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

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#### Abstract

Nano-scale carbon materials such as Ketjenblack (KB) was used to combine with traditional conductive polymer such as poly(3,4-ethylenedioxythiophene) (PEDOT) and  $LiCoO_2$  to prepare composite cathode for lithium-ion (Li-ion) battery. The PEDOT/LiCoO<sub>2</sub>–KB cathodes were made by electrochemical deposition of 3,4-ethylenedioxythiophene (EDOT) monomer on the pre-formed  $LiCoO_2$ –KB electrodes with 1 and 5 wt% of KB content. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were used to confirm the successful coating of PEDOT layer on the  $LiCoO_2$  and KB components. To evaluate the effect of PEDOT coating,  $LiCoO_2$ –KB electrodes with and without PEDOT component were then tested and compared their results from different electrochemical characterizations. Homogeneity of the KB component and the presence of conductive PEDOT layer are found to be important factors in controlling the cathode properties such as the involved capacity, cycle ability, intercalation/de-intercalation rate and rate capability.

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# 1. Introduction

Lithium-ion (Li-ion) battery has become an important component for portable devices due to its higher energy density compared to other rechargeable battery systems such as nickel metal hydride, lead acid, etc. [1]. With a growing interest to develop rechargeable Li-ion batteries for wireless power tools and electric vehicles, the rate capability and cycle life enhancement become the most important challenges for Li-ion batteries. Previously, several carbon materials [2–9] such as carbon fibers (VGCF), acetylene black and Ketjenblack (KB) have been evaluated and implemented in the cathode or anode in real battery products and the resulting materials show very impressive properties. Among them, the incorporation of nanostructured KB with LiCoO<sub>2</sub> [9] was proved to be beneficial to

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the charge–discharge properties of the cathode in Li-ion battery if a well-dispersed suspension of KB can be made. KB, as categorized to the class of so-called "conductive carbon black" is a unique carbon black with extremely small size and high surface area. Therefore, adding the nano-scale KB to cathode should enhance the conductivity of the active materials and therefore the rate capability of battery if a large surface/volume value is the criteria for the enhanced transfer rate of lithium ions.

Electrically conductive polymers (ECPs) represent an interesting family of synthetic materials due to their high electron mobility inside the doped polymer chains [10–13]. The practical application of ECPs often depends on their stability in ambient conditions, in this aspect, great focus had been on polythiophenes 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 [12,13]. With this regard, PEDOT had been incorporated into metal oxides such as LiMn<sub>2</sub>O<sub>4</sub> [14] and V<sub>2</sub>O<sub>5</sub> [15–17] to test their applicability in

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Li-ion battery. 3,4-Ethylenedioxythiophene (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.

Previously, a PEDOT/LiCoO2-carbon fibers (VGCF) composite cathode material had been prepared in our laboratory by a continuous process of electrochemical deposition of EDOT monomer on the pre-formed LiCoO<sub>2</sub>-VGCF electrode [18]. Use of PEDOT in LiCoO<sub>2</sub>–VGCF cathode has enhanced properties such as the cycle ability, electrochemical stability, intercalation/de-intercalation rate of Li ion and rate capability. The electrically conductive PEDOT may serve as outer layer to facilitate the transportation of Li ions between LiCoO<sub>2</sub> and VGCF fibers. Active surface areas of the LiCoO<sub>2</sub> and VGCF components are supposed to be important parameters on controlling the final performance of the composite cathode. With this aspect, alternative composite materials with nano-structured KB to replace the micro-scale VGCF should be considered if active surface is the key factor in controlling the transport rate of Li ion. In this study, LiCoO2/KB cathodes with and without the incorporation of PEDOT layer were prepared and characterized electrochemically. Additional parameter such as the KB loading on the LiCoO<sub>2</sub> cathode was also characterized in order to estimate the effect of active surface.

