Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 41 (2015) 469–474

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Improving the cycling stability of $LiCoO_2$ at 4.5 V through co-modification by Mg doping and zirconium oxyfluoride coating

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

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

Received 5 August 2014; received in revised form 20 August 2014; accepted 23 August 2014
Available online 1 September 2014

Abstract

The co-modification by Mg doping and zirconium oxyfluoride (ZrO_xF_y) coating is employed to improve the cycling stability of $LiCoO_2$ in the voltage range of 3.0–4.5 V. SEM, TEM images and EDS mappings of the modified sample confirm that there is a compact ZrO_xF_y coating layer on the surface of the cathode particles and the doping element (Mg) distributes uniformly in the modified sample. Electrochemical tests demonstrate that the co-modified sample exhibits obviously enhanced cycling stability in the voltage range of 3.0–4.5 V, which maintains 91.2% of its initial capacity after 100 cycles at 1 C rate. That is much more than 64.4% for the pristine sample. Moreover, EIS, XRD and Co dissolution tests of the cycled electrodes reveal that Mg doping stabilizes the crystal structure of $LiCoO_2$ and ZrO_xF_y coating alleviates unwanted interfacial side reactions between the cathode and electrolyte, thereby suppressing Co dissolution and the growth of impedance during prolonged cycling.

Keywords: A. Firing; B. Surfaces; C. Impedance; E. Batteries

1. Introduction

As lithium-ion batteries (LIBs) are expected to be increasingly used as power sources for smart mobile devices, electric vehicles, grid energy storage systems and many other applications, cells with high energy density and long cycling life are strongly demanded [1,2]. Both improvement of the energy density and the cycling life of LIBs are generally limited by the properties of cathode materials. $LiCoO_2$, proposed by Goodenough's group in 1980, has been one of the most predominant cathode materials of LIBs since the first successful commercialization [3,4]. In spite of a high lithium content equivalent to 274 mA h g^{-1}, the practical reversible specific capacity of $LiCoO_2$ is limited to only 160 mA h g^{-1} or less when cycled between 3.0 and 4.3 V (vs. Li/Li^+) in order to maintain a reasonable cycling stability [5]. By charging to higher voltage such as 4.5 V, the capacity of the cell will increase by about 20%. However, it will lead to severe capacity fading due to the structural instability induced by a phase transition and the side reactions between delithiated cathode materials and liquid electrolytes at high voltage [6,7].

So far, a lot of modifications have been attempted to improve the cycling stability of $LiCoO_2$ electrodes at high voltage. One is the doping of suitable metal ions at transition metal sites, such as Mg, Al, Cr, Mn and Zr [8–12]. The doping is quite efficient to enhance the electronic conductivity, suppress the phase transitions and improve the cycling performance at high voltage. However, such improvements have been realized at the expense of specific capacity due to the electrochemically inactive dopants. In addition, the surface of cathode material is still exposed in the electrolyte. The other commonly suggested modification is coating with metal oxides (such as MgO, Al_2O_3, TiO_2 and ZrO_2) [13–15], metal phosphates (such as Li_3PO_4, $AlPO_4$ and $FePO_4$) [16–18], or metal fluorides (such as AlF_3, LaF_3 and MgF_2) [19–21]. The presence of such coatings can protect the active sites of cathode materials from direct contact with the acidic electrolyte, as well as maintaining the Li^+ ionic conduction pathways. However, suppression of the side reactions between

---

*Corresponding author. Tel./fax: +86 731 88836633.
E-mail address: zxwang.csu@hotmail.com (Z. Wang).

http://dx.doi.org/10.1016/j.ceramint.2014.08.093
0272-8842/

electrode and electrolyte alone cannot stabilize the structure of cathode materials significantly when the cells are cycled beyond 4.3 V. Both the strategies mentioned above show positive effects on the electrochemical performance of $LiCoO_2$ cathode material for LIBs [8,17], therefore the co-modification by doping and coating can be attempted to improve the high voltage performance of the material.

In this study, we aim at improving the cycling stability of $LiCoO_2$ at a high cutoff voltage of 4.5 V through co-modification by Mg doping and ZrO_xF_y coating, thus achieving both high capacity and long cycling life. This is a new attempt for depositing ZrO_xF_y onto the surface of Mg-doped $LiCoO_2$ particles. Furthermore, the synergistic effects of Mg doping and ZrO_xF_y coating on the properties of $LiCoO_2$ are investigated.

