



Letter

Remarkable improvement in cell safety for $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ coated with LiFePO_4

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ABSTRACT

$\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ has been synthesized by a co-precipitation method and the surface coated with nanosized LiFePO_4 particles. Structural characterizations were performed by X-ray diffraction (XRD) studies and transmission electron microscopy (TEM) utilized to ensure the coating. A homemade aluminum pouch cell was assembled and studied at different C rates (0.5–20 C). At high current rates, the cell presented very stable discharge behavior. During the safety test, great enhancement of thermal and over-charge behavior was observed for LiFePO_4 -coated $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ material.

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1. Introduction

In recent years, there has been increasing interest to develop cathode materials for lithium batteries with high energy densities and improved safety. Commercially available batteries comprising layered LiCoO_2 as cathode material suffer many problems ranging from poor thermal stability and cost to being environmentally unfriendly. The eco-friendly spinel LiMn_2O_4 has been proposed as an alternative to LiCoO_2 ; however, Jahn-Teller distortions associated with Mn^{3+} dissolution lead to poor capacity retention that hampers the possibility of commercial cell applicability [1].

Ohzuku and Makimura [2] first proposed the attractive $\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ compound as a promising cathode material for lithium ion batteries with exhibited high capacity, structural stability, and excellent cycling behavior. Nevertheless, many issues still require attention, such as low rate capability, poor thermal stability, and considerable capacity loss during high current rates. Many reasons for such problems have been proffered, like direct electrode contact with the electrolyte, mechanical stress caused by volumetric changes during insertion/extraction of the lithium ions, and detachment of the conductive additives from the active material [3]. The introduction of surface coatings by ceramic oxides addressed some of the concerns, but the formation of an inactive

phase on the surface of the material hinders diffusion of lithium ions during the lithiation/delithiation process [4–6].

In the interest of such issues, we have successfully synthesized a core-shell type $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ with minimum Co content by a co-precipitation method. The LiFePO_4 has been coated on the surface of the aforesaid material and effectively improves the safety of pristine $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ under harsh conditions.

2. Experimental

A co-precipitation method was employed to prepare the composite metal hydroxides ($\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}$)-(OH)₂. The starting materials of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (Jinlin Jien, China), $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (Chuodenki, Japan) and $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (Jinlin Jien, China), were the respective sources of Ni, Co, and Mn at stoichiometric ratios. The synthetic procedure contained two steps. In the first step, the source materials were dissolved in purified, ion-exchanged water to prepare the solution and the reaction was performed until formation of slurry containing uniform sizes of metal hydroxides. The second step involved heating the slurry to 300 °C for 12 h and mixing with the lithium source material in 1:1 stoichiometric ratio. The mixture was then calcined at 950 °C for 24 h and again subjected to the calcination process at 500 °C for 24 h to yield the final product. This synthetic procedure is also described elsewhere [7].

The LiFePO_4 material was synthesized from Li_2CO_3 (Sigma-Aldrich, USA), $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (Sigma-Aldrich, USA), and $(\text{NH}_4)_2\text{HPO}_4$ (Sigma-Aldrich, USA) using a solid-state method. A stoichiometric amount of each material was ground and calcined at 400 °C for 1.5 h and then at 660 °C for 2.5 h in an Ar atmosphere using carbon coating in a tubular furnace. The optimum content (1.5 wt%) of the LiFePO_4 , with an average particle diameter D50 of 160 nm, was thoroughly mixed with the composite metal oxides using a dry coating system (NOB-130, Hosokawa micron Ltd., Japan). The mixture was treated at a rotation rate of 2700 rpm for 3 min and heated at 500 °C for 4 h in Ar atmosphere in order to prepare and stabilize a core-shell type cathode material. Particle shape and size distribution of the resulting compound were observed using a transmission electron microscope (TEM, Tec-

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naif20, Philips, Netherlands) and a particle size analysis system (Mastersizer 2000E, Malvern Instrument, UK), respectively.

A homemade, 3.7 mm thick \times 64 mm wide \times 95 mm long aluminum pouch cell bearing a design capacity of 2000 mAh was assembled to study cycling behavior. The cathode material was prepared by a slurry coating procedure at a ratio of 92:4:4 of active material:binder (polyvinylidene fluoride):conducting additive (Teflonized acetylene black). *N*-Methyl pyrrolidone was used as the slurring agent. Porous polypropylene (Celgard 3401) was used as a separator. The 1.2 M LiPF₆ in ethylene carbonate:diethyl carbonate (1:3 v/v), was used as the electrolyte solution. Cycling performances were carried out at room temperature (25 °C) at different C rates between 2.6 and 4.3 V.

