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PAPER

## Enhanced electrochemical performance and thermal stability of CePO<sub>4</sub>-coated Li<sub>1.2</sub>Ni<sub>0.13</sub>Co<sub>0.13</sub>Mn<sub>0.54</sub>O<sub>2</sub> cathode material for lithium-ion batteries

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Layered Li<sub>1.2</sub>Ni<sub>0.13</sub>Co<sub>0.13</sub>Mn<sub>0.54</sub>O<sub>2</sub> cathode is coated with CePO<sub>4</sub> layer via a simple precipitation method. The pristine and CePO<sub>4</sub>-coated Li<sub>1.2</sub>Ni<sub>0.13</sub>Co<sub>0.13</sub>Mn<sub>0.54</sub>O<sub>2</sub> are characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), high resolution transmission electron microscope (HR-TEM) and X-ray photoelectron spectroscopy (XPS), and results indicate that CePO<sub>4</sub> has been uniformly coated on the Li<sub>1.2</sub>Ni<sub>0.13</sub>Co<sub>0.13</sub>Mn<sub>0.54</sub>O<sub>2</sub>. Charge-discharge tests show that the CePO<sub>4</sub>-coated Li<sub>1.2</sub>Ni<sub>0.13</sub>Co<sub>0.13</sub>Mn<sub>0.54</sub>O<sub>2</sub> has an obviously enhanced electrochemical performance compared with the pristine sample: the initial coulombic efficiency from 88.26% to 92.19%, rate capability from 6 to 110 mAh g<sup>-1</sup> at 10 C, high-temperature performance from 59.5 to 219.6 mAh g<sup>-1</sup> at 55 °C after 20 cycles, and low-temperature performance from 128.3 to 246.7 mAh g<sup>-1</sup> at -20 °C. According to the analysis from dc impedance and electrochemical impedance spectra, the improvements on the electrochemical performance are mainly because the coated CePO<sub>4</sub> layer can reduce side reactions of Li<sub>1.2</sub>Ni<sub>0.13</sub>Co<sub>0.13</sub>Mn<sub>0.54</sub>O<sub>2</sub> with the electrolyte, and thus form the cathode-electrolyte interface (CEI) layer with enhanced Li<sup>+</sup> diffusion. In addition, the CePO<sub>4</sub> layer significantly improves the thermal stability of the coexisting systems of charged cathode with the electrolyte. Therefore, CePO<sub>4</sub> coating will be a promising approach to improve the electrochemical performance and thermal stability of Li-rich layered oxide cathode materials.

### Introduction

Developments of electric vehicles (EVs) and smart grids have the increasing demand for advanced rechargeable batteries, among which lithium-ion battery (LIB) is one of the most promising representatives because of its high energy density and successful commercialization in the portable electronic devices [1-3]. The energy density of the state-of-the-art LIBs is mainly governed by the electrode materials, especially the cathode materials [4-6]. In the widely used LiCoO<sub>2</sub>/graphite [4] and LiFePO<sub>4</sub>/graphite [5] cells, the capacity of the cathode materials (~140 mAh g<sup>-1</sup>) is less than half of the graphite anode (~330 mAh g<sup>-1</sup>) [6]. Therefore, the high-capacity candidates of the present cathode materials are needed to meet the demand for development of the advanced LIBs.

Li-rich layered oxide cathode materials, represented by xLi<sub>2</sub>MnO<sub>3</sub>·(1-x)LiMO<sub>2</sub> (M = Ni, Co, Mn or combinations) can deliver a reversible capacity of ~250 mAh g<sup>-1</sup>, which is quite attractive to high-energy LIBs for EVs and smart grid applications [7-9]. However, their drawbacks of large irreversible capacity loss during the initial cycle and poor rate capability limit the commercial utilization [10-14]. One of the main reasons for these drawbacks is the unsatisfying interface chemistry between this kind of cathode and common electrolytes [11]. The high capacity of Li-rich layered oxide cathode materials cannot be achieved until they are charged to an upper cut-off voltage above 4.5 V in order to activate Li<sub>2</sub>MnO<sub>3</sub> component [12]. Such a high voltage is a rigorous challenge to the state-of-the-art carbonate-based electrolytes, and the electrolyte decomposition is unavoidably initiated by strongly oxidative charged electrodes and intermediate oxygen species [15]. In our previous paper [16], it is clearly indicated that the optimized cathode electrolyte interface (CEI) with the help of trimethyl phosphite (TMP) as the high-voltage electrolyte additive has the positive effects on improving

the electrochemical performance and thermal stability of this kind of cathode material.

Besides the reformulation of the electrolytes, surface coating on the cathode material is the alternative effective method to modify the CEI film between the Li-rich layered oxide and the electrolyte [10,17-22]. Coated metal oxides [19-22] on the surface of the Li-rich layered oxide cathode can reduce initial irreversible capacity loss and enhance rate capability. Surface modification with metal phosphate was found to be more effective in lowering the irreversible capacity loss than that with Al<sub>2</sub>O<sub>3</sub> due to the retention of more oxide ion vacancies in the lattice after the first charge [23]. Moreover, metal phosphates have the better thermal stability than its relevant metal oxide due to the strong covalent P-O bonding [23-26]. Recently, rare earth oxides have been coated on the surface of the Li-rich layered oxide cathode and the cycling performance has been improved [27,28], while their phosphates have seldom been considered. CePO<sub>4</sub> coating has been reported to improve the cycling stability of LiCoO<sub>2</sub> and LiMn<sub>2</sub>O<sub>4</sub> at elevated temperature by suppressing Co or Mn dissolution [28-30]. Also, CePO<sub>4</sub> modification can improve the rate capability of LiFePO<sub>4</sub>/C, because CePO<sub>4</sub> as an ionic conductor with stable structure can reduce side reactions and enhances migration of the lithium-ions at the electrode/electrolyte interface [31].

