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# Fabrication of $FePO_4$ layer coated $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$: Towards High-performance Cathode Materials for Lithium Ion Batteries

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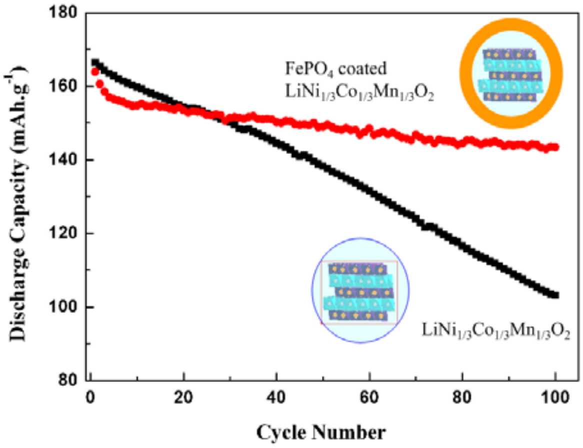
## Abstract

The surface of layered $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ was coated with nano-layer $FePO_4$ by co-precipitation method and followed by heat treatment. The prepared samples were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). $FePO_4$ coated samples exhibited both improved rate and cycle capacity compared with the pristine $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$. The capacity retention after 100 cycles increased from 62.0% to 87.7%. The sample coated with 2 wt.% $FePO_4$ and treated at 400 °C showed the optimum cyclability. The electrochemical impedance spectroscopy (EIS) results indicated that the $FePO_4$ coating layer significantly suppressed the increase of charge-transfer resistance ($R_{ct}$). The activation energy of the charge transfer processes at the electrode/electrolyte interface was reduced by $FePO_4$ coating. Differential scanning calorimetry analysis showed the $FePO_4$ coating improved the thermal stability of the cathode material.

*Keywords:* $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$; $FePO_4$ coating; cycle; charge transfer resistance; activation energy

# Graphical Table of Contents



$FePO_4$ coated $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ showed an improved cycle and rate capacities. The $FePO_4$ coating layer significantly suppressed the increase of charge-transfer resistance ($R_{ct}$) upon cycling and reduced the activation energy of the charge transfer processes.

# 1. Introduction

Cathode material is one of the vital components of lithium ion battery because it not only largely determines the electrochemical performance such as discharge capacity, cyclability, rate performance and thermal stability, but also makes up about 15% of the total battery cost. [1-3] Tremendous efforts have been made to develop an optimum cathode material which can meet the commercial standard for lithium ion battery. Layered $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ is considered as a very promising cathode material since it was proposed by Ohzuku. [4] However, the continuous side-reactions between this electrode and electrolyte upon cycling would lead to the increase of cell resistance, capacity fading and thermal runaway. [5] Surface coating has been proved to be an effective way to improve the electrochemical properties of cathode materials. An proper coating layer can protect the electrode surface from directly contact with the elcctrolyte, and thus suppress the side-reactions which lead to the deterioration of the cell properties. [6] Meanwhile, a coating material, with high ionic/electronic conductivity, can improve the rate capacity since it facilitates the charge transfer at the surface of particle. In addition, the coating layer can also enhance the thermal stability by impedeing the exothermic reaction with the electrolyte. [7-8 ] Up to now, a variety of coatings, such as metal (e.g., Ag) [9], metal oxides (e.g., $Al_2O_3$, $ZrO_2$, $CeO_2$) [10-12], metal fluorides(e.g., $ZrF_2$, $AlF_3$, $SrF_2$) [13-15 ], $LiAlO_2$ [16] and some carbon composites (e.g., PPy, graphene) [17-18] have been shown to enhance both the electrochemical properties and thermal stability.

Recent research progresses indicate that phosphate has become a popular coating material. The strong covalency of the $PO_4$ polyanion with metal ions and the strong P=O bond can stabilize the interface of the electrode and electrolyte and then enhance the resistance of chemical attack. [19] The interest for $FePO_4$ coating layer is related to it is one of the safest environmentally most friendly and less expensive material. It has been coated on the surface of $LiMn_2O_4$, [20] $Li_xNi_{0.9}Co_{0.1}O_2$ [21] and $LiCoO_2$, [22] respectively, and obtained enhanced cycle performance especially at elevated temperature. To our knowledge, $FePO_4$ has not been coated on $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$.

In this paper, we report the effect of $FePO_4$ coating on the electrochemical properties and thermal stability of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ . The synthesis process was conducted in an aqueous solution by co-precipitation method followed by a heat treatment in air. X-ray diffraction (XRD) and Transmission Electron Microscope (TEM) have been conducted to confirm the structure and surface morphology. The cycle and rate performance of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ have been improved by $FePO_4$ coating. Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) were used to investgate the mechanism of the improvement in the electrochemical properties of the $FePO_4$-coated $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ material.

