

# Preparation and electrochemical characterizations of poly(3,4-dioxyethylenethiophene)/LiCoO<sub>2</sub> composite cathode in lithium-ion battery

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## Abstract

A composite electrode material, poly(3,4-ethylenedioxythiophene) (PEDOT)/LiCoO<sub>2</sub>-carbon fibers (VGCF) from a continuous process of electrochemical deposition of 3,4-ethylenedioxythiophene (EDOT) monomer on the pre-formed LiCoO<sub>2</sub>-VGCF electrode, was prepared and characterized to test its applicability in lithium-ion battery. Compared to the bare LiCoO<sub>2</sub>-VGCF electrode, use of PEDOT/LiCoO<sub>2</sub>-VGCF composite as cathode in lithium-ion battery has enhanced properties such as the cyclability, electrochemical stability, intercalation/deintercalation rate of lithium ion and rate capability. Scanning electron microscope shows the successful coating of PEDOT on the LiCoO<sub>2</sub> particles and the VGCF fibers. The differential scanning calorimetry (DSC) scans of the charged cathodes show that incorporation of PEDOT reduces the thermal stability of the cathode.

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## 1. Introduction

Lithium-ion batteries are key components of many portable electronic devices and also show promise for the use in electric vehicles. Due to their high energy density, flexible design, lithium ion batteries have preference over other secondary battery systems, nevertheless, many approaches to alleviate problems such as poor long-term cyclability, worse safety and rate capability [1–4] are still undergoing. Discovery of new composite systems to serve as electrode materials represents a reasonable approach and had been frequently attempted previously.

Electrically conductive polymers (ECPs) represent an interesting family of synthetic materials due to their high electron mobility inside the doped polymer chains [5–9]. The

practical application of ECPs is often dependent on their stability in ambient conditions, in this aspect, great focus had been on polythiophenes (PThs) since they are generally stable in air and moisture. Poly(3,4-ethylenedioxythiophene) (PEDOT), as one member of PTh family, has gained great attention in view of its high electrical conductivity in the p-doped state, good thermal and chemical stability and fast electrochemical switching [7,8]. With this regard, PEDOT had been incorporated into metal oxides such as LiMn<sub>2</sub>O<sub>4</sub> [10] and V<sub>2</sub>O<sub>5</sub> [11–13] and to test their applicability in lithium-ion battery. In this aspect, EDOT monomer can be directly oxidized by the metal oxides to initiate polymerization and form PEDOT polymer into the inner layer of the metal oxides. Use of these PEDOT/metal oxide composites as electrodes showed drastic enhancement on capacity and charge/discharge behavior.

In this study, we attempted to combine PEDOT with vapor growth carbon fiber (VGCF)/LiCoO<sub>2</sub> and to test its capability to serve as cathode materials in lithium-ion battery.

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PEDOT polymer may be electropolymerized between the two kinds of particles to enhance the electronic conductivity of the resulting composite material [14]. Use of VGCF is due to its reported applications [15–17] as filler materials of the electrodes in lithium-ion battery. The unique properties of VGCF, such as the small diameter, large surface area, high electrical conductivity, and the very spacial network morphology on the electrodes, all contribute to the improved performance (e.g. the cycle characteristic) in lithium-ion battery.  $\text{LiCoO}_2$  is the lithium-ion source and is frequently used due to its promising properties in lithium-ion battery. In this study, the PEDOT/ $\text{LiCoO}_2$ -VGCF composite cathode was readily prepared by a continuous process, i.e. direct electrochemical polymerization of EDOT to deposit PEDOT on the pre-formed  $\text{LiCoO}_2$ -VGCF electrode. The resulting PEDOT/ $\text{LiCoO}_2$ -VGCF composite was then used as cathode to test its applicability in lithium-ion battery. For comparison, analogous electrochemical characterizations with  $\text{LiCoO}_2$ -VGCF as cathode were also conducted to distinguish the role of the deposited PEDOT. The results provide the possibility to apply PEDOT/ $\text{LiCoO}_2$ -VGCF composite cathode in current commercial lithium-ion battery.

