



FePO₄-coated Li[Li_{0.2}Ni_{0.13}Co_{0.13}Mn_{0.54}]O₂ with improved cycling performance as cathode material for Li-ion batteries

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Abstract Li[Li_{0.2}Ni_{0.13}Co_{0.13}Mn_{0.54}]O₂ cathode materials were synthesized by carbonate-based co-precipitation method, and then, its surface was coated by thin layers of FePO₄. The prepared samples were characterized by X-ray diffraction (XRD), field emission scanning electron microscope (FESEM), energy-dispersive spectroscopy (EDS), and transmission electron microscopy (TEM). The XRD and TEM results suggest that both the pristine and the coated materials have a hexagonal layered structure, and the FePO₄ coating layer does not make any major change in the crystal structure. The FePO₄-coated sample exhibits both improved initial discharge capacity and columbic efficiency compared to the pristine one. More significantly, the FePO₄ coating layer has a much positive influence on the cycling performance. The FePO₄-coated sample exhibits capacity retention of 82 % after 100 cycles at 0.5 °C between 2.0 and 4.8 V, while only 28 % for the pristine one at the same charge–discharge condition. The electrochemical impedance spectroscopy (EIS) results indicate that this improved cycling performance could be ascribed to the presence of FePO₄ on the surface of Li[Li_{0.2}Ni_{0.13}Co_{0.13}Mn_{0.54}]O₂ particle, which helps to protect the cathode from chemical attacks by HF and thus suppresses the large increase in charge transfer resistance.

Keywords Lithium-ion battery; Cathode material; Coating; Lithium-rich; Iron phosphate

1 Introduction

Lithium-ion battery system is considered to be one of the leading candidates as the power sources for electric vehicles (EV) and plug-in hybrid electric vehicles (PHEV). Li-rich manganese oxides Li[Li_{x/3}Me_{1-x}Mn_{2x/3}]O₂ (Me, 3d-transition metals, such as Co, Ni, and Mn; 0 < x < 1) are the most promising cathode materials for these electric vehicle applications due to their large capacity and low cost [1–4]. The Li-rich manganese oxides have a layered structure, which is often considered as a solid solution of Li₂MnO₃ and LiMeO₂ (Me, 3d-transition metals, such as Co, Ni, and Mn) [5–7], and can also be represented by the chemical formula zLi₂MnO₃-(1-z)LiMeO₂ (0 < z < 1). These Li-rich manganese oxides can deliver much higher capacity (>250 mAh·g⁻¹) than the traditional layered cathode materials (140–200 mAh·g⁻¹). However, they possess several shortcomings, such as high first-cycle irreversible capacity loss, poor rate capability, significant degradation of cycle performance, and decrease in discharge voltage with successive cycling [8–12]. These problems impeded their practical use in high-energy Li-ion batteries, especially in electric vehicle application.

Surface modification was proved to be an effective way to improve the electrochemical performance of these cathode materials. Several studies have reported that the physical and chemical properties of the Li-rich manganese oxides were improved after being coated with metal oxides [13–17], metal phosphates [18–22], or metal fluoride [8, 23, 24]. Among the various coating materials, metal phosphates such as AlPO₄, LiNiPO₄, or Co₃(PO₄)₂ have recently been

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shown to improve both the thermal stability and the rate capability of the Li-rich manganese oxides, because the strong P–O bond of phosphate may lead to better chemical resistance of the cathode to acidic electrolytes [19, 20].

In the family of metal phosphates, FePO_4 is chemically stable and electrochemically active, which makes it to be a very promising coating candidate. FePO_4 was reported as coating layer to improve the electrochemical performance for various cathodes such as LiCoO_2 , LiMn_2O_4 , $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$, $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, and $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ [25–29]. In the case of FePO_4 -treated LiCoO_2 , the FePO_4 layer helps to prevent the interaction between LiCoO_2 and electrolyte and stabilize the structure of LiCoO_2 . In the case of LiMn_2O_4 , the FePO_4 -coated layer helps to prevent the dissolution of Mn to ensure the structural stability, increase the conductivity of solid electrolyte interface (SEI) layer, and facilitate the diffusion of lithium ions through it. Since promising results have been shown in those cathode materials, it is believed that FePO_4 coating can also improve the performance of the Li-rich manganese oxides.

In the present work, FePO_4 was suggested as a coating material for the Li-rich manganese oxides $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}]\text{O}_2$, and the effects of FePO_4 coating on structural and electrochemical properties of the materials were investigated.

