



Short communication

Surface structure investigation of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ by AlPO_4 coating and using functional electrolyte

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ABSTRACT

Surface structures of the bare and AlPO_4 -coated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ particles in two electrolytes after 90°C for 4 h storage were investigated using transmission electron microscope (TEM). The structure of bare $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ particles in common electrolyte has been destructed from the layered structure with space group R-3m at interior region to a rock-salt phase (Fm-3m) at edge of the surface layer of the cycled particles, while AlPO_4 -coated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ particles in common electrolyte has been transformed into a spinel phase (Fd-3m) on the surfaces of the cycled particles. However, the surface structure of bare $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ particles in functional electrolyte has not been changed. The results showed that functional electrolyte can more effectively improve thermal stability of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode cells than the AlPO_4 coating.

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1. Introduction

$\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ has attracted much attention as a 4 V cathode due to its lower price and higher reversible capacity compared with LiCoO_2 . However, the thermal stability of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ must be improved to be used in commercialized batteries because a violent exothermic reaction of the highly delithiated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ with the electrolyte due to the oxygen release is known to occur at around 200°C [1]. To improve thermal stability and cycling performance, one strategy is to coat the cathode material surface with metal oxides such as ZrO_2 [2], SiO_2 [3], Al_2O_3 [4] and AlPO_4 [5,6]. Among those, AlPO_4 -coated LiCoO_2 exhibits low thermal runaway and excellent capacity retention [6]. Another strategy is to use functional electrolytes preventing thermal runaway, although these electrolytes damaged the electrochemical properties of the cathode and anode materials [7]. It is suggested that the interfaces between the cathode material and the electrolyte play an important role, which are the origins of the thermal runaway and the impedance increasing. Therefore knowing the structural variation and compositional modification of the cathode at atomic scale during the electrochemical cycling process is a fundamental object for improving performance of a lithium-ion battery. However, the surface characteristics of cathode active

particles before and after cycling have been paid little attention. Up to now, only Abraham et al. [8] reported the surface changes on $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ particles after extensive cycling, in which a $\text{Li}_x\text{Ni}_{1-x}\text{O}$ -type layer ($0 < x < 0.5$, rock-salt structure, space group Fm-3m) with about 35 nm thickness on the particle surfaces was observed by using transmission electron microscope (TEM). They revealed that the surface layer was a significant contributor to cathode impedance rise. Hence, comparative study of surface structural changes in the uncoated- $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ with and without the functional electrolyte, and AlPO_4 -coated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ with the common electrolyte during electrochemical cycling should provide useful information for improving the performance of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode.

In this work, effects of AlPO_4 coating and functional electrolyte on the surface structure of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ particles after 90°C for 4 h storage have been investigated using TEM.

2. Experimental

$\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ were prepared as follows: $\text{Ni}_{0.8}\text{Co}_{0.2}(\text{OH})_2$ precursors were first synthesized using co-precipitation method. CoCl_2 and NiCl_2 salts were used as starting materials for synthesis of the $\text{Ni}_{0.8}\text{Co}_{0.2}(\text{OH})_2$ powders. The prepared powders were mixed with excess amount of LiOH . After the mixtures were sufficiently ground, the mixtures were heated in air at 680°C for 12 h and followed by slowly cooling to room temperature. The 0.3 wt.% AlPO_4 -coated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ was prepared as described in Ref. [6]. X-ray diffrac-

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tion data shows that the bare and AlPO_4 -coated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ have the same structure with space group R-3m, and the lattice constants, $a = 2.863 \text{ \AA}$, $c = 14.164 \text{ \AA}$, for bare sample, $a = 2.682 \text{ \AA}$, $c = 14.163 \text{ \AA}$, for AlPO_4 -coated sample.

