A facile hydrothermal method is successfully developed for the synthesis of CePO$_4$ coated LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ (NCM 622) cathodes. The as-prepared samples are characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscopy (TEM), electrochemical workstation, electrochemical impedance spectroscopy (EIS) and inductively coupled plasma emission spectrometry (ICP). Compared to the pristine NCM 622 cathode, the rate capacity and cyclic performance are significantly improved after coating. Even under a 10 C charge/discharge rate, the initial discharge capacity of the 3.0-NCM sample is up to 95.2 mAh·g$^{-1}$. Furthermore, the as-prepared 3.0-NCM sample exhibits excellent cyclic performance with 96.8% capacity retention at 1 C under 55°C after 100 cycles, while the pure NCM 622 only delivers poor capacity retention of 71.4%. The above conclusions can be characterized that CePO$_4$ coating layer can effectively avert the secondary reaction between electrolyte and cathode material. In addition, the CePO$_4$ coating layer can significantly suppress the dissolution of cathodes in the electrolyte, which contributes to the excellent rate performance and cycle stability.

**Keywords:** Lithium-ion batteries; LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$; CePO$_4$ coating; Cycling performance

1. **INTRODUCTION**

Lithium-ion batteries (LIBs) are one of the most promising renewable energy sources and have been widely used in electric vehicles, hybrid vehicles and portable devices [1-3]. Recently, the layered
LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2 (NCM 622) cathode has become the hot spot owing to its high specific capacity, high voltage platform, low toxicity and low cost [4-8]. However, despite the mentioned advantages, the large-scale commercial application of NCM 622 cathodes have been restricted owing to irreversible capacity loss during the initial cycle and the unstable structural stability at high temperature or high working voltage. The irreversible capacity loss of NCM 622 can be attributed to the following secondary reaction between active materials and electrolytes [9,10]: (1) the dissolution of cathodes during the charge/discharge process, (2) metal fluorides with high resistance tends to deposit on the electrode surface.

Surface modification is an effective way to suppress the side reactions between cathodes and electrolytes. The materials such as Al_2O_3 [11,12], ZrO_2 [13], TiO_2 [14], MgO [15], WO_3 [16], Li_2ZrO_3 [17] have been reported to prevent the NCM 622 cathode and improve electrochemical performance. According to the previous report, the strong covalent interaction between PO_4^{3-} groups and metal ions can ameliorate the thermal stability of the coatings [18-20]. Suk-Woo Lee et al. [21] prepared Li_3PO_4 coated NCM 622 cathode and the capacity retention rate was increased from 63.9% to 79.7% after 100 cycles. Bai et al. [22] synthesized FePO_4 coated NCM 622 cathode via a solid-state calcination route, which exhibited a promising initial discharge capacity. After 50 cycles, it still maintains a promising capacity retention of 91.2% under a high voltage of 4.6 V. Furthermore, CePO_4 is a kind of electronic ceramics, with excellent electrical conductivity, and Ce^{3+} has strong oxidizing properties, which can consume the HF in the electrolyte and prevent secondary reaction between active materials and electrolytes. P Mohan et al. [23] synthesized CePO_4 coated LiMn_2O_4 which displayed promising specific capacity of 91 mAh·g^{-1} at 1 C rate with a capacity retention of 86% after 100 cycles. Although phosphate coating is widely used in cathode materials, the current literature on CePO_4 coated NCM 622 cathode materials have not been reported.

Here we designed the CePO_4 coated NCM 622 cathodes with three different coatings amount (denoted as 1.0-NCM, 3.0-NCM and 5.0-NCM, respectively) via a facial hydrothermal method. The structure, morphology and electrochemical performance of NCM 622 anode materials with different CePO_4 coating amount were studied. The as-prepared CePO_4 coated NCM 622 cathodes optimal coating amount (3.0-NCM) delivers high rate performance and excellent cyclic stability. This method has a prospect for application to high nickel-based cathode materials for advanced lithium-ion batteries.

