a linear relation between the charge and the output potential, as reported

previously [11]. The cell with the pure CB cathode provides a capacity of 8.8 mAh g^{-1} in the potential range 4.0–2.0 V vs. Li/Li$^+$ at the discharge rates from 0.05 to 5.0 C. The response of CB was also the characteristics of a capacitor. In the case of CB about 10% of excess charge was observed in the first scan, since the redox function groups such as quinone, ketone and carboxylic groups onto the carbon surface, are produced on the surface of CB as CB is making.
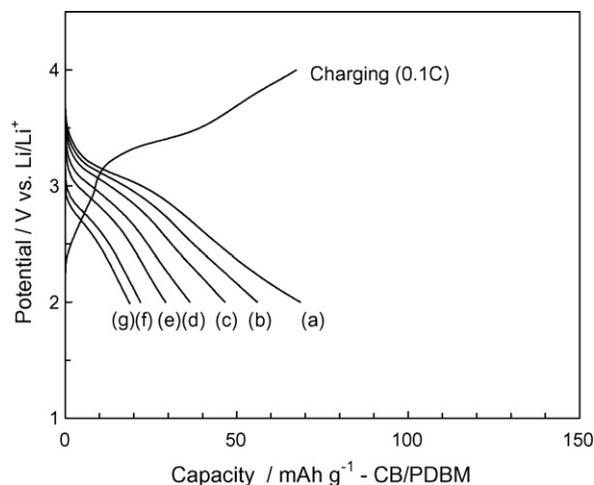
Fig. 4. Charge–discharge curves of a test cell built with the use of the composite cathode having the CB/PDBM (1/1) + PVdF (10 wt%) at various discharge rates of (a) 0.05 C, (b) 0.10 C, (c) 0.20 C, (d) 0.50 C, (e) 1.0 C, (f) 2.0 C, and (g) 5.0 C. The cell was charged up to 4.0 V vs. Li/Li$^+$ at a constant current 0.025 mA cm^{-2} at 20 °C.
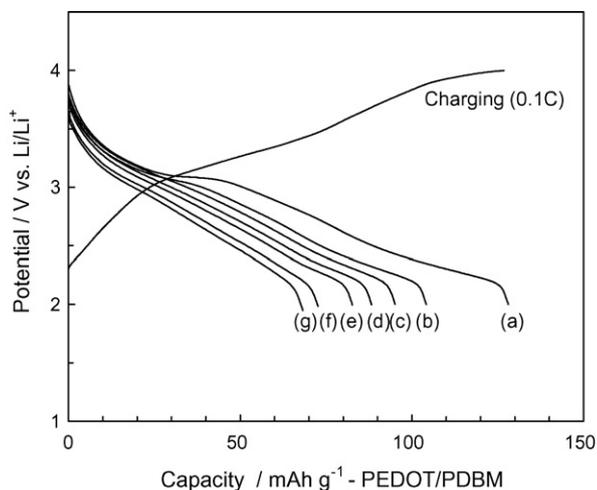
Fig. 5. Charge–discharge curves of a test cell built with the use of the composite cathode having the PEDOT/PDBM (1/1) + PVdF (10 wt%) at various discharge rates of (a) 0.05 C, (b) 0.10 C, (c) 0.20 C, (d) 0.50 C, (e) 1.0 C, (f) 2.0 C, and (g) 5.0 C. The cell was charged up to 4.0 V vs. Li/Li$^+$ at a constant current 0.025 mA cm^{-2} at 20 °C.
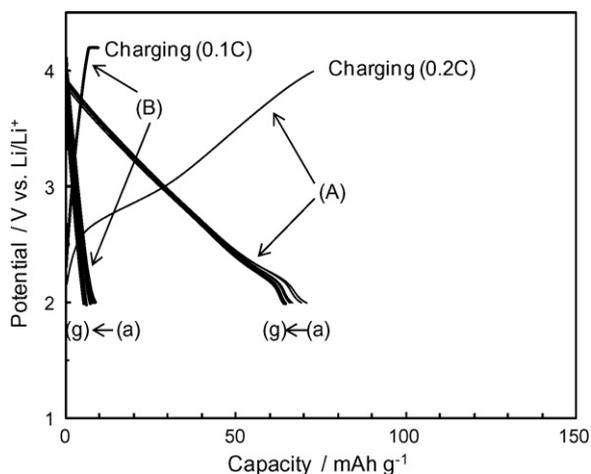
Fig. 6. Charge–discharge curves of test cells built with the use of the composite cathode having the PEDOT + PVdF (10 wt%) (A) and the CB + PVdF (10 wt%) (B) at various discharge rate of (a) 0.05 C, (b) 0.10 C, (c) 0.20 C, (d) 0.50 C, (e) 1.0 C, (f) 2.0 C, and (g) 5.0 C. The cell was charged up to 4.0 V vs. Li/Li$^+$ at a constant current of (A) 0.050 mA cm^{-2} and (B) 0.025 mA cm^{-2}, respectively, at 20 °C.