Positive electrodes were made by coating a paste of the bare or AlPO_4 -coated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ active material, acetylene black (as a conducting additive), and polyvinylidene fluoride (PVDF) binder (93:3.5:3.5 (wt.%)) on an aluminum foil collector. The negative electrode was prepared by mixing graphite with 10 wt.% PVDF binders, and the prepared paste was coated on a copper foil. The electrodes were then dried under vacuum (5×10^{-2} Torr) for 24 h at 120°C . The common electrolyte was 1 M $\text{LiPF}_6/\text{EC}:\text{DEC}:\text{DMC}$ (1:1:1, v/v), the functional electrolyte was 1 M $\text{LiPF}_6/\text{EC}:\text{DEC}:\text{DMC}$ (1:1:1, v/v) + 3 wt.% TPP (triphenylphosphate). The cells were assembled inside an Ar-filled dry-box and were evaluated using aluminum shell 053048-cells (thickness: 5 mm, width: 30 mm, height: 48 mm). For the elevated temperature storage test, the cells were charged to 4.2 V at a rate of 0.1 C firstly and held there until the current decreased to 10%, then were heated to 90°C for 4 h, followed by cooling to room temperature and discharged to 3.0 V at 1 C, finally disassembled inside an Ar-filled dry-box. In order to avoid damaging the cycled particle surfaces, Pieces of the cathodes

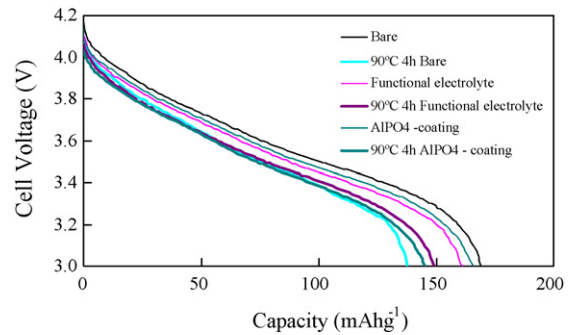


Fig. 1. Discharge curves of bare and 0.3 wt.% AlPO_4 -coated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ in common and functional electrolytes in the voltage range of 4.2–3.0 V at a rate of 1 C before and after 90°C for 4 h storage.

obtained from the disassembled cell were ultrasonically deagglomerated in acetone and dispersed on a holey carbon film supported by a Cu grid for TEM observation. A JEOL-2010 transmission electron microscope operating at 200 kV accelerating voltage was used for imaging and electron diffraction.