Herein, we performed the CePO<sub>4</sub> coating on the 0.5Li<sub>2</sub>MnO<sub>3</sub>·0.5LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> cathode (denoted as Li<sub>1.2</sub>Ni<sub>0.13</sub>Co<sub>0.13</sub>Mn<sub>0.54</sub>O<sub>2</sub>, and abbreviated as LNCMO) by a simple precipitation reaction. After the structures of the cathode materials with and without coating have been identified, the effects of CePO<sub>4</sub> coating on the electrochemical performance and thermal stability of the Li-rich layered oxide cathode are systemically investigated. Definitely, compared with the pristine LNCMO, the CePO<sub>4</sub>-coated Li<sub>1.2</sub>Ni<sub>0.13</sub>Co<sub>0.13</sub>Mn<sub>0.54</sub>O<sub>2</sub> (abbreviated as CP-LNCMO) shows an obvious improvement on

initial coulombic efficiency, rate capability, high-temperature and low-temperature performance.

## Experimental

### Materials synthesis

The pristine LNCMO was prepared by a co-precipitation method, as described previously [16]. Surface coating of LNCMO with  $\text{CePO}_4$  were carried out as follows:  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (54.9 mg) and  $(\text{NH}_4)_2\text{HPO}_4$  (16.8 mg) were dissolved in distilled water until a white suspension (of  $\text{CePO}_4$ ) was obtained. The pristine LNCMO powder was then added to the suspension and was magnetically stirred for 20 min to form a slurry. The weight ratio of  $\text{CePO}_4$  and LNCMO was 3:100. Subsequently, the slurry was dried in an oven for 12 h at 100 °C, and annealed at 400 °C for 5 h in a furnace to obtain the CP-LNCMO.

### Characterization and electrochemical measurements

The crystalline structures of the pristine LNCMO and CP-LNCMO were identified by X-ray diffraction (XRD) using a diffractometer (D/MAX2500 V, Cu K $\alpha$  radiation). The diffraction patterns were recorded in the 2 theta range from 10° to 80°. The particle size and morphology of the pristine LNCMO and CP-LNCMO were observed by field-emission scanning electron microscopy (FE-SEM, Hitachi SU8020) and high resolution transmission electron microscope (HR-TEM, JEM-2100F). X-ray photoelectron spectroscopy (XPS, ESCALAB250) was performed to characterize the surface state of the obtained products.

The electrochemical performances of the pristine LNCMO and CP-LNCMO were investigated using CR2032 coin-type cells assembled in an argon-filled glove box (MBraun). In order to make the electrode laminate, a slurry containing 84 wt.% active material, 8 wt.% acetylene black and 8 wt.% polyvinylidene fluoride (PVDF) dispersed in N-methyl-2-pyrrolidinone (NMP) was cast onto an aluminum current collector. After vacuum drying at 70 °C, the laminate was punched into discs ( $\Phi$ 14 mm) for assembling the coin cells. The mass loading in the electrode was controlled at about 2.5 mg  $\text{cm}^{-2}$ . Celgard 2400 microporous polypropylene membrane was used as separator. Highly pure lithium foil was used as the counter electrode and reference electrode for the cell assembly. The electrolyte was 1 M  $\text{LiPF}_6/\text{ethylene carbonate (EC) + dimethyl carbonate (DMC)}$  (1:1 w/w). The cell performance of the pristine LNCMO and CP-LNCMO were evaluated on a multichannel battery cycler (Neware BTS2300). All the cells were initially cycled twice between 2.5 and 4.8 V at a current rate of 0.1 C (1 C=200 mA  $\text{g}^{-1}$ ). Then the cycling tests were performed at a current rate of 0.5 C in the constant current-constant voltage (CC-CV) charge mode and constant current (CC) discharge mode between 2.5 and 4.6 V. For the high temperature tests, the cells were galvanostatically cycled between 2.5 and 4.6 V at 55 °C at a current rate of 0.5 C. For the low temperature tests, the cells were galvanostatically charged to 4.6 V at room temperature then discharged at 0 °C or -20 °C at a current rate of 0.1 C. Cyclic voltammograms (CV) were performed over the potential range of 2.5-4.8 V at a scanning rate of 0.2  $\text{mV s}^{-1}$  on a CHI 604D electrochemical workstation (Shanghai Chenhua Instruments Co. Ltd.). The electrochemical impedance spectra of the cells were also measured on the CHI electrochemical workstation with the frequency range and potential perturbation set as 1 MHz to 0.01 Hz and 10 mV at the state of charge (SOC) of 50%. The internal resistance of the cells was measured by a current interruption technique. This was done by cutting off the current intermittently for 1 min through the process of charge and recording the voltage

change after interruption. Thus, the dc impedance of a cell ( $R_{\text{dc}}$ ) can be calculated as  $R_{\text{dc}} = \Delta U/\Delta I$ , where  $\Delta U$  is the difference between the voltage of before and after the 1-min interruption [32]. Thermal stability of the coexisting systems of the charged LNCMO and CP-LNCMO cathode with electrolyte was evaluated by using a Calvet-type calorimeter (Setaram C80). 23 mg cathode materials (after charged to 4.6 V in the cells and disassembled in the glove box) and 50 mg electrolyte were placed in a high-pressure stainless steel vessel with dry argon atmosphere. The measurement was performed at a heating rate of 0.2 °C  $\text{min}^{-1}$  from room temperature to 300 °C, and the C80 calculations were based on the weight of the electrolyte. More details can be found in our previous report [33]. All the testing above was performed at room temperature unless otherwise specified.