3. Results and discussion

Figure 1 represents the typical X-ray diffractions of the materials synthesized. A hexagonal structure with a *R3m* space group for both pristine and LiFePO₄-coated material was apparent. No new peak was observed for the coated LiFePO₄ material, due potentially to less material coating the surface, inducing few if any structural changes [8]. The lattice parameters were calculated ($a = 2.8721$ Å and $c = 14.2574$ Å) for Li[Ni_{0.5}Co_{0.2}Mn_{0.3}]O₂ and were in good agreement with the earlier report by Liu et al. [9] Notwithstanding, a slight difference ($a = 2.8712$ Å and $c = 14.2596$ Å) has been observed for LiFePO₄-coated material.

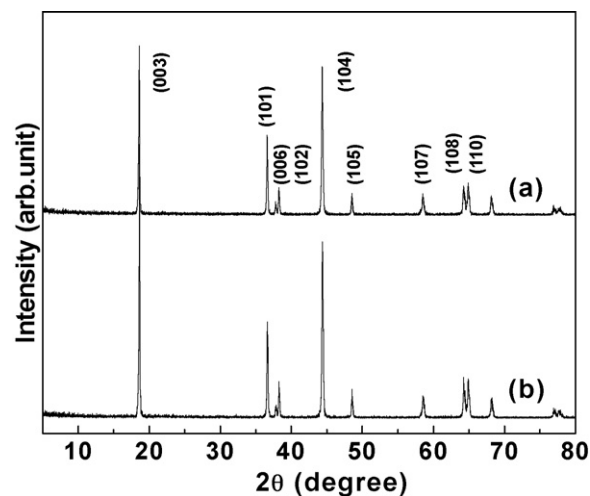


Fig. 1. X-ray diffractions of: (a) Pristine Li[Ni_{0.5}Co_{0.2}Mn_{0.3}]O₂; (b) 1.5 wt.% LiFePO₄-coated Li[Ni_{0.5}Co_{0.2}Mn_{0.3}]O₂.

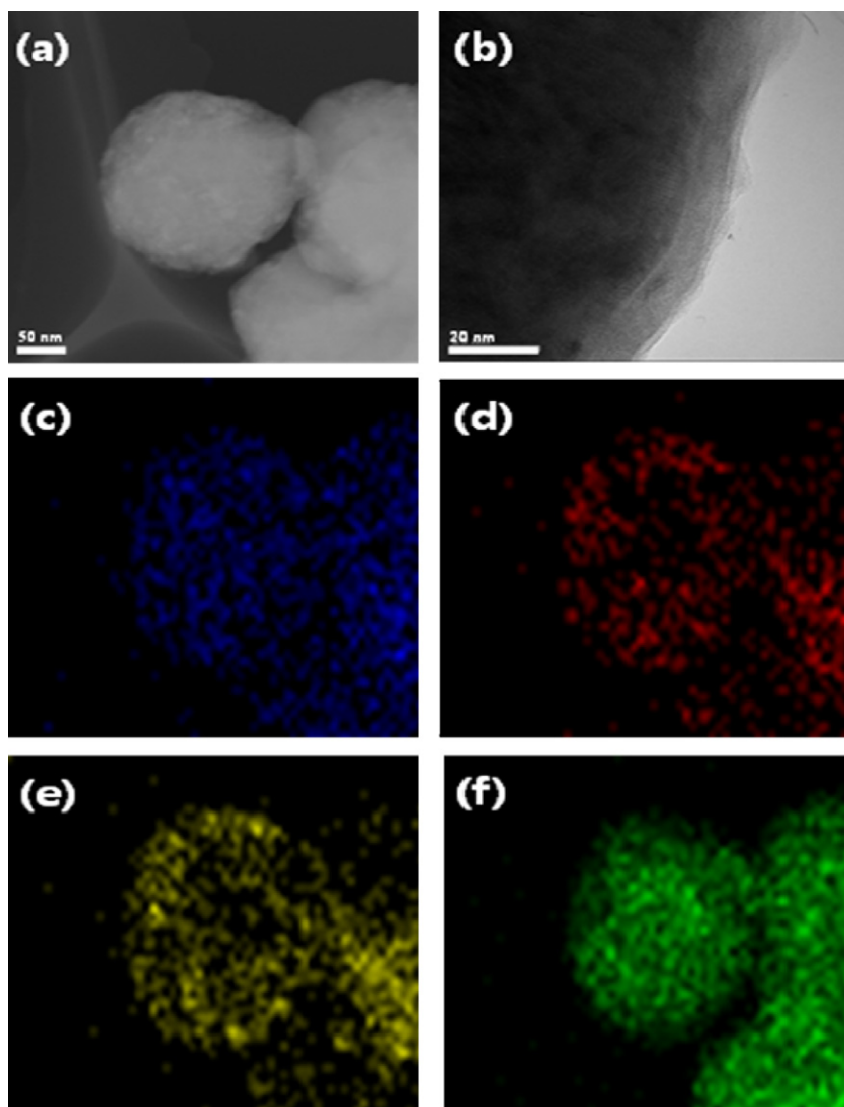


Fig. 2. (a) TEM image of 1.5 wt.% LiFePO₄-coated Li[Ni_{0.5}Co_{0.2}Mn_{0.3}]O₂, (b) HRTEM image showing coating layer, (c) mapping of Co, (d) mapping of Mn, (e) mapping of Ni, and (f) mapping of Fe.

