



# Polypyrrole-coated LiCoO<sub>2</sub> nanocomposite with enhanced electrochemical properties at high voltage for lithium-ion batteries



Jingchao Cao, Guorong Hu, Zhongdong Peng, Ke Du, Yanbing Cao\*

School of Metallurgy and Environment, Central South University, Changsha 410083, China

## HIGHLIGHTS

- PPy-coated LiCoO<sub>2</sub> particles are prepared by a chemical polymerization method.
- The PPy film, like a capsule shell, avoids LiCoO<sub>2</sub> corrosion from HF attacking.
- The PPy film builds a conductive network and increases the electronic conductivity.
- The electrochemical properties of LiCoO<sub>2</sub> are enhanced after coating with PPy.

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## ABSTRACT

A conducting polypyrrole thin film is successfully coated onto the surface of LiCoO<sub>2</sub> by a simple chemical polymerization method. The structure and morphology of pristine LiCoO<sub>2</sub> and PPy-coated LiCoO<sub>2</sub> are investigated by the techniques of X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscope (TEM). Energy dispersive X-ray spectroscopy (EDXS), Fourier transform infrared spectrometry (FTIR) and thermogravimetric analysis (TGA) further demonstrate the existence of PPy. The electrochemical properties of the composites are investigated by galvanostatic charge–discharge test and AC impedance measurements, which show that the conductive PPy film on the surface significantly decrease the charge-transfer resistance of LiCoO<sub>2</sub>. The PPy-coated LiCoO<sub>2</sub> exhibits a good electrochemical performance, showing initial discharge capacity of 182 mAh g<sup>-1</sup> and retains 94.3% after 170 cycles. However, the retention of pristine LiCoO<sub>2</sub> is only 83.5%. The rate capability results show that the reversible capacity retention (10C/0.2C) of LiCoO<sub>2</sub> increases from 52.4% to 80.1% after being coated with PPy. The continuously coated thin PPy film is just like a capsule shell, which can protect the core (LiCoO<sub>2</sub>) from corrosion causing by the HF attacking and greatly reduce the dissolution of Co into electrolyte.

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## 1. Introduction

Lithium-ion batteries (LIBs) have been extensively used for a wide variety of applications, for instance, from portable electronic equipments to hybrid and electric vehicles. The performance of the batteries is often decided by the properties of cathode material. Among various cathode materials, lithium cobalt oxide (LiCoO<sub>2</sub>) is currently one of the most popular cathode materials in batteries for portable devices due to its high energy density, ease of preparation, good C-rate capacity and long cycle life [1–5]. LiCoO<sub>2</sub> has a specific capacity of 137 mAh g<sup>-1</sup> during the (de)lithiation process from 2.75

to 4.2 V vs. Li/Li<sup>+</sup>, only 0.5 Li<sup>+</sup> per molecule of LiCoO<sub>2</sub> can be extractable [6,7]. Increasing the reversible capacity is strongly demanded with rapidly growing demands for higher energy density lithium-ion batteries. One promising attempt to increase the capacity of LiCoO<sub>2</sub> is charging cells above 4.2 V [8,9]. However, the structural instability and capacity fading is more severely which is caused by easy dissolution of Co<sup>4+</sup> into the acidic electrolyte medium, as well as a large number of side reactions on the surface of the cathode particles [4,10].

Meanwhile, attempts have been made to resolve the problems by doping non-transition and transition metal ions into the LiCoO<sub>2</sub> structure by partial substitution of cobalt, but capacity fading has been still observed even though some improvement has been achieved [5,11]. As an alternative, the surface modification of LiCoO<sub>2</sub> with inorganic materials such as LiFePO<sub>4</sub> [12], LiMgPO<sub>4</sub> [13],

\* Corresponding author.

E-mail address: [cybcsu@csu.edu.cn](mailto:cybcsu@csu.edu.cn) (Y. Cao).

LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>2</sub> [8], LiNbO<sub>3</sub> [14], LiMn<sub>2</sub>O<sub>4</sub> [15], Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> [16], Li [Li<sub>0.2</sub>Mn<sub>0.6</sub>Ni<sub>0.2</sub>O<sub>2</sub>] [17], Al<sub>2</sub>O<sub>3</sub> [18], ZnO [19], LiF [20], MgF<sub>2</sub> [21] and FePO<sub>4</sub> [22] has been extensively investigated and achieved good effect on inhibiting capacity fading. However, the inorganic materials are discontinuously deposited onto the surface of LiCoO<sub>2</sub>, tending to act as an inert layer regarding ionic conduction and also require complex coating process.

Polypyrrole (PPy), a typical soft conducting polymer with good mechanical flexibility and chemical stability during the electrochemical process, has been attracted much attention. PPy can act as a host material for Li<sup>+</sup>-ion insertion/extraction in the voltage range of 2.0–4.5 V versus Li/Li<sup>+</sup>, with a theoretical capacity of 72 mAh g<sup>-1</sup> [23]. Therefore, PPy additives can be used as both conductive agents and cathode materials. The application of PPy to improve electrochemical performance of electrode materials for lithium ion batteries have been reported, such as Fe<sub>3</sub>O<sub>4</sub>/PPy [24], Fe<sub>2</sub>O<sub>3</sub>/PPy [25], LiMn<sub>2</sub>O<sub>4</sub>/PPy [26], LiV<sub>3</sub>O<sub>8</sub>/PPy [27,28], LiFeO<sub>2</sub>/PPy [29], LiFePO<sub>4</sub>/PPy [30] and LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>/PPy [31]. But up till now, using PPy as a coating layer to improve the electrochemical properties of LiCoO<sub>2</sub> at high voltage has not been reported.

In this study, LiCoO<sub>2</sub>-PPy nanocomposite was synthesized using a chemical polymerization method. The structure, morphology and electrochemical performance of the LiCoO<sub>2</sub>-PPy are discussed and compared with the performance of bare LiCoO<sub>2</sub> cathode material.

## 2. Experimental

### 2.1. Synthesis of nanoarchitected PPy-coated LiCoO<sub>2</sub>

LiCoO<sub>2</sub> powder with an average particle size of 10 μm was prepared in our previous work [17]. The PPy-coated LiCoO<sub>2</sub> composite powder was prepared by the chemical polymerization with sodium *p*-toluenesulfonate (AR, 99%) as the dopant. In order to avoid the introduction of impurity ions such as Fe<sup>3+</sup>, H<sub>2</sub>O<sub>2</sub> (AR, H<sub>2</sub>O<sub>2</sub> ≥ 30%) was chosen to use as the oxidant. LiCoO<sub>2</sub> (5 g), H<sub>2</sub>O<sub>2</sub> (2 mL) and *p*-toluenesulfonate (0.5 g) were dispersed into alcohol solution (50 mL), pyrrole (0.1 g) was diluted into 10 mL with alcohol, and then was slowly added to the mixture with continuously magnetically stirred for 15 h. The final products were filtered and washed with deionized water several times and dried at 60 °C in a vacuum oven for 12 h. In order to calculate the PPy content, pure PPy powder was also prepared using the same method above.

### 2.2. Materials characterization

X-ray diffraction (XRD, D/max-r A type Cu Kα, 40Kv, 300 mA) was employed to identify the crystalline phase of the products. The scan range was 10–80° with a scan speed of 0.02° min<sup>-1</sup>. The morphological and compositional characterization of the as-prepared compound was performed by means of scanning electron microscopy (SEM, JEOLJSM-6360LV), transmission electron microscope (TEM, JEOL, 2010) and energy dispersive X-ray spectroscopy (EDXS). Fourier transform infrared spectrometry (FTIR) measurements were carried out on a Hitachi FTIR-8900 spectrometer (Japan) in wave-numbers ranges of 400–4000 cm<sup>-1</sup> using a KBr wafer. Thermogravimetric analysis (TGA) was carried out on a TG 209 F1 Iris under air atmosphere in the temperature range of 30–800 °C at a heating rate of 5 °C/min. The dissolution of Co into electrolyte was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Optima 4300DV).