## 2. Experimental

$\text{LiCoO}_2$  (Nippon Chemical Industrial Co.) used in this work has an average particle size of 11.5  $\mu\text{m}$ , and a Brunauer–Emmett–Teller (BET) surface area of 0.21  $\text{m}^2 \text{g}^{-1}$ . VGCF (diameter 150 nm, length 5–10  $\mu\text{m}$ , Showa Denko) with a BET of 13  $\text{m}^2 \text{g}^{-1}$  was used as the conductive carbon of the composite cathode. Electrodes were prepared by combining solid components of VGCF (5 wt.%), polyvinylidenedifluoride (5 wt.%, PVDF, Kureha Chemical Industry Co.) and  $\text{LiCoO}_2$  (90 wt.%) in *N*-methylpyrrolidinone (NMP, Merck) solvent of equal weight. The mixed slurry was then coated on an aluminum foil (20  $\mu\text{m}$ , Nippon Foil Co.) and dried at 90 °C. The dried electrode was compressed by a roller at room temperature to make a smooth and compact film structure. The composite cathode electrode was required to store in the glove box (with its oxygen and humidity content maintained below 5 ppm) for more than 24 h before the electrochemical polymerization step.

The electrochemical deposition of PEDOT was performed by an Autolab electrochemical analyzer with a current sensitivity of 1 nA (Autolab PGSTAT30, Eco Chemie) [9]. A one-compartment three-electrode glass cell was used and the whole apparatus was settled in the glove box. The working electrode is the composite  $\text{LiCoO}_2$ -VGCF electrode prepared by the above procedure with a dimension of 1 cm  $\times$  1 cm. Both the counter and reference electrodes are lithium metal (FMC). PEDOT was deposited on the  $\text{LiCoO}_2$ -VGCF electrode in 1M  $\text{LiPF}_6$  (Kanto Denka Kogyo Co. Ltd.)/propylene carbonate (PC, Ferro) solution with 0.05 M 3, 4-ethylenedioxy thiophene (EDOT) monomer by a constant

current of 0.5 mA for 400 s (equal to 200 mC). The resulting composite electrode of PEDOT/ $\text{LiCoO}_2$ -VGCF was washed by PC for several times before further test for its capability as cathode materials in lithium-ion battery.

The composite cathodes of PEDOT/ $\text{LiCoO}_2$ -VGCF and  $\text{LiCoO}_2$ -VGCF electrodes were tested by repeated cyclic voltammetry (CV) at 50  $\text{mV s}^{-1}$  in 1 M electrolyte of  $\text{LiPF}_6$  in ethylene carbonate: dimethyl carbonate (EC:DMC = 1:1) (Merck, LP 30). A three-electrode glass cell with lithium foil as counter and reference electrodes was used and operation was performed in a glove box. Otherwise, the electrodes were tested by CV at various scan rates in the same system in order to compare the ionic transfer rate of the two composite cathodes. Since the real applications of cathodes in lithium ion battery are the charge/discharge behavior at the constant current mode, the electrodes were therefore charged to 4200 mV at 0.1  $\text{mA cm}^{-2}$  before the subsequent discharge to 2700 mV at either rate of 0.1 or 1.0  $\text{mA cm}^{-2}$  to check the rate capability performance of the composites. The results should be consistent with those from the CV test.

Differential scanning calorimetry (DSC) experiments were carried out after charging the electrodes to 4.3 V at 0.1 C rate. A DSC Perkin-Elmer calorimeter was used. Approximately 4 mg of the cathode composite containing the electrolyte were hermetically sealed in an aluminum DSC pan in a glove box. The samples were analyzed in the DSC using a temperature scan rate of 10 °C  $\text{min}^{-1}$  from 30 to 430 °C.

Surface morphology and surface composition of the composite electrodes were detected by scanning electron microscope (SEM, JEOL JSM35 model, operating at 20 kV) and energy dispersive spectroscopy (EDS), respectively. Specimen of PEDOT/ $\text{LiCoO}_2$ -VGCF was firstly washed by PC and then dried at 90 °C for 24 h before inspected by SEM. In contrast,  $\text{LiCoO}_2$ -VGCF specimen was inspected directly as its prepared status.