2 Experimental

$\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}]\text{O}_2$ powder was synthesized by carbonate-based co-precipitation method. Firstly, the metal sulfates (molar ratio of Ni/Co/Mn = 0.13:0.13:0.54) were dissolved in distilled water to get an aqueous solution with a concentration of $2.0 \text{ mol}\cdot\text{L}^{-1}$. The metal sulfate solution and Na_2CO_3 solution ($2 \text{ mol}\cdot\text{L}^{-1}$) were added synchronously into a reactor drop by drop, in which distilled water was added under vigorous stirring. At the same time, the desired amount of $\text{NH}_3\cdot\text{H}_2\text{O}$ solution was fed into the reactor to control the pH of the reaction system. During the reaction process, the stirring speed ($600 \text{ r}\cdot\text{min}^{-1}$), temperature ($50 \text{ }^\circ\text{C}$), reactor pH (7.5), and reaction time (12 h) of mixture in the reactor were all controlled carefully. The precipitate was filtered, washed, and dried. The obtained carbonate was mixed with Li_2CO_3 (3 % excess) in an agate mortar and preliminarily annealed at $480 \text{ }^\circ\text{C}$ for 5 h in air and then sintered at $900 \text{ }^\circ\text{C}$ for 20 h in air to obtain crystalline $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}]\text{O}_2$.

Then, to prepare FePO_4 -coated samples, $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ and $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}]\text{O}_2$ were dispersed and mixed in distilled water with vigorous stirring. $(\text{NH}_4)_2\text{HPO}_4$ solution was added drop by drop into the mixture. Afterward, the pH value of the solution was adjusted to 7.0 by ammonia solution. The solution was constantly stirred at $80 \text{ }^\circ\text{C}$ for 5 h, accompanied by slow

evaporation of the solvent. The obtained powders were heated at $500 \text{ }^\circ\text{C}$ for 5 h in air to get the FePO_4 -coated $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}]\text{O}_2$ samples. In this work, the coating amount of the FePO_4 is 4 wt%.

X-ray diffraction (XRD) analyses on the powders were carried out using a PANalytical X-Pert PRO MPD diffractometer with $\text{Cu K}\alpha$ radiation in 2θ ranging from 10° to 90° . The surfaces of the coated and uncoated powders were observed using a field emission scanning electron microscope (FESEM, S-4800, HITACHI) and transmission electron microscopy (TEM, TECNAI F30, FEI). Electrochemical characterization on the powders was performed by fabricating 2032 coin cells. The working electrodes were composed of 80 wt% $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ powder, 10 wt% super-P conductive carbon, and 10 wt% poly-vinylidene fluoride (PVDF) binder dissolved in N-methyl-2-pyrrolidone (NMP), onto an aluminum current collector. After drying the electrode overnight at $80 \text{ }^\circ\text{C}$ in vacuum, the coin cells were assembled in an MBraun argon-filled glove box. $1 \text{ mol}\cdot\text{L}^{-1}$ LiPF_6 in molar ratio of ethylene carbonate (EC)/dimethyl carbonate (DMC)/methyl ethyl carbonate (EMC) of 1:1:1 was used as electrolyte, lithium foil as anode, and Celgard 2400 membrane as separator. The cells were permitted to rest for 10 h and charge–discharged on a battery tester (LAND CT-2001A, China) between 2.0 and 4.8 V (vs. Li/Li^+) at room temperature. Alternating current impedance measurements were taken using an electrochemical work station (PARSTAT 2273, Prinstone, USA) over the frequency range of 1 MHz to 10 mHz with amplitude of 10 mV.

3 Results and discussion

Figure 1 displays XRD patterns of pristine and 4 wt% FePO_4 -coated $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}]\text{O}_2$ powders. Both of them exhibit layered hexagonal characteristics, and all the

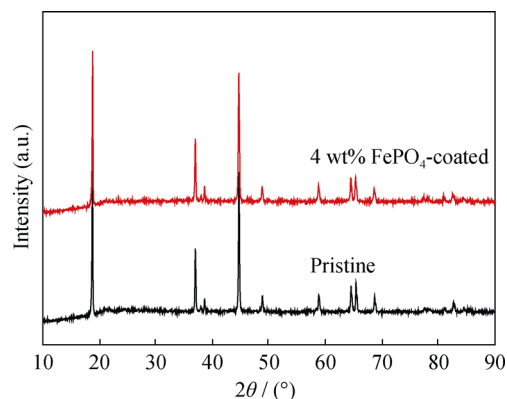


Fig. 1 XRD patterns of pristine and FePO_4 -coated $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}]\text{O}_2$ powders

