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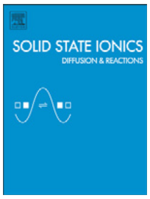

Enhanced electrochemical properties of $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ via lithium boron oxide glass surface treatment

Maohui Bai, Zhixing Wang *, Xinhai Li, Huajun Guo, Zhenjiang He, Junkai Zhao

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

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ABSTRACT

A $Li_2O \cdot 2B_2O_3$ layer is successfully coated on the surface of Li-rich layered cathode $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$, which is demonstrated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The electrochemical performance of the pristine and LBO-coated materials have been investigated by galvanostatic charge/discharge. The experiment results indicate that the electrochemical performances of Li-rich cathode materials are obviously improved by LBO surface modification. Particularly, the sample with 3 wt.% LBO-coating shows the best cycling performance, with capacity retention of 92% after 100 cycles, which is much better than the pristine one. Electrochemical impedance spectroscopy (EIS) reveals that the enhanced electrochemical performances of the LBO-coated sample are due to the enhancement of surface electronic conductivity and the suppression of the decomposition of electrolyte.

1. Introduction

With the development of hybrid electric vehicles (HEVs) and electric vehicles (EVs), the high-energy and high-power Li-ion batteries (LIBs) are in great demand [1–5]. As compared with the conventional cathode materials such as layered $LiCoO_2$ [6] and olivine $LiFePO_4$ [7], Li-rich layered-oxide positive electrode materials are more attractive due to the higher theoretical specific capacity as large as 250 mAh g^{-1} and relative low cost. The successful application of these materials can increase the energy density of Li-ion batteries, such as $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$.

Nevertheless, the Li-rich Mn-based oxide materials have several shortcomings [8], including poor rate capacity and insufficient capacity retention, which greatly impeded their actual applications. Various effective methods have been adopted to solve these critical problems via coatings of sundry materials [9–13], such as metal oxides [14,15], metal phosphates [16,17], and metal fluorides [18]. A proper coating layer can defend the electrode surface from direct contact with the electrolyte and reduce the side-reactions between the electrolyte and electrode [19,20].

Lithium boron oxide (Li_2O-$2B_2O_3$,or LBO) glass is typically solid lithium ionic conductor with good lithium ionic conductivity and electrochemical stability against high oxidation potential. In addition, good wetting properties and relatively low viscosity of the LBO allow easy processing and result in even coverage with the use of a minimal amount of materials [21,22]. Based on the above statements, the presence of LBO at the surface of host materials might help to improve cycling stability and the rate capability even at high voltage. Also this work has not yet been reported, so LBO glass has been employed as a suitable coating for $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$.

2. Experimental

2.1. Powder preparation

The bare $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ powder was synthesized by oxalate co-precipitation method [23] and annealing at 950 °C in air for 16 h. To prepare sample coated with LBO, stoichiometric $LiOH \cdot H_2O$ and H_3BO_3 (1:2 in molar) was dissolved in alcohol under gently stirring. Then, Bare $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ powder was added into the solution stirred continually, and heated at 80 °C until the solvent completely evaporated. In the end, the remaining powder was calcined in air at 500 °C for 10 h to obtain the sample. For this research, the $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ powder was coated with different amounts of LBO glass in the range of 1 to 5 wt.%. We defined the LBO-glass-coated composites with coating treatment of 0 wt.%, 1 wt.%, 2 wt.%, 3 wt.%, and 5 wt.% as LBO0, LBO1, LBO2, LBO3, and LBO5 respectively.

2.2. Physical characterizations

The powder X-ray diffraction (XRD, Rint-2000, Rigaku, Japan) using Cu Kα radiation was employed to identify the crystalline phase of the synthesized materials. The morphology of the composites was measured by scanning electron microscopy (SEM, Sirion 200), and by transmission electron microscope (Tecnai G12, 200KV).

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* Corresponding author.
E-mail address: zxwang_csu@163.com (Z. Wang).

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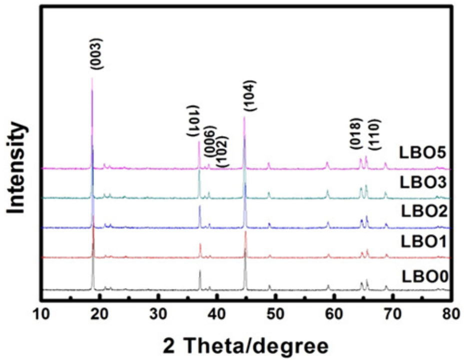

Fig. 1. XRD patterns of LBO0, LBO1, LBO2, LBO3, LBO5.

2.3. Electrochemical tests

The electrochemical characterizations were detected by using a standard CR2025 coin-type cell composed of the cathode, metallic lithium anode, a commercial polypropylene micro-porous separator, and 1 mol/L $LiPF_6$ in EC, EMC and DMC (1:1:1 v/v/v). The samples were prepared by coating homogenous slurries on an aluminum foil. The slurry was mixed with 10% conductive-carbon, and 10% PVDF binder was coated onto an aluminum foil current collector and dried for 6 h at 120 °C. Then it was cut into the shape of circular disks and kept in a vacuum drying oven prior to use. The assembly of the cells was executed in an argon-filled glove box. The cells are charged and discharged over a voltage range of 2.5–4.6 V versus Li/Li^+ electrode at current density of 0.2 C, 0.5 C, and 1 C (250 mA g^{-1}) at room temperature.

