



# Enhanced high-voltage electrochemical performance of LiCoO<sub>2</sub> coated with ZrO<sub>x</sub>F<sub>y</sub>



Zhiguo Wang, Zhixing Wang\*, Huajun Guo, Wenjie Peng, Xinhai Li, Jiexi Wang

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

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## ABSTRACT

LiCoO<sub>2</sub> is successfully coated with oxyfluoride ZrO<sub>x</sub>F<sub>y</sub> by a chemical deposition method for the first time. The formation of a uniform coating layer on the surface of the cathode particles is confirmed by SEM, TEM, EDX and XPS. The coated sample maintains the pristine layered structure according to the XRD result. Compared with pristine LiCoO<sub>2</sub>, the ZrO<sub>x</sub>F<sub>y</sub>-coated sample exhibits enhanced electrochemical performance especially at high cutoff voltage. Similar discharge capacities are delivered by both pristine and coated samples in various voltage ranges. However, the coated sample shows improved cycling performance, maintaining 56.4%, 32.8% capacity retention after 200 cycles, which is much more than 30.3%, 10.5% that is shown by the pristine sample in the voltage range of 3.0–4.5 V and 3.0–4.6 V, respectively.

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## 1. Introduction

Up to now, LiCoO<sub>2</sub> still occupies the major cathode material position in commercialized lithium ion batteries due to its easy synthesis, high electronic conductivity, excellent cycle performance, and reasonable rate capability [1,2]. Though LiCoO<sub>2</sub> has a high theoretical specific capacity (274 mAh g<sup>-1</sup>), the reversible specific capacity is limited to only 160 mAh g<sup>-1</sup> or less when cycled between 3.0 and 4.3 V (vs. Li/Li<sup>+</sup>) [3]. Increasing power consumption of mobile devices like notebook computers and cellular phones has demanded smaller, thinner batteries with high capacity [4]. Therefore, many studies have been focused on achieving higher capacity by charging the cell beyond 4.3 V, but it leads to structural damage and severe capacity decay of the cathodes [5,6].

Many efforts have been made to improve the electrochemical performances of LiCoO<sub>2</sub> at high cutoff voltages. One of the useful strategies is the surface modification of active materials by thin coating layer of metal oxides [3,7], metal phosphates [8,9], and metal fluorides [10,11]. The presence of such coatings can improve the stability of the electrode surface by protecting the active oxides (3d metal ion) particles from direct contact with the acidic electrolyte when the cells were cycled beyond 4.3 V [3,12]. However, different coating materials lead to different performance of the cathode [13]. In this study, the oxyfluoride ZrO<sub>x</sub>F<sub>y</sub> is introduced

as coating material of LiCoO<sub>2</sub> cathode for the first time. Chemical deposition route is adopted here for its easy control and homogeneous coverage. We expect the ZrO<sub>x</sub>F<sub>y</sub> coated LiCoO<sub>2</sub> to exhibit improved electrochemical performance, particularly at high cutoff voltages of 4.5 and 4.6 V.

## 2. Experimental

Pristine LiCoO<sub>2</sub> powder was prepared by mixing Co<sub>3</sub>O<sub>4</sub> and Li<sub>2</sub>CO<sub>3</sub> at a molar ratio of 1:1.04, and firing at 950 °C for 16 h in air. A chemical deposition method was used to obtain ZrO<sub>x</sub>F<sub>y</sub>-coated LiCoO<sub>2</sub> that is inspired by deposition of ZrO<sub>x</sub>F<sub>y</sub> via adding NH<sub>4</sub>F in Zr<sup>4+</sup> aqueous solution. Zr(NO<sub>3</sub>)<sub>4</sub> · 5H<sub>2</sub>O and NH<sub>4</sub>F were separately dissolved in distilled water, and then NH<sub>4</sub>F aqueous solution was slowly added to Zr(NO<sub>3</sub>)<sub>4</sub> aqueous solution, in which the molar ratio of Zr to F was controlled to be 1:4. After constantly stirring for 10 min at 25 °C, the prepared LiCoO<sub>2</sub> powder was immersed into the resulting solution. The weight ratio of elemental Zr to LiCoO<sub>2</sub> powder was 0.3 wt%. The mixed solution was stirred at 25 °C for 1 h, and then dried at 60 °C in a vacuum oven. The resulting solid was calcined at 400 °C for 5 h in flowing argon to obtain ZrO<sub>x</sub>F<sub>y</sub>-coated LiCoO<sub>2</sub>.