Table 1

Discharge capacity (mAh g^{-1}) of PDBM observed with different discharge current rates of the PDBM composite cathode materials (20 mm × 20 mm) having the weight ratios of (a) 2/1, (b) 1/1 and (c) 1/2 for the PDBM/PEDOT, and (d) 1/1 for the PDBM/CB at 20 °C.

Rate (C)	Weight ratio of PDBM to PEDOT or CB			
	2/1[a]	1/1[b]	1/2[c]	1/1[d]
0.05	175	188	136	149
0.1	158	140	127	112
1.0	106	96	100	59

All of the composites contain 10 wt% of PVdF as a binder and their thickness was 25 μm. The cell was charged up to 4.00 V vs. Li/Li$^+$ at a current 0.050 mA cm^{-2} and discharged to a cut off potential of 2.00 V vs. Li/Li$^+$.

The produced group probably results in the observed capacity. As compared with the capacity of CB, the high capacity for PEDOT was observed. This is because the redox reaction of thiophene function group of the polymer chain contributes to the charging–discharging capacity.

The both backside parts of the test cells used in Figs. 4–6 are pressed with holders under a constant pressure, as described in the experimental section. Therefore, the amount of electrolyte salt and solvent does not present sufficiently at the electrolyte layer (containing a separator) between the anode and cathode. It is worth noting that in the case where the cell with the pure PEDOT cathode does not contain the sufficient amount of electrolyte salt without being pre-doped the cathode with the anion, the less discharge capacity is observed because the electro-activity of the PEDOT is attained with the movement of anion but not cation (Li$^+$). However, even if in the case where the cells with the both CB/PDBM and PEDOT/PDBM composite cathodes do not contain the sufficient amount of electrolyte salt without being pre-doped the cathode with the anion, the sufficient discharge capacities was observed. It seems to be that the activity of the PDBM is kept with the movement of Li$^+$ ion which is served from the Li foil anode by oxidation. This means that the charge–discharge responses of the composite cathode are accompanied mainly by Li$^+$ ion or by self-doping of the cationic PEDOT moieties with the anionic PDBM moieties in the range of potential between 2.0 and 3.5 V vs. Li/Li$^+$, where about 75% of the observed discharge capacity is provided. In the range of potential from 2.0 to 3.5 V vs. Li/Li$^+$, the redox reaction between the semi-quinone and the quinone groups of PDBM moieties is fully performed, as seen from Fig. 1(A), and the thiophene groups of PEDOT moieties are partially oxidized as seen from Fig. 2(A). (Here, it should be noted that the value of potential 0.0 V vs. Ag/Ag$^+$ in a AN solution can be converted to that potential 3.3 V vs. Li/Li$^+$ in EC/DMC (1/2) solution.) Consequently, we can consider that the cells having the composite cathodes reasonably are performed with the rocking-chair mode of Li$^+$ ion.