## 3. Results and discussion

The target material, PEDOT/ $\text{LiCoO}_2$ -VGCF cathode, was readily made by direct electrochemical deposition of EDOT to the preformed  $\text{LiCoO}_2$ -VGCF electrode. The successful incorporation of PEDOT into the  $\text{LiCoO}_2$  and VGCF components can be verified by comparison of the surface morphology of  $\text{LiCoO}_2$ -VGCF and PEDOT/ $\text{LiCoO}_2$ -VGCF. SEM micrographs of different magnifications (4000 $\times$  and 10,000 $\times$ ) shown in Fig. 1 were selected to focus on the  $\text{LiCoO}_2$ - and VGCF-rich areas, respectively. For the large  $\text{LiCoO}_2$  particles in  $\text{LiCoO}_2$ -VGCF composite (Fig. 1a), several small  $\text{LiCoO}_2$  scraps are visible on the surface area. On the contrary, the large  $\text{LiCoO}_2$  particles in PEDOT/ $\text{LiCoO}_2$ -VGCF composite (Fig. 1c) show no traces of small  $\text{LiCoO}_2$  fragments, which suggests the fact that the surfaces of  $\text{LiCoO}_2$  in the PEDOT/ $\text{LiCoO}_2$ -VGCF sample are covered by the PEDOT polymer. VGCF fibers in  $\text{LiCoO}_2$ -

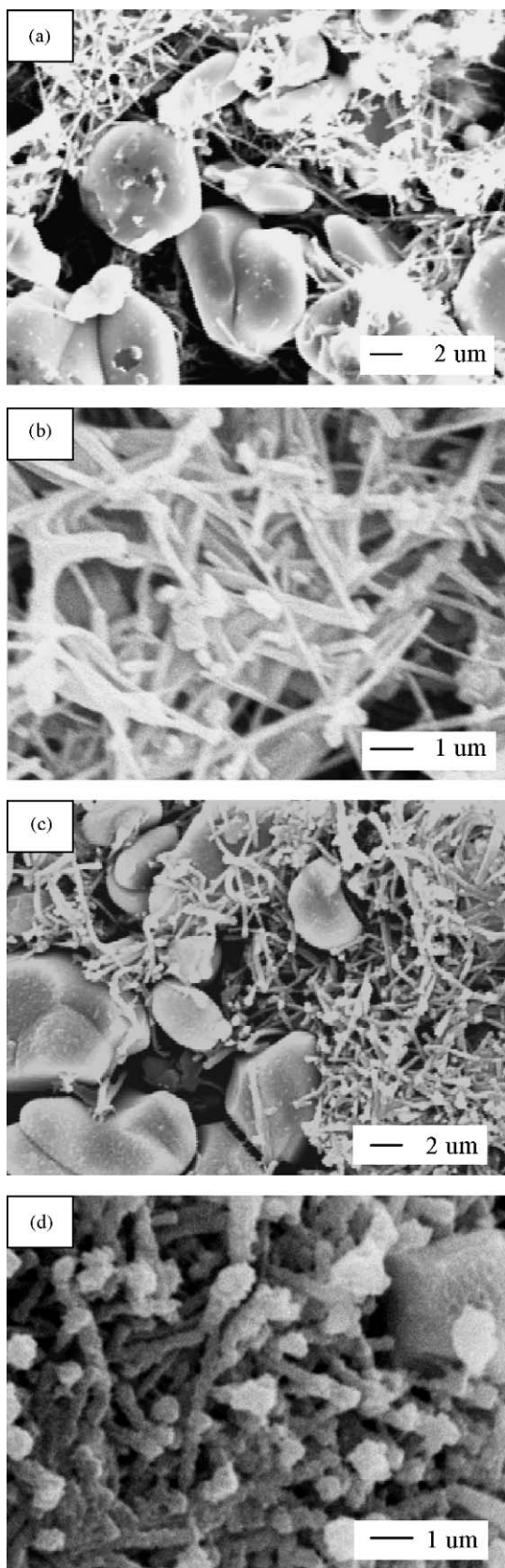


Fig. 1. SEM micrographs of the  $\text{LiCoO}_2$ -VGCF composite cathode at a magnification of (a)  $4000\times$ , (b)  $10,000\times$  and the PEDOT/ $\text{LiCoO}_2$ -VGCF composite cathode at a magnification of (c)  $4000\times$  and (d)  $10,000\times$ .

VGCF composite (Fig. 1b) are randomly distributed over the specimen and have their diameters ranged from 60 to 300 nm. Upon incorporating with PEDOT, VGCF fibers in PEDOT/ $\text{LiCoO}_2$ -VGCF composite become larger (diameters ranged from 150 to 500 nm, Fig. 1d) than the un-coated ones and have their both tips covered by clumps of PEDOT polymer. During the stage of electrochemical deposition, high current density is involved on the tip areas and this may contribute to the preferable deposition of PEDOT on the tips. Also, the defects concentrated on the tips are supposed to be the preferable nucleation sites for the growing PEDOT chains during electrochemical deposition. SEM micrographs in Fig. 1 show the primary evidence of a successful coating of PEDOT polymer on both the  $\text{LiCoO}_2$  and VGCF components.