### 2. Experimental

LiCoO<sub>2</sub> (Nippon Chemical Industrial Co.) used in this work had an average particle size of 11.5 µm, and a Brunauer–Emmett–Teller (BET) surface area of  $0.21 \text{ m}^2 \text{ g}^{-1}$ . Ketjenblack (particle diameter 39.5 nm, Ketjenblack International) with a BET of  $800 \text{ m}^2 \text{ g}^{-1}$  and an empty core (ca. 60 vol% ratio) morphology was used as the conductive carbon in the composite cathode. Electrodes with two levels of KB content (1 and 5 wt%) were prepared by combining solid components of KB, polyvinylidenedifluoride (5 wt%, PVDF, Kureha Chemical Industry Co.) and LiCoO<sub>2</sub> (94 and 90 wt%) in Nmethylpyrolidone (NMP, Merck) of equal weight. The mixed slurry was then coated on an aluminum foil (20 µm, Nippon Foil Co.) and dried at 90 °C. The dried electrodes were compressed by a roller at room temperature to make a smooth and compact film structure. The composite cathode electrodes need to be stored 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) [19]. 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 LiCoO<sub>2</sub>–KB electrode prepared by the above procedure with a dimension of  $1 \text{ cm} \times 1 \text{ cm}$ . Both the counter and reference electrodes are lithium metal (FMC). PEDOT was deposited on the LiCoO<sub>2</sub>–KB electrode in 1M LiPF<sub>6</sub> (Kanto Denka Kogyo Co. Ltd.)/propylene carbonate (PC, Ferro) solution with 0.05 M 3,4-ethylenedioxythiophene (EDOT, Aldrich) monomer by a constant current of 0.5 mA for 400 s (equal to 200 mC). The resulting composite electrode of PEDOT/LiCoO<sub>2</sub>–ECP was washed by PC for several times before further test for its capability.

The composite cathodes of PEDOT/LiCoO<sub>2</sub>–KB and LiCoO<sub>2</sub>–KB electrodes were tested by repeated cyclic voltammetry (CV) at 50 mV s<sup>-1</sup> in 1 M electrolyte of LiPF<sub>6</sub> in ethylene carbonate:dimethyl carbonate (EC:DMC=1:1, as LP30, Merck). A three-electrode glass cell with lithium foil as the counter and reference electrodes were used and the operation was performed in the glove box. The electrodes were also tested by CV at various scan rates in the same system in order to compare the ionic transfer rate of the composite cathodes. Since the real applications of cathodes in Li-ion battery are the charge/discharge behavior at the constant current mode, the electrodes were therefore charged to 4200 mV at a rate of 0.1 mA cm<sup>-2</sup> before the subsequently discharged to 2500 mV at a rate of 0.1 or  $1.0 \text{ mA cm}^{-2}$  to check the rate capability of the composites.

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. Specimens of PEDOT/LiCoO<sub>2</sub>–KB were firstly washed by PC and dried at 90 °C for 24 h before inspected by SEM. In contrast, LiCoO<sub>2</sub>–KB specimens were examined directly as in the prepared states.

### 3. Results and discussion

Electrochemical deposition of EDOT on the pre-formed LiCoO<sub>2</sub>-KB electrode was firstly tested in the galvanostatic mode and measurements without EDOT monomer (i.e. without complication from polymerization) were also made for comparison. In each set of experiments, LiCoO2-KB electrodes of two KB contents (1 and 5 wt%, designated as LiCoO<sub>2</sub>-KB-1 and LiCoO<sub>2</sub>–KB-5, respectively) were applied. Curves (a and b) in Fig. 1 represent those without the EDOT monomer and curves (c and d) are from results with EDOT monomer in the electrolytes. Since there is no EDOT monomer in the reaction, the voltage responses in curves (a and b) come exclusively from the constant current charge with LiCoO<sub>2</sub>-KB electrode. Curve (a) has higher voltage response than curve (b) during the whole process, indicating that the resistance of the cathode electrode with 1 wt% KB is higher than cathode with 5 wt% KB. In considering KB is a conductive (conductivity =  $33 \text{ S cm}^{-1}$ ) additive, higher KB content should result in reduced resistance on the corresponding LiCoO<sub>2</sub>-KB-5 cathode.

