Poly[dithio-2,5-(1,3,4-thiadiazole)] (PDMcT)–poly(3,4-ethylenedioxythiophene) (PEDOT) composite cathode for high-energy lithium/lithium-ion rechargeable batteries

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Abstract

We present a characterization of the redox behavior of organosulfur-based composite cathodes composed of poly[dithio-2,5-(1,3,4-thiadiazole)] (PDMcT), which is a polymer derived from 2,5-dimercapto-1,3,4-thiadiazole (DMcT), and poly(3,4-ethylenedioxythiophene) (PEDOT) in a carbonate-based mixed solvent containing 1.0 M LiBF$_4$. We have previously shown that PEDOT films, electrochemically generated at glassy carbon electrode surfaces, gave rise to a dramatic enhancement of the interfacial charge transfer kinetics of DMcT in solution. In a similar fashion, chemically prepared PEDOT films exhibited dramatic electrocatalytic activity towards the redox reactions of PDMcT in the composite cathodes. While the composite cathode exhibited a very high capacity of 205 mAh g^{-1} (based on the electroactive mass) at the first discharge, in subsequent charge/discharge tests, the capacity of the PDMcT–PEDOT composite cathode (1:1 mole ratio) decreased significantly because of dissolution of the reduction products of PDMcT into the electrolyte solution. We also found that an ionic polymer, consisting of a mixture of PEDOT and polystyrene sulfonate (PEDOT–PSS) could electrostatically, but not physically, prevent, at least in part, leaching of the DMcT species into the electrolyte solution, thus improving the coulomb efficiency for the redox reactions of DMcT in a PDMcT–PEDOT composite film during charge/discharge cycles.

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1. Introduction

For over 15 years, organosulfur-based compounds with multiple thiol groups or disulfide moieties have received attention as potential cathode electroactive materials for lithium/lithium-ion rechargeable batteries due to their high theoretical capacity and chemical tunability [1–15]. More importantly, the capability of the thiolate system to release and capture lithium-ions during charge/discharge cycles allows their easy incorporation into the so-called "rocking-chair" type system employed in current lithium-ion battery technologies [16]. Additionally, organic materials offer the advantage of making them relatively low

cost and derived from abundant resources, being particularly suitable to applications requiring large amounts of electroactive materials, such as power sources for pure electric vehicles (PEVs) and hybrid electric vehicles (HEVs). However, the practical application of these compounds has been hindered because of the sluggish kinetics of the redox reactions at room temperature [3,17,18], the lack of electronic conductivity, and the poor charge/discharge durability in liquid electrolyte systems [19].

We have studied organosulfur-based composite systems in which a conducting polymer (e.g., PEDOT) is employed as an efficient electrocatalyst to accelerate the redox reactions of organosulfur compounds such as 2,5-dimercapto-1,3,4-thiadiazole (DMcT) [9,19]. An additional advantage of conducting polymers is that they possess their own redox reactions, and thus can also be used as an electroactive material in their own right [20]. DMcT, which possesses two thiol groups,

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is oxidized to form a disulfide polymer by a two-electron process upon electrochemical oxidation, providing 362 mAh g^{-1} of theoretical capacity. We previously reported that the redox reactions of DMcT are dramatically accelerated by the conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) [9], and proposed full redox reaction schemes for DMcT at a PEDOT film-modified glassy carbon electrode (GCE) based upon cyclic voltammetry (CV), electrochemical quartz crystal microbalance (EQCM), and acid–base chemistry studies [19]. However, in the mechanistic studies, when CV studies were carried out for composite film-coated GCEs composed of DMcT polymer (PDMcT) and PEDOT, it was observed that the redox current responses of PDMcT decreased with increasing number of potential cycles as a result of dissolution and leaching of the reduction products of PDMcT, such as the DMcT monomer, into the bulk electrolyte solution. This dissolution precluded the consistent charge/discharge durability and energy output required for application in lithium-ion rechargeable batteries.

In this study, we have fabricated a prototype lithium battery with a PDMcT–PEDOT composite cathode, and characterized the redox response, charge/discharge capacities as well as the durability in a carbonate-based mixed solvent (ethylene carbonate (EC) and diethyl carbonate (DEC), 1:3 volume ratio) containing 1.0 M lithium tetrafluoroborate (LiBF$_4$) as a supporting electrolyte via CV and charge/discharge tests at a constant current density. PDMcT and PEDOT were chemically synthesized to make the composite films and the amount of PEDOT required for efficient electrocatalysis was also optimized. On the basis of their theoretical gravimetric capacities (362 and 115 [21] mAh g^{-1} for PDMcT and PEDOT, respectively), the higher the fraction of PDMcT that a composite film contains, the higher the capacity that one can obtain from it.

Furthermore, in order to obtain better charge/discharge cycle durability for a PDMcT–PEDOT composite cathode, we have employed an ionic polymer, a mixture of PEDOT and polystyrene sulfonate (PEDOT–PSS) at the interface between the composite cathode film and the electrolyte solution. Due to the electrostatic interaction between the ionic polymer and DMcT species generated upon reduction of PDMcT, it was anticipated that the DMcT species would be retained inside the composite film, leading to an improvement of the charge/discharge durability of the composite film. The effects of the ionic polymer on the redox behavior of PDMcT–PEDOT composite films are discussed in detail.

2. Experimental

2.1. Materials

2,5-Dimercapto-1,3,4-thiadiazole (DMcT) (battery grade) was purchased from Toyo Kasei Co. (Japan) and used without further purification. 3,4-Ethylenedioxythiophene (EDOT, Baytron M) and polyethylenedioxythiophene polystyrene sulfonate (PEDOT–PSS) aqueous dispersion (Baytron P) were obtained from Bayer Co. (Germany) and used as received. High-purity HPLC-grade acetonitrile (AN) was purchased from Burdick and Jackson, dried over 3 Å molecular sieves,

and used for electrochemical measurements. 1-Methyl-2-pyrrolidinone (NMP) (HPLC grade, 99+%), lithium perchlorate (LiClO$_4$, 99.99%), copper (II) tetrafluoroborate hydrate (Cu(BF$_4$)$_2$·xH$_2$O), ammonium hexafluorophosphate (NH$_4$PF$_6$, 99.99%), and AN anhydrous (99.8%) were purchased from Aldrich Chemical Co. and used as received. A carbonate-based mixed solvent (EC and DEC, 1:3 volume ratio) containing 1.0 M LiBF$_4$ was purchased from Kishida Chemical Co. (Japan) and used as received. Carbon black (CB, #3350B) and poly(vinylidene fluoride) (PVdF, KF polymer, #9130) were purchased from Mitsubishi Chemical Co. (Japan) and Kureha Co. (Japan), respectively. Carbon-coated aluminum (C-Al) sheet and lithium metal sheet were purchased from Toyo Aluminum K.K. (Japan) and Honjo Metal Co., Ltd. (Japan), respectively. Polyolefin porous film (Hipore^{TM}) was purchased from Asahi Kasei Co. (Japan).