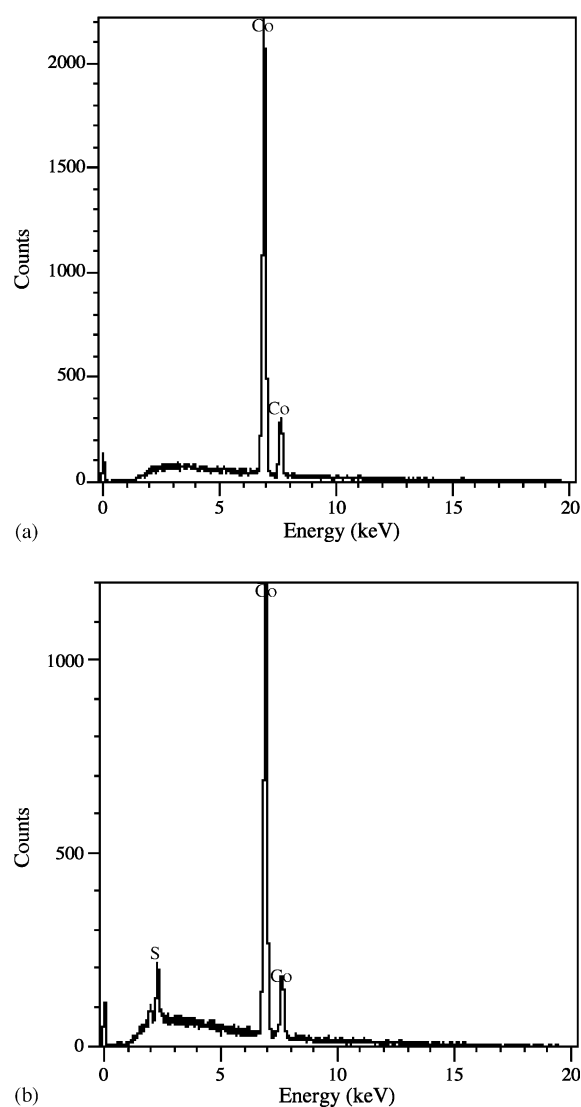


Fig. 2. EDS of (a)  $\text{LiCoO}_2$ -VGCF and (b) PEDOT/ $\text{LiCoO}_2$ -VGCF cathode materials. The composite cathode of PEDOT/ $\text{LiCoO}_2$ -VGCF was prepared by electrochemical deposition of EDOT (0.05 M) monomer on  $\text{LiCoO}_2$ -VGCF cathode under constant current ( $0.5 \text{ mA cm}^{-2}$ ) in 1 M  $\text{LiPF}_6/\text{PC}$  solution.

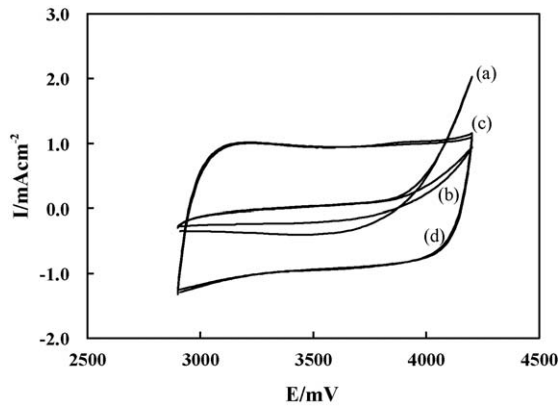


Fig. 3. Cyclic voltammograms from (a) the second scan of  $\text{LiCoO}_2$ -VGCF, (b) the tenth scan of  $\text{LiCoO}_2$ -VGCF, (c) the second scan of  $\text{PEDOT/LiCoO}_2$ -VGCF, and (d) the tenth scan of  $\text{PEDOT/LiCoO}_2$ -VGCF cathodes. Scan rate:  $50 \text{ mV s}^{-1}$ , potential range:  $2900\text{--}4200 \text{ mV}$ .