## 2. Experimental

$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powder was synthesized by co-precipitation method using carbonate as precipitant. [23] Coating process was conducted in aqueous suspension by coprecipitation. $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (2 g) dispersed in 20 ml deionized water. After that, aqueous solution of $FeCl_3$ (with certain amount) was added to the slurry with vigorous stirring for 30 min. Then, stoichiometric amount of $NH_4H_2PO_4$ was added with stirring for 4 h. The slurry was dried at 80 °C for one night. Finally, the obtained powder was annealed in air at different temperature. The coating amount were changed from 1 wt.% to 5 wt.% and heat treat temperature from 300 to 600 °C. For convenience, the samples are marked with X wt%- T °C in which X represent the coating amount and T represent the annealed temperature.

XRD (Bruker D8 with Cu $K_{\gamma}$ radiation, $\lambda$=0.15406 nm) was employed to analyze the structure of the pristine and coated samples. The surface morphology before and after surface coating were examined by TEM on a JEOL 3100F instrument with a voltage of 300 KV.

The electrochemical performance of all the samples were conducted by coin cells (CR 2032) consisting of a cathode, metallic lithium anode, polypropylene separator and an electrolyte of 1M $LiPF_6$ in EC/DMC (1:2 vol.%). The cathode was faricated from a 80:15:5 (mass%) mixture of active material:acetylene black:polytetra-fluoroethylene (PTFE). The above mixture were mixed and grounded in an agate mortar and then pressed onto a aluminum mesh which served as a current collector and then dried at 80 °C for 12 h at vacuum. The cells were assembled in an Ar-filled glove box and subjected to galvanostatic cycling using a Hokuto Denko in a potential range of 2.8-4.5 V (versus $Li^+/Li$) at certain current densities. The specific capacity and current density are based on the mass of synthesized cathode materials (for the coated materials, the coating layer has been included). Cyclic Voltammetry (CV) were done with coin cells on a Solartron Instrument Model 1287 with a scan rate of 0.2 mV/s using lithium metal as both counter and reference electrodes. The electrochemical impedance spectroscopy (EIS) were also done with coin cells on a Solartron Instrument Model 1287 electrochemical interface and a 1255 B frequency response analyzer controlled by Z-plot. The measurements were performed in the frequency range 0.5 MHz to 0.01 Hz with an ac signal amplitude of 5 mV. Data analysis was done using the software Zview 2.70 (Scribner Associates Inc., USA). The thermal stability after surface coating was examined by differential scanning calorimetry measurement (Pyris 1), where the cell first charge to 4.5 V by a current of 15 mA/g and charge at this voltage for 5 h. The cells were disassembled in an Ar filled glove box to collect the charged cathode. Approximately 4 mg of the samples were hermetically sealed in a high-presure DSC pan. The measurement was conducted in a temperature range of 25-350 °C at a heating rate of 10 °C $min^{-1}$ under a nitrogen atmosphere.

## 3. Results and discussion

Fig.1 shows the XRD patterns of pristine and $FePO_4$ coated powders (1, 2, 3, 4, 5 wt.%). For the patterns of pristine, all the peaks can be indexed to the hexagonal $\alpha\text{-}NaFeO_2$ structure with $R\bar{3}m$ space group. The splitting of the [(108),(110)] and [(006),(102)] indicate that the materials have a well ordered structure. The intensity ratio of $I_{(003)}/I_{(004)}$ has been reported to be strongly correlated to undesirable cation mixing. The layered cathode materials with a ratio of $I_{(003)}/I_{(004)}$ >1.2 is an indication of desirable cation mixing and will show good electrochemical performance. [24-25] For the patterns of the coated samples, no impurities and secondary phases have been observed. In order to confirm the contents of coating layer, the $FePO_4$ coating layer was synthesized using the same route without adding of layered $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$. The XRD patterns (Fig. 1b) show that it can indexed to JCPDS card 01-071-3497 as compound $FePO_4$ with hexagonal structure. However, there are no corresponding peaks can be detected in the XRD patterns of coated samples. It is considered that such a lower amount of $FePO_4$ in coated samples can not be detected due to the accuracy limited of X-ray diffraction. Fig. 2 shows the TEM images of pristine and 2 wt%-400 °C coated samples to confirm the surface morphology.The pristine sample shows a very smooth edges and there are no other layers on the surface in Fig. 2a. However, as shown in Fig. 2b, we find that the surface of coated sample was homogeneously covered by a $FePO_4$ layer with a thickness about 20-30 nm. The distribution of $FePO_4$ coating layer on the surface of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ were measured by EDS mapping. As shown in Fig. 3, the bright spots correspond to the presence of each element and the spot intensity is an indicator of the concentration of element. Based on the mapping, Fe in the sample is homogeneously distributed in the composite, indicating uniform distribution of $FePO_4$ on the surface of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$.