3. Results and discussion

XRD patterns of pristine and LBO coated samples are shown in Fig. 1. Except for the weak peaks located at $2\theta = 20$–25°, the weak peaks located are caused by the short-ranged superlattice ordering of the Li, Ni and Mn atoms in the transition metal layers [24,25]. The other peaks in the XRD pattern of LBO0 can be indicated to the α-$NaFeO_2$ structure with space group of R-3m. In addition, strong and narrow diffraction peaks as well as clear peak splits of (006)/(102) and (018)/(110) reveal the highly ordered layered structure of $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ powders. The diffraction peaks of the modified samples (LBO1–LBO5) show almost no differences with those of the pristine material, indicating that the LBO coating layer has little influence on the bulk structure of the bare sample. Since no other diffraction peaks show up, it is believed that amorphous LBO glass is well coated onto the surface of the pristine material.

In order to confirm further information of the coating layer on the materials, SEM and TEM were used to study surface morphologies and microstructures of these samples. Fig. 2(a) and (b) shows SEM images of LBO0 and LBO3 samples which exhibit similar surface morphologies. The particle size of LBO3 remains unchanged and there is less agglomeration after modification. Fig. 2(c) and (d) shows TEM images of LBO0 and LBO3 particles. An apparent thin coating layer with a thickness of approximately 8 nm is observed on the surface of LBO3. This phenomenon suggests that the coating layer has been formed on the surface of $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ powders. The EDS images of LBO3 are shown in Fig. 3 and confirm that the B elements are distributed in the samples homogenously.

The initial discharge curves of all samples in the range of 2.5–4.6 V at a current density of 12.5 mA g^{-1} is shown in Fig. 4(a). The initial discharge capacities of the samples are 255, 240, 232, 228, 213 mAh g^{-1}, respectively. The decrease of capacity means the LBO glass in the LBO coated samples is a non-electroactive species. Fig. 4(b) is the influence of LBO coating layer on the capacity retention of Li-rich cells in the range of 2.5–4.6 V at 0.2 C, 0.5 C and 1 C (250 mA g^{-1}) rates, respectively. Apparently, pristine Li-rich electrode suffers fast capacity decay during the cycle process. At the current density of 250 mA g^{-1}, it displays an initial discharge capacity of 150 mAh g^{-1}, which sharply decreases to 106 mAh g^{-1} after 100 cycles, with a capacity retention of only 70%. As can be clearly observed in this figure, LBO surface modification greatly improves the cycleability of $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$. In

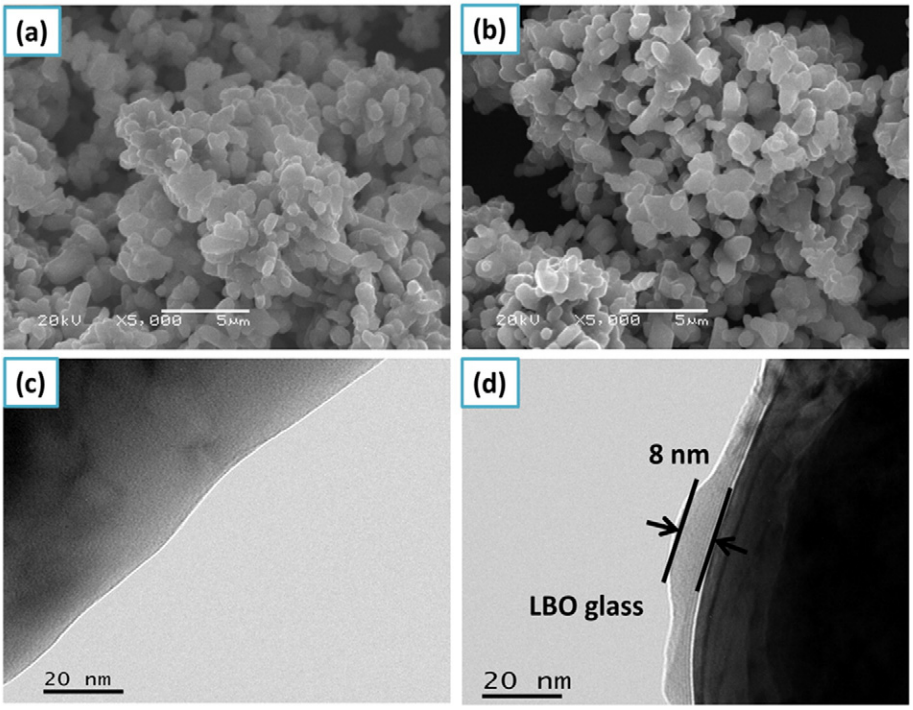

Fig. 2. SEM images of LBO0 (a) and LBO3 (b), TEM images of LBO0 (c) and LBO3 (d).