2. Experimental

Pristine $LiCoO_2$ powder was prepared by mixing Co_3O_4 and Li_2CO_3 at a molar ratio of 1:1.04, and firing at 950 °C for 16 h in air. Mg-doped $LiCoO_2$ powder was prepared by heating the mixture of Co_3O_4, MgO and Li_2CO_3 under the same condition. The molar ratio of Mg was 0.05. A chemical deposition method was used to obtain ZrO_xF_y-coated sample that is inspired by deposition of ZrO_xF_y via adding NH_4F into Zr^{4+} aqueous solution. $Zr(NO_3)_4 \cdot 5H_2O$ and NH_4F were separately dissolved in distilled water, and then NH_4F aqueous solution was slowly added into $Zr(NO_3)_4$ 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 Mg-doped $LiCoO_2$ powder was immersed into the resulting solution. The weight ratio of elemental Zr to $LiCoO_2$ 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_xF_y-coated sample. For convenience, pristine $LiCoO_2$, Mg-doped $LiCoO_2$ and ZrO_xF_y-coated sample are labeled as LCO, LCMO and LCMO/ZFO, respectively.

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, Hitachi, H-800, 200 kV). The powder X-ray diffraction (XRD, Rigaku, Rint-2000) measurement using Cu*K*α radiation was employed to identify the crystal structure of the cycled electrodes. The amount of dissolved Co into the electrolyte was detected by an inductively coupled plasma optical emission spectrometer (ICP-OES, IRIS Intrepid II XSP).

CR2025 coin-type cells were assembled with metallic lithium anodes for electrochemistry studies. The positive electrodes were fabricated by casting a slurry consisting of as-prepared sample (80 wt%), acetylene black (10 wt%) and

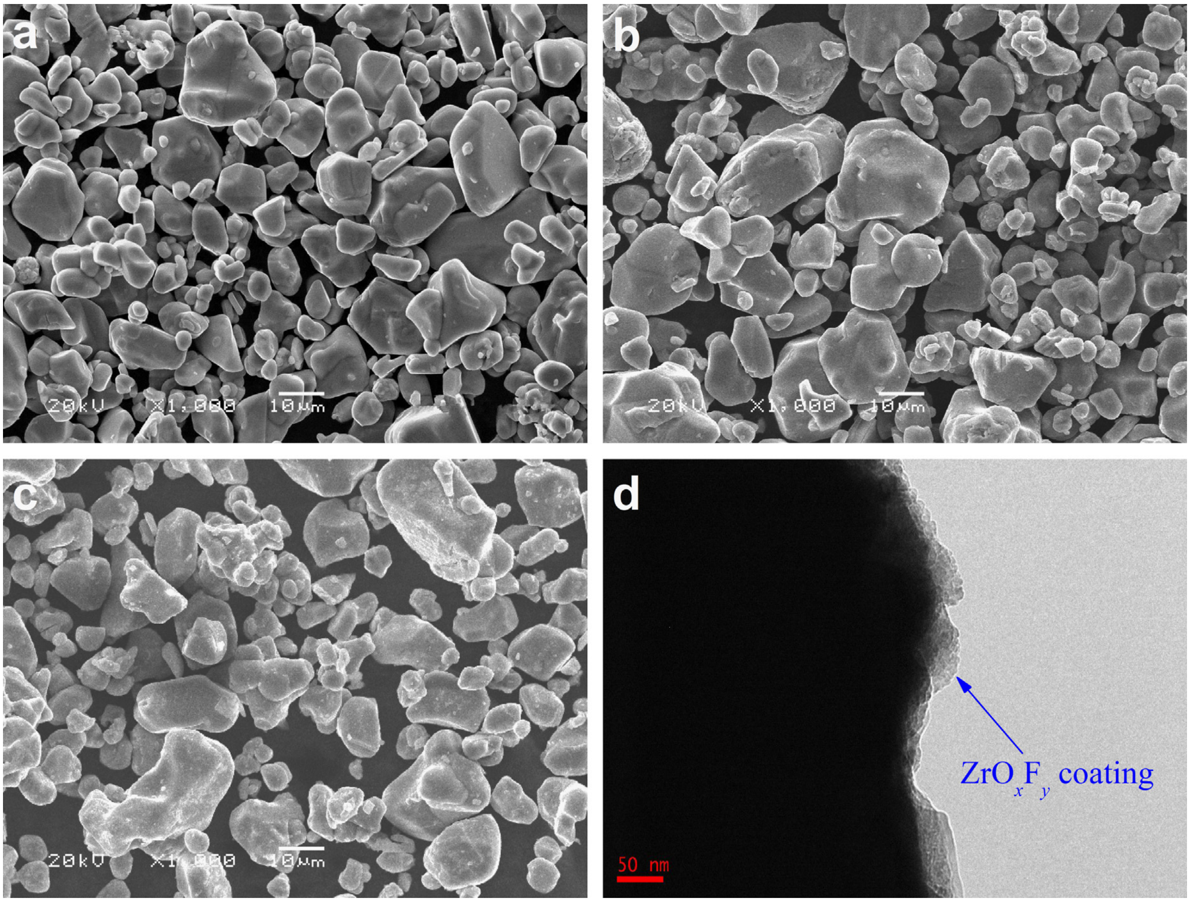

Fig. 1. SEM images of LCO (a), LCMO (b) and LCMO/ZFO (c) samples; TEM (d) image of LCMO/ZFO sample.