The cycle performance and rate capability of pristine and coated $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ were tested to investigate the effect of $FePO_4$ coating. The cycle performances of coated samples with different $FePO_4$ contents and heat treated temperature are shown in Fig.4. These charge-discharge were conducted at a current of 150 mA/g in the voltage range of 2.8-4.5V. As shown in Fig.4a, with 1 wt.%, 2 wt.%, 3 wt.%, 4 wt.% and 5 wt.% coating, the discharge capacities are 138.4, 143.5, 132.1, 101.3 and 61.8 mAh/g at the $100^{th}$ cycle, respectively. Meanwhile, the discharge capacities is about 103.2 mAh/g at the $100^{th}$ cycles for the pristine samples. It is indicated that cycle performance has been improved by $FePO_4$ coating with a coating amount of 1 wt.% to 3 wt.%. However, the discharge capacity decreased obviously when the coating amount increase to 4 wt.% and 5 wt.%. Therefore, this result indicates that only an appropriate amount of $FePO_4$ coating can facilitate the diffusion of Li ions. With a thicker layer, the excess insulating $FePO_4$ may inhibit the intercalation-deintercalation of Li cations and lead to a worse electrochemical performance. [20] The optimal coating amount is 2 wt.% according the capacity retention.

The effect of heat treat temperature on cycle performance were also investigated as shown in Fig.4b. At $100^{th}$ cycle, the discharge capacity are 123.42 mAh/g (2 wt.%-300 ºC), 143.45 (2 wt.%-400 ºC), 129.82 (2 wt.%-500 ºC), and 120.35 (2 wt.%-600 ºC), respectively. Obviously, the sample which was heat treated at 400 ºC showed the bigger discharge capacity among all the measured samples. Although, the reason why the sample with heat at 400 ºC exhibited the best cycle performance is unclear, we considered that with low heat treat temperature, the contact between the coating layer and the cathode material is not very closely, so that the coating layer may peel off from the cathode surface during charge-discharge cycles. However, with high heat treated temperature, the coating layer may diffusion into the cathode and affect the crystal lattice thus lead to bad Li ion transport between the electrode and electrolyte. So, an appropriate heat treat temperature would largely affect the electrochemical performance. Based on the above data, we conclude that the 2 wt.%-400 ºC sample showed the optimum $FePO_4$ coating condition. In order to confirm whether the increase of discharge capacity of coated sample due to the react between the $FePO_4$ coating layer and $Li^+$, the cycle performance of pristine and 2 wt.%-400 ºC coated sample were also tested at the voltage range of 4.5-3.4 V as shown in Fig.S1. Table 1 summarized the discharge capacity of pristine and 2 wt.%-400 ºC for the 1st, 50th and 100th cycles with different cut-off voltage. It demonstrates that the capacity fading can be significantly prevented by surface $FePO_4$ coating. As we know, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ is still stable when it is charged to 4.5V. [26] The capacity fading of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ at this cut-off voltage is originated from the side-reactions between the electrode and electrolyte. We have further tested CV to confirm whether there were some redox reactions in $FePO_4$ coating layer with different coating amount and heat treated temperature as shown in Fig.S2. Thus, the final results indicated that $FePO_4$ coating just suppress the side reactions to improve the cycle performance.

Fig. 5a, 5b show the charge and discharge curves of pristine and 2 wt.% -400 ºC $FePO_4$ coated samples at different cycles at a constant current of 150 mA/g (about 1 C rate) in the potential range of 2.8-4.5 V versus $Li/Li^+$. The first charge/discharge curves of both samples show a typical potential plateaus of layered compound at about 3.9 V region, originating from the $Ni^{2+}/Ni^{4+}$ redox couples. [27] The first discharge capacities are 166 mAh/g and 164 mAh/g for pristine and the 2 wt.%-400 °C coated sample, respectively. However, at the 50th cycles, the discharge capacity of 2 wt.%-400 °C coated sample is 149.0 mAh/g, however, the discharge capacity of pristine is only 138.3 mAh/g. Furthermore, the discharge capacities of coated samples is 143.5 mAh/g, much higher than the pristine of 103.2 mAh/g at the 100th cycles. Meanwhile, there is also an increase of charge plateaus and a decline of discharge plateaus with the increase of cycles. This phenomenon is considered as originating from the increase of electrode polarization which caused by the side-reactions between the electrode and electrolyte. For the pristine sample, the charge plateau increase to above 4.0 V at the 100th cycle. However, for the coated samples, the charge plateau is still lower than 3.9 V at the 100th cycle. The changes of behaviors for discharge curves is more obvious than the charge curves. At the 100th cycles, the discharge plateau of pristine is diminished, meanwhile, there is only a small changes for the coated samples.

The changes of voltage at the state half of charge/discharge were also tracked as shown in Fig. 5c. Until the first 50 cycles, there is little changes of the charge or discharge potentials for the pristine sample. As the charge-discharge cycle continues, there is an obvious increase of charge potential and a decrease of discharge potential. However, for the 2 wt.%-400 °C $FePO_4$ coated samples, the changes of potential is relatively small. We can conclude that the $FePO_4$ coating layer suppressed the increase of interfacial polarization and therefore decreasing the capacity fading.