Three potential reactions including electrochemical polymerization of EDOT monomer, the electrochemical oxidation of the deposited PEDOT and the de-intercalation of the Li ions from the LiCoO<sub>2</sub> particles are supposed to occur during the electrochemical process shown in curves (c and d) of Fig. 1. This electrochemical polymerization of EDOT monomer resulted in a lower voltage profile in curves (c and d) as compared to those in curves (a and b). This result can be the evidence for



Fig. 1. The voltage profiles of LiCoO<sub>2</sub>–KB cathodes with (a) 1 wt% KB and (b) 5 wt% KB in 1 M LiPF<sub>6</sub>–propylene carbonate (PC) solution, and (c) 1 wt% KB and (d) 5 wt% KB in EDOT (0.05 M)/LiPF<sub>6</sub>–PC (1 M) solution (under constant current of 0.5 mA cm<sup>-2</sup> for 400 s).

a successful PEDOT deposition since the continuous incorporation of PEDOT on the pre-formed LiCoO<sub>2</sub>–KB cathode helps to reduce the electrode resistance. Here, voltages involved for PEDOT/LiCoO<sub>2</sub>–KB-1 electrode (curve (c)) are even lower than those for LiCoO2–KB-5 electrode (curve (b)), which suggests that the incorporated PEDOT exerts a greater effect on reducing the corresponding polarization potential than the KB component.

The surface morphology of all electrodes was then examined by SEM. LiCoO2-KB electrodes were examined by SEM and the results were shown in Fig. 2. Under low magnification  $(500 \times, \text{Fig. } 2(a'))$ , no obvious KB particles can be resolved for LiCoO<sub>2</sub>-KB-1 since the nano-scale KB particle (with a diameter of  $\sim$ 39.5 nm, Fig. 2(a)) is difficult to be observed at such a low magnification. With a higher magnification  $(4000 \times)$ , the corresponding micrograph in Fig. 2(a) shows that most of the LiCoO<sub>2</sub> particles are covered by rough surfaces presumably constituted by KB aggregates. Morphological variation is more significant for LiCoO<sub>2</sub>-KB-5, where fewer particles than expected are observed under low magnification (500×, Fig. 2(b')) and most areas are flat regions with certain visible crack lines. With 60 vol% of empty core, KB component in LiCoO<sub>2</sub>-KB-5 electrode actually occupies a large volume fraction (calculated volume ratio of KB and LiCoO<sub>2</sub> is 1–2.8). If inspected under high magnification as in Fig. 2(b), the KB residues found on the surface of LiCoO<sub>2</sub> are fewer than expected if compared to Fig. 2(a). Reasonably, the surplus KB particles (LiCoO<sub>2</sub>-KB-5 versus LiCoO<sub>2</sub>-KB-1) tend to form separated aggregates due to the strong van der Waal interactions among the hydrophobic carbon atoms in KBs. Therefore, large portions of the flat regions must be constituted by KB components and most likely by their aggregate. This non-uniform dispersion of KB particles is supposed to have influence on the resulting properties just as the reported case of carbon black on Li-ion batteries, where the uniformity of the carbon black largely affects the reversible capacity [20].

Under 500× magnification, PEDOT/LiCoO<sub>2</sub>–KB-1 has a morphology (Fig. 2(c')) similar with LiCoO<sub>2</sub>–KB (Fig. 2(a)) and micrograph under high magnification  $(4000 \times, \text{Fig. 2(c)})$  shows

the prevalence of small particles covered by rough surfaces. Presumably, these rough surfaces are due to the resulting PEDOT layers, a problem will be further verified by EDS provided next. The resulting morphology for PEDOT/LiCoO<sub>2</sub>–KB-5 (Fig. 2(d and d')) is similar to that of LiCoO<sub>2</sub>–KB-5. Careful inspection may suggest an inhomogeneous coating of PEDOTs over the resolved particles; suggestively, covering of PEDOT over an originally non-uniform LiCoO<sub>2</sub>–KB composite will end in a similar non-uniformity, too.

Incorporation of PEDOT to LiCoO<sub>2</sub>–KB composite can be further verified by the EDS spectra shown in Fig. 3. Both LiCoO<sub>2</sub>–KB-1 (Fig. 3(a)) and LiCoO<sub>2</sub>–KB-5 (Fig. 3(b)) have peaks attributed to the K $\alpha$  and K $\beta$  diffractions of Co at the respective positions of 6.925 and 7.649 keV. Existence of PEDOT in PEDOT/LiCoO<sub>2</sub>–KB-1 and PEDOT/LiCoO<sub>2</sub>–KB-5 cathodes can be confirmed by the extra peak at 2.307 keV (K $\alpha$  diffraction of S atom in PEDOT) in Fig. 3(c and d). Here, the small amount of phosphorus diffraction is due to the LiPF<sub>6</sub> residues from the electrolyte. In combination with the SEM results, we may conclude a successful electrochemical deposition of PEDOT to the LiCoO<sub>2</sub>–KB composites.