## Results and discussion

The XRD patterns of the pristine LNCMO and CP-LNCMO samples are shown in Fig. 1. All the major diffraction peaks can be indexed as a layered oxide lattice based on a hexagonal  $\alpha\text{-NaFeO}_2$  type structure with a space group R-3m [18]. Both (006)/(102) and (108)/(110) doublets are clearly split, suggesting that the material crystallized in the layered structure without formation of any spinel structure [23]. The weak peaks between 20° and 25° (marked by \*) are reflected by a monoclinic unit cell with a C2/m symmetry, due to a  $\text{LiMn}_6$  cation arrangement that occurs in the transition metal layers of  $\text{Li}_2\text{MnO}_3$  region. No peak of  $\text{CePO}_4$  is observed due to its low quantity, illustrating that the coating processes do not destroy the structure of the Li-rich layered oxides and no impurity appears in the XRD patterns.

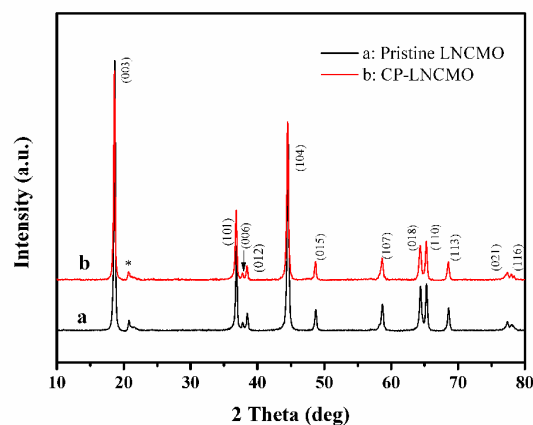
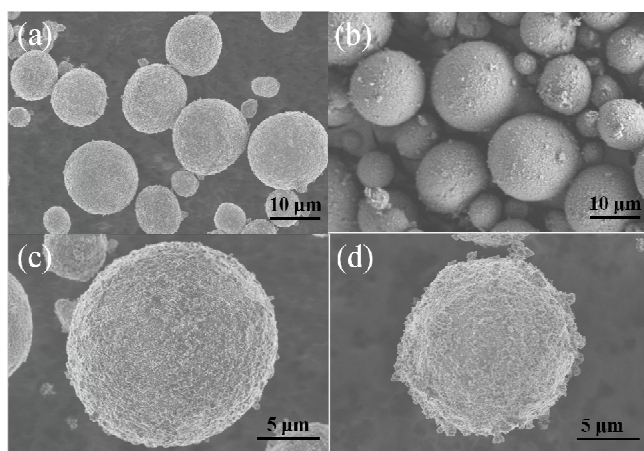
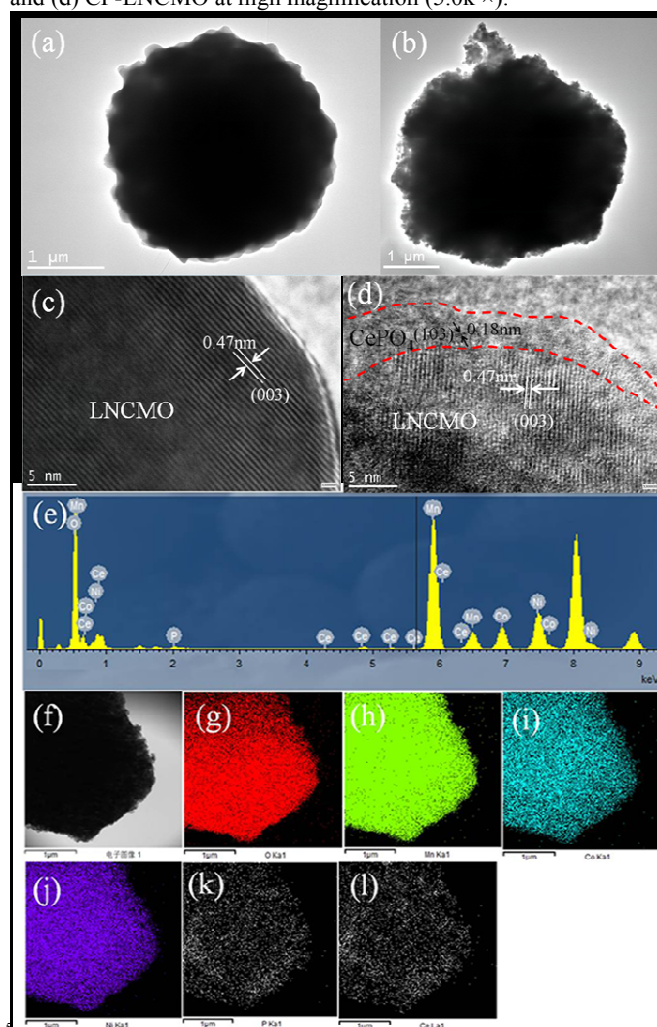


Fig. 1 XRD patterns of the pristine LNCMO and CP-LNCMO.