Rate capability is also an important feature in judging their use in practical lithium ion batteries. The $FePO_4$-coating layer may improve the C-rate performance of the coated samples because of the phosphate coating layer can facilitate the charge transfer between the electrode and electrolyte. [28] Fig.6 shows the discharge capacities gradually decrease with increasing the charge-discharge current. Meanwhile, it is clearly observed that the 2 wt.%-400 ºC coated sample has better rate capability than the pristine sample, especially at high rates. This result make us believe that the $FePO_4$ coating layer on $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ can functions as an promoter for Li transport to the host structure as a result of the reduced interfacial resistance between the electrode and electrolyte. This is also been certified by the following impedance experiments.

EIS test was carried out to further understand the $FePO_4$ coating effect on charge-discharge process. EIS plots of the pristine and 2 wt.%- 400 ºC sample at 4.5 V, after the $1^{st}$ and $100^{th}$ cycle, are shown in Fig.7a and Fig.7b, respectively. Before each measurement, the cells were first galvanostatically charge-discharge to the desired cycles (at a current of 150 mA/g with a voltage range of 4.5-2.8V), followed by charging the cells to 4.5V at a current of 15 mA/g and then charged for 3 h at this voltage. The Nyquist plots were fitted to the model in Fig.7c. Generally, an Nyquist plots include three parts, a semicircle in the high frequency range which correspond to the $R_{sei}$ (the impedance of the natural and artificial solid electrolyte interface and the impedance of electrons through the active materials) in the model, a semicircle in the medium-to-low frequency range which correspond to the $R_{ct}$ (charge-discharge resistance at the interface of electrode and electrolyte) and a sloping line at low frequency which correspond to $Z_w$ (diffusion of lithium ion in the solid electrode). The fitting result are listed in Table.2. At the $1^{st}$ cycle, the $R_{ct}$ of 2 wt.%-400 ºC is a little smaller than the $R_{ct}$ of the pristine. It is because the $FePO_4$ coating layer can facilitate the Li ion transport and reduce the charge transfer resistance. This is also why the coated sample showed an improved rate capacity.The $R_{ct}$ of pristine sample increase to about 40 times larger at the $100^{th}$ cycles than that at the $1^{st}$ cycle. However, the $R_{ct}$ of 2 wt.%-400 ºC is only two times of the initial value. This EIS results clearly indicate that the $FePO_4$ coating layer can significantly suppress increase of $R_{ct}$ with cycling. The increase of $R_{ct}$ of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ is mainly caused by side-reactions between the electrode and electrolyte. [29]

As we know, the interfacial charge transfer at the interface of electrode and electrolyte is the rate determine step in the whole Li ion transfer process. Moreover, the activation energy of that process can be calculated by the temperature dependence charge-transfer resistance ($R_{ct}$). The plots of log(T/$R_{ct}$) against 1000/T showed linear relationship obeying the Arrhenius equation. [30]

$$\ln \frac{T}{Rct} = \ln A - \frac{Ea}{R}\frac{1}{T}$$

Here $E_a$ is the activation energy, T is absolute temperature, $R_{ct}$ is the charge transfer resistance, R is gas constant, A is the pre-exponential factor. According this equation, the $E_a$ can be calculated from the slope of plots. Thus, the temperature dependence charge-transfer resistance ($R_{ct}$) were tested. As shown in Fig.8a, $E_{a2}$ of 2 wt.%-400 ºC sample is 17.60 kJ/mol, which is lower than $E_{a1}$ (33.95 kJ/mol) of the pristine sample. The $FePO_4$ coating layer decreased the activation energy of the charge transfer process, somewhat acted as a \`catalyst\`, which speed up the charge transfer processes at the interface of electrode and electrolyte.

Fig.9 shows the DSC profiles of pristine and 2 wt.%-400 ºC electrodes at charged state of 4.5 V. The small peaks at 245 and 283 ºC for the pristine and the 2wt.% - 400 ºC samples were attributed to the absorption of gas on the surface of the electrode materials. The pristine $Li_{1-x}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$ showed an exothermic peak at 332.9 ºC with an exothermic heat generation of 66.2 J/g. While the $FePO_4$ coated samples showed an exothermic peak at 337.9 ºC with an exothermic heat generation of 49.6 J/g. The enhanced thermal stability of the $FePO_4$ coated sample should be attributed to the stabilization of cathode surface by $FePO_4$ coating. As reported by other phosphate coated samples, the strong P=O bond and the strong covalency between the $PO_4$ polyanions and $Fe^{3+}$ can stabilize the cathode surface and thus strengthen the thermal stability of the materials. [31]

## 4. Conclusion

In this paper, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ is successfully coated with different amounts of $FePO_4$ by a co-precipitation method followed with heat treatment at different temperature. Among all the coated samples, the one with 2 wt.% $FePO_4$ and treated at 400 °C showed the best performance in terms of cycle and rate capacities. The effect of $FePO_4$ coating layer are as follows: (1) prevent from the side-reaction at the interface of electrode and electrolyte and thus suppressing the increase of charge transfer resistance upon charge-discharge cycles; (2) decrease of the activation energy of the charge transfer process and can speed up the charge transfer processes at the interface of electrode and electrolyte; (3) stabilize the cathode surface by the strong P=O bond and the strong covalency between the $PO_4$ polyanions and $Fe^{3+}$ and thus improve the thermal stability of the materials.