CV scans with LiCoO2-KB or PEDOT/LiCoO2-KB composite cathodes were performed in the standard LP30 electrolytes and the corresponding curves were illustrated in Fig. 4. For  $LiCoO_2$ –KB-1 (curve (a)), the onset potential of the anodic sweep is not easy to locate but for the 5 wt% counterpart shown in curve (c), the onset anodic and oxidation cathodic sweeps at the respective 3900 and 3550 mV are clearly visible. These values are coincided with the typical CV behavior of LiCoO<sub>2</sub> [21]. Here, we observe that the involved capacity increases with the KB content in all composite cathodes. However, with the incorporation of PEDOT component, the involved capacity is obviously larger in cathodes containing PEDOT than those without it. For PEDOT/LiCoO<sub>2</sub>-KB-1, the corresponding response in curve (b) is rather symmetric on either the anodic or cathodic sweeps, a characteristic had been reported for PEDOT coated LiCoO<sub>2</sub> previously [19]. The onset potentials for both PEDOT/LiCoO2-KB-1 and PEDOT/LiCoO2-KB-5 are the same irrespective of the difference on the KB content. A cross examination on the involved capacity might suggest that KB content is the controlling factor since the capacity difference (117 mC) between PEDOT/LiCoO<sub>2</sub>-KB-1 and PEDOT/LiCoO<sub>2</sub>-KB-5 (curve (b) versus curve (d)) is quite close to that (110 mC) between LiCoO<sub>2</sub>-KB-1 and LiCoO<sub>2</sub>-KB-5 cathodes (curve (a) versus curve (c)).

Electrochemical stability of cathodes can be evaluated by integrating the cathodic and anodic currents from 2900 to 4200 mV during continuous CV cycling and the capacity ratio used to quantify the stability is the ratio between the second and the further cycles. Fig. 5 shows the capacity ratio fading curves, where result from LiCoO<sub>2</sub>–KB-1 is slightly different from the other. Excellent stability is observed for LiCoO<sub>2</sub>–KB-5 and PEDOT/LiCoO<sub>2</sub>–KB-1 and PEDOT/LiCoO<sub>2</sub>–KB-5 since the capacity fading ratio is less than 1% for curves (b–d). Even for LiCoO<sub>2</sub>–KB-1, the stability is also good since after 60 cycles the capacity fading is less than 2%. The capacity retentions after 60 cycles for LiCoO<sub>2</sub>–KB-1 and PEDOT/LiCoO<sub>2</sub>–KB-



Fig. 2. SEM micrographs of the LiCoO<sub>2</sub>–KB-1 composite at a magnification of (a)  $4000 \times$  and (a')  $500 \times$ ; LiCoO<sub>2</sub>–KB-5 composite at a magnification of (b)  $4000 \times$  and (b')  $500 \times$ ; PEDOT/LiCoO<sub>2</sub>–KB-1 composite at a magnification of (c)  $4000 \times$  and (c')  $500 \times$ ; PEDOT/LiCoO<sub>2</sub>–KB-5 composite at a magnification of (d)  $4000 \times$  and (d')  $500 \times$ :



Fig. 3. EDS of (a)  $LiCoO_2$ –KB-1, (b)  $LiCoO_2$ –KB-5, (c) PEDOT/LiCoO\_2–KB-1 and (d) PEDOT/LiCoO\_2–KB-5 composite cathode materials. The composite cathodes of PEDOT/LiCoO\_2–KB were prepared from electrochemical deposition of PEDOT on the corresponding  $LiCoO_2$ –KB composites under constant current density of 0.5 mA cm<sup>-2</sup> in 0.05 M EDOT and 1 M LiPF<sub>6</sub>–PC solution.



Fig. 4. Cyclic voltammograms of (a) LiCoO<sub>2</sub>–KB-1, (b) PEDOT/LiCoO<sub>2</sub>–KB-1, (c) LiCoO<sub>2</sub>–KB-5 and (d) PEDOT/LiCoO<sub>2</sub>–KB-5 composite cathodes in LP30 electrolyte at a scan rate of  $10 \text{ mV s}^{-1}$ .