XPS measurements were also performed with the film electrodes of PEDOT/PDBM having weight ratio of 1/1. In the case where the used electrodes were altered to the oxidized form, being charged up to +4.0 V vs. Li/Li$^+$ at a current 0.050 mA cm^{-2}, and the reduced form, being discharged down to +2.0 V vs. Li/Li$^+$ at a current 0.050 mA cm^{-2}, after 20 cycles of charge–discharge process. After that the cells were broken up elements and then the resulting cathodes were pretreated to make the samples of XPS measurements in a argon gas flow dry box, as following. The electrodes under the oxidized and the reduced forms are soaked in EC/DEC (weight ratio of 1/3) solution for 10 min, washed with the EC/DEC to eliminate the excess presence of supporting electrolyte LiPF$_6$ in the film, again soaked in pure EC/DEC (weight ratio of 1/3) solution for 2 hrs for three times, then dried under the vacuum oven at 60 °C for 12 h. The resulting electrodes were set-up on sample holder. Interestingly in XPS the predominate Li$_{1S}$ peak was observed clearly at the reduced
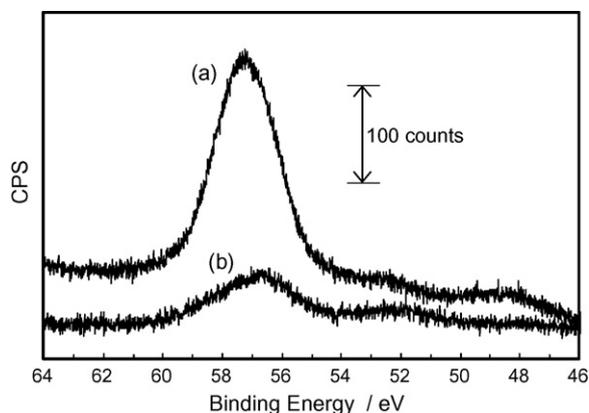
Fig. 7. X-ray photoelectron Li$_{1s}$ spectra for the film electrodes of PEDOT/PDBM (weight ratio 1/1): (a) reduced form being discharged down to +2.0 V vs. Li/Li$^+$, and (b) oxidized form being charged up to +4.0 V vs. Li/Li$^+$, after 20 cycles of charge–discharge process.

(discharged) form of the composites. However this peak was significantly reduced at the oxidized (charged) form of it, as shown in Fig. 7, being expected from the rocking-chair mode of Li$^+$ ion. In addition, the F$_{1S}$ and P$_{2S}$ peaks were also appeared in the spectra of the both forms. Their intensities (CPS) between the both oxidation states for the F$_{1S}$ and P$_{2S}$ peaks remained almost unaltered. The presence of PF$_6^-$ anion (or F$^-$ anion produced by decomposition of PF$_6^-$) in the discharged film could not be ruled out completely with the repeated washing. Therefore, the formation of electrostatic complex with charged moieties of polymer probably brings about the presence of the PF$_6^-$ anion in the film. Charge distribution within the film under the charged and discharged states can probably be depicted by Scheme 2.

Table 1 summarizes the PDBM capacities observed with three kinds of composite cathodes, whose PEDOT/PDBM weight ratio were 2/1, 1/1 and 1/2, and with the composite cathode of the CB/PDBM weight ratio of 1/1. As being seen in Table 1, the composite cathode having a PEDOT/PDBM weight ratio of 1/1 shows gravimetric capacity of 129 mAh g^{-1} (corresponding to 188 mAh g^{-1} for PDBM and 70 mAh g^{-1} for PEDOT) at current densities of 0.025 mA cm^{-2}. The value of 188 mAh g^{-1} for PDBM

Fig. 9. Cycle-life performance of the cells using the composite cathodes of (A) the PEDOT/PDBM having the weight ratios of (a) 2/1, (b) 1/1, and (c) 1/2 with different discharge rates (0.2 C → 5 C → 0.2 C → 0.05 C) after 100 cycles, and (B) the CB/PDBM having the weight ratio of 1/1 with different discharge rates(0.1 C → 0.05 C → 0.1 C → 0.2 C → 0.5 C → 1.0 C → 3.0 C → 5.0 C → 0.1 C) after the 8th cycle. The cell was charged up to 4.0 V vs. Li/Li$^+$ at a current 0.050 mA cm^{-2} at 20 °C. The value of percentage at each cycle was normalized with the discharged capacity observed at 1st cycle with 0.1 C rate.

means 1.1–1.2 electron exchange per quinone unit of polymer moieties. The theoretical maximum discharge capacity of PDBM is 161 mAh g-cathode^{-1} under the condition, where one electron-transfer reaction is assumed to occur per quinone unit of PDBM moieties. Therefore, the experimentally evaluated discharge capacity of 188 mAh g^{-1} is then 110–120% of the overall theoretical capacity.