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# Figure Caption

Figure 1. XRD patterns of pristine and $FePO_4$-coated $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powder (a) and $FePO_4$ (b);

Figure 2. TEM images of (a) pristine and (b) 2 wt%-400 ºC $FePO_4$-coated sample;

Figure 3. (a) Cycling performance of pristine and $FePO_4$-coated $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ in the voltage range of 2.8-4.5 V at a current of 150 mA $g^{-1}$; (b) Cycle performance of 2 wt% $FePO_4$-coated $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ with different sintered temperature;

Figure 4. The charge-discharge curves of (a) pristine; (b) 2 wt% -400 ºC $FePO_4$-coated $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ in the voltage range of 2.8-4.5 V at a current of 150 mA $g^{-1}$ and (c) changes of voltage at half charge/discharge capacity with different cycles;

Figure 5. Rate capabilities of pristine and 2 wt% $FePO_4$-coated $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ in the voltage range of 2.8-4.5 V;

Figure 6. EIS Nyquist plots of pristine and 2wt% $FePO_4$-coated $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ with cycling, (a) at the 1st cycles; (b) at the 100th cycles discharge to 2.8 V; (c) Voigt-type of equivalent circuit;

Figure 7. (a)Temperature dependency for interfacial charge-transfer resistance of pristine and 2 wt%-400 ºC sample; (b) Image figure of improvement of activation energy by $FePO_4$ coating;

Figure 8. DSC profiles of pristine and 2 wt% $FePO_4$-coated $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ electrode charged to 4.5 V.

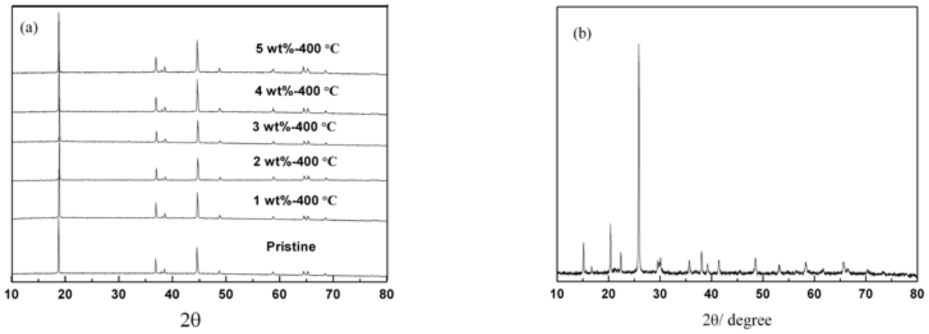


Figure 1

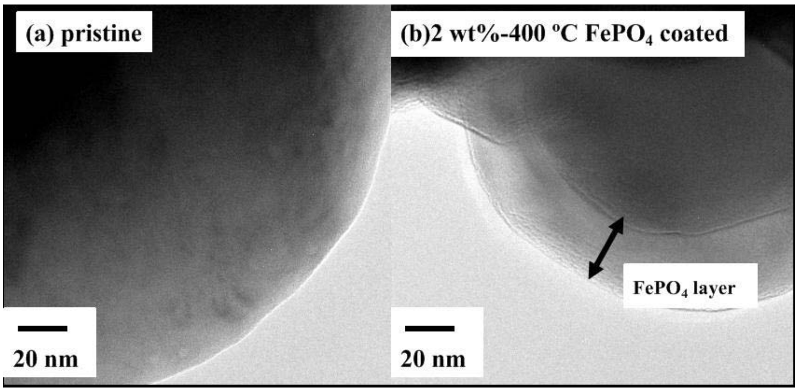
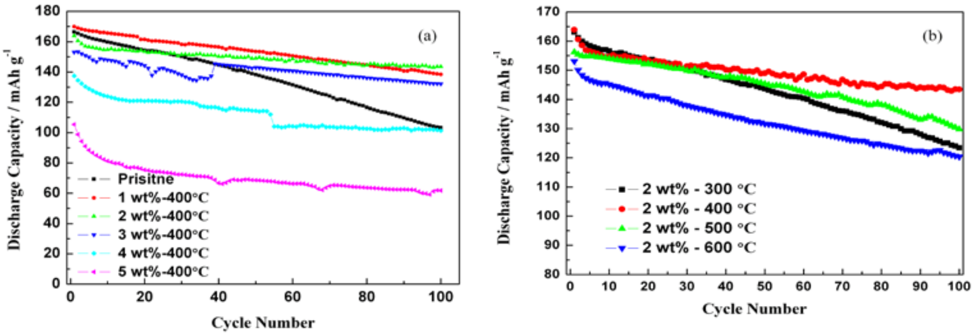