Poly[dithio-2,5-(1,3,4-thiadiazole)] (PDMcT) was prepared by chemical polymerization of DMcT monomer following the procedure previously reported [22]. 4 g (26.6 mmol) of DMcT were dissolved in 300 ml of a H$_2$O:CH$_3$OH mixed solvent (1:1 volume ratio). 100 ml of a CH$_3$OH solution containing 6.7 g (26.4 mmol) of iodine were added dropwise to the DMcT monomer solution and stirred for 24 h at room temperature and 4 h at 50 °C under an argon atmosphere. The light brown precipitate obtained was filtered and washed with H$_2$O and CH$_3$OH. The precipitate was dried under vacuum at 70 °C for 24 h and a pale yellow powder was obtained. Poly(3,4-ethylenedioxythiophene) (PEDOT) was chemically prepared from EDOT monomer using Cu(BF$_4$)$_2$ as an oxidizing agent. 14.2 g (0.1 mol) of EDOT were dissolved in 200 ml of anhydrous AN. 200 ml of an AN solution containing 47.4 g (0.2 mol) of Cu(BF$_4$)$_2$ were added dropwise to the EDOT monomer solution and stirred for 24 h at room temperature under an argon atmosphere. The dark blue precipitate obtained was then filtered, washed with H$_2$O, CH$_3$OH, and acetone, and dried under vacuum for 72 h.

2.2. Apparatus and experimental procedure

Electrochemical characterizations were carried out at room temperature via a battery (charge/discharge) test (Keisokuki Center Co. Ltd. (Japan), model JSM-5800) and cyclic voltammetry (CV) (Hokuto Denko Co. (Japan), model HSV-100).

For CV studies, measurements were taken in a prototype cell prepared for charge/discharge tests or in a three-electrode cell configuration using a glassy carbon electrode (GCE) (Bioanalytical Systems (BAS), 3.0 mm diameter or Pine Instrument Co., 5.0 mm diameter), a large area Pt coil counter electrode, and a Ag/Ag$^+$ (0.1 M LiClO$_4$/AN or 1.0 M LiBF$_4$/EC:DEC solutions containing 0.05 M AgClO$_4$) reference electrode. All potentials are reported against Ag/Ag$^+$–AN, Ag/Ag$^+$–EC:DEC, or Li/Li$^+$. All the experiments were carried out in either a 0.1 M LiClO$_4$/AN solution or a 1.0 M LiBF$_4$/EC:DEC 1:3 vol% solution, which were thoroughly purged using pre-purified argon gas.

For studies on the electrocatalytic effect of PEDOT towards the redox reactions of DMcT in solution, films of PEDOT were prepared on GCEs by oxidative polymerization of EDOT

monomer at a concentration of 20 mM in a 0.1 M LiClO$_4$/AN solution via potential cycling at 20 mV s^{-1} over the potential range from −0.60 V to +0.90 V versus Ag/Ag$^+$–AN. The charge consumed during electropolymerization of EDOT to generate a PEDOT film was estimated by coulometry (via a coulometer attached to Hokuto Denko Co., model HABF 1510m). The film thickness of PEDOT was correlated to the charge, estimated during the electrochemical polymerization, with a previously-established calibration curve obtained from profilometry using a Tencor Instruments, model Alpha-Step 500 surface profiler [23]. After polymerization, the films were thoroughly rinsed with the electrolyte solution employed and subsequently used for the characterization of the redox behavior of DMcT in an AN solution.

"Electrochemically-prepared" DMcT–PEDOT composite films were prepared by cycling the potential of a PEDOT modified GCE in 0.1 M LiClO$_4$/AN containing 5 mM DMcT over the potential range from −0.60 V to +0.80 V versus Ag/Ag$^+$–AN, and arresting the potential scan at +0.80 V in order to deposit the DMcT polymer into the PEDOT film. The resulting composite film was thoroughly rinsed with a 0.1 M LiClO$_4$/AN solution and subsequently used for characterization of the redox behavior in a 0.1 M LiClO$_4$/AN solution without dissolved DMcT.

"Chemically-prepared" PDMcT–PEDOT composite film-modified GCEs were prepared by casting slurries containing PDMcT, PEDOT, CB, PVdF, and NMP. The slurry was prepared by mixing 13.2 mg (34.6 mM) of PDMcT, 12.5 mg (34.6 mM) of PEDOT, 13.2 mg of CB, 12.5 mg of PVdF, and 2.58 g of NMP. The mixture was sonicated for 30 min to homogenize it. 1 μl of the slurry was cast on a GCE with a micro-syringe and subsequently dried under vacuum at room temperature for an hour to obtain the film-modified GCEs.

For charge/discharge tests, prototype lithium-battery cells were fabricated with a PDMcT–PEDOT composite cathode, a lithium-metal anode, polyolefin porous films (as separators), current collectors (C-Al for the cathode and copper for the anode), and Teflon-coated metal plates in a dry room (dew point: −50 °C on average). PDMcT–PEDOT composite cathodes were prepared from slurries composed of PDMcT, PEDOT, CB, PVdF, and NMP. The slurry for the composite film (PDMcT:PEDOT = 1:1 mole ratio) was prepared by mixing 264.2 mg (1.8 mmol) of PDMcT, 250.4 mg (1.8 mmol) of PEDOT, 121.0 mg of CB, 65.4 mg of PVdF, and 2.84 g of NMP, and pasted on a C-Al current collector by using a "doctor blade" (Imoto Machinary Co. Ltd. (Japan), flame applicator). The C-Al sheet was subsequently dried under vacuum at 80 °C, and cut into 2 cm × 2 cm size electrodes. All tests were carried out in a mixture of EC:DEC (1:3 volume ratio) solution containing 1.0 M LiBF$_4$ at a rate of 0.1 C. Cut-off potentials for charge and discharge were set at 3.7 V and 2.0 V (versus Li/Li$^+$), respectively. The surface morphology of PDMcT–PEDOT composite films after charge/discharge tests was analyzed using scanning electron microscopy (SEM) (JEOL Ltd., model JSM-5800). After the first charge/discharge cycle in a battery test, the PDMcT–PEDOT composite cathodes, removed from the prototype lithium-battery cells, were washed with acetone and used immediately for SEM analysis.