2. EXPERIMENTAL METHODS

2.1. Synthesis of CePO_4 coated NCM 622 cathodes

The commercial NCM 622 cathodes were purchased from Hunan Shanshan New Material Co., Ltd. CePO_4 coated NCM 622 samples were carried out through a hydrothermal method. Firstly, 0.1 g (NH_4)_2HPO_4 (Shanghai Aladdin Reagent, 99.9%) and Ce(NO_3)_3·6H_2O (Shanghai Aladdin Reagent, 99.9%) (0.1 g, 0.3 g and 0.5 g, respectively) were fully dissolved in 60 mL deionized water with vigorously stirring. And then 2.0 g pristine NCM 622 powders were then added to the suspension and was magnetically stirred for 20 min. After that, the obtained mixed solution was transferred into a 100-mL Teflon-lined autoclave and reacted at 100°C for 10 hours. Subsequently, the slurry was dried in an oven for 12 h at 100°C. Finally, the obtained powder was sintered at 400°C for 6 h to obtain the CePO_4 coating.
coated NCM 622 with different amounts of CePO₄ coating (denoted as 0.0-NCM, 1.0-NCM, 3.0-NCM and 5.0-NCM).

**Figure 1.** Schematic diagram of coating CePO₄ by sol-gel method

### 2.2. Material Characterization

The sample was analyzed by the X’ pert 3 power X-ray diffractometer from the Dutch. The CuKα (λ = 0.15405 nm) source was used, the accelerating voltage was 40 kV, the tube current was 100 mA, and the scanning angle range was 10-80°. The surface morphology, element distribution and interior structure of the original NCM 622 and CePO₄ coated NCM 622 samples were observed by scanning electron microscopy (SEM, Zeiss Supra 55VP), and transmission electron microscopy (TEM, FEI Tecnai F20). The amounts of cathode dissolution were measured by inductively coupled plasma emission spectroscopy (ICP, Thermo-6000).

### 2.3. Electrochemical measurements

The coin cell preparation and detailed electrochemical analysis procedures were following our previous reports [24,25]. For electrochemical performance evaluating, the charge-discharge tests were carried out with a LAND-CT2001A test system (Shenzhen, China). The electrochemical impedance spectra (EIS) was conducted using an electrochemical workstation (CHI660E, Chenhua, China) in a frequency range from 1 mHz to 1 MHz with an amplitude of 5 mV.

### 3. RESULTS AND DISCUSSION

Figure 2 shows the XRD patterns of NCM 622 materials. All of the as-prepared samples have a typical hexagonal structure with a layered rhombohedral α-NaFeO₂-type with R₃m space group [26,27] and no impurity peaks observed, which means that CePO₄ coating do not change the crystal structure of
the host material [28]. What’ more, both of the samples exhibit the obvious peaks splitting of (006)/(102) and (108)/(110) [29,30], indicating that as-prepared deliver high crystallinity layered structure.

**Figure 2.** XRD patterns of 0.0-NCM, 1.0-NCM, 3.0-NCM and 5.0-NCM sample, respectively.

**Figure 3.** SEM images of 0.0-NCM, 1.0-NCM, 3.0-NCM and 5.0-NCM sample, respectively; TEM image of the 3.0-NCM sample.
The morphology of as-prepared samples was analyzed by SEM. Figure 3 displays the SEM images of pure and CePO$_4$-coated NCM 622 samples, respectively. All of the samples have similar uniform spherical-structure with the particle size of 10-15 μm. The spherical particles consist of nanosized primary particles and the surface of the primary particles in the bare sample has a smooth appearance. Through comparison of the surface for different samples, it is not difficult to observe a rougher coating layer on the CePO$_4$-coated NCM 622 samples. From the side view in the TEM image of 3.0-NCM particles (Figure 3e), the rough coating film (around 5 nm) appears on the surface of the LNMO bulk, which is formed by the CePO$_4$ nanosized particles with irregular shapes. In order to confirm the successful coating of CePO$_4$ on the particle surface, the EDS analysis for 3.0-NCM was carried out and displayed in Figure 4. It can be clearly seen that Ce and P elements are homogeneously distributed, indicating that the CePO$_4$ particles are uniformly coated on the interface of NCM 622 cathodes.

![Figure 3](image)

**Figure 4.** EDS mapping of 3.0-NCM sample

![Figure 5](image)

**Figure 5.** Initial charge-discharge curves of as-prepared CePO$_4$-coated NCM 622 samples

Figure 5 exhibits the initial charge-discharge curves of pure NCM 622 and CePO$_4$-coated NCM 622 samples at 0.2 C in the voltage range of 2.8 V to 4.3 V, respectively. The initial charge/discharge capacity and Coulombic efficiency for the bare and CePO$_4$-coated samples are listed in Table 1. It can
be observed that all the coated samples exhibit similar voltage plateaus compared to the pristine one, indicating that the CePO₄ coating does not introduce any electrochemical side reactions. In addition to, the initial discharge specific capacities of 0.0-NCM, 1.0-NCM, 3.0-NCM, 5.0-NCM samples are 159.5, 155.8, 149.9 and 147.8 mAh·g⁻¹, respectively. With increasing of coating amount, the mass of active material per unit area on the electrode is also reduced, leading to a decrease of the initial discharge capacity. The decrease of the initial capacity of as-prepared after CePO₄ coating can be attributed to the reduction in the mass of active material on electrode.