The morphologies of the pristine LNCMO and CP-LNCMO samples were investigated by FE-SEM, as shown in Fig. 2. From Fig. 2a and 2c, the pristine LNCMO spherical particles are 2-10  $\mu\text{m}$  in diameter. As shown in Fig. 2b and 2d, the surface of the CP-LMNCO is coated by  $\text{CePO}_4$  particles, and becomes rough. From the FE-SEM results, we expect that  $\text{CePO}_4$  coating of LNCMO can effectively decrease the direct contact area between the high-voltage cathode material and the electrolyte. Fig. 3 shows the HRTEM images of the pristine LNCMO and CP-LNCMO particles. Compared with the surface of the pristine LNCMO (Fig. 3a), the surface of CP-LNCMO is quite rough and scattered by  $\text{CePO}_4$  particles (Fig. 3b). The distance between two



**Fig. 2** SEM images of (a) the pristine LNCMO and (b) CP-LNCMO at low magnification (2.0k  $\times$ ), (c) the pristine LNCMO and (d) CP-LNCMO at high magnification (5.0k  $\times$ ).

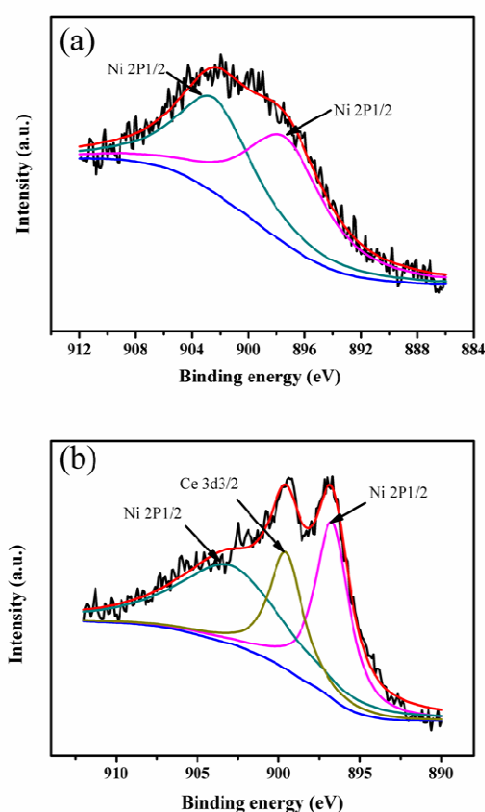


**Fig. 3** TEM images of the pristine LNCMO (a, c) and CP-LNCMO (b, d), the EDS (e) and maps (f-l) of the CP-LNCMO.

lattice fringes of the pristine LNCMO is calculated to be 0.47 nm, which is assigned to (003) plane of LNCMO (Fig. 3c). In Fig. 3d, the distances between two lattice fringes on the internal and surface of the CP-LNCMO are 0.47 nm and 0.18 nm, assigned to (003) plane of LNCMO and (103) plane of CePO<sub>4</sub>, respectively,

implying that the CePO<sub>4</sub> coating processes do not destroy the structure of the Li-rich layered oxides (in agreement with the XRD results) and the coated CePO<sub>4</sub> is crystalline. EDS analysis is performed and the results are shown in Figs. 3e-l. The EDS analysis (Fig. 3e) reveals the presence of Ni, Co, Mn, O, Ce and P in the CP-LNCMO sample. The EDS element maps (Figs. 3f-l) clearly reveal that the Ce and P elements in the composite are uniformly distributed on the surface of LNCMO particles, illustrating that the CePO<sub>4</sub> is homogeneously coated on the surface of LNCMO particles.

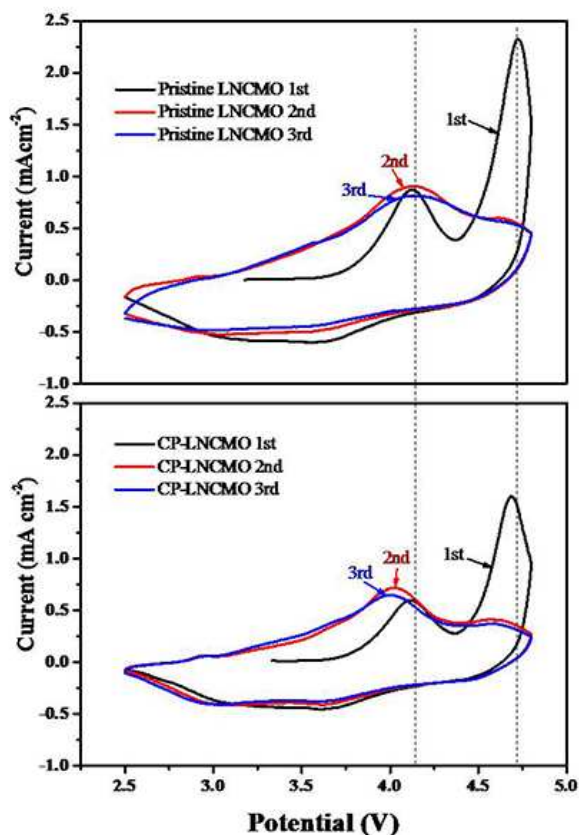
The XPS spectra of the pristine LNCMO and CP-LNCMO samples are shown in Fig. 4. As shown in Fig. 4a, the two peaks at 902.4 and 897.4 eV are assigned to Ni 2p<sub>1/2</sub> [34,35] on the surface of the pristine LNCMO. After coating CePO<sub>4</sub>, in Fig. 4b, the signal at 901.1 eV (assigned to Ce 3d<sub>3/2</sub>) is characteristic of Ce<sup>3+</sup> [36,37]. The XPS results indicate that it is Ce (III) spectrum that is detected and definitely the coating layer is CePO<sub>4</sub>, combined with EDS results.