Consequently, as one reason, we imagine that the reduced form of quinone group of PDBM moieties is not only monoanionic semi-quinone but also partially dianionic alkoxide of PDBM moieties through interaction of quinone moieties with PEDOT. In the literature [23], Pham and coworkers have shown that charge-transfer interaction occurs between aryl–amine groups of polyaniline (PANi) and quinones moieties with investigation method of in situ multiple internal reflection Fourier transform infrared spectroscopy (MIRFTIRS). Changes of bands at 1655 cm^{-1} (quinoid form), 1140 cm^{-1} (semi-quinoid), and 1624 cm^{-1} (C=O stretch of quinine) for the quinones moieties were investigated during the film reduction after pre-oxidation of the film. Therefore, the MIRFTIRS seems to be suitable for examining the interaction between quinone moieties of PDBM and a conducting polymer of

Fig. 8. Change in capacity for the test cells having (a) the CB/PDBM (1/1), (b) the PEDOT/PDBM (2/1), (c) the PEDOT/PDBM (1/1), and (d) the PEDOT/PDBM (1/2) cathode as the discharge rate from 0.05 to 5.0 C at 20 °C. The cell was charged up to 4.0 V vs. Li/Li$^+$ at a current 0.050 mA cm^{-2} and discharged to a lower cut off voltage of 2.0 V vs. Li/Li$^+$.
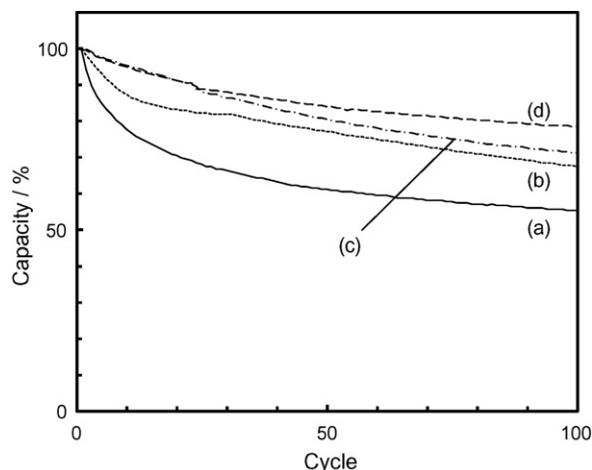
Fig. 10. Relative capacity change of the test cells having (a) CB/PDBM (1/1), (b) PEDOT/PDBM (1/2), (c) PEDOT/PDBM (1/1), and (d) PEDOT/PDBM (2/1) cathodes by the charge-discharge cycles. The cell was charged up to 4.0 V vs. Li/Li+ at a current 0.050 mA cm^{-2} and discharged to a lower cut off voltage of 2.0 V vs. Li/Li+ at a current 0.050 mA cm^{-2} at 20 °C.

PEDOT. However the related research is beyond the scope of the present paper.

As another reason, we can consider that the capacity of 70 mAh g^{-1} observed with the pure PEDOT cathode is developed to the value of 97 mAh g^{-1} in the presence of quinone moieties within the film, in the case where the capacity of PDBM is kept to 161 mAh g^{-1}. Increasing the discharging rate, the capacity decreased, as seen from Table 1 and Figs. 4 and 5. However, 96 mAh g^{-1} capacity was still obtained at 0.25 mA cm^{-2} (=1.0 C rate) with the composite cathode having the PEDOT/PDBM weight ratio of 2/1. In the case where the test cells were charged at 0.025 mA cm^{-2} and discharge at 0.0125 mA cm^{-2} (0.05 C) to 1.25 mA cm^{-2} (5.0 C), the discharge capacities of both the CB/PDBM and PEDOT/PDBM cathodes decreased as increasing of discharging currents. As being found in Fig. 8, at higher discharge currents the discharge capacity showed lower values and the capacity fading was more pronounced. In the case that the discharge current is 1.25 mA cm^{-2} (5.0 C) at the PEDOT/PDBM, the evaluated value was closed to 70 mAh g^{-1}, which is the value obtained with the pure PEDOT cathode under the same discharge current. However, approximately the initial value of the capacity was retained by setting the discharging current smaller. That is, the capacity fading is in most part reversible, as described below.

