



Lithium Cobalt Oxides Functionalized by Conductive Al-doped ZnO Coating as Cathode for High-performance Lithium Ion Batteries



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ARTICLE INFO

Article history:

Received 9 July 2016

Received in revised form 29 November 2016

Accepted 7 December 2016

Available online 10 December 2016

Keywords:

lithium ion batteries

lithium cobalt oxide

Al-doped ZnO

electronic conduction

high discharging rate capability

ABSTRACT

LiCoO₂ (LCO) has been functionally modified with electronic conductive Al-doped ZnO (AZO) via a sol-gel method. The physicochemical characterization results demonstrate that the AZO layer is coated onto the surface of LiCoO₂ particles successfully, and the AZO-coated LCO material shows a higher electronic conductivity than pristine sample. The LCO sample coated by 2 wt.% AZO shows the excellent cyclability with a capacity retention of 98.2% after 50 cycles in the voltage range of 2.75–4.5 V under room temperature. More importantly, this material exhibits outstanding rate capability and delivers a quite high capacity of 156 mA h g⁻¹ at the rate of 8 C (1600 mA g⁻¹), corresponding to 86.6% of the capacity at the rate of 0.1 C. Such superior electrochemical performance results from the effective coating of AZO layer which not only acts as a physical protection layer to stabilize the surface structure, but also supplies the conductive networks to decrease charge transfer impedance. The conducting functionalized AZO coating is a facile and efficient approach to improve the electrochemical performance of LCO at a high cut-off voltage of 4.5 V vs. Li⁺/Li for large-scale application of high energy density lithium ion batteries.

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1. INTRODUCTION

Since commercialized in 1990s, lithium ion batteries (LIBs) have become the irreplaceable portable power sources in our daily life, and their applications are currently expanding from consumer electronics to electric vehicles, hybrid electrical vehicles and stationary power grid storage. The ever-enlarging market requires batteries with enhanced energy density, power density, cyclability and safety. In order to get better performance to meet all of the requirements, the research and development of new cathode materials with high capacity and high operating voltage for LIBs have been boosted [1,2].

As a mature commercial cathode material for lithium ion batteries, the layered oxide of LiCoO₂ (LCO) has been utilized for more than two decades in batteries for consumer electronic devices. However, due to the intrinsic structural instability of the LCO material with high delithiated state, it can only deliver a reversible capacity of about 136 to 140 mA h g⁻¹ (corresponding to

charge/discharge between 3–4.2 V vs. Li⁺/Li), which is just half of its theoretical capacity (273 mA h g⁻¹) [3]. In this regard, great efforts have been made to increase the specific capacity, capacity retention and rate performance at high cut-off voltage of LiCoO₂ [4,5]. Among them, forming a passive layer onto the surface of LCO is considered as an effective strategy to improve the electrochemical performance [6]. The coating materials investigated to date are given as follows: (1) metal oxides, including Al₂O₃ [7–10], MgO [11–13], ZrO₂ [14,15], ZnO [16], and so on; (2) phosphates and silicates, such as AlPO₄ [17,18], Li₂SiO₃ [19], MnSiO₃ [20]; (3) fluorides, for instance, MgF₂ [21], AlF₃ [22]; and (4) other inactive material in nonaqueous electrolyte environment, like AlW_xF_y [23], BaTiO₃ [24], etc. Meanwhile, coating materials are generally unfavorable for both lithium ion and electron conduction of cathode, which results in deterioration of electrochemical properties, especially the rate performance.

ZnO normally has the similar hexagonal structure to LCO [25], where the zinc atom layers alternate with layers occupied by oxygen atoms. This characteristic contributes to the ZnO layer epitaxial growth onto LCO surface easily. More importantly, while ZnO, a wide band gap (3.37 eV) semiconductor, is doped with Al, In or Ga, its electronic conductivity will increase obviously [26]. In a previous study, Dai et al. [27] coated Al₂O₃-doped ZnO layer on the