Figure 2



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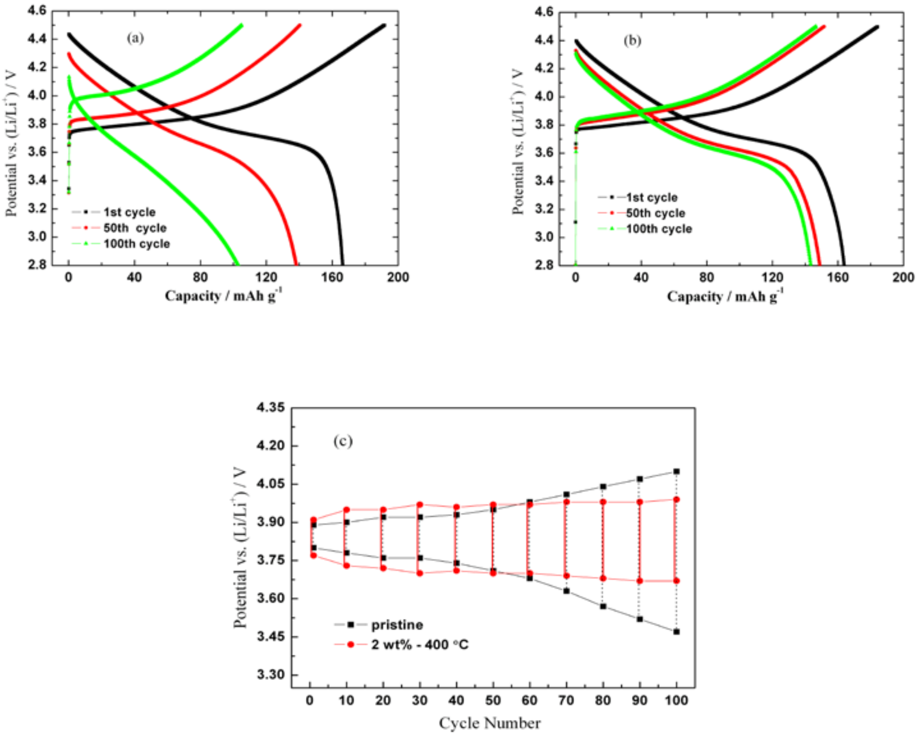

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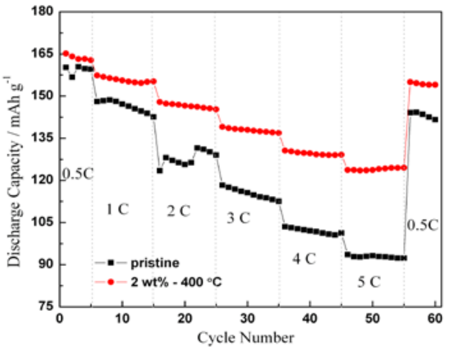

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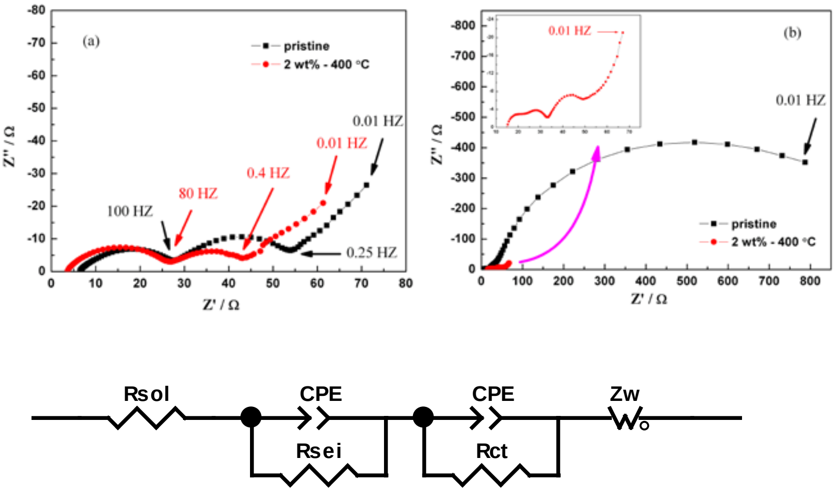

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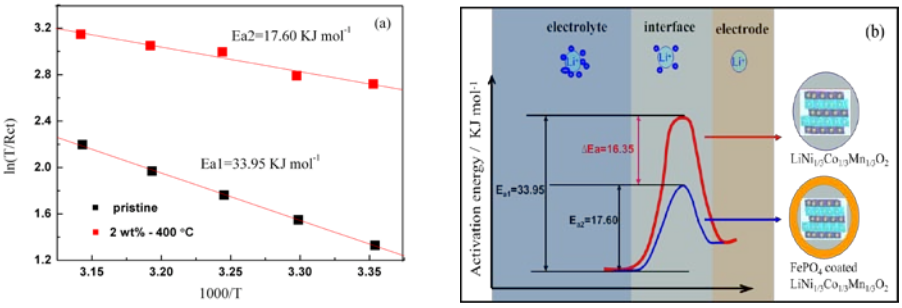

