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Short Communication

Enhanced electrochemical performance of Li-rich layered cathode materials by surface modification with P_2O_5

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ABSTRACT

Rate capability and charge/discharge coulombic efficiency of Li-rich layered oxides was greatly improved by surface modification with P_2O_5 through a gas–solid reaction. The P_2O_5 treatment results in forming a uniform nanoscale coating layer of ionically conductive Li_3PO_4 and spinel-like material on Li-rich layered oxide particles. The resulting material delivers a charge/discharge coulombic efficiency of 90% compared with 81% of the pristine sample during the first cycle. The treated electrode also exhibits improved rate capability with a reversible capacity of 148 mAh g^{-1} at 4 C-rate vs. 269 mAh g^{-1} at 0.1 C-rate between 2.0 and 4.8 V.

1. Introduction

Lithium-rich layered oxide (represented by either $Li_{1+x}MO_2$ or $xLi_2MnO_3 \cdot (1-x)LiMO_2$, ($0 < x < 1$, M = Mn, Ni, Co)) has been proposed as a promising candidate for next generation lithium-ion batteries due to its extra high specific capacity [1–3]. For example, $0.5Li_2MnO_3 \cdot 0.5LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ prepared by a molten salt method can deliver a reversible discharge capacity as high as 313 mAh g^{-1} at room temperature [4], which makes this material a promising cathode for high energy density LIBs. Although Li-rich layered oxides are considered to have enormous potential in the future, there are still several major issues to be resolved, including large irreversible capacity at the first cycle, poor rate capability and cycling stability.

Surface modification has been proven to be an effective way to improve the performances of cathode materials. In the previous studies, many compounds, such as phosphates [5], oxides [6,7] and fluorides [8], have been synthesized by wet-chemical methods as coating agents to improve the electrochemical performance of Li-rich layered oxides. However, most of these surface coatings are realized through wet-chemical methods, which results in rough coating with nanoparticles loading on the surface (uncontinuous coating layer) [9]. Although atomic layer deposition (ALD) coatings can provide pinhole free complete protection for cathode materials [10], this process is expensive and relatively difficult to realize. In the present study, we report a new strategy to achieve a uniform and continuous surface modification using a simple gas–solid reaction between sublimated P_2O_5 and Li-rich cathode particles. For P_2O_5, sublimation starts from ca. 300 °C [11]. During the heat treatment process, P_2O_5 solids was sublimated and become gaseous phase, P_2O_5 and cathode particles can contact well with each other, ensuring a uniform surface treatment. The schematic of different types of surface coating mentioned above is shown in Fig. 1. The electrochemical profile of the resulting material was evaluated in comparison with pristine material. We demonstrate that Li-rich layered oxide electrodes with P_2O_5 treatment can greatly improve the electrochemical performances compared to untreated particles.

2. Experimental

Pristine $0.5Li_2MnO_3 \cdot 0.5LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ was prepared by a co-precipitation method according to a previous report, using transitional metal sulfates and lithium hydroxide as starting materials [12]. The P_2O_5 treatment process was conducted immediately after the pristine sample was obtained. The reactor used for the treatment was an inner ceramic container with a stainless steel shell sealed with a graphite sealing ring. To prepare the experiment, firstly, all the things used for the treatment were transferred into the glove box. In the glove box, 0.05 g of P_2O_5 powder was added on the bottom of the ceramic container, and then 1 g of pristine powder was put on a gas-permeable sample holder in the ceramic container fixed over P_2O_5 powder. After hermetically sealing with a graphite sealing ring, the reactor was transferred to a muffle furnace preheated to 350 °C and kept at that temperature for 1 h. After heat-treatment, the treated cathode powder was washed with deionized water and vacuum dried overnight.

The morphology, structure and surface state of the samples were characterized using X-ray diffraction (XRD, Bruker D8), transmission

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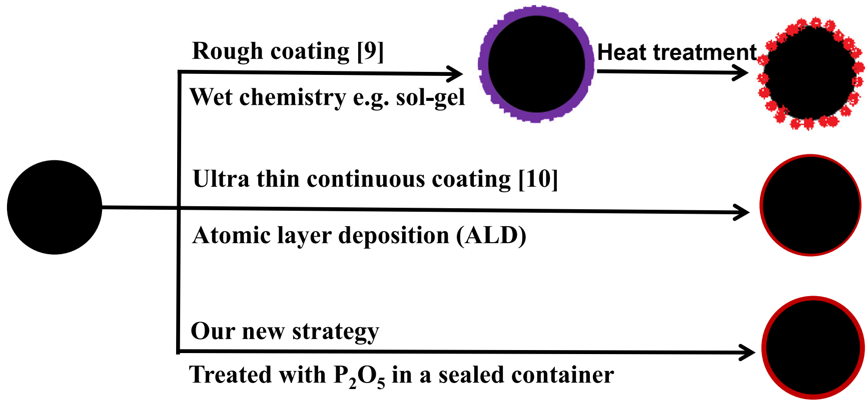

Fig. 1. Schematic of different types of surface modification.

electron microscopy (TEM, Joel JEM2010), X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra), and Fourier-transform infrared spectroscopy (FTIR, NICOLET 6700). The collected intensity data of XRD were analyzed by the Rietveld method using the TOPAS package.