### 2.3. Electrochemical measurements

Electrochemical properties of the materials were investigated by using coin cells (2025 type). The working electrodes were

prepared by dispersing the 85 wt. % cathode materials, 10 wt. % acetylene black and 5 wt. % polyvinylidene fluoride (PVDF) binder in *N*-methyl-2-pyrrolidinone (NMP). The slurry was coated on an aluminum foil and then dried at 120 °C for 20 h under vacuum. The cells were assembled in an argon filled glove box with electrolyte of 1 mol L<sup>-1</sup> LiPF<sub>6</sub> in EC-DMC-EMC (1:1:1 volume ratio) solution, metallic Li as anodes and polypropylene separators (Celgard 2400). The cells galvanostatically charged and discharged in the potential range of 3.0–4.5 V (vs. Li/Li<sup>+</sup>) at different current densities using LAND CT2001A test system. Cyclic voltammograms measurements were done by a Solartron 1287 electrochemical interface between 2.8 and 4.6 V at a scan rate of 0.1 mV s<sup>-1</sup>. Electrochemical impedance spectroscopy (EIS) analysis was carried out with a three electrode cell system from 1 MHz to 1 mHz by using the potentiostat/galvanostat Model 2273A potentiostat and the Model 5210 lock-in amplifier with 5 mV ac excitation. All tests were performed at room temperature.

## 3. Results and discussion

The XRD patterns of pristine LiCoO<sub>2</sub> and PPy-coated LiCoO<sub>2</sub> are presented in Fig. 1. It is observed that the pristine LiCoO<sub>2</sub> shows a well-defined α-NaFeO<sub>2</sub> structure with no minor phases. The PPy-coated LiCoO<sub>2</sub> composite also conform to a single-phase hexagonal structure of α-NaFeO<sub>2</sub> structure is attributed to LiCoO<sub>2</sub> structure, and PPy phase is not observed in this pattern.

SEM images of the pristine LiCoO<sub>2</sub> and the PPy-coated LiCoO<sub>2</sub> composite are shown in Fig. 2(a) and (b). The particle size of pristine LiCoO<sub>2</sub> powder is about 10 μm. It can be seen from Fig. 2(a) the surface of pristine LiCoO<sub>2</sub> is smooth and clean. After intruding the PPy, the PPy-coated LiCoO<sub>2</sub> exhibits an anomalous coating layer, which is featured with a thin and highly continuous morphology. TEM photograph of PPy-coated LiCoO<sub>2</sub> exhibits the thickness of PPy coating layer is approximately 20 nm. In order to further confirm the presence of PPy, energy dispersive X-ray (EDX) mapping was used to observe the distribution of PPy (Fig. 2(e)–(g)). The element of N and C are only existed in PPy. It obviously can be seen from Fig. 2(f) and (g) that the N and C are distributed uniformly throughout the whole area, which indicates that the PPy film had uniformly coated on the surface of LiCoO<sub>2</sub> powders.

FT-IR spectra obtained for the KBr diluted pellets of pristine

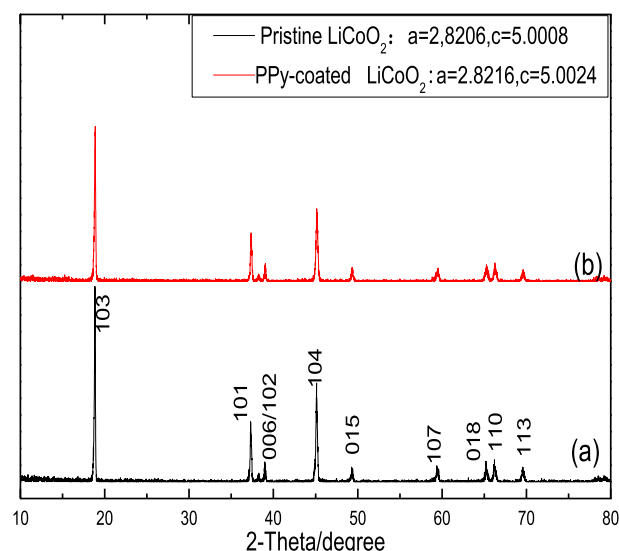


Fig. 1. XRD patterns of LiCoO<sub>2</sub> and PPy-coated LiCoO<sub>2</sub> composite.

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