The powder X-ray diffraction (XRD, Rigaku, Rint-2000) measurement using CuKα radiation was employed to identify the crystalline phase of the prepared materials. The particle morphology and elemental mapping of the prepared powders were observed by scanning electron microscope (SEM, JEOL, JSM-5612LV, 20 kV) and transmission electron microscope (TEM,

\* Corresponding author. Tel./fax: +86 731 88836633.

E-mail address: [zxwang\\_csu@163.com](mailto:zxwang_csu@163.com) (Z. Wang).

Hitachi, H-800, 200 kV). The X-ray photoelectron spectroscopy (XPS, Perkin-Elmer, PHI 5600) measurements were performed to get information on the surface of the materials.

The electrochemical characterizations were performed using CR2025 coin-type cell. For positive electrode fabrication, the prepared powders were mixed with 10 wt% acetylene black as conducting agent, and 10 wt% polyvinylidene fluorides as binder in N-methyl pyrrolidinone until slurry was obtained. Then, the blended slurries were pasted onto an aluminum current collector, followed by drying at 120 °C for 12 h. The test cell consisted of the positive electrode and lithium foil negative electrode separated by a porous polypropylene film, and 1 M LiPF<sub>6</sub> in EC/EMC (1:2 in wt%) as electrolyte (Jiangxi Youli New Materials Co. Ltd., China). The assembly of the cells was carried out in a dry argon-filled glove box. The cells were cycled in the voltage ranges of 3.0–4.5 V and 3.0–4.6 V at room temperature.

### 3. Results and discussion

Prior to preparing ZrO<sub>x</sub>F<sub>y</sub>-coated LiCoO<sub>2</sub>, we first obtain the coating material by using a chemical deposition method. The molar ratio of Zr to F is controlled to be 1:4. The XRD result shows that the phase of the coating material is ZrO<sub>x</sub>F<sub>y</sub> (zirconium oxyfluoride). Meanwhile, the amount of the coating material is optimized through electrochemical performance firstly. In our

preliminary experiments, when the weight ratio of elemental Zr to LiCoO<sub>2</sub> powder was 0.3 wt%, the sample shows the best electrochemical performance.

Typical SEM and TEM images of pristine and ZrO<sub>x</sub>F<sub>y</sub>-coated LiCoO<sub>2</sub> are shown in Fig. 1. In comparison with pristine sample having smooth surfaces and well-defined edges, the surfaces of coated sample is rough and coated with an apparently continuous layer. Fig. 1e and f are the HRTEM pictures of the selected area “1” and “2” in Fig. 1c and d, respectively. It can be clearly seen that a distinguishable and translucent compact coating layer exists on the surface of the modified LiCoO<sub>2</sub> particles (dark opaque region).

Fig. 2a exhibits the XRD patterns of pristine and ZrO<sub>x</sub>F<sub>y</sub>-coated LiCoO<sub>2</sub>. All the diffraction peaks of the both samples can be indexed on hexagonal α-NaFeO<sub>2</sub> structure type with a space group of *R*3*m*, no extra peaks from related impurity phases exist. The XPS analysis of pristine and ZrO<sub>x</sub>F<sub>y</sub>-coated LiCoO<sub>2</sub> was carried out and given in Fig. 2. Zr 3d and F 1s peaks are detected for the coated sample, but absent for the pristine sample. The binding energies of Zr 3d and F 1s for the coated sample are 180.8 and 685.5 eV, respectively, which indicates the presence of Zr<sup>4+</sup> and F<sup>−</sup> at the surface. Both the samples have Li 1s and Co 2p peaks without remarkable chemical shift of the binding energy, indicating that the ion environments have no changes in the surface structure. It is noted that the intensities of Li 1s and Co 2p peaks on the surface of coated sample are lower than that of pristine sample. It is interesting that the shape of O 1s spectra is little changed.