Incorporation of PEDOT in composites can be further confirmed by the EDS results (Fig. 2). Here,  $\text{LiCoO}_2$ -VGCF sample (Fig. 2a) show only peaks at 6.925 and 7.649 keV, which are attributed to the Co  $\alpha$  and  $\beta$  in  $\text{LiCoO}_2$ , respectively. In contrast, extra peak at 2.307 keV due to the S  $\alpha$  of PEDOT can be detected for  $\text{PEDOT/LiCoO}_2$ -VGCF (Fig. 2b). In combining the SEM results, successful deposition of PEDOT to  $\text{LiCoO}_2$ -VGCF by electrochemical reaction can be demonstrated.

CV scan with  $\text{LiCoO}_2$ -VGCF or  $\text{PEDOT/LiCoO}_2$ -VGCF as cathode was performed in the standard LP30 electrolytes and the representative results from the second and the tenth cycles were shown in Fig. 3. With  $\text{LiCoO}_2$ -VGCF as cathode, curves from the second (curve (a)) and the tenth cycles (curve (b)) have their onset potentials of the anodic currents at  $\sim 3800 \text{ mV}$ , however, the curve shapes are basically varied, which refers to the occurrence of certain irreversible processes on prolonged cycling. The situation is different for the  $\text{PEDOT/LiCoO}_2$ -VGCF case since there is little differ-

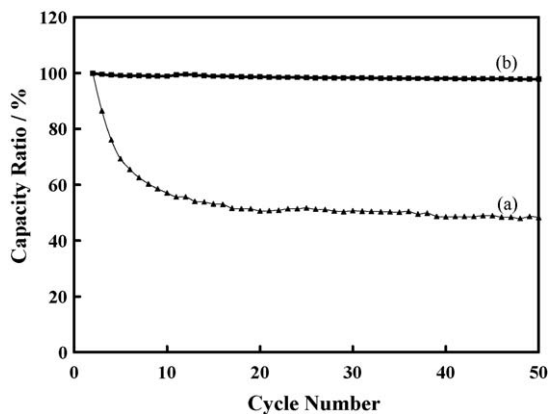


Fig. 4. Capacity ratio as a function of the cycle number with (a)  $\text{LiCoO}_2$ -VGCF and (b)  $\text{PEDOT/LiCoO}_2$ -VGCF cathodes in LP 30 electrolytes. Scan rate:  $50 \text{ mV s}^{-1}$ , potential range:  $2900\text{--}4200 \text{ mV}$ .

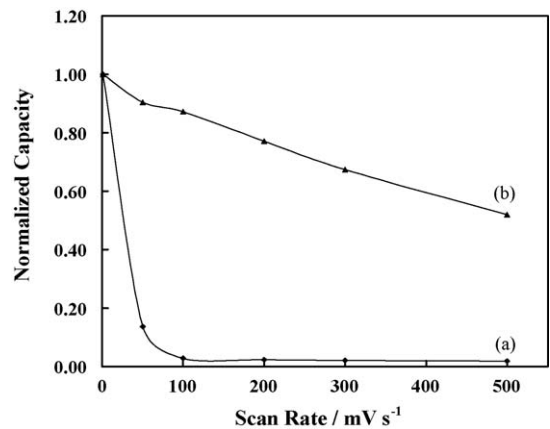


Fig. 5. Normalized capacity (in respect to that at scan rate of  $1 \text{ mV s}^{-1}$ ) as a function of scan rate with (a)  $\text{LiCoO}_2$ -VGCF and (b)  $\text{PEDOT/LiCoO}_2$ -VGCF cathodes. Scan rate: 1, 50, 100, 200, 300 and  $500 \text{ mV s}^{-1}$ , potential range:  $2900\text{--}4200 \text{ mV}$ .

ence between results from the second (curve (c)) and the tenth (curve (d)) cycles. The rather symmetric shape for the CV curve of the  $\text{PEDOT/LiCoO}_2$ -VGCF cathode results in better reversible capacity of the cathodes, which may refer to the potential application in capacitor. CV results in Fig. 3 suggest the better reversibility of the  $\text{PEDOT/LiCoO}_2$ -VGCF over the  $\text{LiCoO}_2$ -VGCF cathodes.

Electrochemical stability was then tested by measuring the capacity variation during further cycling. Here, capacity was obtained by integrating the cathodic and anodic currents from 2900 to 4200 mV and the capacity ratio comes from the ratio between the second and the further cycles and is used to quantify the stability. Drastic difference can be observed from Fig. 4, where use of  $\text{PEDOT/LiCoO}_2$ -VGCF as cathode resulted in no capacity change despite the continuous cycling up to the fiftieth cycle but for  $\text{LiCoO}_2$ -VGCF case, quick drop of capacity ratio was observed right from the beginning and remained at ca. 50% value after the twentieth cycle.