**Fig. 4** XPS of the pristine LNCMO (a) and CP-LNCMO (b).

Fig. 5 shows the CV profiles of the pristine LNCMO and CP-LNCMO. By comparing the pristine LNCMO with the CP-LNCMO, the anodic/cathodic behaviors are quite similar. During the first cycle, the anodic peaks of both samples are located at about 4.2 V which is associated with Ni<sup>2+</sup> and Co<sup>3+</sup> oxidation processes, while the second anodic peaks at above 4.5 V is predominantly associated with oxygen release and Li<sup>+</sup> extraction from the Li<sub>2</sub>MnO<sub>3</sub> component [38]. For the CP-LNCMO sample, the peak shifts to lower potential and around 4.1 V during the following two cycles. Such relatively low oxidation potential is beneficial to the effective Li<sup>+</sup> extraction in the cathode-active material after the CePO<sub>4</sub> coating. Furthermore, in the cathodic

process, despite the broad slope above 3.5 V related to the reductions of  $\text{Ni}^{4+} \rightarrow \text{Ni}^{2+}$  and  $\text{Co}^{4+} \rightarrow \text{Co}^{3+}$ , the apparent 3.1 V peak must be associated with the partial reduction of  $\text{Mn}^{4+}$  to  $\text{Mn}^{3+}$  in the transformed  $\text{Li}_{1-x}\text{MnO}_2$  [39]. Compared with the pristine LNCMO, the cathodic curves of the CP-LNCMO are more repeatable, implying that the coated  $\text{CePO}_4$  restrains LNCMO structural evolution.

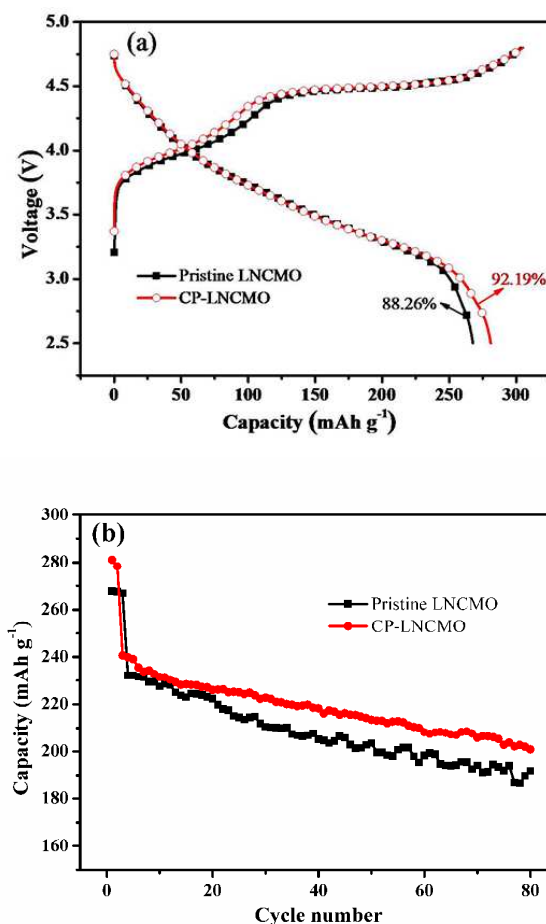


**Fig. 5** Cyclic voltammety of the pristine LNCMO and CP-LNCMO electrodes at  $0.2 \text{ mV s}^{-1}$  scan rate.

The initial charge-discharge curves and the cycling performance of the pristine LNCMO and CP-LNCMO samples are shown in **Fig. 6**. As shown in **Fig. 6a**, the initial charge and discharge capacities for the pristine LNCMO are  $302$  and  $267 \text{ mAh g}^{-1}$  at  $0.1 \text{ C}$ , respectively. So the irreversible capacity is  $35 \text{ mAh g}^{-1}$  and coulombic efficiency is  $88.26\%$ . As for CP-LNCMO, the initial charge and discharge capacities are  $305$  and  $281 \text{ mAh g}^{-1}$ , respectively. Therefore, CP-LNCMO has the lower irreversible capacity of  $23 \text{ mAh g}^{-1}$  and higher coulombic efficiency of  $92.19\%$  than the pristine LNCMO. This should be attributed to the suppressed side reactions between the electrolyte and the LNCMO cathode by  $\text{CePO}_4$  coating. **Fig. 6b** shows the cycling performance of the pristine LNCMO and the CP-LNCMO. After two formation cycles at  $0.1 \text{ C}$ , the discharge capacities of the pristine LNCMO are about  $230$ ,  $203$  and  $191 \text{ mAh g}^{-1}$  at the 3rd, 50th and 80th cycle at  $0.5 \text{ C}$ , whereas those of CP-LNCMO are about  $240$ ,  $213.5$  and  $201 \text{ mAh g}^{-1}$  at the 3rd, 50th and 80th cycle, respectively. These results suggest that the coated  $\text{CePO}_4$  effectively improved the cycling stability of LNCMO and bulk structure evolution have been restrained.