Fig. 5. Capacity ratio of CV as a function of the cycle number in LP30 electrolyte at various cathodes as (a) LiCoO<sub>2</sub>–KB-1, (b) PEDOT/LiCoO<sub>2</sub>–KB-1, (c) LiCoO<sub>2</sub>–KB-5 and (d) PEDOT/LiCoO<sub>2</sub>–KB-5 composites. The scan rate is  $50 \text{ mV s}^{-1}$  and the curves were scanned from 2900 to 4200 mV vs. Li/Li<sup>+</sup>.



Fig. 6. Normalized capacity of CV (in respect to that at scan rate of  $1 \text{ mV s}^{-1}$ ) as a function of scan rate in LP30 electrolyte with (a) LiCoO<sub>2</sub>–KB-1, (b) PEDOT/LiCoO<sub>2</sub>–KB-1, (c) LiCoO<sub>2</sub>–KB-5 and (d) PEDOT/LiCoO<sub>2</sub>–KB-5 cathode. The potential range is from 2900 to 4200 mV.

1 are 98.3 and 99.6%, respectively; therefore, deposition of PEDOT on the LiCoO<sub>2</sub>–KB cathode does not enhance the electrochemical stability. This is also true for the 5 wt% KB composites.

Intercalation/de-intercalation rate of the Li ion was further evaluated by CV scans at different rates. The resulting capacity of each scan rate was normalized with respect to the capacity at  $1 \text{ mV s}^{-1}$  and results were shown in Fig. 6. LiCoO<sub>2</sub>-KB-5 cathode shows a higher normalized capacity than LiCoO2-KB-1 cathode at various scan rates, indicating that higher KB content is helpful in increasing the intercalation/de-intercalation rate of the Li ion. With the participation of PEDOT component, PEDOT/LiCoO2-KB cathodes (cf. curves (b and d)) have higher normalized capacities than LiCoO<sub>2</sub>-KB (cf. curves (a and c)). Cross examination shows that PEDOT/LiCoO2-KB-1 (curve (b)) has better intercalation/de-intercalation rate than  $LiCoO_2-KB-5$  (curve (c)). This result suggests that the deposited PEDOT layer helps to reduce the resistance of LiCoO<sub>2</sub> and small amounts of PEDOT actually exerts more effect than larger quantities of KBs.

The performances of all composite cathodes can be further revealed by the rate capability test. Here, the corresponding electrodes are fully charged to 4200 mV at a constant current of 1.0 mA cm<sup>-2</sup> and then discharged under two different currents of 0.1 and 1.0 mA cm<sup>-2</sup> to test its response toward capacity. Fig. 7 shows the results from the LiCoO<sub>2</sub>–KB-1 and PEDOT/LiCoO<sub>2</sub>–KB-1 cathodes. At either discharge rate, the PEDOT/LiCoO<sub>2</sub>–KB cathodes have a higher voltage profile than LiCoO<sub>2</sub>–KB. The  $V_{1/2}$  (voltage at 50% of discharge) values for LiCoO<sub>2</sub>–KB-1 and PEDOT/LiCoO<sub>2</sub>–KB-1 (curves (a and c)) are 3720 and 3864 mV, respectively. It suggests that the polarization of PEDOT/LiCoO<sub>2</sub>–KB-1 is less than simple LiCoO<sub>2</sub>–KB-1 electrode. The curves at 1.0 mA discharge current also exhibit the same trend, i.e. the discharge voltage in curve (d) is higher than that in curve (b). Apparently, cathode



Fig. 7. Rate capability with LiCoO<sub>2</sub>–KB-1 cathode at a discharge current of (a) 0.1 mA cm<sup>-2</sup> and (b) 1.0 mA cm<sup>-2</sup>, and with PEDOT/LiCoO<sub>2</sub>–KB-1 wt% cathode at a current of (c) 0.1 mA cm<sup>-2</sup> and (d) 1.0 mA cm<sup>-2</sup>. The system was charged to 4200 mV at 0.1 mA cm<sup>-2</sup> before discharged to 2500 mV in LP30 electrolyte.

with PEDOT coating has lower resistance than cathode without this conductive layer.