### Table 1. The initial charge/discharge capacity and coulombic efficiency of as-prepared samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial charge capacity (mAh g⁻¹)</th>
<th>Initial discharge capacity (mAh g⁻¹)</th>
<th>Initial coulombic efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0-NCM</td>
<td>197.2</td>
<td>159.5</td>
<td>80.88%</td>
</tr>
<tr>
<td>1.0-NCM</td>
<td>183.8</td>
<td>155.8</td>
<td>84.77%</td>
</tr>
<tr>
<td>3.0-NCM</td>
<td>181.7</td>
<td>149.9</td>
<td>82.50%</td>
</tr>
<tr>
<td>5.0-NCM</td>
<td>177.9</td>
<td>147.8</td>
<td>83.08%</td>
</tr>
</tbody>
</table>

In addition, to evaluate the rate performance, all the samples were tested at different charge and discharging current rates of 0.1, 0.2, 0.5, 2, 5 and 10 C and then return to 0.1 C, within the voltage range of 3.0-4.3 V, as shown in Figure 6a. With the increase of current density, compared with pure NCM 622, CePO₄-coated samples exhibit significantly improved capacities, even at a high current density of 10 C, the discharge capacity of 3.0-NCM can still remain up to 95.2 mAh·g⁻¹. What’s more, the discharge capacity of 3.0-NCM can be recovered to its initial value when the current density returns to 0.1 C, indicating that CePO₄-coated samples have good electrochemical reversibility and structural stability. In order to evaluate the cycle life of NCM 622 before and after coating, the cycling property for pure and CePO₄-coated electrodes are tested between 3.0-4.3 V at 1 C under 55°C, as can be seen in Figure 6b. After 100 cycles, the specific capacity of 0.0-NCM decays rapidly and delivers an almost ignorable capacity of 104.6 mAh·g⁻¹. The declined capacities at elevated temperature can be attributed to the accelerated Mn dissolution in the electrolyte. For comparison, the 3.0-NCM delivers the capacity of 134.9 mAh·g⁻¹ with an excellent capacity retention of 96.8%. In addition, we compared the cycle performance of 3.0-NCM cathode with some previous reports of surface-modified NCM-622 cathodes and the relevant data are shown in the Table 2. It is noted that even after 100 cycles, the as-prepared 3.0-NCM cathode still exhibits excellent capacity retention under both normal and high ambient temperature. These results further demonstrate that the CePO₄ coating layer can protect cathode from the corrosion of HF assigned to the decomposition of organic electrolyte.

In order to study the protection of CePO₄ coating, all of the as-samples were immersed in the electrolyte solution for two weeks. The amount of transition metal in the electrolyte was determined by ICP measurements after 2 weeks of storage in LiPF₆/ DEC: EC (1:1) electrolyte at 55°C. Figure 7 shows the dissolution histogram of the metal transitions in the active material. It can be clearly seen from Table 3 that the amount of metal dissolution in the electrolyte for CePO₄ coated sample is significantly reduced compared to the original sample. These results indicate that CePO₄ coating layer can effectively suppress
the dissolution of the cathodes in the electrolyte, which contributes significantly to the favorable rate performance and cycle stability of the NCM 622 cathode.

**Figure 6.** The rate performance at different current density (a) and cycling performances at 1 C under 55°C of pure and CePO₄-coated NCM cathodes at different current density (b).

**Table 2.** The comparison for the cycling performance with some previous reports of surface-modified NCM-622 cathodes.

<table>
<thead>
<tr>
<th>Coating materials</th>
<th>Discharge capacity and capacity retention after several cycles at a certain rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>CePO₄ (our work)</td>
<td>55°C, 134.9 mAh·g⁻¹, 96.8%, 100 cycles, 1 C</td>
</tr>
<tr>
<td>Co₃O₄[31]</td>
<td>25°C, 114.1 mAh·g⁻¹, 60.3%, 100 cycles, 0.1 C</td>
</tr>
<tr>
<td>Li₂SiO₃[32]</td>
<td>25°C, 167.6 mAh·g⁻¹, 85.5%, 100 cycles, 0.2 C</td>
</tr>
<tr>
<td>Li₃PO₄[21]</td>
<td>25°C, 79.7 mAh·g⁻¹, 79.7%, 100 cycles, 1 C</td>
</tr>
<tr>
<td>Li₂ZrO₃[33]</td>
<td>25°C, 161.5 mAh·g⁻¹, 85%, 100 cycles, 0.1 C</td>
</tr>
<tr>
<td>Carbon[34]</td>
<td>25°C, 138.2 mAh·g⁻¹, 84.3%, 50 cycles, 0.1 C</td>
</tr>
</tbody>
</table>