The effects of a PEDOT–PSS film on the redox behavior of a PDMcT–PEDOT composite film were studied via CV. A PEDOT–PSS film-coated PDMcT–PEDOT (PDMcT–PEDOT/PEDOT–PSS) film modified GCE was prepared by casting a PEDOT–PSS solution (PEDOT: ca. 35.7 mM, PSS: ca. 21.8 mM) on a PDMcT–PEDOT film-modified GCE. A PEDOT film-coated PDMcT–PEDOT film (PDMcT–PEDOT/PEDOT) modified GCE was prepared by casting a NMP solution containing PEDOT (36.2 mM) on a PDMcT–PEDOT film-modified GCE. The electrodes were dried under vacuum at room temperature for an hour to obtain the PDMcT–PEDOT/PEDOT–PSS and PDMcT–PEDOT/PEDOT films.

3. Results and discussion

3.1. Electrocatalytic effect of PEDOT film-coated GCEs towards the redox reactions of DMcT in solution

We first present the redox reactions of DMcT in solution at a PEDOT film-modified GCE in order to exemplify the dramatic electrocatalytic effect of PEDOT towards the reactions [9]. Fig. 1a-1 presents a CV for a 5 mM DMcT solution at a bare GCE in a 0.1 M LiClO$_4$/AN solution. An expanded current scale CV, recorded over different potential regions is also shown in Fig. 1a-2 for comparison. Over the potential region from −1.00 V to +0.20 V versus Ag/Ag$^+$–AN (Fig. 1a-2), an anodic current peak, due to oxidation of DMcT to generate the dimer, was observed at −0.13 V, and the corresponding cathodic current peak was observed at −0.66 V. The redox current peak potential separation, ΔE_p, was 530 mV, indicating that the charge transfer kinetics of the dimerization process are electrochemically irreversible. Moreover, over the potential region from −0.60 V to +0.80 V, a larger anodic current response was observed with an onset potential of ca. +0.32 V. This is due to the subsequent oxidation of the DMcT dimer to the polymer. On the other hand, the corresponding reduction current response was not observed over the same potential region, indicating that both oxidations of DMcT monomer and the dimer obtained at an unmodified GCE are electrochemically irreversible at room temperature.

However, at a PEDOT film-coated GCE, DMcT exhibited quite different redox responses, indicative of the dramatic electrocatalytic effect of the PEDOT film-modified GCE towards the redox reactions of DMcT. Fig. 1a-4 presents a representative CV for 5 mM DMcT at a PEDOT film-coated GCE in a 0.1 M LiClO$_4$/AN solution. Fig. 1a-3 shows a CV for a PEDOT film-coated GCE in a 0.1 M LiClO$_4$/AN solution without DMcT for comparison. The film thickness of the PEDOT film was approximately 2 μm. Over the potential region from −0.60 V to +0.80 V versus Ag/Ag$^+$–AN, the current response did not exhibit any characteristic redox peaks, while scanning to −1.20 V resulted in the development of oxidation and reduction peaks typical of PEDOT films (see Fig. 2) [24,25]. In Fig. 1a-4, a set of well-defined oxidation and reduction waves, which were absent at an unmodified GCE, were observed at formal potential values of −0.3 V and +0.4 V, respectively. Based on our previous stud-
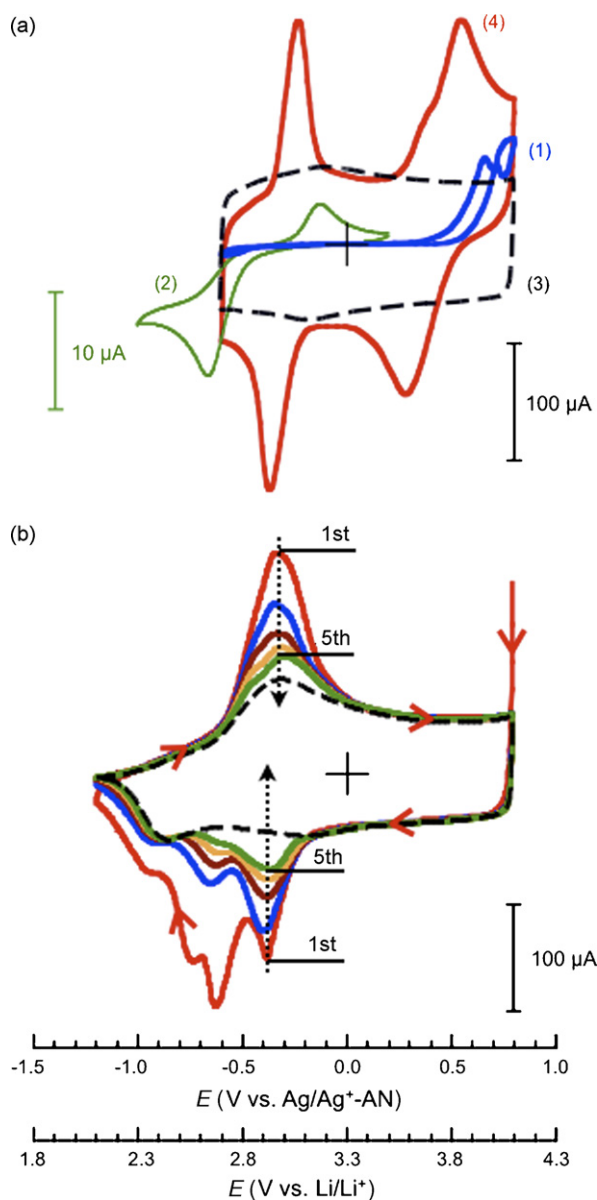
Fig. 2. (a) Representative CV for a PEDOT film-modified GCE in 0.1 M LiBF$_4$/EC:DEC. Scan rate was 20 mV s^{-1}. (b) Cathodic capacity obtained at different scan rates. (c) Cathodic charge obtained from different PEDOT coverages.