The electrochemical properties of the pristine and P_2O_5-modified materials were measured using 2016 coin-type cells with a LAND CT2001A Battery Cycler (Wuhan, China). For fabrication of the electrodes, the cathode powders were mixed with conductive carbon and polyvinylidene fluoride (80:10:10 by weight) in N-methylpyrrolidinon. The electrolyte solution used was 1 M $LiPF_6$ dissolved in a 1:1:1 volume ratio mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC). 1 C-rate is equivalent to 200 mA g^{-1} in our definition, for the reason that the total discharge time is about one hour at this current density.

3. Results and discussion

Rietveld refinement profiles of pristine and P_2O_5 treated samples of pristine and P_2O_5-treated samples using $R\bar{3}m$ and C2/m symmetry are shown in Fig. 2a. The phase fractions of rhombohedral and monoclinic components of pristine material were 50.3% and 49.7%, respectively, compared to 51.9% and 48.1% of the P_2O_5-treated material. Before treatment, all peaks of the XRD patterns can be indexed as an O_3-type structure, except for the superlattice peaks between 21 and 25°, which can be attributed to the ordering of Li and Mn in the transition-metal layer. However, after heat-treatment, there is no detectable phase due to the treatment of P_2O_5 as no extra peak can be found in the XRD pattern of the treated sample. Lattice constants were determined by fitting the peak positions with a $R\bar{3}m$ space group. The lattice parameters of the

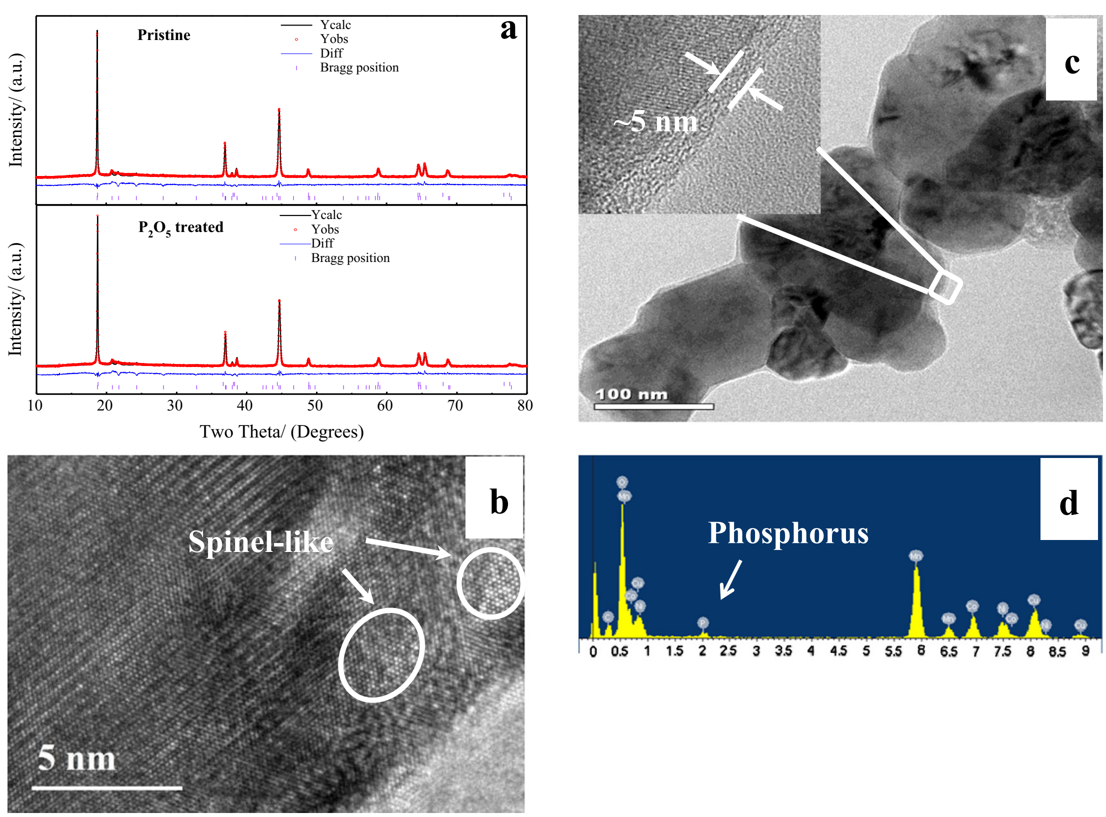

Fig. 2. (a) Rietveld refinement profiles of pristine and P_2O_5 treated samples, (b) high and (c) low magnification TEM images, and (d) EDX spectrum of P_2O_5 treated samples.