**Figure 7.** Histogram of transition metal dissolution in the active materials
Table 3. The ICP test results for pure NCM 622 and CePO$_4$-coated NCM 622 cathodes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dissolved amount of Ni$^{2+}$/ ppm</th>
<th>Dissolved amount of Ni$^{2+}$/ ppm</th>
<th>Dissolved amount of Ni$^{2+}$/ ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>The pristine</td>
<td>247.2</td>
<td>176.4</td>
<td>384.9</td>
</tr>
<tr>
<td>1.0-NCM</td>
<td>88.93</td>
<td>65.72</td>
<td>136.5</td>
</tr>
<tr>
<td>3.0-NCM</td>
<td>55.74</td>
<td>38.16</td>
<td>88.23</td>
</tr>
<tr>
<td>5.0-NCM</td>
<td>52.33</td>
<td>36.74</td>
<td>82.51</td>
</tr>
</tbody>
</table>

Figure 8. Nyquist plots of the 0.0-NCM and 3.0-NCM sample before (a) and after 100 cycles (b); the equivalent circuit (c).

Electrochemical impedance spectroscopy (EIS) was also performed to study the effect of CePO$_4$ coating on the NCM 622 cathodes. Figure 8 a and b plot the Nyquist graphs of 0.0-NCM and 3.0-NCM before and after 100 cycles. Both of the as-prepared samples show typical Nyquist plots, including the depressed semicircles at the high-frequency range and the oblique line at the low-frequency range. The depressed semicircle is associated with the charge transfer resistance in the electrode/electrolyte interfaces, while the inclined line is attributed to Warburg impedance ($Z_w$) [35,36]. Based on the previous reports [37-39], $R_s$ is the solution resistance, while $R_{ct}$ represents the charge transfer resistance. The fitted results of solution resistance ($R_s$) and charge transfer resistance ($R_{ct}$) were fitted through the equivalent circuit (Figure 8 c) and the results are listed in Table 4. Both of the samples deliver the almost similar $R_s$ and $R_{ct}$ before cycling, indicating that the CePO$_4$ coating layer does not act as a barrier to the Li$^+$
diffusion. However, a remarkable divergence in the impedance change between 0.0-NCM and 3.0-NCM electrode after cycling can be observed. it can be clearly seen from Figure 8 b that Rs for the 3.0-NCM electrode (100.1 Ω) is much smaller than that for the 0.0-NCM electrode (246.6 Ω). These results illustrate that the CePO4 coating is beneficial to alleviate the growth of the SEI layer, which can suppress the side reactions between electrolyte and cathodes.

Table 4. Impedance data for 0.0-NCM and 3.0-NCM samples before cycling and after 100 cycles.

<table>
<thead>
<tr>
<th>Cycle number</th>
<th>0.0-NCM</th>
<th>3.0-NCM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rs/ohm</td>
<td>Rct/ohm</td>
</tr>
<tr>
<td>0</td>
<td>2.783</td>
<td>40.9</td>
</tr>
<tr>
<td>100th</td>
<td>3.307</td>
<td>246.6</td>
</tr>
</tbody>
</table>

4. CONCLUSIONS

In summary, CePO4 coated LiNi0.6Co0.2Mn0.2O2 with different coating amount were successfully synthesized by a facile hydrothermal strategy. Structure and morphology measurements show that the CePO4 nanoparticles are successfully coated on the surface of LiNi0.6Co0.2Mn0.2O2 cathode. High rate capability and excellent cyclic performance at a cutoff voltage of 4.3 V can be achieved after CePO4 coating. 3.0-NCM delivers 95.2 mAh·g⁻¹ at 10 C rate and maintains 96.8% of its initial capacity at 1 C even under 55°C. Furthermore, the EIS measurement shows that the Rct value of 3.0-NCM is significantly reduced, which contributes to the improved electrochemical cycling stability and rate performances. The surface modification using CePO4 has been proved to be an effective measure to develop high nickel-based cathode materials.

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References


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