Fig. 1. (a) CVs for a 5 mM DMcT-2H solution at a bare GCE in 0.1 M LiClO$_4$/AN. The potential regions investigated were (1) −0.60 V to +0.80 V and (2) −1.00 V to +0.20 V. CVs for (3) 0 mM and (4) 5 mM DMcT-2H solutions at PEDOT film-modified GCEs in 0.1 M LiClO$_4$/AN. (b) CVs for a DMcT–PEDOT composite film-coated GCE in 0.1 M LiClO$_4$/AN solution (solid lines). CVs for a PEDOT film-coated GCE obtained in 0.1 M LiClO$_4$/AN are also shown for comparison (dashed lines). The scan rate in all cases was 20 mV s^{-1}.

ies on the acid–base chemistry for this system [19], the redox response at −0.3 V was assigned to oxidation (dimerization) of singly-protonated DMcT (DMcT-1H) to generate the dimer. In addition, the redox reaction of DMcT-1H proceeded not only at the surface of the PEDOT film but also inside the film [19]. Moreover, the redox response at +0.4 V was assigned to oxidation (polymerization) of the protonated DMcT dimer [19]. From the observed dramatic decrease in the overpotentials, it was evident that both the dimerization and polymerization processes of DMcT are greatly electrocatalyzed at a PEDOT film-modified GCE, and thus, the use of this electrocatalytic effect was deemed to be a promising strategy for organosulfur compounds such
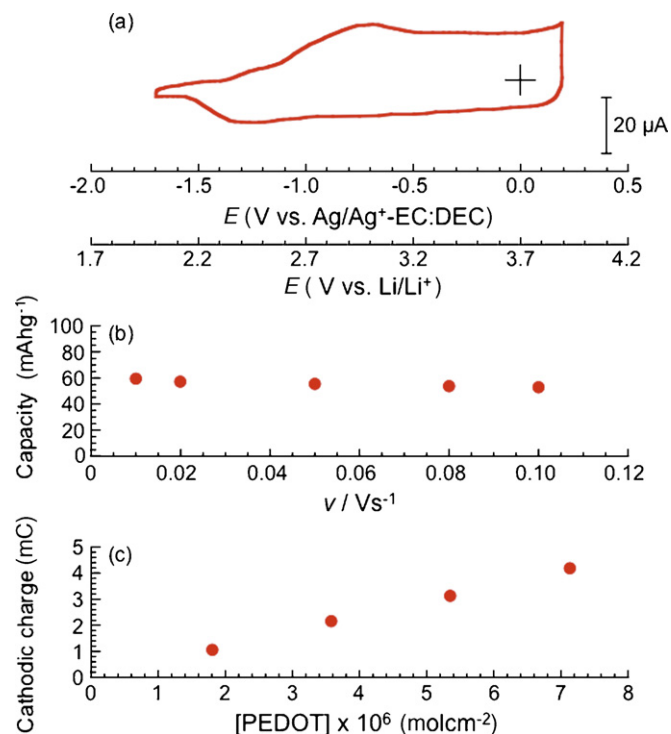
as DMcT to be of practical use as high-energy cathodes for lithium-ion batteries.

Next, the redox behavior of "electrochemically-prepared" PDMcT–PEDOT composite films was studied. In this system, DMcT is deposited on and into an electrochemically prepared PEDOT film and thus, all of the electroactive components are confined to the electrode surface as a composite film. Therefore, the behavior of this system provides a better point of comparison to conditions employed in practical applications. Moreover, the system allows for the elimination of the effects of protons on the redox behavior of DMcT, which is the most important point to consider for cathodes in lithium-ion batteries (no protons are available in the device and thus, hydrogen evolution is precluded).

Fig. 1b shows the CV response for an "electrochemically-prepared" PDMcT–PEDOT composite film in a 0.1 M LiClO$_4$/AN solution over the potential range from −1.20 V to +0.80 V versus Ag/Ag$^+$–AN (solid lines). The CV for a PEDOT film-coated GCE obtained in the same solution is also shown for comparison (dashed line). As would be anticipated, the redox couple previously observed at +0.4 V in a DMcT solution (Fig. 1c) is absent since no protons are available [19]. Instead, multiple reduction peaks were observed over the potential range from −0.20 V to −1.20 V, while the oxidation response was observed as a single peak at −0.34 V. The responses can be assigned to the reduction of PDMcT to doubly deprotonated DMcT (DMcT^{2-}) through the dimer, and the corresponding oxidation of DMcT^{2-} to the polymer. The multiple cathodic peaks are likely due to the reduction of different lengths of polymers (or

oligomers). In addition, the amplitude of the response decreased with increasing number of cycles, indicating the dissolution of DMcT monomer during reductive potential cycles. These results indicate that, for practical applications, the catalyzed anodic and cathodic reactions of DMcT would be available at −0.34 V (∼3 V versus Li/Li⁺) and over the range from −0.20 V to −1.20 V (ca. 2–3 V versus Li/Li⁺), respectively.

3.2. Redox behavior of PEDOT film-modified GCEs and PDMcT–PEDOT composite cathodes

Next, we investigated the redox behavior and charge/discharge performance of "chemically-prepared" PDMcT–PEDOT composite cathodes in a 1.0 M LiBF₄/EC:DEC solution. The redox behavior of chemically-prepared PEDOT, which was employed to prepare DMcT–PEDOT composite cathodes, was first studied in detail. Fig. 2a shows a representative CV obtained at 20 mV s⁻¹ for a PEDOT film-modified GCE in a 1.0 M LiBF₄/EC:DEC solution. Over the potential region from −1.20 V to 0.20 V versus Ag/Ag⁺–EC:DEC, oxidation of the PEDOT film (the *p*-type doping process) started at −1.39 V and a current peak was observed at −0.70 V, followed by a plateau current response due mostly to its capacitance. It is well known that the capacitance of conducting polymer films is strongly dependent on the applied potential [26,27] because of the change in the capacitance due to the changes in the electronic state and morphology of the films involved in the redox reactions. In the case of PEDOT, the capacitance of the film increases during the oxidation and reaches a steady value of capacitance after the completion of the oxidation, resulting in a plateau current response over the potential region where the faradic current response of the PEDOT film is not dominant. The corresponding reduction current peaks were observed at −0.77 V and −1.25 V, respectively. Thus, both chemically and electrochemically prepared PEDOT films exhibited similar onset potentials for oxidation and windows of conductivity, indicating that both materials have similar electronic structures. Consequently, we anticipated a similar electrocatalytic activity towards the redox reactions of DMcT.

Fig. 2b shows a plot of the gravimetric capacity (mAh g⁻¹) obtained at different scan rates. The capacity obtained was approximately 59 mAh g⁻¹ and, as would be anticipated, was not significantly dependent on the scan rate. These results indicate that the PEDOT film is completely oxidized/reduced over the time scales employed and that the number of electrons actually obtained from the film is approximately 0.3 per monomer unit over the potential region examined. Moreover, as shown in Fig. 2c, the cathodic charge obtained was proportional to the PEDOT coverage (mol cm⁻²). Thus it was confirmed that, as would be anticipated, the redox reaction of chemically-prepared PEDOT is a surface process and that charge propagation is facile.