Figure 7

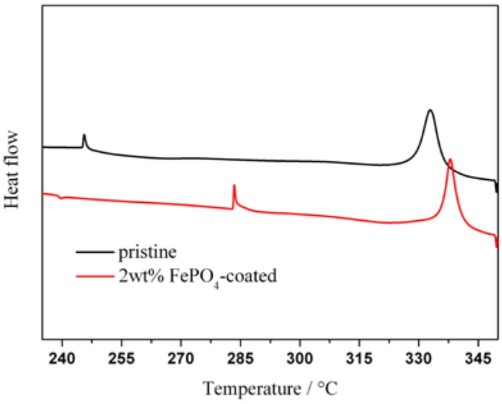

Figure 8

Table 1. Discharge capacities of pristine and 2 wt% -400 ºC $FePO_4$-coated $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ electrodes during 100 cycles in the voltage range of 4.5-2.8 V

| | 1st ( mAh $g^{-1}$) | 50th (mAh $g^{-1}$) | 100th (mAh $g^{-1}$) |
|---|---|---|---|
| Pristine(3.4V) | 166.4(155.5) | 138.3(129.8) | 103.2(105.7) |
| 2 wt% -400 ºC $FePO_4$-coated(3.4V) | 163.9(138.9) | 149.0(129.1) | 143.4(121.7) |

Table 2. Fitting results of the AC impedance parameters

| Samples | $R_{sol}$ / Ω At the 1st | $R_{sol}$ / Ω At the 100th | $R_{sei}$ / Ω At the 1st | $R_{sei}$ / Ω At the 100th | $R_{ct}$ / Ω At the 1st | $R_{ct}$ / Ω At the 100th |
|---|---|---|---|---|---|---|
| Pristine | 6.34 | 5.26 | 22.55 | 16.31 | 28.38 | 1129 |
| 2 wt% -400 ºC $FePO_4$-coated | 3.51 | 8.37 | 22.97 | 22.23 | 20.47 | 56.78 |

# *Supporting Information*

# Fabrication of $FePO_4$ layer coated $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$: Towards High-performance Cathode Materials for Lithium Ion Batteries

**Xizheng Liu,[b,a] Huiqiao Li,[a] Eunjoo Yoo,[a] Masayoshi Ishida,[b] and Haoshen Zhou,*[a]**

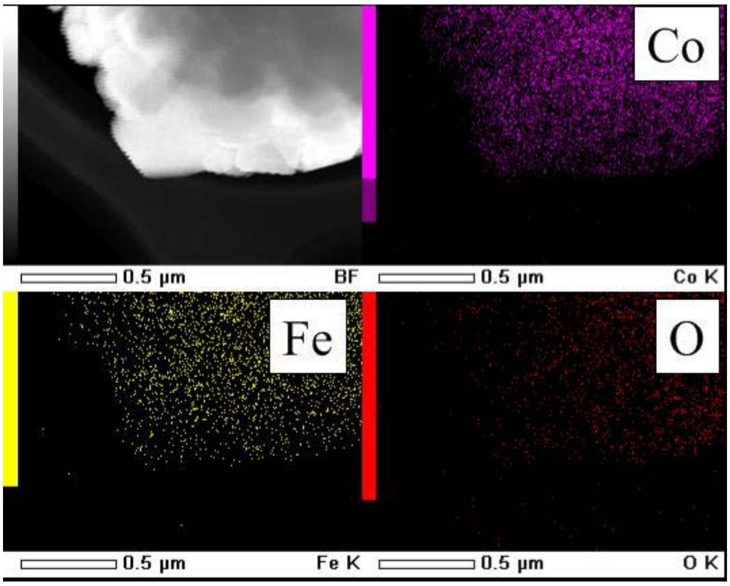

Fig. S1 EDS mapping patterns of 2 wt%-400 ºC $FePO_4$-coated sample;

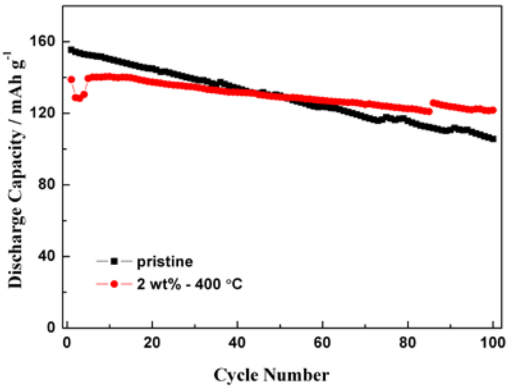

Fig.S2 Cycling performance of pristine and 2 wt% $FePO_4$-coated $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ in the voltage range of 3.4-4.5 V at a current of 150 mA $g^{-1}$

The cycle performance were tested in a voltage range of 2.8-4.5 V, however, the reaction $FePO_4 + Li^+ + e \leftrightarrow LiFePO_4$ occurs at about 3.45 V. [1] So it is necessary to confirm whether the increase of discharge capacity of coated sample due to the react between the $FePO_4$ coating layer and $Li^+$. The cycle performance of pristine and 2 wt%-400 ºC coated sample were tested at the voltage range of 4.5-3.4 V (Fig.S1). Even at such a high cut-off voltage, the 2 wt%-400 ºC coated sample still showed an improved cycle performance than that of the pristine. Thus, the $FePO_4$ coating layer showed little discharge contribution in the above experiments.