fundamental peaks could be indexed on the basis of α -NaFeO₂ except the weak reflections around 22° to 25°. These weak reflections are characteristics of the monoclinic Li₂MnO₃-like (*C2/m*) superlattice [30], which correspond to the ordering of the metal ions (Li, Ni, Co, and Mn) in the transition metal layer [4]. In the case of FePO₄-coated Li[Li_{0.2}Ni_{0.13}Co_{0.13}Mn_{0.54}]O₂, its XRD pattern is identical to that of the pristine sample with no impurity peaks, which suggests that the FePO₄ coating layer on the particle surface alone does not induce any change in the crystal structure of the host material. The absence of any reflections corresponding to FePO₄ in the coated sample is due to the lower concentration or/and intrinsic amorphous structure of the FePO₄ coating layer.

Figure 2 shows FESEM images of pristine and FePO₄-coated Li[Li_{0.2}Ni_{0.13}Co_{0.13}Mn_{0.54}]O₂ powders. There is no significant difference between the SEM images of the two samples. Both of them consist of particles with a diameter of 200–400 nm.

Figure 3 presents TEM images of pristine and the 4 wt% FePO₄-coated samples. As shown in Fig. 3a, the pristine sample shows good crystallinity with lattice fringe extending to the grain boundary, and there are no other layers on the surface. However, the 4 wt% FePO₄-coated Li[Li_{0.2}Ni_{0.13}Co_{0.13}Mn_{0.54}]O₂ material exhibits a coated layer with thickness of about 2 nm on the surface, as shown in Fig. 3b. The distribution of FePO₄-coated layer on the surface of the Li-rich materials was also measured by EDS mappings. As shown in Fig. 4, the bright spots correspond

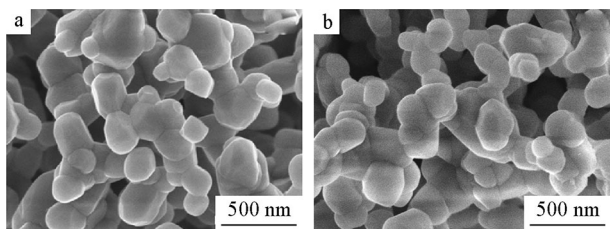


Fig. 2 SEM images of **a** pristine and **b** FePO₄-coated Li[Li_{0.2}Ni_{0.13}Co_{0.13}Mn_{0.54}]O₂ powders

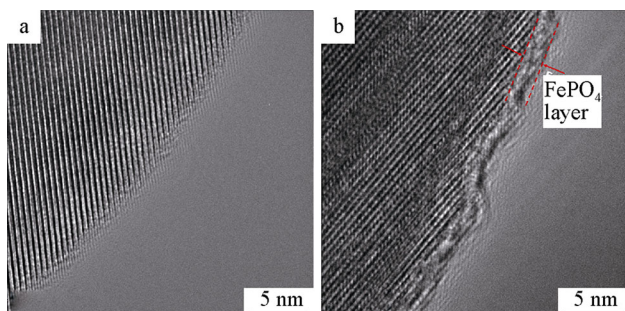


Fig. 3 TEM images of **a** pristine and **b** FePO₄-coated Li[Li_{0.2}Ni_{0.13}Co_{0.13}Mn_{0.54}]O₂ powders

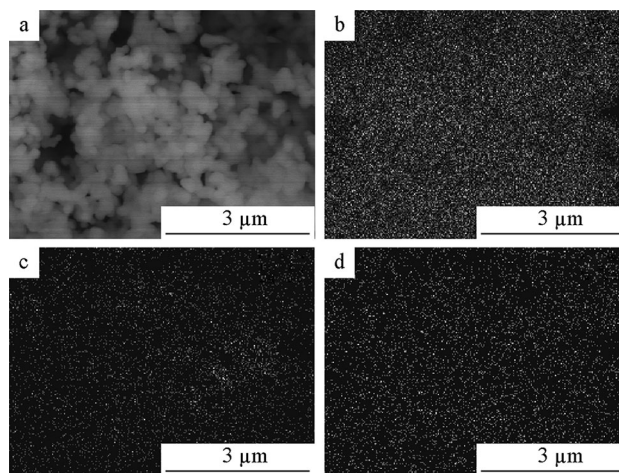


Fig. 4 FESEM image **a** and EDS elemental mappings for Mn **b**, P **c**, and Fe **d** of 4 wt% FePO₄-coated Li[Li_{0.2}Ni_{0.13}Co_{0.13}Mn_{0.54}]O₂ powder

to the presence of each element, and the spot intensity is an indicator of element concentration. Based on the mappings, Fe and P in the sample are homogeneously distributed in the composite, indicating uniform distribution of FePO₄ on the surface of the Li-rich materials. This FePO₄ layer will separate the direct contact between the electrode and electrolyte and suppress the side reaction when charged to high voltage up to 4.8 V.