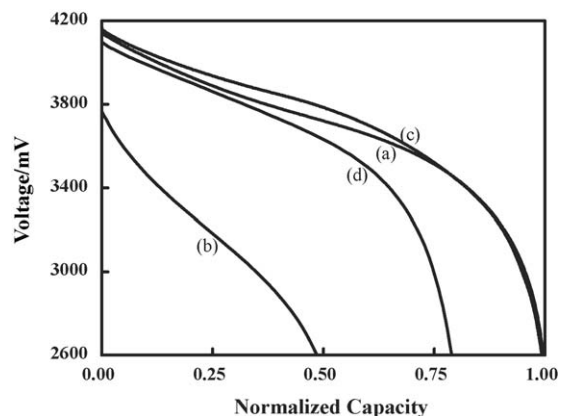


Fig. 6. Rate capability of  $\text{LiCoO}_2$ -VGCF cathode at a current of (a)  $0.1 \text{ mA cm}^{-2}$ , (b)  $1.0 \text{ mA cm}^{-2}$  and  $\text{PEDOT/LiCoO}_2$ -VGCF cathode at current of (c)  $0.1 \text{ mA cm}^{-2}$  and (d)  $1.0 \text{ mA cm}^{-2}$ . The system was charged to  $4200 \text{ mV}$  at  $1.0 \text{ mA cm}^{-2}$  before discharged to  $2700 \text{ mV}$  in LP30 electrolyte.

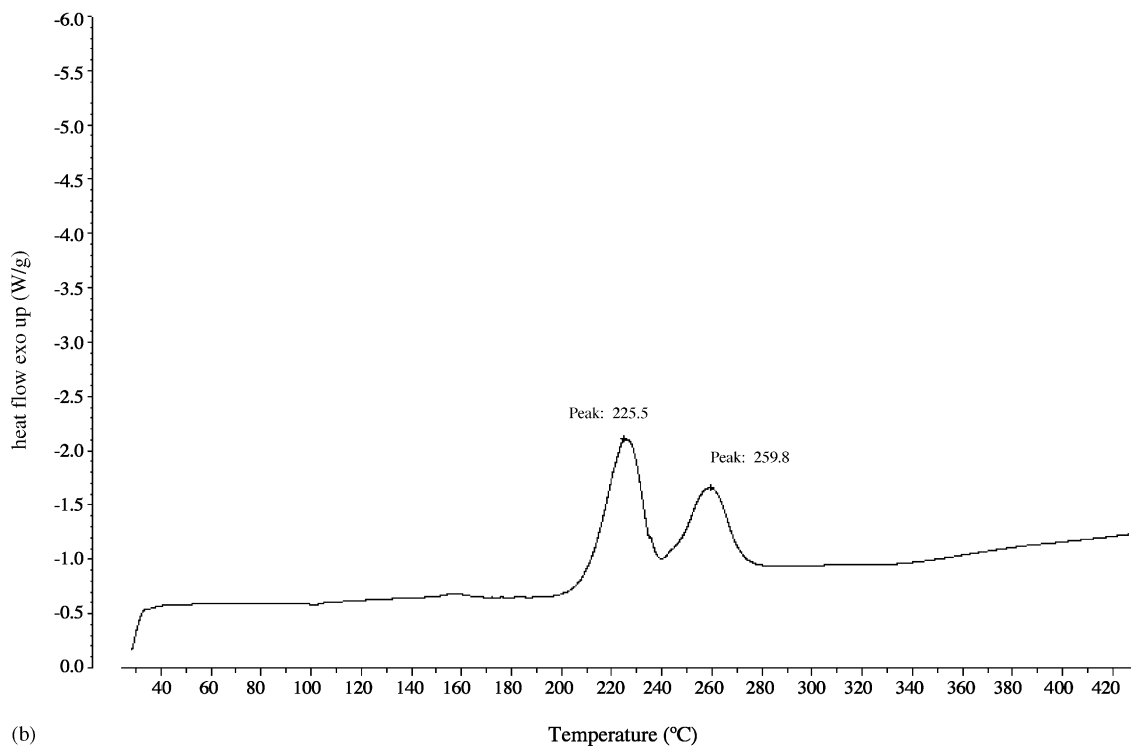
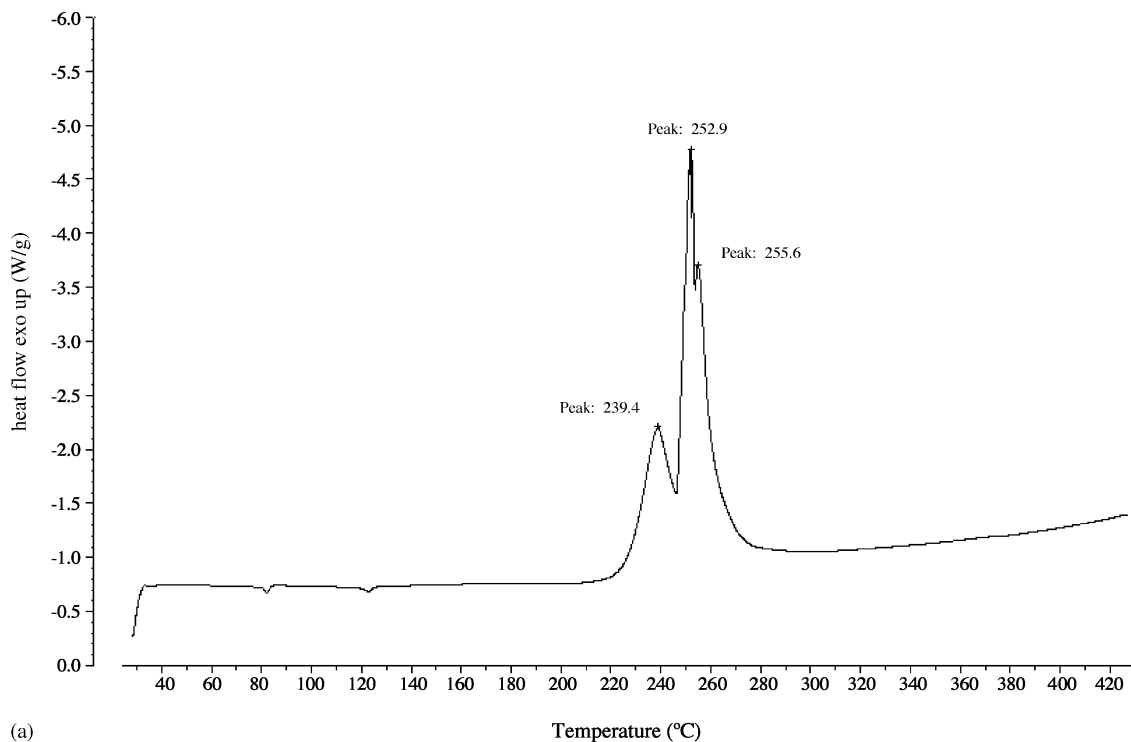