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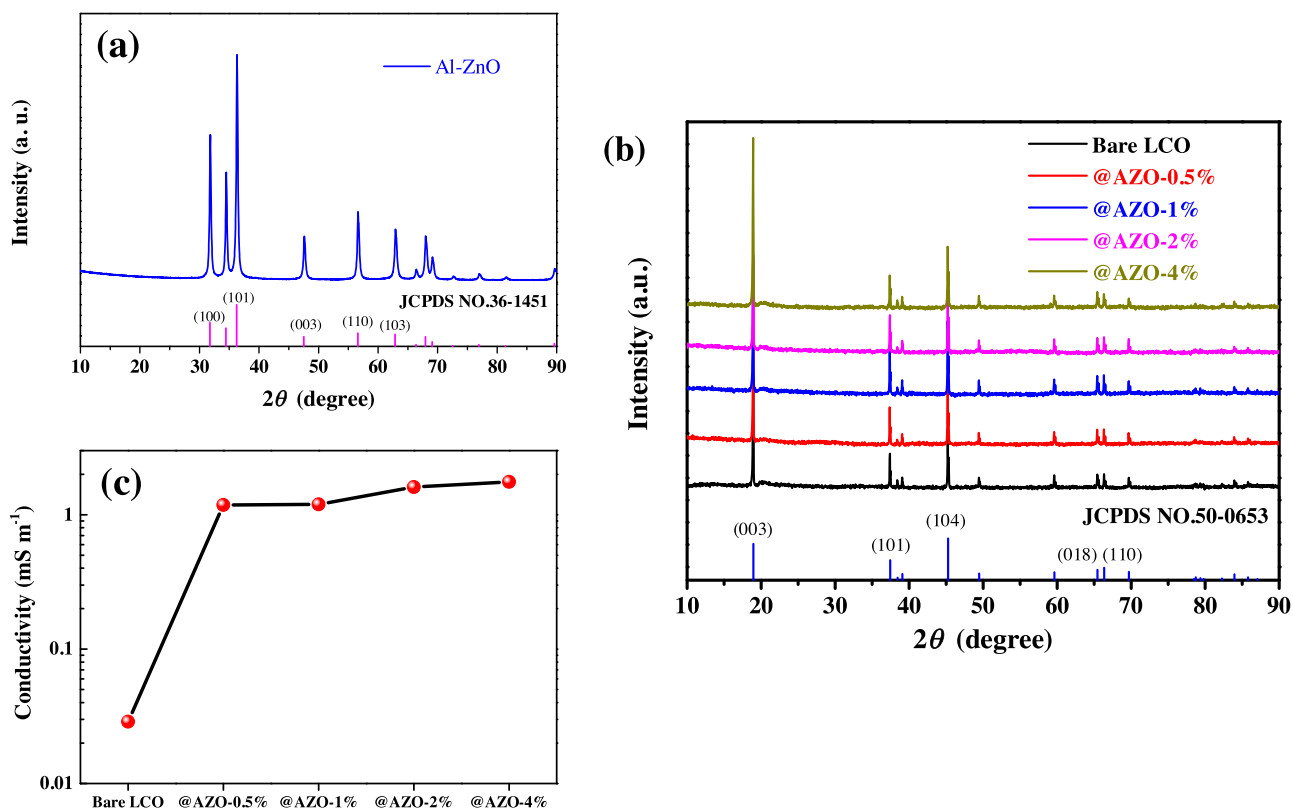


Fig. 1. (a) XRD pattern of AZO powder. (b) XRD patterns of Bare-LCO and AZO-coated LCO samples. (c) Electronic conductivities of Bare-LCO and AZO-coated LCO.

LiCoO₂ electrode by magnetron sputtering. The AZO was directly deposited onto the LiCoO₂ porous composite electrode including conductive agent and binder by the magnetron sputtering method. So, except to outer particle, the LCO particles were rarely coated by AZO layer. Thus it is hardly to maximize AZO layer's advantage of excellent electronic conduction. Moreover, this method can be hardly adopted for practical battery applications due to its high cost. In this paper, the Al-doped ZnO (AZO)-coated LiCoO₂ powders were prepared by a facile sol-gel method, exhibiting the improved structural stability at high state of charge and electric conductivity. The cycling behavior and rate performance of AZO-coated LiCoO₂ material were evaluated using coin-type lithium ion cells between 2.75 and 4.5 V.

2. EXPERIMENTAL SECTION

2.1. Preparation of AZO-coated LCO powders

Commercial LiCoO₂ powders with the median particle size (d₅₀) of 11.9 μm were obtained from Pulead Technology Industry

Co., Ltd. as pristine material (denoted as Bare-LCO). The AZO precursor solution was prepared as follows: Zinc acetate dehydrate (Zn(CH₃COO)₂·2H₂O) and aluminum nitrate nonahydrate (Al(NO₃)₃·9H₂O) were dissolved in a solution of absolute ethanol with monoethanolamine (MEA) as a sol stabilizer. The concentration of Al as a dopant was fixed at 2.0 at.% with respect to Zn, which was considered to reveal the most excellent electron conduction [28,29]. The resultant solution was stirred at 60 °C for 2 h to yield a clear solution, then aged at room temperature for 24 h. Thereafter, LiCoO₂ was immersed into the solution with the total AZO amount of 0.5 wt.%, 1 wt.%, 2 wt.%, and 4 wt.% in the coated LiCoO₂ powders. The obtained samples were denoted as @AZO-0.5%, @AZO-1%, @AZO-2%, and @AZO-4%, respectively. After thorough stirring for 1 h, the slurry was then dried in an oven at 100 °C for 10 h and finally calcined at 600 °C for 4 h in air. Specially, the samples prepared for electron conduction testing were pressed into discs with 15 mm in diameter and about 2 mm in thickness before calcination.

2.2. Materials Characterizations

The morphology of the coated LCO samples was characterized by scanning electron microscope (SEM, HELIOS NanoLab 600i, FEI Company) and transmission electron microscopy (TEM, Tecnai G2 F30, FEI Company). The element mapping is performed by energy dispersive spectroscopy (EDS) using the same instrument with the SEM characterization. The crystal structure of the obtained materials was characterized by X-ray diffraction using Cu Kα radiation (XRD, λ = 1.54056 Å, X'Pert ProMPD, Panalytical company) in the 2θ range of 10–90°. The electronic conductivities of the samples were investigated by the four-point probe method. Surface and atomic composition analyzes were performed by an

Table 1
Structural Parameters of Bare-LCO and AZO-Coated LCO Obtained from the Rietveld Refinement of X-ray Diffraction Data.

Samples	a (Å)	c (Å)	V (Å ³)
Bare-LCO	2.81594(1)	14.05256(4)	95.60
@AZO-0.5%	2.81669(3)	14.05287(1)	96.55
@AZO-1%	2.81645(3)	14.05529(1)	96.55
@AZO-2%	2.81614(1)	14.05380(5)	96.52
@AZO-4%	2.81641(3)	14.05384(1)	96.54

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