1. Huang, Y. H.; Goodenough, J. B. High-Rate $LiFePO_4$ Lithium Rechargeable Battery Promoted by Electrochemically Active Polymers. *Chem. Mater*. **2008**, *20*, 7237–7241.

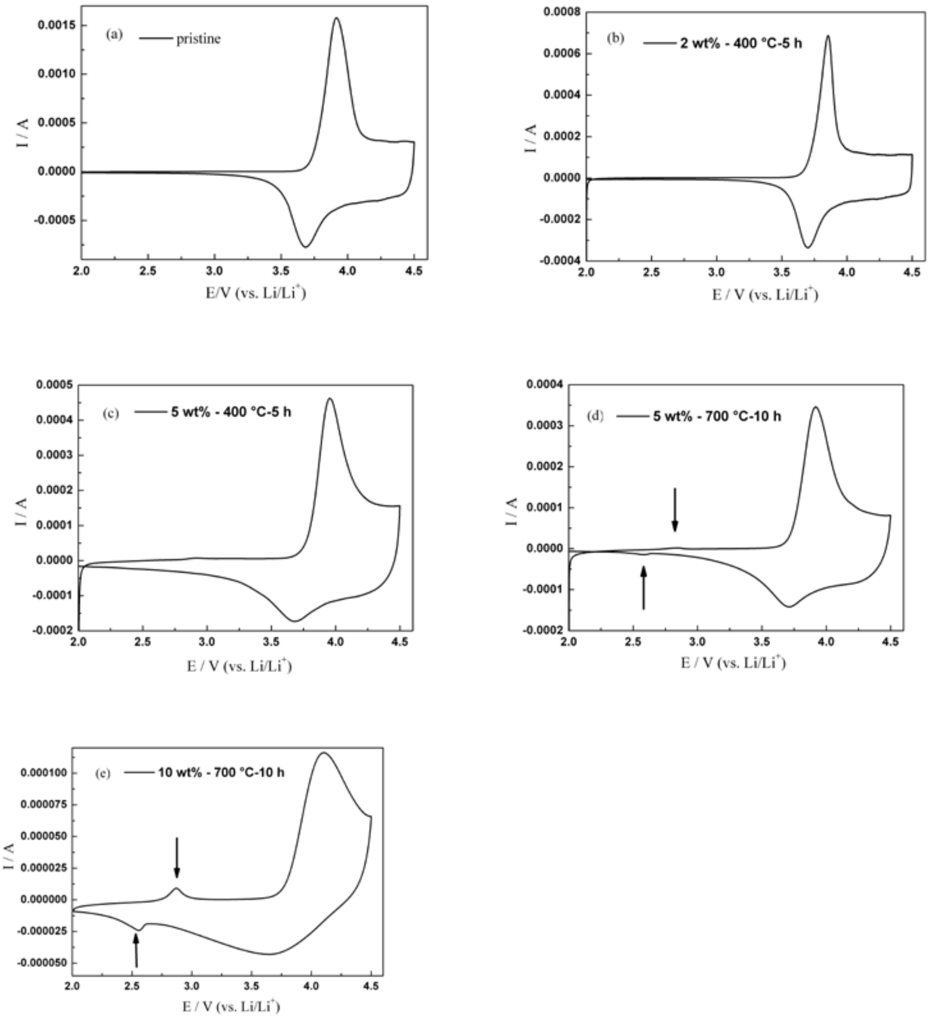

Fig. S3 Cyclic voltammograms of pristine and $FePO_4$-coated samples (with different synthesis conditions), at scan rate of 0.2 mV/s between 2.0 and 4.5 V.

For the pristine, 2 wt%-400 ºC and 5 wt%-400 ºC coated samples, only a couple of peaks which can be attributed to the redox reactions of $Ni^{2+}/Ni^{4+}$. [2] With increaseing the coating amount and heat treated temperature, a 10 wt.% and heat treated at 700 ºC, a couple of redox peaks appeared at 2.55 V / 2.84 V, which can be assigned to the redox of $Fe^{2+}/Fe^{3+}$ (Fig.S3d and S3e). Thus, we can conclude that the coated samples which with a coating layer less than 5 wt% and heat treated temperature at 400 ºC showed no $Fe^{2+}/Fe^{3+}$ redox reactions and also no charge/discharge capacity contributions.

2. Koyama, Y.; Yabuuchi, N.; Tanaka, I.; Adachi, H.; Ohzuku, T. Solid-State Chemistry and Electrochemistry of $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ for Advanced Lithium-Ion Batteries. *J. Electrochem. Soc.* **2004**, *151*, A1545-A1551.