Fig. 3 presents a CV obtained at 0.5 mV s⁻¹ for a PDMcT–PEDOT composite cathode in a 1.0 M LiBF₄/EC:DEC solution. The CV was obtained from a prototype cell (see experimental section) and the molar ratio of PDMcT to PEDOT in the composite cathode was 1:1. The film thickness was approximately 50 μm and the open-circuit potential was 3.20 V versus
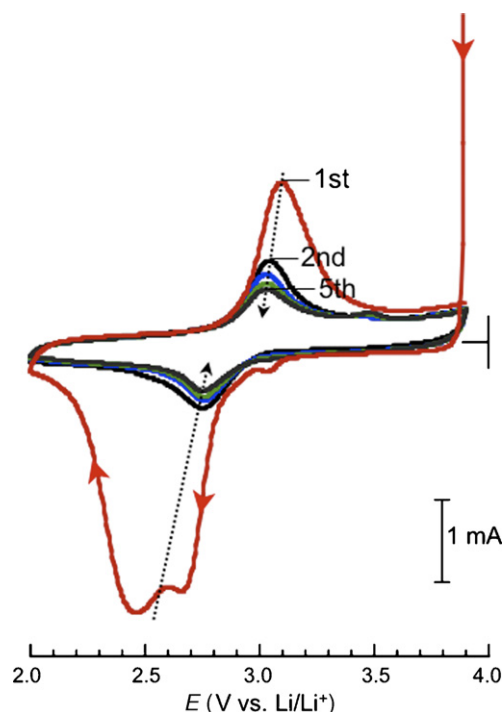

Fig. 3. CV for a PDMcT–PEDOT composite cathode (1:1 mole ratio, C-Al current collector) in 1.0 M LiBF₄/EC:DEC. Scan rate was 0.5 mV s⁻¹.

Li/Li⁺. In the first reduction (discharge), a large cathodic current with peak potentials at 2.66 V and 2.48 V, due to reduction of PDMcT, was observed as a result of electrocatalysis by the PEDOT film. The gravimetric capacity obtained at the first discharge was 177 mAh g⁻¹ (based on mass of PDMcT and PEDOT) which is 74% of the theoretical capacity. It is worth noting that the large anodic transient current observed at 3.90 V at the first discharge is due to the double layer charging current of the film and not to further oxidation of PDMcT. Moreover, the charge obtained (area under the transient) is clearly negligible when compared to the faradic charge obtained from the reduction of PDMcT. In the reverse potential scan (recharge), while the corresponding anodic current due to regeneration of PDMcT was observed with a peak potential at 3.10 V, the gravimetric capacity decreased significantly resulting in only 64 mAh g⁻¹. After the first cycle, the charge obtained from the redox reaction of PDMcT gradually decreased with increasing number of potential cycles. The redox response with anodic and cathodic current peaks at 3.02 V and 2.75 V, respectively, observed during fifth cycle, can be assigned to the redox reactions of DMcT dissolved in the electrolyte solution (*vide infra*). Additionally, the difference observed in the current response from the film shown in Fig. 8 relative to the one described above is due most likely to the difference in their thickness (50 μm versus 2 μm) and their cell configurations (a prototype cell versus a conventional three-electrode cell).

Fig. 4a presents potential profiles during charge/discharge obtained for a PDMcT–PEDOT composite cathode in a 1.0 M LiBF₄/EC:DEC solution. The 1:1 mole ratio PDMcT–PEDOT composite film exhibited a capacity of 205 mAh g⁻¹ (based on electroactive mass) with a potential plateau at 2.80 V at the
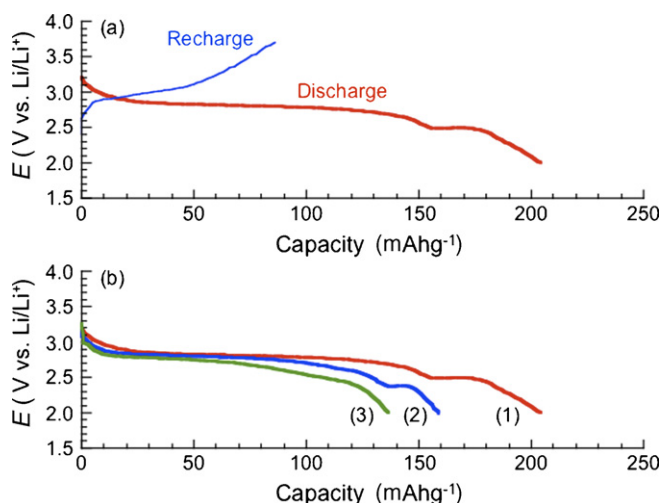
Fig. 4. (a) Potential profiles during the first charge/discharge cycle obtained for a PDMcT–PEDOT composite cathode (1:1 mole ratio) in 1.0 M LiBF$_4$/EC:DEC. Charge/discharge rate employed was 0.1 C (3.7 V cut) and 0.1 C (2.0 V cut) for charge and discharge, respectively. (b) First discharge curves obtained for PDMcT–PEDOT composite cathodes with different composition in 1.0 M LiBF$_4$/EC:DEC: (1) PDMcT:PEDOT = 1:1, (2) 2:1, and (3) 5:1 mole ratio.
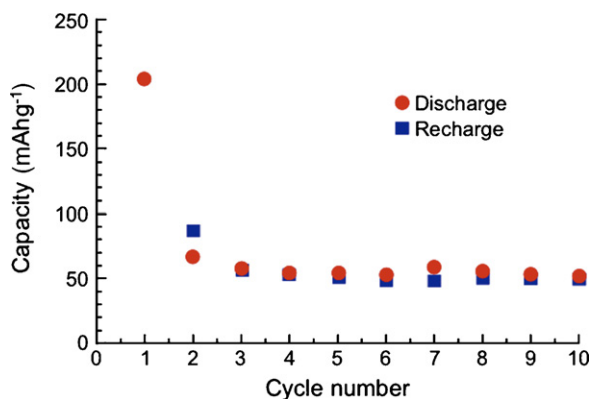

Fig. 5. Charge/discharge cycle performance obtained for a PDMcT–PEDOT composite cathode (1:1 mole ratio) in 1.0 M LiBF$_4$/EC:DEC.

first discharge, corresponding to 574 Wh kg^{-1} of energy density. Based upon CV studies for the composite film discussed above, the plateau observed at 2.80 V was ascribed to the electrocatalytic reduction of PDMcT by PEDOT. On the other hand, the capacity obtained at the first recharge was only 88 mAh g^{-1} (43% of coulomb efficiency) and the discharge capacity eventually reached approximately 50 mAh g^{-1} after the third cycle as shown in Fig. 5. From these results as well as the results obtained from "electrochemically-prepared" composite films, we believe that the loss of capacity occurs as a result of dissolution and leaching of the reduction products of PDMcT, particularly the DMcT monomer, into the electrolyte solution during discharge.