3.4. Correlation among composition, discharge current and cycle life

Using different weight-ratio of the PEDOT/PDBM composite as a cathode material, we made test cells and examined charge-discharge characteristics by changing the discharge current (=rate). In the case where the test cells were charged at 0.050 mA cm^{-2} and discharge at 0.025–1.25 mA cm^{-2}, the discharge capacity of both the PEDOT/PDBM and the CB/PDBM cathodes decreased little by little as the charge–discharge process was repeated. The capacity fading was faster at higher discharge currents. During high-rate discharging of the high current, a region where electrical conductivity is unexpectedly low is not fully discharged, since discharging in this region is slower than in the other region. Within the redox-active film on the cathodic current collector, there is inhomogeneous distinction of electronic conductive region. If the charging and discharging currents are made smaller after the cell capacity has faded,

the capacity returns near to one before being faded, as shown in Fig. 9.

The PEDOT/PDBM cathode showed good charging–discharging efficiency and retained approximately 80% of its initial capacity, after 100 cycles as shown in Fig. 10. In this figure are shown the three kinds of the PEDOT/PDBM composites cathodes which are PEDOT/PDBM weight ratio of (a) 1/2, (b) 1/1 and (c) 2/1 and the CB/PDBM composite cathode at weight ratio of 1/1. When the PEDOT composite of the 1/1 ratio is compared with the CB composite of the 1/1 ratio, the degradation of the PEDOT composite was markedly reduced. In addition, as PEDOT/PDBM ratio increased, the degradation was also reduced. The cell with composition cathode having a PEDOT/PDBM weight ratio of 2/1 was less degraded and its capacity was maintained at 80% of the initial one after 100 cycles under the present conditions. Here, we sense that this 20% deterioration in capacity after 100 cycles mainly results in the inactivation of the Li anode used in the present work. However, the use of Li-intercalated graphite is beyond the scope of the present work.

4. Conclusion

By using the addition of electro-conducting polymer PEDOT to PDBM, the significant effects on the electrochemical responses of the PDBM cathode for rechargeable Li batteries were observed as follows: (1) PEDOT/PDBM film having a weight ratio of 1/1 shows gravimetric capacity of 129 mAh g^{-1} (corresponding to 188 mAh g^{-1} for PDBM and 70 mAh g^{-1} for PEDOT). (2) The highest energy density observed was 140 mAh g^{-1} (406 mWh g^{-1}) for the composite cathode having PEDOT/PDBM weight ratio of 1/2 under the discharge rate of 0.05 C (current: 0.0125 mA). (3) Smooth discharge curve in the range of potential 3.8–2.0 V vs. Li/Li+ was obtained with the rocking-chair mode of lithium ion. (4) Nyquist plots showed the decrease of an electron-transfer resistance for the PEDOT/PDBM film. (5) Oxidized PEDOT suppressed the solubility of quinone polymer under the semi-quinone state and good cycleability above 100 cycles was attained with PEDOT-PDBM film. (6) Improvement of the electronic contact to connect with all the redox active sites of quinone group will further rise up the gravimetric capacity of an organic cathode.

In this paper, it was found that the PEDOT was superior to the carbon usually mixed the electroactive material electrodes to improve their electronic conductivity. That is, the PEDOT functions as an electronic conductor and is electroactive in the same potential range, where the reaction of a redox couple between semi-quinone and quinoid occurs. In addition, it was revealed that the redox reaction of the quinone group is accelerated with the PEDOT.

Finally, it should be mentioned that this high gravimetric density observed with present work will, to some extent, be offset by the low physical density of organic materials. Our composite electrodes should be therefore applied for new demands, where weight rather than volume is critical, together with the benefit of flexible property of organic materials [24]. In addition, in the case of an organic polymer there is the characteristic of electrode preparation method, by which an organic polymer as a viscous "ink" can be spread simply on a current collector substrate.

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[16] Here, a two-electrode cell is used instead of a three electrode cell, since the parts of the Li metal/electrolyte/separator/electrolyte is common to the cells of Li metal/electrolyte/separator/electrolyte/the cathode (prepared in this work). Thus, we expect that the differences of the charge-transfer kinetics and charge distribution dynamic equilibrium for the prepared cathodes will be confirmed by comparison of the Nyquist AC impedance responses observed.

[17] In the case of the PEDOT film, it has been known that the PEDOT powder, even if this is under both the oxidized state and the reduced state, was insoluble in any solvents[11].

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