Fig. 7. DSC curves of charged cathodes containing bare (up) and PEDOT (down) coated  $\text{LiCoO}_2$ -VGCF. Cathode materials charged to 4.3 V at 0.1 C rate.

Enhanced electrochemical stability for the PEDOT/ $\text{LiCoO}_2$ -VGCF cathode is thus demonstrated.

Intercalation/deintercalation rate of lithium ion was further evaluated by CV scans at different rates. Six scan

rates (1, 50, 100, 200, 300, 500  $\text{mV s}^{-1}$ ) were used and the resulting capacity was normalized with respect to the capacity at 1  $\text{mV s}^{-1}$ . The results in Fig. 5 demonstrate that the ion intercalation/deintercalation rates between the

LiCoO<sub>2</sub>-VGCF and PEDOT/LiCoO<sub>2</sub>-VGCF systems are significantly different. With LiCoO<sub>2</sub>-VGCF cathode, the resulting capacity decreased rapidly and dropped to near zero at scan rates >100 mV s<sup>-1</sup>. The situation is clearly different for PEDOT/LiCoO<sub>2</sub>-VGCF case, where the capacity decreased steadily and with the highest scan rate 500 mV s<sup>-1</sup>, 50% of the capacity still involved. The enhanced response rate for PEDOT/LiCoO<sub>2</sub>-VGCF shows its advantage over LiCoO<sub>2</sub>-VGCF cathode.