Fig. 8 shows the results from the LiCoO<sub>2</sub>–KB-5 and PEDOT/LiCoO<sub>2</sub>–KB-5 composite cathodes. Comparatively, PEDOT/LiCoO<sub>2</sub>–KB-5 has a higher voltage profile than LiCoO<sub>2</sub>–KB-5 and the involved  $V_{1/2}$  values for curves (a and c) are 3750 and 3854 mV, respectively. The normalized capacity and voltage profile involved in curves (b and d) also lead to the same conclusion as in Fig. 7, i.e. cathode with PEDOT deposition is beneficial in enhancing the discharge voltages and rate capability of the corresponding cathode.

To access the effect of KB component, results from simple  $LiCoO_2$  (without KB) electrode was added in Fig. 9 to compare with the performance from  $LiCoO_2$ –KB-1 and  $LiCoO_2$ –KB-5. Here, direct current resistance (DCR) was calculated from the voltage difference divided by the current difference involved in the discharge curves (such as curves in Fig. 7) under 0.1 and  $1.0 \text{ mA cm}^{-2}$  currents. With the inclusion of 1 wt% KB, a



Fig. 8. Rate capability with LiCoO<sub>2</sub>–KB-5 cathode at a discharge current of (a)  $0.1 \text{ mA cm}^{-2}$  and (b)  $1.0 \text{ mA cm}^{-2}$ , and with PEDOT/LiCoO<sub>2</sub>–KB-5 cathode at a current of (c)  $0.1 \text{ mA cm}^{-2}$  and (d)  $1.0 \text{ mA cm}^{-2}$ . The system was charged to 4200 mV at  $0.1 \text{ mA cm}^{-2}$  before discharged to 2500 mV in LP30 electrolyte.



Fig. 9. Direct current resistance of  $LiCoO_2$ –KB composite cathode electrodes: (a) 0% KB, (b) 1% KB and (c) 5% KB. The value of DCR was calculated from the voltage difference divided by the current difference between 0.1 and 1.0 mA cm<sup>-2</sup> discharge curves.

notable decrease on DCR was observed if results from  $LiCoO_2$  (curve (a)) and  $LiCoO_2$ –KB-1 (curve (b)) were compared. Further DCR reduction for  $LiCoO_2$ –KB-5 electrode was also observed (curve (c)), however, the magnitude of reduction is below what we anticipated from its KB loading. Suggestively, optimal KB loading is supposed to lie in between 1 and 5 wt%, a similar observation had been reported previously [9] for  $LiCoO_2$ –KB systems and homogeneity of the dispersed KB component is supposed to be key factor in controlling the final performance.

Qualitative discussion on the potential roles of PEDOT and KB should be addressed here. As cited above [14-17], electron mobility of the metal oxide composite can be enhanced by the addition of electrically conductive polymers, i.e. PEDOT. The higher conductivity of PEDOT  $(330-550 \,\mathrm{S \, cm^{-1}})$  as compared to KB  $(33 \text{ S cm}^{-1})$  makes it as an important component in promoting the electron conductivity of the involved cathodes (cf. results from Figs. 4 and 6). Applicability of the corresponding cathodes in Li-ion battery is also facilitated by the incorporation of PEDOT component. For KB component, its uniformity turns out to be crucial on the transfer of the Li ions in composites with and without PEDOT component. As the morphology from SEM suggests, certain KB particles separate from LiCoO<sub>2</sub> particles and form large aggregates in distinct areas from LiCoO<sub>2</sub> particles. As suggested by the SEM micrographs (cf. Fig. 2), the density-induced heterogeneity becomes pronounced when KB content reaches 5 wt%. These separated KB aggregates are supposed to be less effective in transporting the Li ions than the KB residues on the surfaces of LiCoO<sub>2</sub> particles since they are more remote from LiCoO<sub>2</sub> and their effective surface/volume ratios are largely reduced when aggregated. With low KB content (e.g. 1 wt%), less separate KB domains are present in the system and most of them are in direct contact with LiCoO<sub>2</sub> and function appropriately in transporting the Li ion. Continuous PEDOT coating on the originally non-uniform LiCoO<sub>2</sub>-KB-5 cathode will result in a similar non-uniformity. Therefore, in-proportional performance enhancement is also observed between PEDOT/LiCoO<sub>2</sub>-KB-1 and PEDOT/LiCoO<sub>2</sub>-KB-5 cathodes, too.