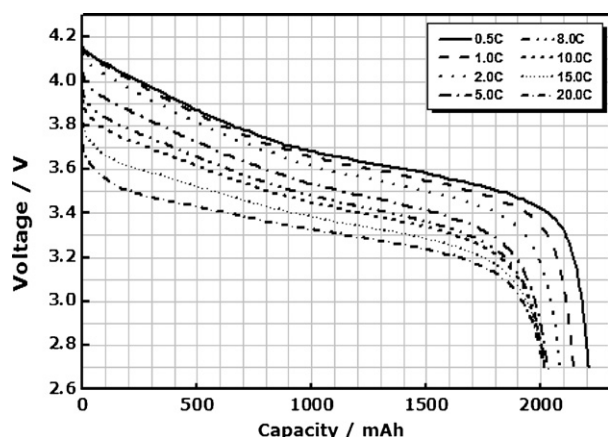


Fig. 3. Discharge capacity vs. voltage profile of 1.5 wt.% LiFePO₄-coated Li[Ni_{0.5}Co_{0.2}Mn_{0.3}]O₂ at room temperature.

Figure 2 represents the transmission electron microscopic (TEM) images of LiFePO₄-coated Li[Ni_{0.5}Co_{0.2}Mn_{0.3}]O₂ material. As shown in Fig. 2b, the nanosized LiFePO₄ particles were homogeneously coated on the surface, easily discerned from the intersection of the core shell type Li[Ni_{0.5}Co_{0.2}Mn_{0.3}]O₂ material. Figure 2(c–f) present the distribution of the constituent metal ions in the Li[Ni_{0.5}Co_{0.2}Mn_{0.3}]O₂ coated with LiFePO₄. All metal ions (Co, Mn, Ni) were uniformly distributed in the all range of particle and LiFePO₄ material was also well coated on the surface of parent Li[Ni_{0.5}Co_{0.2}Mn_{0.3}]O₂. We strongly emphasize that the coating technique used in this study is not wet coating, but dry coating method. It is recently start to report that dry coating technique by Nobilta system (NOB-130) is an excellent tool, which can produce well-coated material in a short time using very powerful rotation, shear, and collision at the same time. It is expected that the LiFePO₄ material with quite reduced particle size (<100 nm) through the coating process easy to stuck into the surface of parent Li[Ni_{0.5}Co_{0.2}Mn_{0.3}]O₂ particle, which results in a formation of dense and thin (10–20 nm) coating layer after coating process. This protective coating layer provided a huge safety to the cell during the safety and overcharge studies and will be discussed in detail later in this paper.

Several inert metal oxides, MgO, Al₂O₃, CeO₂, ZrO₂, and TiO₂ have been used to encapsulate the cathode material in order to improve capacity and safety [5,8,9]. We herein report the coating of LiFePO₄ on Li[Ni_{0.5}Co_{0.2}Mn_{0.3}]O₂. The advantage of LiFePO₄ coating is 2-fold: extension of the capacity into certain levels: protective layer for cathode materials. The LiFePO₄ is an attractive cathode compared to other positive electrodes because of its salient features, namely, low cost, high thermal and chemical stability, and lower voltage (3.4 V vs. Li⁺/Li), making it less reactive towards electrolytes with a higher electrochemical stability window [10–12]. Further, high surface area LiFePO₄, having a wide range of non-stoichiometry, improves the rate of the Li⁺ ion insertion reaction via lithium diffusion kinetics during the charge-discharge process [11–14].