It is widely reported that the rate capability of Li-rich layered oxide cathode is poor, which becomes one of main drawbacks of this material for the commercial utilization [10]. The poor rate capability is usually ascribed to the formation of a

high-resistance CEI layer on the cathode surface owing to electrolyte oxidation at high potentials [15,16]. **Fig. 7** shows rate



**Fig. 6** Initial voltage profiles of the pristine LNCMO and CP-LNCMO electrodes at  $0.1 \text{ C}$  (a), cycling performance of both electrodes at  $0.5 \text{ C}$  (b).

capability of the pristine LNCMO and the CP-LNCMO. After two formation cycles at  $0.1 \text{ C}$ , the discharge capacities of the pristine LNCMO and the CP-LNCMO are comparative at  $0.5 \text{ C}$ . When the current rates increase to  $1 \text{ C}$ ,  $2 \text{ C}$ ,  $5 \text{ C}$  and  $10 \text{ C}$ , the discharge capacities of the pristine LNCMO, rapidly drop to  $171$ ,  $103$ ,  $48$  and  $6 \text{ mAh g}^{-1}$ , respectively. However, for the CP-LNCMO, the discharge capacities are  $231$ ,  $205$ ,  $172$  and  $110 \text{ mAh g}^{-1}$  at  $1 \text{ C}$ ,  $2 \text{ C}$ ,  $5 \text{ C}$  and  $10 \text{ C}$ , respectively. That is, the rate capability of LNCMO can be remarkably improved by the  $\text{CePO}_4$  coating. In addition, when the current rate returns back to  $0.5 \text{ C}$ , the discharge capacities of both samples can be restored.

At elevated temperatures, Mn and Co dissolutions from LNCMO result in serious capacity fading during charge and discharge [29]. **Fig. 8** reveals the cycling performance of the pristine LNCMO and the CP-LNCMO cathodes at elevated temperature. After two formation cycles at room temperature, the initial discharge capacities at  $55 \text{ }^\circ\text{C}$  of the pristine LNCMO and CP-LNCMO are  $241.1$  and  $280.8 \text{ mAh g}^{-1}$ , respectively. After 20 cycles, the capacity of the pristine LNCMO rapidly fades to  $59.6 \text{ mAh g}^{-1}$ , with the low capacity retention of  $24.7\%$ . However, the CP-LNCMO still keeps a quite high capacity of  $219.6 \text{ mAh g}^{-1}$ , and the capacity retention is as high as  $78.2\%$ . In order to figure out the reason for the improvement on high-temperature capacity

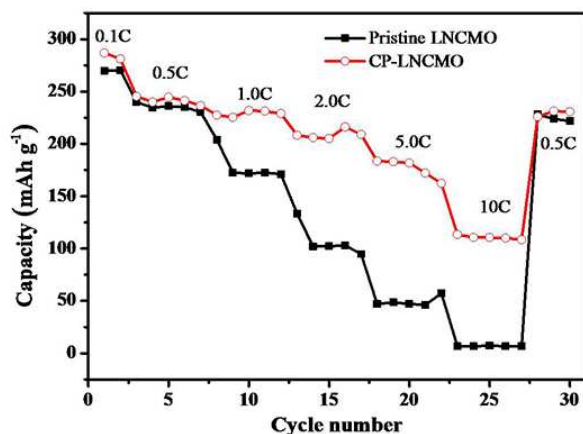


Fig. 7 Rate capability of the pristine LNCMO and CP-LNCMO electrodes.

retention from the  $\text{CePO}_4$  coating, both the pristine LNCMO and the CP-LNCMO electrodes were soaked in 6 g electrolyte and stored at  $55^\circ\text{C}$ . After 60 h, as shown in the insets of Fig. 8, the electrolyte stored with the pristine LNCMO became light brown, while that with the CP-LNCMO electrode was still colorless. The color change of the former is probably due to the dissolution of Mn and Co into the electrolyte at  $55^\circ\text{C}$ . Therefore, it can be concluded that the coated  $\text{CePO}_4$  can effectively prevent Mn and Co ions from dissolving into the electrolyte at elevated temperature, and improve the high-temperature cycling stability of the LNCMO.

Up to now, low-temperature performance of LIBs keeps a big challenge to meet the requirements of EVs, because of the decrease in the both discharge capacity and voltage plateau [40]. To the best of our knowledge, low-temperature performance of Li-rich layered oxide cathode materials has seldom been investigated in previous literatures. Here, we compare the low-temperature performance of the pristine LNCMO and the CP-LNCMO cathodes at  $0^\circ\text{C}$  and  $-20^\circ\text{C}$ , as shown in Fig. 9. For the pristine LNCMO, the discharge capacities are  $234.7\text{ mAh g}^{-1}$  at  $0^\circ\text{C}$  and  $128.3\text{ mAh g}^{-1}$  at  $-20^\circ\text{C}$ . However, the CP-LNCMO can deliver the discharge capacities of  $278.5$  at  $0^\circ\text{C}$  and  $246.7\text{ mAh g}^{-1}$  at  $-20^\circ\text{C}$ , respectively. As far as the capacity retention at low temperature is concerned, the discharge capacities of the pristine LNCMO and CP-LNCMO at  $-20^\circ\text{C}$  are 44.8% and 83.1% of the corresponding capacities at room temperature, respectively. In addition, the discharge voltage plateau of the CP-LNCMO is higher than that of the pristine LNCMO at the same temperatures. Therefore, the low-temperature performance of the LNCMO can be significantly improved by the  $\text{CePO}_4$  coating. Herein, since the main difference is on the CEI interface, the improved low-temperature performance of CP-LNCMO is resulted from the optimized CEI interface by the  $\text{CePO}_4$  coating.