# 4. Conclusions

PEDOT/LiCoO<sub>2</sub>-KB composites can be readily prepared from the electrochemical polymerization of EDOT on the preformed LiCoO<sub>2</sub>-KB electrodes. Results from the voltage profiles of the electrochemical polymerization, SEM and EDS suggest the successful deposition of PEDOT on the LiCoO2-KB composites. With high KB content (e.g. 5 wt%), the nano-scale KB particles tend to separate from LiCoO<sub>2</sub> particles to form large aggregated domains, which are less effective in transporting the Li ions than the KB particles directly attached to the LiCoO<sub>2</sub> particles. The performance enhancement on LiCoO2-KB-5 and PEDOT/LiCoO<sub>2</sub>-KB-5 cathodes is therefore not so much as expected due to the non-uniform dispersion of the KB particles. Electrochemical characterizations on the LiCoO2-KB and PEDOT/LiCoO<sub>2</sub>-KB cathodes suggest that incorporation of the conductive PEDOT into cathode enhances the intercalation/deintercalation of Li ion and also the rate capability.

#### References

- [1] D. Im, A. Manthiram, Solid State Ionics 150 (2003) 249.
- [2] M. Endo, Y.A. Kim, T. Hayashi, K. Nishimura, T. Matusita, K. Miyashita, M.S. Dresselhaus, Carbon 39 (2001) 1287.
- [3] N. Li, C.R. Martin, J. Electrochem. Soc. 148 (2001) A164.
- [4] G.T. Wu, C.S. Wang, X.B. Zhang, H.S. Yang, Z.F. Qi, P.M. He, W.Z. Li, J. Electrochem. Soc. 146 (1999) 1696.
- [5] F. Marken, M.L. Gerrard, I.M. Mellor, R.J. Mortimer, C.E. Madden, S. Fletcher, K. Holt, J.S. Foord, R.H. Dahm, F. Page, Electrochem. Commun. 3 (2001) 177.
- [6] A.M. Wilson, J.R. Dahn, J. Electrochem. Soc. 142 (1995) 326.
- [7] X.W. Zhang, P.K. Patil, C. Wang, A.J. Appleby, F.E. Little, D.L. Cocke, J. Power Sources 125 (2004) 206.
- [8] T. Takamura, M. Saito, A. Shimokawa, C. Nakahara, K. Sekine, S. Maeno, N. Kibayashi, J. Power Sources 90 (2000) 45.
- [9] S. Kuroda, N. Tobori, M. Sakuraba, Y. Sato, J. Power Sources 119–121 (2004) 924.
- [10] H.S. Nalwa (Ed.), Organic Conductive Molecules and Polymers, vol. 1–4, Wiley, New York, 1997.
- [11] K. Gurunathan, A.V. Murugan, R. Marimuthu, U.P. Mulik, D.P. Amlnerkar, Mater. Chem. Phys. 61 (1999) 173.
- [12] L.A.A. Pettersson, F. Carlsson, O. Inganäs, H. Arwin, Thin Solid Films 313–314 (1998) 356.
- [13] A. Czardybon, M. Lapkowski, Synth. Met. 119 (2001) 161.
- [14] C. Arbizzani, M. Mastragostino, M. Rossi, Electrochem. Commun. 4 (2002) 545.
- [15] A.V. Murugan, B.B. Kale, C.-W. Kwon, G. Campet, K. Vijayamohanam, J. Mater. Chem. 11 (2001) 2470.
- [16] A.V. Murugan, C.-W. Kwon, G. Campet, B.B. Kale, J. Power Sources 105 (2002) 1.
- [17] C.-W. Kwon, A.V. Murugan, G. Campet, J. Portier, B.B. Kale, K. Vijaymohanan, J.-H. Choy, Electrochem. Commun. 4 (2002) 384.
- [18] L.J. Her, J.L. Hong, C.C. Chang, J. Power Sources 157 (2006) 457.
- [19] C.C. Chang, L.J. Her, J.L. Hong, Electrochim. Acta 50 (2005) 4461.
- [20] D. Linden, Handbook of Batteries, second ed., McGraw-Hill, New York, 1995.
- [21] R. Dominko, M. Gaberšček, J. Drofenik, M. Bele, J. Jamnik, Electrochim. Acta 48 (2003) 3709.