The amount of PEDOT required for the electrocatalysis in the composite film was also investigated. Clearly, the more PDMcT in a PDMcT–PEDOT composite film, the higher the gravimetric capacity. The theoretical capacities of PDMcT and PEDOT are 362 mAh g^{-1} and 115 mAh g^{-1}, assuming that the numbers of electrons transferred are 2 and 0.6 [21], respectively. Fig. 4b presents the first discharge curves for PDMcT–PEDOT composite cathodes with different composition in a EC:DEC solution. While the 1:1 mole ratio PDMcT–PEDOT composite film (Fig. 4b-1) exhibited high efficiency, 86% of theoretical capacity, the value decreased with increasing amount of PDMcT relative to PEDOT (57% and 43% for PDMcT:PEDOT = 2:1 and 5:1 mole ratios, respectively, Fig. 4b-2 and b-3). These results indicate that a minimal amount of PEDOT is required as an electrocatalyst in order to utilize the redox charge of PDMcT efficiently, and that the optimized molar composition appears to be approximately 1:1.

To further investigate the redox capacity loss observed in PDMcT–PEDOT composite films, SEM images were obtained for a 1:1 mole ratio PDMcT–PEDOT composite film cathode before (Fig. 6a) and after (Fig. 6b) the first charge/discharge cycle. It can be seen from Fig. 6a that PDMcT particles appear as approximately 3–5 µm in size and are brighter than PEDOT and CB (carbon black) particles due to its lower conductivity. By comparing the images, it is also evident that the number of PDMcT particles decreased significantly after the first charge/discharge cycle. Moreover, after the battery cell was dis-
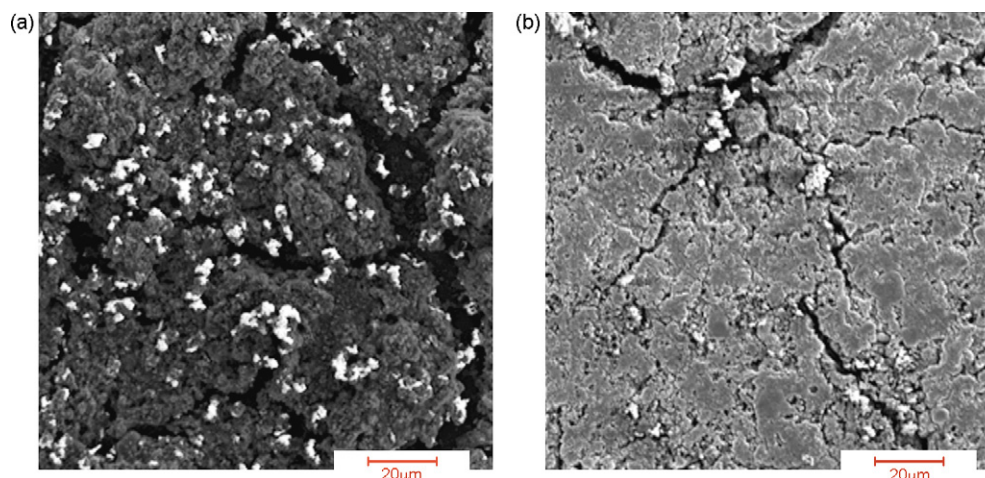

Fig. 6. SEM images of a PDMcT–PEDOT composite cathode: (a) before and (b) after the first charge/discharge cycle.
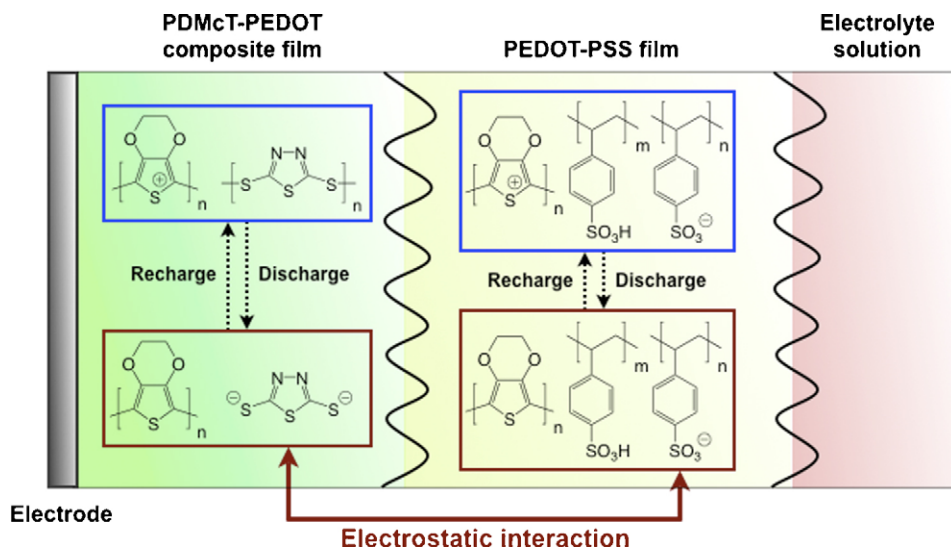
Fig. 7. Schematic depiction of the effect of the ionic polymer PEDOT–PSS on the redox behavior of a PDMcT–PEDOT composite cathode via the electrostatic interaction between the reduction products of PDMcT, generated during discharge, and the sulfonate groups of PSS.

assembled, the electrolyte solution had turned yellow, which is the color of the DMcT species. Thus it is evident from the results that reduction products of PDMcT, generated during the first discharge, had dissolved into the electrolyte solution to a significant extent, resulting in the experimentally observed large decrease in the redox capacity of the composite film.

3.3. Effect of PEDOT–PSS film on the redox behavior of PDMcT–PEDOT composite cathodes

In the previous section, it was shown that PDMcT–PEDOT composite cathodes lost a significant amount of redox capacity during multiple charge/discharge cycles because of dissolution of reduction products of PDMcT, such as the DMcT monomer, into the electrolyte solution. In order to improve the charge/discharge cyclability of PDMcT–PEDOT composite cathodes (i.e., in order to prevent leaching of DMcT species), the effect of employing an ionic polymer, PEDOT–PSS, on the redox behavior of PDMcT–PEDOT was investigated. The expectation was that, by coating the PDMcT–PEDOT composite film with PEDOT–PSS, the electrostatic interaction between the reduction products of PDMcT and the sulfonate groups of PSS would prevent the DMcT species from leaching into the electrolyte solution from the composite cathode (Fig. 7).

