



Tri-functional coating to enhance the capacity retention of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ for high power lithium ion battery

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ABSTRACT

$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is a promising cathode material for high power lithium ion batteries (LIBs) for electric vehicles (EVs) and hybrid electric vehicles (HEVs). For the first time we design a tri-functional coating to improve the cycling performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. With the designed BiPO_4 coating, the capacity retentions of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ are largely improved from 84.3% to 93.6% at 0.5 C after 50 cycles and from 80.6% to 96.2% at 10 C after 100 cycles. The tri-functional coating reduces the charge transfer resistance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode and plays a critical role in enhancing the electrochemical performance and lifetime. This strategy provides a new way to modify electrode materials to elevate the performance of LIBs.

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1. Introduction

Spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with a high power density and energy density is a promising cathode material for LIBs for applications in electric vehicles (EVs) and hybrid electric vehicles (HEVs) [1–3]. It can reversibly intercalate/deintercalate lithium ions at ~ 4.7 V with a specific capacity over 130 mAh g^{-1} . Because of a fast lithium ion diffusion and a high operating voltage, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ shows much higher power density than LiMn_2O_4 and LiFePO_4 , which are prevalent cathode materials for EVs [4]. However, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ suffers from three problems for the practical application. First, a high temperature required in the sintering process often triggers Mn reduction to produce oxygen defects and the residual impurity phase $\text{Li}_x\text{Ni}_{1-x}\text{O}$ [5]. Second, Ni and Mn can be dissolved in the electrolyte during the charging and discharging process, resulting in a collapse of the spinel structure. Last but not least, the traditional organic electrolyte undergoes oxidized decomposition on the cathode surface, especially at an operating voltage as high as 4.9 V [6], which deteriorates the cycling performance of the battery. It is well known that surface modification is an effective way to solve the last two problems mentioned above.

Bi_2O_3 [7], SiO_2 [8], BiOF [9], AlF_3 [10], Al_2O_3 [11], Fe_2O_3 [12], TiO_2 [13], and AlPO_4 [14] have been investigated for coating on the surface of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. These coating materials are able to stabilize the interface between the cathode materials and electrolyte to suppress Mn dissolution and oxidation of electrolyte, but the performances of these coated cathodes will degrade with an increasing applied current, which is due to their poor lithium ion transport properties. It is worth noting that the fast migration of lithium ions and electrons is very important for cathode materials in the power LIBs. Herein, we propose that BiPO_4 , which has extensive applications in photocatalyst [15], is possible to be an appropriate coating material for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, considering that lithium ions can react with BiPO_4 at around 3 V to produce metal bismuth and Li_3PO_4 [16]. The BiPO_4 coating have three functions. Firstly, it can decrease the charge transfer resistance (R_{ct}) and improve the diffusion coefficient of lithium ions through the electrode (D_{Li^+}). Secondly, it enhances the interface stability because P–O bonds in BiPO_4 are strong enough to defend against hydrofluoric acid (HF) attacks. Thirdly, it reduces the direct contact of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with the electrolyte to minimize undesirable side reactions.

2. Experimental

$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was prepared by a modified solid-state method [10]. 30 mM $\text{Mn}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ and 10 mM $\text{Ni}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ were

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dissolved in 20 ml distilled water with intensive stirring at 90 °C for 5 h. The solution was evaporated at 120 °C in air for 10 h to form solid-state mixtures. The mixtures were ball-milled for 1 h at 500 rpm and then calcined at 400 °C for 6 h. The resulting powder was mixed with Li_2CO_3 and sintered at 900 °C for 16 h in a muffle furnace, followed by an annealing process at 650 °C for 10 h during the cooling process to obtain $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powder.

$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ were first mixed in distilled water under vigorous stirring at 80 °C. Then $\text{NH}_4\text{H}_2\text{PO}_4$ solution was added into the suspension drop by drop. The mixture was heated at 80 °C until the solvent was completely evaporated.

The powders were then calcined at 550 °C for 5 h to transform to 1 wt% BiPO_4 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Preparation of 1 wt% AlF_3 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ follows the process reported previously [10].

Electrochemical performances of the as-prepared cathode materials were evaluated by CR2025 coin cells using Celgard 2400 as the separator and Li slice as the anode. The cathode was composed of 80 wt% BiPO_4 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, 12 wt% acetylene black and 8 wt% PVDF binder. The electrolyte was 1 mol/L LiPF_6 in a mixture of ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC), and fluoroethylene carbonate (FEC) (1:1:1:1, v/v). Galvanostatic cycling was carried out between 3.5 and 4.9 V at 0.5 and 10 C on a multi-channel battery test system (Neware CT-3008 W).