Figure 5 shows the first charge–discharge profiles of pristine and 4 wt% FePO₄-coated samples between 2.0 and 4.8 V at room temperature with a current rate of 0.1C. Both of the two samples exhibit two plateaus during the first charge, due to the existence of two different lithium deinsertion processes [5]. The former plateau is located at 3.8–4.4 V, corresponding to the oxidation of Ni²⁺→Ni⁴⁺ and Co³⁺→Co⁴⁺. The latter one is observed at above 4.4 V, corresponding to the removal of oxygen from the

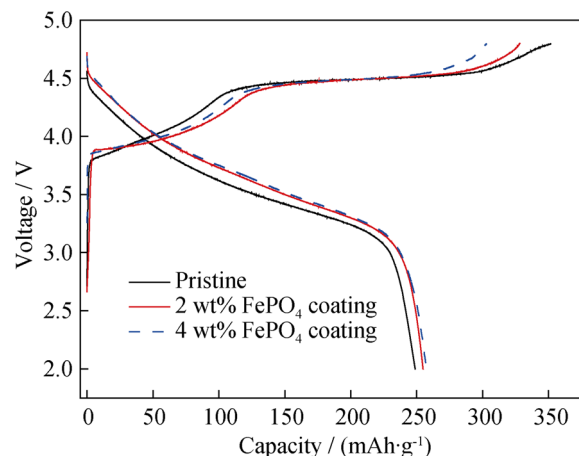


Fig. 5 Initial charge–discharge profiles of pristine and FePO₄-coated Li[Li_{0.2}Ni_{0.13}Co_{0.13}Mn_{0.54}]O₂ electrodes

cathode accompanied by diffusion of transition metal ions from surface to bulk where they occupy vacancies created by lithium removal [31]. Compared to pristine sample, the second plateau at above 4.4 V for FePO₄-coated sample is much shorter, which gives a smaller charge capacity and then less irreversible capacity loss. The initial discharge capacity of the pristine sample is 248.9 mAh·g⁻¹ with a columbic efficiency of 70.8 %, while the FePO₄-coated sample exhibits higher initial discharge capacity of 257.3 mAh·g⁻¹ and higher columbic efficiency of 84.9 %. Similar results can be found in other reports which demonstrated that various cathode coatings can reduce first-cycle irreversible capacity losses and improve the columbic efficiency [16, 18].

More significant improvements in the performance of the FePO₄-coated cathode materials are observed in capacity retention with cycling. Figure 6 gives the cycling performances of pristine and 4 wt% FePO₄-coated Li[Li_{0.2}Ni_{0.13}Co_{0.13}Mn_{0.54}]O₂ electrodes cycled at 2.0–4.8 V, 0.5C, and room temperature after activation at 0.1C for one cycle. The deliver capacities of pristine and the FePO₄-coated electrodes are 229.0 and 228.9 mAh·g⁻¹ in the initial cycle at 0.5C, respectively, very close to each other. However, much difference appears in the following cycles. The cycling behavior of the FePO₄-coated Li[Li_{0.2}Ni_{0.13}Co_{0.13}Mn_{0.54}]O₂ is greatly improved, showing a capacity retention of 82 % after 100 cycles, while the pristine electrode shows a quick decrease in capacity especially after 50 cycles, leading to a capacity retention of only 28 % during the same cycling period. The results show that the FePO₄-coated layer could distinctly improve the cycling performance of the cathode materials. The possible reason for the capacity fading of the uncoated Li[Li_{0.2}Ni_{0.13}Co_{0.13}Mn_{0.54}]O₂ is the big increase in internal resistance, which will be shown in electrochemical impedance spectroscopy (EIS).