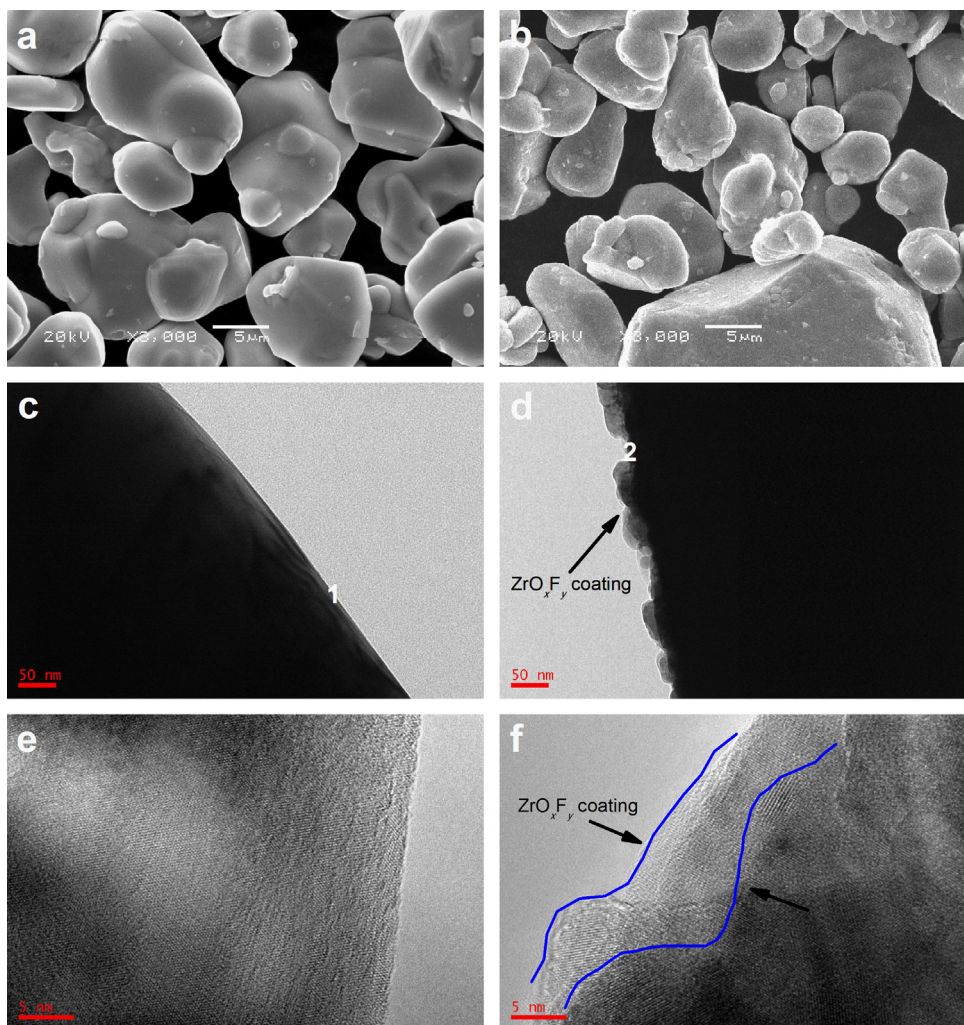


Fig. 1. Typical SEM and TEM images of pristine (a and c) and ZrO<sub>x</sub>F<sub>y</sub>-coated LiCoO<sub>2</sub> (b and d); HRTEM images (e and f) of the selected areas 1 and 2 in c and d.

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