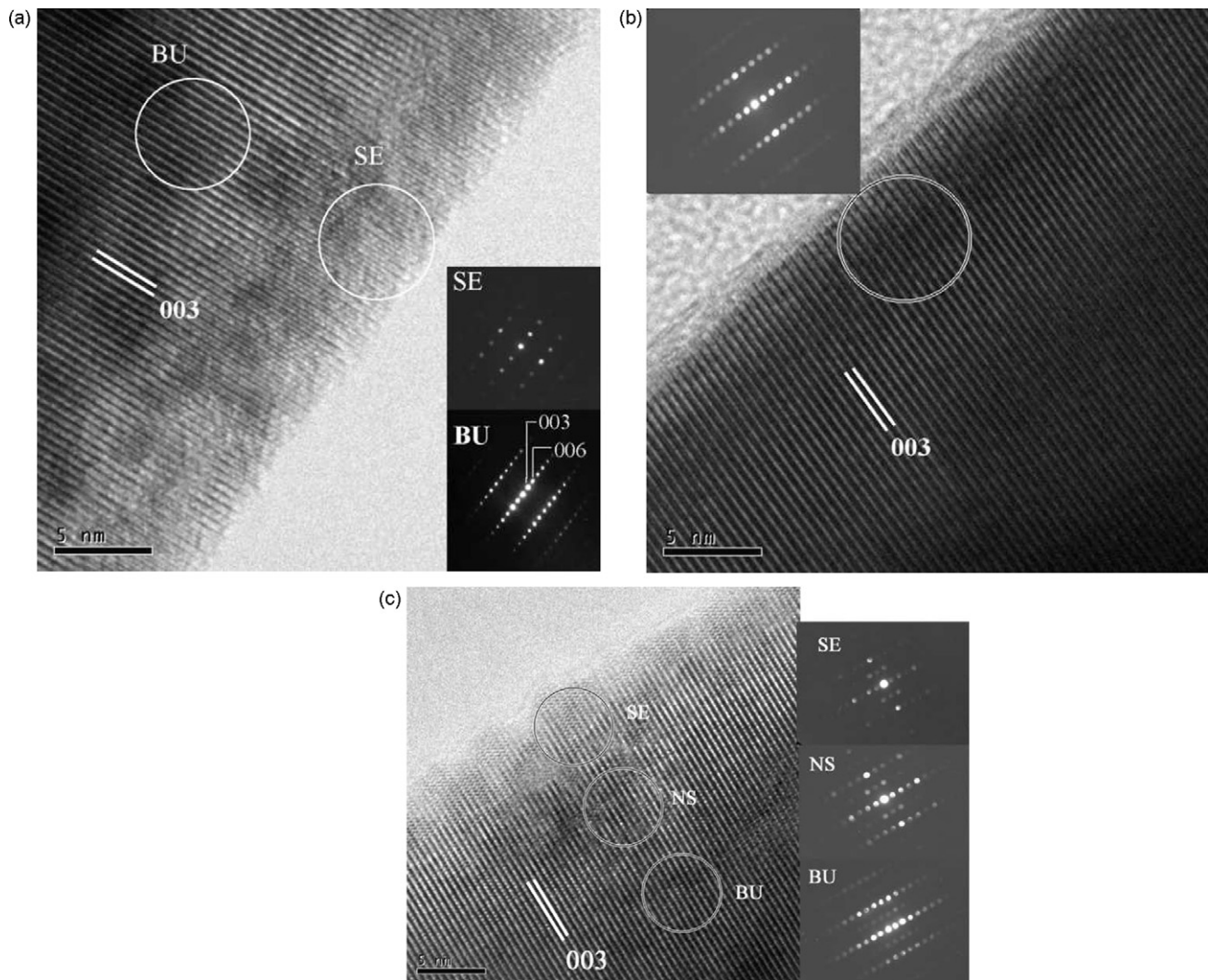


Fig. 2. HRTEM images of the particles after 90°C for 4 h storage in 1 1 0 orientation of $\alpha\text{-NaFeO}_2$ lattice show the detail structural features of (a) bare $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ in common electrolyte, (b) bare $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ in functional electrolyte, and (c) 0.3 wt.% AlPO_4 -coated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ in common electrolyte. The inserted micro-diffraction patterns taken from the region of BU, NS and SE marked in the images.

Table 1Results of electrochemical experiments for bare and 0.3 wt.% AlPO₄-coated LiNi_{0.8}Co_{0.2}O₂ in common and functional electrolytes.

	Bare LiNi _{0.8} Co _{0.2} O ₂ in common electrolyte	0.3 wt.% AlPO ₄ -coated LiNi _{0.8} Co _{0.2} O ₂ in common electrolyte	Bare LiNi _{0.8} Co _{0.2} O ₂ in functional electrolyte
Initial discharge capacity (1 C)	170 mAh g ⁻¹	166 mAh g ⁻¹	160 mAh g ⁻¹
Thickness increase ratio of the cells after 90 °C for 4 h storage	~70%	~40%	~2%
Capacity retention after 90 °C for 4 h storage	81%	86%	93%