Fig. 8 presents a representative CV obtained at $20\,mV\,s^{-1}$ for a 1:1 mole ratio PDMcT–PEDOT composite film-coated GCE in a 0.1 M LiClO$_4$/AN solution. The inset is an identical, but enlarged, CV of the one shown in the main panel (for comparison with Fig. 9). The potential was swept from +0.80 V to −1.20 V versus Ag/Ag$^+$–AN. In the first reductive potential sweep, a large current response, due to reduction of PDMcT, was observed at −0.86 V. The cathodic charge obtained indicated that the efficiency for reduction of PDMcT to its monomer was approximately 100% under the conditions employed. As was the case for a "chemically-prepared" PDMcT–PEDOT composite film (Fig. 3), the anodic current response observed at

+0.80 V versus Ag/Ag$^+$–AN at the first discharge is due to the charging current of the composite film and thus, the charge obtained from the process does not affect the comparison of cathodic charges obtained from PDMcT shown in Fig. 10. Additionally, the slight difference observed in the current response from an "electrochemically-prepared" composite film (Fig. 1b) is likely due to differences in their physicochemical properties such as the polymer lengths (chemical versus electrochemi-
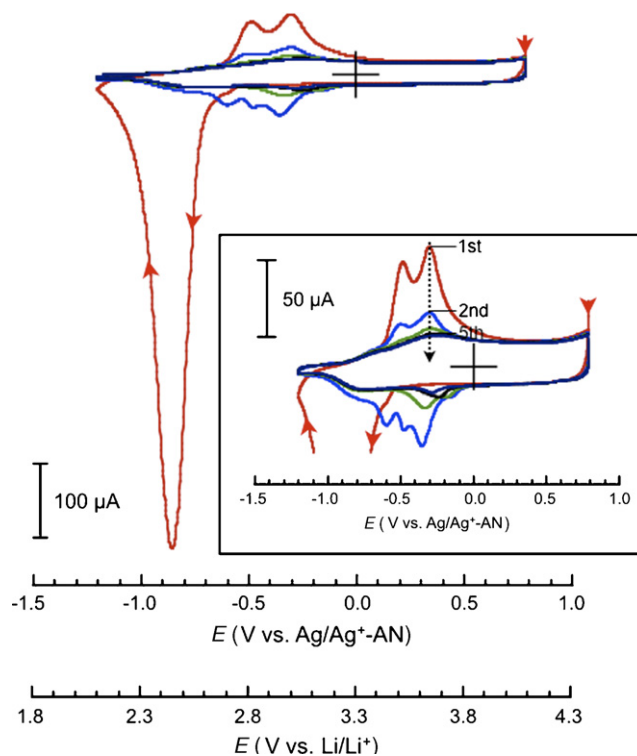

Fig. 8. CV for a 1:1 mole ratio PDMcT–PEDOT composite film-modified GCE in 0.1 M LiClO$_4$/AN. Scan rate was $20\,mV\,s^{-1}$. The inset is an identical, but enlarged CV of the one shown in the main panel.
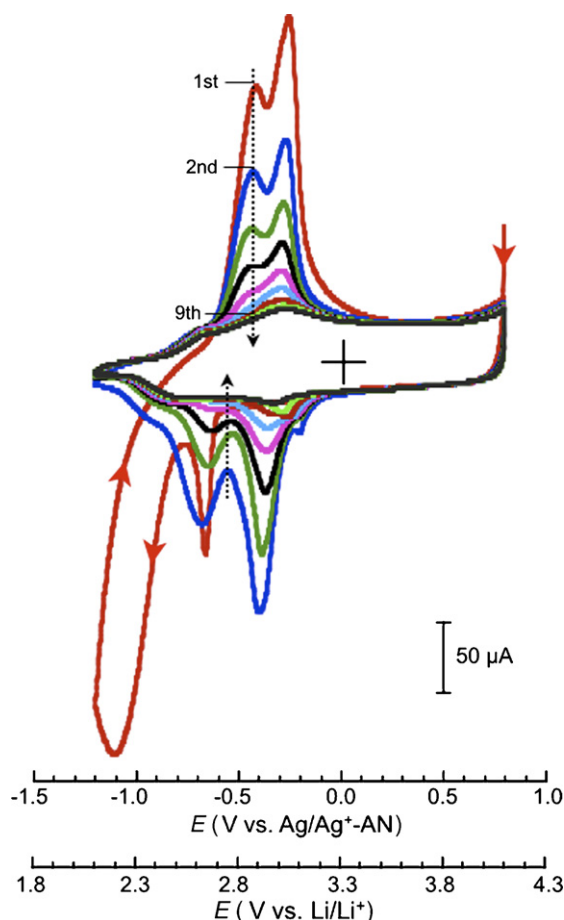
Fig. 9. CV for a PDMcT–PEDOT/PEDOT–PSS composite film-coated GCE in 0.1 M LiClO$_4$/AN. Scan rate was 20 mV s^{-1}.

cal polymerizations) and their distribution within the films. On the other hand, in the reverse potential scan (recharge), the anodic current response, with peak potentials at −0.48 V and −0.30 V, due to regeneration of PDMcT, significantly decreased as was previously observed for an "electrochemically-
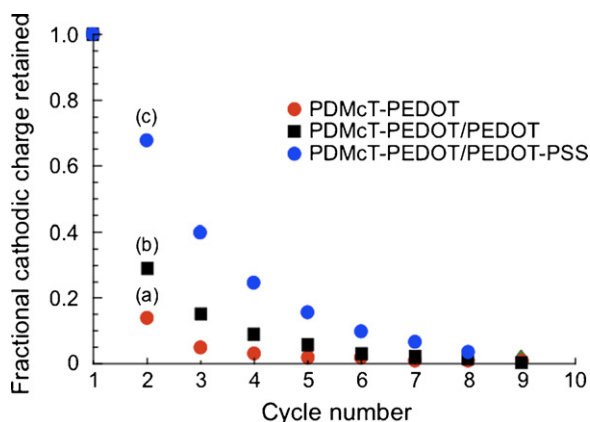

Fig. 10. Cathodic charge obtained from reduction of PDMcT in (a) PDMcT–PEDOT, (b) PDMcT–PEDOT/PEDOT, and (c) PDMcT–PEDOT/PEDOT–PSS films in a 0.1 M LiClO$_4$/AN solution. The cathodic charge obtained at the tenth cycle was set as the background in order to subtract the current response due to PEDOT, and the charge at first cycle was set to 1.

prepared" PDMcT–PEDOT composite film (Fig. 1b) and a PDMcT–PEDOT composite film in a prototype cell (Fig. 3). The response was ascribed to oxidation of DMcT^{2-} to its dimer (at −0.48 V), and the further oxidation to PDMcT (at −0.30 V). After the first cycle, the charge obtained from the redox reaction of PDMcT decreased with increasing number of potential cycles, eventually leaving only the redox response of PEDOT itself. In addition, after the first cycle, the reduction of PDMcT occurred at more positive potentials when compared to the response at the first cycle, suggesting that DMcT polymer, regenerated during the anodic potential sweep, possesses somewhat different physicochemical properties such as polymer chain length, from the starting polymers (prepared either chemically or electrochemically).