Rate capability tests were then performed. The corresponding electrodes were fully charged to 4200 mV at constant current of 1.0 mA cm<sup>-2</sup> and then discharged under two different currents (0.1 and 1.0 mA cm<sup>-2</sup>) to test its response toward capacity (Fig. 6). With the same current (either 0.1 or 1.0 mA cm<sup>-2</sup>), PEDOT/LiCoO<sub>2</sub>-VGCF cathode shows better discharge rate as compared to LiCoO<sub>2</sub>-VGCF cathode. An examination of Fig. 6 also shows that the voltage of discharge on PEDOT/LiCoO<sub>2</sub>-VGCF cathode is higher than that on LiCoO<sub>2</sub>-VGCF cathode. SEM micrographs in Fig. 1 shows that VGCF distribution in cathode materials is non-uniform. PEDOT is quite uniformly deposited onto all active particles (e.g. VGCF and LiCoO<sub>2</sub>) surface. The difference in the PEDOT treatment is clearly reflected in cathode polarization and, consequently, in reversible capacity the cathode with PEDOT gives a smaller polarization (Fig. 6) and higher reversible capacity (Fig. 3). Apparently, cathode with PEDOT coating has lower resistance than cathode without PEDOT component.

A DSC study was performed after charging the cathodes to 4.3 V to evaluate the effect of the PEDOT/LiCoO<sub>2</sub>-VGCF on the thermal stability of the charged cathode. The thermal stability of bare and PEDOT-coated LiCoO<sub>2</sub>-VGCF cathodes are given in Fig. 7. The onset temperatures for thermal decomposition of LiCoO<sub>2</sub>-VGCF and PEDOT/LiCoO<sub>2</sub>-VGCF are 220 and 201 °C, respectively. An examination of Fig. 7 shows that the first exothermic peak for bare LiCoO<sub>2</sub>-VGCF locates at 239.4 °C. For an PEDOT/LiCoO<sub>2</sub>-VGCF cathode, this peak shifts to 225.5 °C. The total exothermic peaks area of PEDOT/LiCoO<sub>2</sub>-VGCF (−245 J g<sup>-1</sup>) is smaller than that of LiCoO<sub>2</sub>-VGCF (−337 J g<sup>-1</sup>). The onset temperature and the peak area of first exothermic peak results show that PEDOT coating on LiCoO<sub>2</sub>-VGCF surface may reduce the thermal stability of the cathode for lithium ion battery.

The enhanced properties of PEDOT/LiCoO<sub>2</sub>-VGCF over LiCoO<sub>2</sub>-VGCF cathodes indicate certain roles of the PEDOT on the constituent components, LiCoO<sub>2</sub> particles and VGCF fibers. The potential functions of PEDOT on the LiCoO<sub>2</sub> particles may be multiple. Firstly, PEDOT polymer was formed between the active particles surface (such as VGCF and LiCoO<sub>2</sub>) to enhance the electronic conductivity of the resulting composite electrode [14]. Secondly, it may function as protection layer for LiCoO<sub>2</sub> particles. Oxidation of the non-aqueous electrolytes (i.e. propylene carbonate, EC or DMC as used in this study) had been reported previously [18,19] and this resulted in the undesired deposition

of the oxidized products to form a solid electrolyte interface (SEI) on the LiCoO<sub>2</sub> particles [18]. With PEDOT as the protection layer of LiCoO<sub>2</sub>, deposition of the oxidized products on the particle might be avoided. Thirdly, PEDOT to coordinate lithium ions was well-documented [20] and this should enhance the intercalation/deintercalation of lithium ions from the inner LiCoO<sub>2</sub> core to the outer PEDOT layer. Transportation of lithium ions in LiCoO<sub>2</sub> with and without PEDOT should be greatly different (cf. the CV scans shown in Fig. 3).

#### 4. Conclusion

PEDOT/LiCoO<sub>2</sub>-VGCF can be readily prepared from the electrochemical deposition of EDOT on the pre-formed LiCoO<sub>2</sub>-VGCF electrode and was directly used as cathode materials in lithium-ion battery. Results from SEM and EDS suggest the successful coating of PEDOT on both the LiCoO<sub>2</sub> particles and the VGCF fibers. Further electrochemical characterizations on system with PEDOT/LiCoO<sub>2</sub>-VGCF cathode suggest better cyclability, electrochemical stability, response rate and rate capability than that with LiCoO<sub>2</sub>-VGCF cathode. DSC results of charged cathodes containing LiCoO<sub>2</sub>-VGCF and PEDOT/LiCoO<sub>2</sub>-VGCF show that PEDOT coating on LiCoO<sub>2</sub>-VGCF surface may reduce the thermal stability of the cathode. Important role of the polymeric PEDOT on improving the electrochemical properties is thus evident.

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