3. Results and discussion

Table 1 shows the electrochemical experiment results, the thickness of bare LiNi_{0.8}Co_{0.2}O₂ cell with functional electrolyte has not been almost changed after 90 °C for 4 h storage, while the thickness increase of bare and 0.3 wt.% AlPO₄-coated LiNi_{0.8}Co_{0.2}O₂ cells with 1 M LiPF₆/EC:DEC:DMC (1:1:1, v/v) are about 70 and 40%, respectively. The discharge curves of the three cells between 4.2 and 3.0 V at a rate of 1 C before and after 90 °C for 4 h storage are compared in Fig. 1. The bare LiNi_{0.8}Co_{0.2}O₂ cell with functional electrolyte exhibits higher capacity retention than the bare and 0.3 wt.% AlPO₄-coated LiNi_{0.8}Co_{0.2}O₂ cells with the common electrolyte after 90 °C for 4 h storage, although its initial discharge capacity (1 C) is lower than that of the bare and 0.3 wt.% AlPO₄-coated LiNi_{0.8}Co_{0.2}O₂ cells with the common electrolyte. These results indicate that functional electrolyte can more effectively improve thermal stability of LiNi_{0.8}Co_{0.2}O₂ cathode cells than the AlPO₄ coating, but meanwhile decreased Li⁺ diffusion during electrochemical cycling.

Fig. 2 shows the surface structures of bare and AlPO₄-coated LiNi_{0.8}Co_{0.2}O₂ particles in two electrolytes after the elevated temperature storage. In Fig. 2(a), the HRTEM image of the bare LiNi_{0.8}Co_{0.2}O₂ particles in common electrolyte shows (003) plane lattice fringes were clearly visible in the bulk regions, however, the parallel (003) plane lattice fringes disappeared and were replaced by thin lattice fringes at edge of the surface layer of the particles. As well know, the (003) plane is characteristic of the layered LiNi_{0.8}Co_{0.2}O₂, its absence means a random distribution of atoms on the 3a(Li) and 3b(Ni,Co) sites of the layered LiNi_{0.8}Co_{0.2}O₂. The inserted micro-diffraction patterns taken from the region of BU and SE marked in the image indicates that the structure of bare LiNi_{0.8}Co_{0.2}O₂ particles in common electrolyte has been destructed from the layered structure with space group R-3m at interior region to a rock-salt phase (Fm-3m) at edge of the surface layer of the cycled particles. In Fig. 2(b), the HRTEM image of the bare LiNi_{0.8}Co_{0.2}O₂ particles in functional electrolyte shows (003) plane lattice fringes were clearly visible on the overall surface layer of the particles. The inserted micro-diffraction pattern taken from the region of SE marked in the image presents the typical electron diffraction pattern of the [110] zone of the layered LiNi_{0.8}Co_{0.2}O₂. These structural characteristics demonstrate the functional electrolyte has effectively prevented the structural change of the LiNi_{0.8}Co_{0.2}O₂ particles during 90 °C for 4 h storage. In comparison with Fig. 2(b), besides (003) plane lattice fringes, some lattice fringes were clearly observed in the HRTEM image (in

Fig. 2(c)) of AlPO₄-coated LiNi_{0.8}Co_{0.2}O₂ particles in common electrolyte. In addition, new diffraction spots appeared in the inserted micro-diffraction patterns taken from the region of BU, NS and SE marked in Fig. 2(c), which indicates that a spinel phase (Fd-3m) is present on the surfaces of the AlPO₄-coated LiNi_{0.8}Co_{0.2}O₂ particles.

Because the phase transition from the layered structure to a rock-salt phase releases more amounts of oxygen than to a spinel phase [3], thermal stability improving of LiNi_{0.8}Co_{0.2}O₂ cathodes resulted in structural stability for functional electrolyte and AlPO₄ coating that maintained an original layered structure and blocked the phase transition to a rock-salt phase, respectively.

4. Conclusion

The surface structures of bare and AlPO₄-coated LiNi_{0.8}Co_{0.2}O₂ particles in common electrolyte showed different phase transformation paths during 90 °C for 4 h storage. The layered structure of bare cathode particles has been converted to a rock-salt phase (Fm-3m) at edge of the particle surface, while the AlPO₄-coated sample was transformed to a spinel phase (Fd-3m) with the less loss of oxygen on the particle surfaces. The functional electrolyte maintained the original hexagonal phase, and is very effective in retarding the oxygen loss.

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