To further understand the electrochemical processes in the CP-LNCMO, dc resistance is tested. As shown in Fig. 10, the dc resistance measurements show that the CP-LNCMO has a lower dc resistance than the pristine LNCMO, especially at high potential ( $> 4\text{ V}$ ). We speculate that the lower dc resistance results from the coated  $\text{CePO}_4$  layer, which can suppress the electrochemical reactions between the electrolyte and charged LNCMO cathode. Furthermore, Fig. 11 shows that the Nyquist plots of the pristine LNCMO and CP-LMNCO electrodes at the SOC of 50% after the 3rd and 100th cycle, respectively. EIS

results were fitted by using an equivalent circuit, in which  $R_e$ ,  $R_f$ ,  $R_{ct}$  and  $W$  stand for internal resistance of the cell, the impedance of  $\text{Li}^+$  diffusion in the interface (herein CEI) film, the impedance

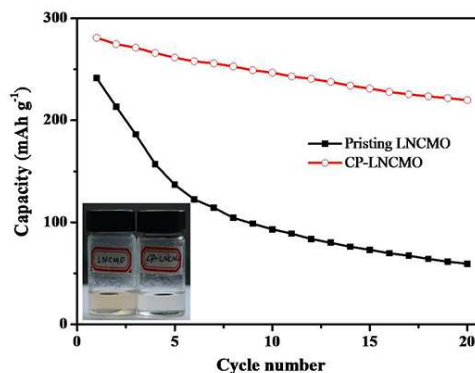


Fig. 8 Capacity retention of the pristine LNCMO and CP-LNCMO electrodes at  $55^\circ\text{C}$ , the insets show both electrodes stored in the electrolyte at  $55^\circ\text{C}$  for 60 h.

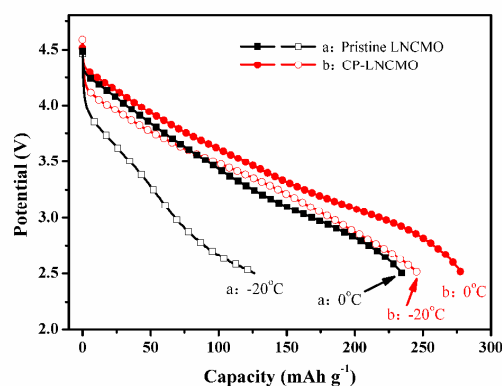


Fig. 9 Discharge curves of the pristine LNCMO and CP-LNCMO electrodes at low temperatures.

of charge transfer and Warburg impedance, respectively [41,42]. The fitted impedance parameters of the equivalent circuit are listed in Table 1. The values of  $R_e$  of the CP-LNCMO are relatively smaller than those of the pristine LNCMO at the same cycle, which suggests that the  $\text{CePO}_4$  coating can reduce the negative effect on the electrolyte from the LNCMO cathode. The values of  $R_f$  of the pristine LNCMO are  $236.8$  and  $270.4\ \Omega$ , much higher than those of the CP-LNCMO ( $84.2$  and  $199.5\ \Omega$ ) after the 3rd and 100th cycle, respectively. This result supports that the coated  $\text{CePO}_4$  suppresses the growth of CEI film on the LNCMO cathode. The values of  $R_{ct}$  of pristine LNCMO drastically increase from  $276.7$  to  $867.4\ \Omega$ , while those of the CP-LNCMO show negligible change from  $105.8\ \Omega$  at the 3rd cycle to  $103.8\ \Omega$  at the 100th cycle. Herein, the low and stable charge transfer impedance suggests that the coated  $\text{CePO}_4$  layer can reduce side reactions of LNCMO with the electrolyte, and thus form the CEI layer with enhanced  $\text{Li}^+$  diffusion [12], which is the main reason for the improvement of the  $\text{CePO}_4$  on the electrochemical performance of the LNCMO. XPS results of the electrodes after two formation cycles also support the point that  $\text{CePO}_4$  coating can minimize the electrolyte decomposition at high voltage and suppress the growth of CEI film. In Fig.12, because of the

protection of the coated  $\text{CePO}_4$ , the CP-LNCMO electrode has the decreased C 1s peak and the enhanced Mn 2p3/2 peak, which indicate less CEI formation and Mn dissolution.

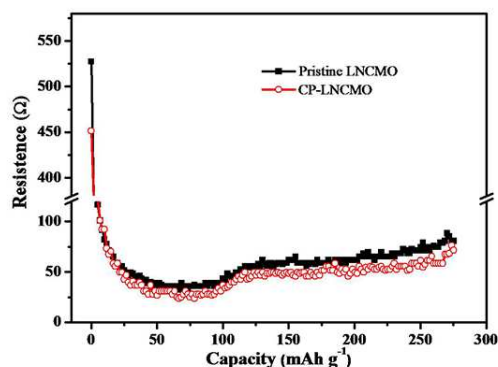


Fig. 10 Relationship between special capacity and dc resistance of the pristine LNCMO and CP-LNCMO electrodes.