EIS is a widely employed technique to understand the various phenomena occurring at the interface of the

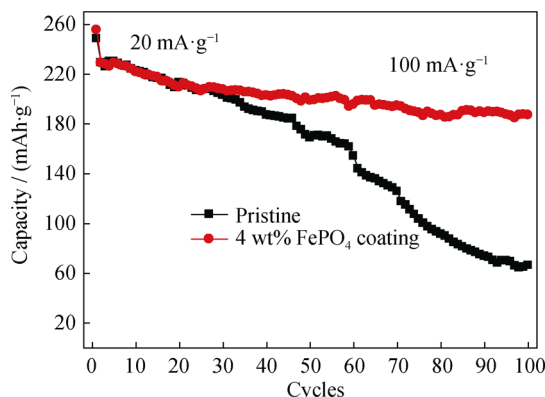


Fig. 6 Cycling performances of pristine and FePO₄-coated Li[Li_{0.2}Ni_{0.13}Co_{0.13}Mn_{0.54}]O₂ electrodes

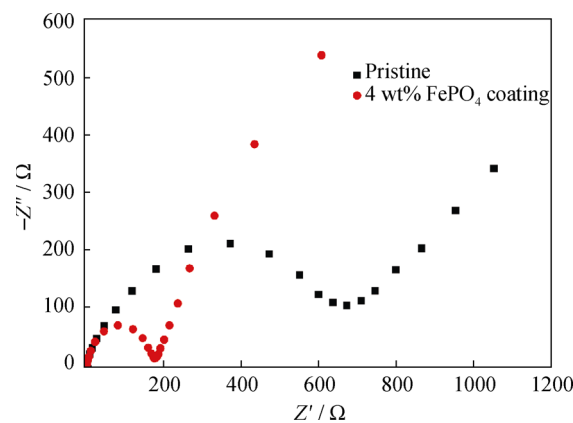


Fig. 7 Nyquist plots obtained from EIS spectroscopy of pristine and FePO₄-coated Li[Li_{0.2}Ni_{0.13}Co_{0.13}Mn_{0.54}]O₂ electrodes after 100 cycles at 0.5 °C

electrode and electrolyte. The Z' and $-Z''$ denote the real and imaginary part of impedances, respectively. Here in this work, EIS was used to detect the differences in the electrode interfaces of pristine and FePO₄-coated Li[Li_{0.2}Ni_{0.13}Co_{0.13}Mn_{0.54}]O₂ cathodes. EIS plots of pristine and FePO₄-coated electrodes at 4.3 V after the 100th cycle are shown in Fig. 7. Generally, Nyquist plots include three parts, a semicircle at the high-frequency range which corresponds to R_{sl} (resistance of the solid-state interface layer including the SEI film and the surface modification layer), a semicircle at intermediate frequency range which corresponds to R_{ct} (charge–discharge resistance at the interface of electrode and electrolyte), and a inclined line at low frequency which corresponds to Z_w (diffusion of lithium ion in the solid electrode). In Fig. 7, the two different semicircles are overlapped to form a suppressed semicircle in the Nyquist plot, which is similar as that reported in previous studies [14, 15, 32, 33]. It is clear that the internal resistance of the pristine sample is much bigger than that of FePO₄-coated one after cycling for 100 cycles at 0.5C. The large increase in internal resistance of the uncoated sample is mainly caused by the formation of micro-cracks at the crystal surface due to HF attack and then the distortion of crystal periodicity after some charge–discharge cycles [34]. The smaller internal resistance of the FePO₄-coated Li[Li_{0.2}Ni_{0.13}Co_{0.13}Mn_{0.54}]O₂ indicates better charge transfer kinetics against high current burdens [35, 36], which leads to a better cycle ability. The role of FePO₄ layer is to protect the surface from HF attacking and then suppress the significant increase in internal resistance.

4 Conclusion

In this study, the surface of the Li[Li_{0.2}Ni_{0.13}Co_{0.13}Mn_{0.54}]O₂ cathode material synthesized by carbonate-based co-precipitation method was coated with a thin FePO₄ layer. The effect

of the FePO₄ coating on the structure, morphology, and electrochemical properties was studied. The presence of FePO₄-coated layer was confirmed by TEM and EDS studies. XRD and TEM results reveal that the FePO₄ coating does not make any major change in the crystal structure. Electrochemical characterization shows that the FePO₄-coated Li[Li_{0.2}Ni_{0.13}Co_{0.13}Mn_{0.54}]O₂ exhibits a better electrochemical performance compared to the pristine Li[Li_{0.2}Ni_{0.13}Co_{0.13}Mn_{0.54}]O₂, especially in cycling stability. The EIS study indicates that the FePO₄-coated sample has lower internal resistance value compared to the pristine one. The improvement could be attributed to the protection of crystal surface from HF attacking and the suppression of the increase in internal resistance. Surface modification by FePO₄ is an effective way to improve the performance of the Li-rich manganese oxide cathode materials for lithium-ion batteries. Those improved properties would be applied for the Li-ion secondary battery system.

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