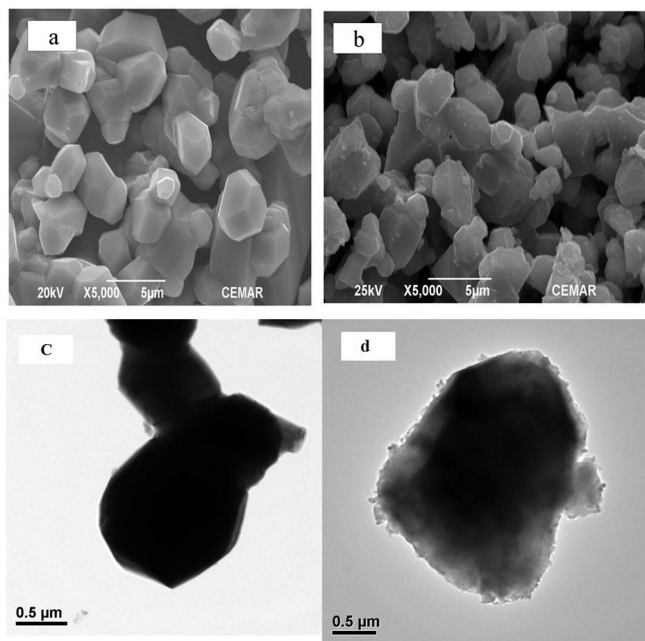


Fig. 1. SEM images of samples: (a) pristine, and (b) BiPO_4 -coated. TEM images of samples: (c) pristine, and (d) BiPO_4 -coated.

3. Results and discussions

SEM images of pristine and BiPO_4 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ are illustrated in Fig. 1 a and b. In comparison to the clean and smooth surface of pristine $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, BiPO_4 -coated particles display a rough surface. TEM images of pristine and BiPO_4 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, as shown in Fig. 1 c and d, present that the edge of bare particles is well fined, while that of the BiPO_4 -coated is covered with small particles of ten nanometers.

Fig. 2 shows the composition of the BiPO_4 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ via Energy Dispersive X-ray (EDX) analysis. In Fig. 2b, strong peaks for Ni, Mn and O elements are observed while only weak peaks can be distinguished for Bi and P elements. EDX mapping results from Fig. 2c to f confirm the homogeneous presence of Bi and P on the surface of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles.

XRD patterns of the pristine and BiPO_4 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ are shown in Fig. 3a. The intense peaks indicate a good crystallinity. Both samples are indexed to a spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with a space group $\text{Fd}\bar{3}\text{m}$. No structural change is found after the BiPO_4 coating. The tiny diffraction peaks around 37° and 44° are corresponding to $\text{Li}_x\text{Ni}_{1-x}\text{O}$ according to the previous report [17]. The ratios of the diffraction peak (3 1 1) to (4 0 0) for pristine and BiPO_4 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ are 1.04 and 1.02, respectively. Both values are within the range from 0.96 to 1.1, which have been

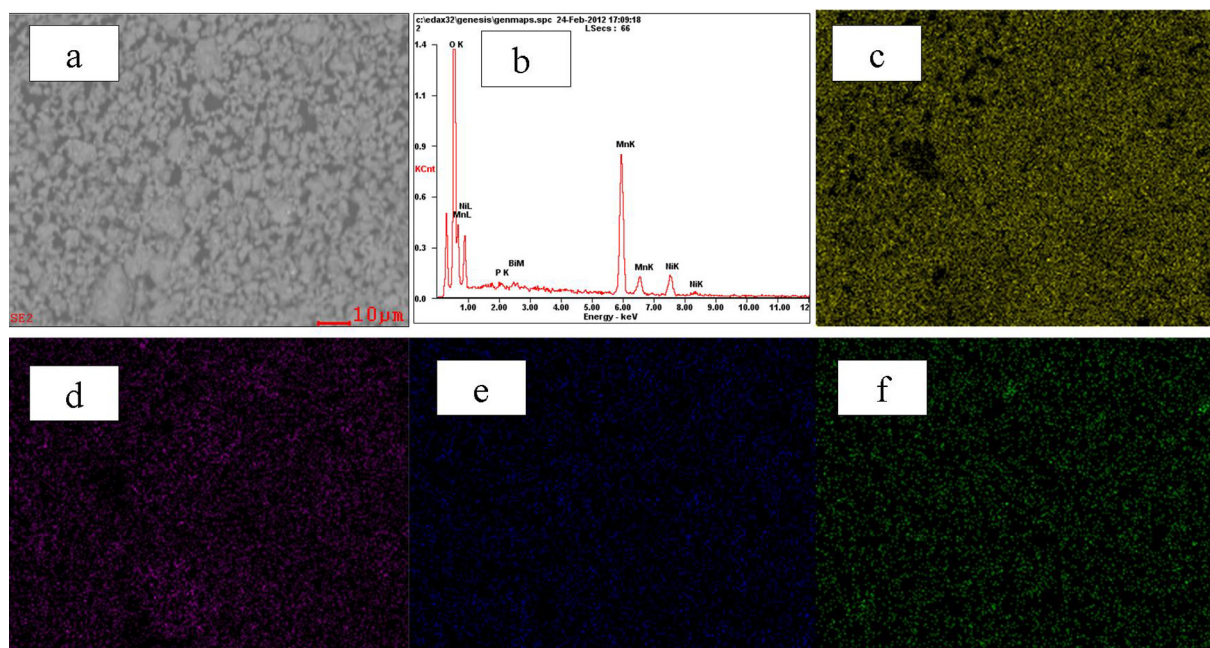


Fig. 2. SEM image (a), EDX spectrum (b) and EDX mappings for Mn (c), Ni (d), Bi (e) and P (f) elements of BiPO_4 -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

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