Fig. 9 presents a representative CV obtained at 20 mV s^{-1} for a PEDOT–PSS film-coated PDMcT–PEDOT composite film (PDMcT–PEDOT/PEDOT–PSS) modified GCE in a 0.1 M LiClO$_4$/AN solution. In the first reductive potential sweep, the cathodic current peak due to reduction of PDMcT shifted negative (relative to a PDMcT–PEDOT composite film) and appeared at −1.10 V, resulting in a decrease in the cathodic charge obtained, due to reduction of PDMcT, over the potential regime under study (+0.80 V to −1.20 V). This may be due to the negative charges in the PEDOT–PSS film retarding lithium-ion diffusion into the PDMcT–PEDOT composite system to compensate the negative charges generated upon reduction of PDMcT as well as to potential ohmic drops. In fact, an increase in the concentration of LiClO$_4$ in the AN solution lead to a shift of the cathodic peak potential, associated with reduction of PDMcT, towards positive values at the first cycle, and to a decrease in the peak separation for the redox reactions of PDMcT (see supporting information, Fig. S1). This result indicates that under these conditions the redox reactions of PDMcT are lithium-ion diffusion-controlled processes. In the reverse potential scan (recharge), the oxidation current peaks, corresponding to oxidation of DMcT^{2-} to its dimer and the further oxidation to PDMcT, were observed at −0.42 V and −0.30 V, respectively, and the corresponding reduction current peaks were observed at −0.67 V and −0.38 V, respectively. The increase in the peak separation for the redox reactions of DMcT in the presence of the PEDOT–PSS film, compared to a PDMcT–PEDOT film, also indicates that there are lithium-ion diffusion-controlled processes and ohmic effects. Furthermore, and most importantly, while the redox current response of DMcT decreased with the increasing number of potential cycles, the anodic charge obtained at the first recharge significantly increased compared to a PDMcT–PEDOT composite film without PEDOT–PSS. This result suggests that PEDOT–PSS films are capable of preventing DMcT species from leaching out into the electrolyte solution due to the electrostatic interaction between DMcT species and sulfonate groups of PSS.

In order to make a better comparison between PDMcT–PEDOT and PDMcT–PEDOT/PEDOT–PSS films, the cathodic charge retained was estimated for the two films. The cathodic charge obtained at the tenth cycle was set to the background to subtract the current response due to PEDOT, and the charge at first cycle was set to 1. In addition, a PEDOT

film-coated PDMcT–PEDOT (PDMcT–PEDOT/PEDOT) film was also prepared for comparison to evaluate the effect of PSS on the PEDOT–PSS film. Fig. 10 presents the fractional cathodic charges obtained from reduction of PDMcT in PDMcT–PEDOT (Fig. 10a), PDMcT–PEDOT/PEDOT (Fig. 10b), and PDMcT–PEDOT/PEDOT–PSS (Fig. 10c) films in a 0.1 M LiClO$_4$/AN solution. It can be seen that, while all of three films exhibited a decrease in the cathodic charge retained with increasing number of potential cycles, the cathodic charge retained in the PDMcT–PEDOT/PEDOT–PSS film (Fig. 10c) was significantly greater than that in the PDMcT–PEDOT film (Fig. 10a). In particular, the charges retained in PDMcT–PEDOT/PEDOT–PSS and PDMcT–PEDOT films at the second cycle were 68% and 14%, respectively. Furthermore, the PDMcT–PEDOT/PEDOT film (Fig. 10b) only exhibited a slight improvement over the PDMcT–PEDOT film. Therefore, it is evident that the PEDOT–PSS film is electrostatically, but not physically, capable of preventing DMcT species from leaching into the electrolyte solution, thus improving the coulomb efficiency for the redox reactions of DMcT in PDMcT–PEDOT composite films during charge/discharge cycles.

4. Conclusions

In this study, the redox behavior of PEDOT and PDMcT–PEDOT composite films has been characterized in detail in a EC:DEC solution using chemically-prepared PDMcT and PEDOT. As was the case for the redox reactions of DMcT dissolved in solution at a PEDOT film-modified GCE, the redox reactions were also dramatically electrocatalyzed by PEDOT in chemically-prepared PDMcT–PEDOT composite films. The PEDOT film exhibited 59 mAh g^{-1} of gravimetric capacity and facile charge propagation. It was also found that a lithium battery cell, with a PDMcT–PEDOT (1:1 mole ratio) composite film as cathode, exhibited 205 mAh g^{-1} with a potential plateau at 2.80 V versus Li/Li$^+$ at the first discharge. These values correspond to an energy density of 574 Wh kg^{-1}, comparable to lithium metal oxides currently used as cathode materials for practical batteries. However, the capacity decreased significantly with increasing number of potential cycles due to dissolution of the reduction products of PDMcT generated during discharge. The poor charge/discharge durability precludes the use of this system for practical application in lithium-ion rechargeable batteries.

Furthermore, it was observed that the use of the ionic polymer PEDOT–PSS can electrostatically, but not physically, prevent the leaching, at least in part, of DMcT species into the electrolyte solution, improving the coulomb efficiency for the redox reactions of DMcT in a PDMcT–PEDOT composite film. However, it was also observed that coating PEDOT–PSS to a PDMcT–PEDOT composite film impeded lithium-ion diffusion into the PDMcT–PEDOT film layer, which could result in a decrease in the charge/discharge rate capability. Nevertheless, the use of electrostatic interactions shows potential to be a viable solution to the improvement of the charge/discharge cyclability of PDMcT–PEDOT composite cathodes. We are exploring this

as well as other alternatives which we will report on in the future communications.

5. Supporting Information

A figure of CV for a PDMcT–PEDOT/PEDOT–PSS composite film-coated GCE in a 1.0 M LiClO$_4$/AN solution.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jpowsour.2007.04.086.

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