Figure 3 shows the voltage profile and cycle performance of the LiFePO₄-coated cathode, between the 2.6–4.3 V window and the various C rates from 0.5 to 20C, at 25 °C. The cell experiences a discharge capacity of 2200 mAh (153 mAhg^{−1}) at a 0.5C rate. At high current rates, beyond 2C, it is interesting to see that only a very meager capacity fade is observed. A similar kind of behavior is extended up to 20C. This high rate performance is due also to the coating of LiFePO₄ on Li[Ni_{0.5}Co_{0.2}Mn_{0.3}]O₂. The coated LiFePO₄ also acts as a cathode and can form a protective layer that prevents unwanted reaction with the electrolyte and

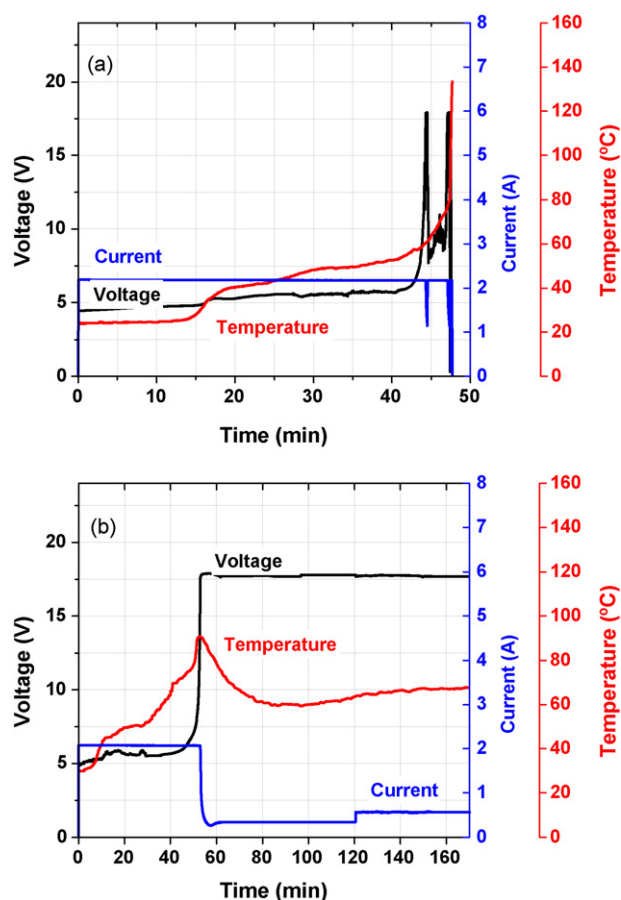


Fig. 4. Voltage and surface temperature profiles of cells with: (a) Pristine Li[Ni_{0.5}Co_{0.2}Mn_{0.3}]O₂; (b) 1.5 wt.% LiFePO₄-coated Li[Ni_{0.5}Co_{0.2}Mn_{0.3}]O₂ cathode, as a function of time. The cell was initially charged at 5 V and then charged up to 18 V.

Co⁴⁺ dissolution [4–6,15]. A similar type of LiFePO₄ particle coating procedure on LiCoO₂ was reported by Wang et al. [16]. In this study, coating of LiFePO₄ particles substantially increased the Li ion diffusion rate into the core material. Furthermore, LiFePO₄-coated cathode also present very excellent cycle behavior until 250 cycles with a retention rate over 89% (>8% improvement against parent Li[Ni_{0.5}Co_{0.2}Mn_{0.3}]O₂ cell) at 50 °C, although it was not presented in this text. It will be reported elsewhere in the near future.

The overcharge safety test also has been conducted for both pristine and LiFePO₄-coated cells at 18 V, under a current density of 1 C (2000 mAh). Figure 4(a) represents the voltage and cell surface temperature of the pristine cell during the 18 V overcharge test. Overcharging to this voltage increased the rate of decomposition of the electrolyte, as well as internal resistance. In any situation, direct contact between the anode and cathode leads to short-circuiting of the cell. For the applying voltage (18 V), the separator tends to melt down for both cases, while simultaneously, the temperature of the internal cell reaches 130 °C for the pristine LiFePO₄ cell. Decomposition of electrolytes occurred at a ~5 V plateau, after decomposition, with the cell voltage reaching its maximum (18 V) within a very short period. Immediately, the cell voltage dropped to 0 V and the cell burned out for the uncoated example. Concerning the LiFePO₄-coated Li[Ni_{0.5}Co_{0.2}Mn_{0.3}]O₂ cell, after reaching a maximum voltage (18 V), there is no contact between the anode and cathode due to the coating of the LiFePO₄, thus exhibiting very stable behavior for a prolonged time. The coating of polyanionic substances, especially nanosized LiFePO₄ particles, also suppresses the surface temperature of the cell (<100 °C), which may be due to

the strong covalent nature of the PO_4 anions with cations. The very strong P–O bonding also restricts chemical attack during decomposition, leading to a drastic improvement in thermal stability over extended periods of time [17,18].

4. Conclusions

The core shell type $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ material was synthesized by a co-precipitation method and coated with nanosized LiFePO_4 particles. The coating of LiFePO_4 certainly improved capacity at higher current rates at room temperature due to the dual action of the coated material. The coating of LiFePO_4 on the $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ material resulted in remarkable improvement of thermal and over-charge tolerance over a prolonged period of time.

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