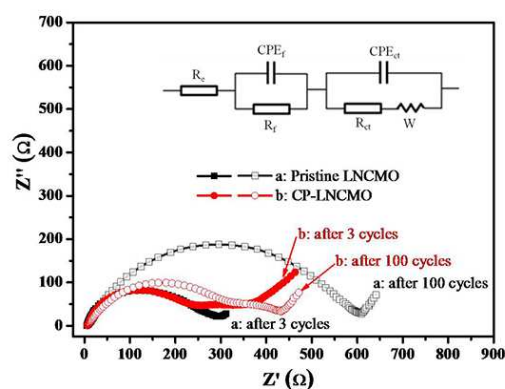


Fig. 11 EIS results of the pristine LNCMO and CP-LNCMO electrodes, the inset shows equivalent circuit for Nyquist plots.

Table 1 Fitted impedance parameters of the pristine LNCMO and CP-LNCMO.

Sample	$R_c$ ( $\Omega$ )	$R_f$ ( $\Omega$ )	$R_{ct}$ ( $\Omega$ )	$W$ ( $S \text{ sec}^{1/2}$ )
Pristine LNCMO (3 <sup>rd</sup> )	6.8	236.8	276.7	0.02839
Pristine LNCMO (100 <sup>th</sup> )	8.5	270.4	867.4	0.02097
CP-LNCMO (3 <sup>rd</sup> )	4.6	84.2	105.8	0.08808
CP-LNCMO (100 <sup>th</sup> )	7.3	199.5	103.8	0.05458

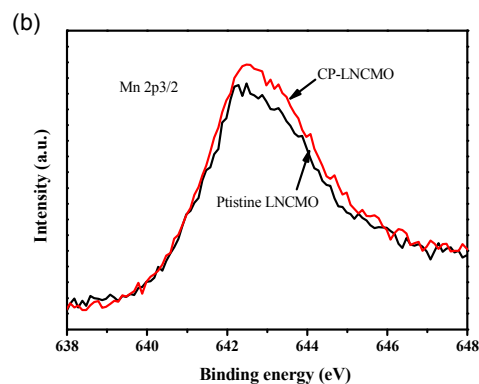
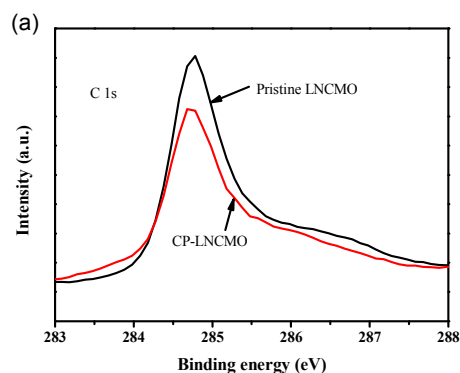


Fig. 12 XPS spectra of the pristine LNCMO and CP-LNCMO electrodes after 2 formation cycles.

Fig. 13 shows the C80 heat flow curves of the charged 20 pristine LNCMO and CP-LNCMO cathode materials with the electrolyte. As we reported previously [33], the maximal heat flow and its corresponding temperature both have very important effect on the thermal stability of LIBs. Herein, the system with the CP-LNCMO has an onset exothermic temperature of 185 °C, 25 higher than that (160 °C) of the system with the pristine LNCMO. Meanwhile, the main exothermic peak of the system with the CP-LNCMO was delayed to 211 °C from 182 °C of the pristine LNCMO. In conclusion, all the C80 results support the viewpoint that  $\text{CePO}_4$  coating has significantly enhanced the thermal 30 stability of the coexisting systems of charged LNCMO cathode and the electrolyte.

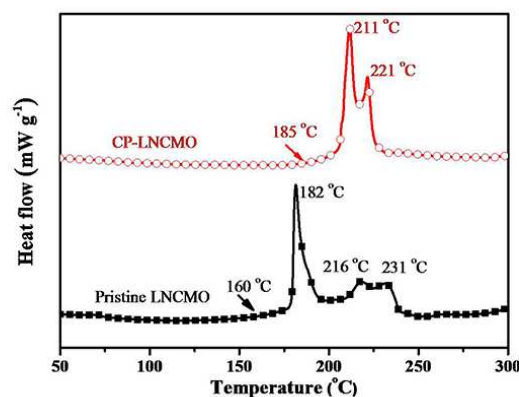


Fig. 13 C80 heat flow curves of coexistence systems of 50 mg electrolyte and 23 mg charged cathode materials (charged to 4.6 35 V) at a heating rate of 0.2 °C min<sup>-1</sup>.

## Conclusions

$\text{CePO}_4$  was uniformly coated on the surface of the Li-rich layered oxide  $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$  particles via a simple 40 precipitation method. The coated  $\text{CePO}_4$  can not only suppress the side reactions between the cathode and the electrolyte, but also increase the  $\text{Li}^+$  migration rate at the interface and improve the thermal stability of the coexisting systems of the charged LNCMO cathode and the electrolyte. As a result, the rate 45 capability, high-temperature and low-temperature performance of

the LNCMO have been significantly improved from CePO<sub>4</sub> coating. The Li-rich layered cathode with uniformly CePO<sub>4</sub> layer coated by a simple and effective method could be a significant breakthrough in the development of advanced LIBs with higher energy, longer cycle life and stronger safety.

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## Notes and references

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