

CaF₂ Coated Li_{1.2}Mn_{0.56}Ni_{0.16}Co_{0.08}O₂ Microspheres with Enhanced Electrochemical Performances as Lithium Ion Battery Cathode

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Surface modification has been one of most effective methods to improve the electrochemical performance of lithium rich layered oxides. In this paper, the Li_{1.2}Mn_{0.56}Ni_{0.16}Co_{0.08}O₂ microspheres are prepared by urea assisted combustion route, and then coated with proper amount of CaF₂. XRD and SEM results show surface modification has not changed the structure of Li_{1.2}Mn_{0.56}Ni_{0.16}Co_{0.08}O₂, and a uniform coating layer can be obtained. As lithium ion battery cathode, the optimal CaF₂ (i.e., 2 wt.%) coated sample presents a high initial discharge capacity of 223 mAh·g⁻¹ with Coulombic efficiency of 80.5 % at 0.1 C, which is much better than that of pristine sample. Also, a high discharge capacity of 119 mAh·g⁻¹ can be obtained for CaF₂ coated sample at 5 C. The improved electrochemical performance may be attributed the formation of fast Li ion conductor on the surface supported by EIS study.

Keywords: Li_{1.2}Mn_{0.56}Ni_{0.16}Co_{0.08}O₂ microspheres, CaF₂ coated, surface modification, Li ion battery.

1. INTRODUCTION

To meet the demand of high-performance lithium ion battery, improvement of cathode materials with high safety, low cost, long cycling life and high energy density have become one of most important topics in the field of lithium ion battery [1, 2]. Among all kinds of candidates, the lithium rich layered oxides (LLOs) have attracted more and more attentions due to their high discharge capacity up to 250 mAh/g or more. However, the high irreversible loss and poor rate capability still hinder their possible commercialization [3–5]. In order to overcome above shortcoming, some methods including doping, surface modification or optimization of chemical composition has been widely developed to improve the electrochemical performance of LLOs [6–8].

Among all modification methods, the surface modification has been regarded as one of most effective methods. In general, the surface modification with fast Li ion conductor (e.g., Li₃PO₄) or electron conductor (e.g., carbon) can elevate the electrochemical conductivity of LLOs [9–11], as well as inhibit the dissolution of electrode materials, which should be important to overcome shortcoming of LLOs. CaF₂, one of common metal fluorides, has been widely used as surface modification for cathode materials, and the electrochemical performances of LiMn₂O₄ or LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ can be greatly improved [12–14]. As one of two components, Ca²⁺ has the ionic radii of 0.102 nm, bigger than the ionic radii of Mn⁴⁺ (i.e., 0.067 nm). Thus, some surface defect can be obtained by effective surface modification, which is useful for the diffusion of Li ion. Also, F⁻ can induce the formation of surface fast Li ion conductor. Therefore, the

CaF₂ should be a suitable surface modification agent^[12–14]. In this paper, the CaF₂ is used as surface modifier for Li_{1.2}Mn_{0.56}Ni_{0.16}Co_{0.08}O₂ microspheres. The structure and electrochemical performance of CaF₂ coated sample is clearly studied, as well as the coating amount.

2. EXPERIMENTAL

Synthesis of Li_{1.2}Mn_{0.56}Ni_{0.16}Co_{0.08}O₂ microspheres: All of reagents are A.R. grade used as received. The Li_{1.2}Mn_{0.56}Ni_{0.16}Co_{0.08}O₂ microspheres are prepared by urea assisted combustion route described as follow [15]: 2.602 g aqueous solution of Mn(NO₃)₂ (50 wt.%, Sinopharm Chem.), 2.196 g CO(NH₂)₂ (Sinopharm Chem.), 1.0114 g LiNO₃ (5 % Li excess, Sinopharm Chem.), 0.2794 Co(NO₃)₂·6H₂O (Sinopharm Chem.) and 0.5584 g Ni(NO₃)₂·6H₂O (Sinopharm Chem.) are dissolved together into 10 ml distilled water to form a uniform solution. Afterwards, the obtained mixed solution was heated in a muffle furnace at 450 °C for 40 minutes in air to remove organic component. Then, the powder is heat treated inside a muffle furnace at 850 °C for 10 h under air atmospheres with heating rate of 5 °C/min. After cooling to room temperature naturally, the Li_{1.2}Mn_{0.56}Ni_{0.16}Co_{0.08}O₂ microspheres can be obtained.

Synthesis of CaF₂ coated Li_{1.2}Mn_{0.56}Ni_{0.16}Co_{0.08}O₂: A certain amount of Li_{1.2}Mn_{0.56}Ni_{0.16}Co_{0.08}O₂ microspheres are added into as-prepared Ca(NO₃)₂ (Sinopharm Chem.) solution. Then, the NH₄F (Sinopharm Chem.) solution (the molar ratio of Ca to F is set as 0.5 based on the chemical formula of CaF₂) is added into above suspension drop by drop under stirring. After complete evaporation of water at the temperature of 80 °C, the obtained powder is annealed at 450 °C for 4 h under a N₂ atmospheres. In previous literatures [13, 14], a coating amount nearby 3wt% may be promising for cathode materials. Thus, various CaF₂ coated amounts are studied and denoted as 2 wt.%, 3 wt.% or

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4 wt.% coated $\text{Li}_{1.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}\text{O}_2$ to obtain an optimal value.

Structure characterization: The crystal phase of bare and CaF_2 coated $\text{Li}_{1.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}\text{O}_2$ are examined by X-ray diffraction (DX-2700 Dandong), within 2θ range from 10 to 80° at a scanning rate of 0.06 degree per second. The morphologies and particle size of samples are observed by scanning electron microscope (SEM, Hitachi S3400N).

Electrochemical properties: CR2016 coin cell are used throughout the electrochemical experiments. The working electrode is fabricated as follows: Active material, polyvinylidene fluoride (PVDF) binder and acetylene black in a ratio of $80:10:10$ together with a certain amount of N-methyl-2 pyrrolidine (NMP) solvent, and then the prepared slurry is pasted on aluminum foil. After drying at 80°C overnight, the decorated aluminum foil were punched into discs with a diameter of 14 mm and used as working electrode. The coin cells are assembled in the Ar-filled glove box. Highly pure lithium foils are used as reference and counter electrode. Celgard 2500 microporous polypropylene membrane is used as separator and Commercial LBC-301 LiPF_6 solution (ShenZhen XinZhouBang) is used as electrolyte. The electrochemical properties are conducted in the NEWARE battery test system within the voltage window of 2.0 – 4.7 V and the current density is fixed as 0.2 C, 0.5 C, 1 C, 2 C and 5 C (1 C = 200 mAh·g $^{-1}$).

3. RESULTS AND DISCUSSION

3.1. Structural study

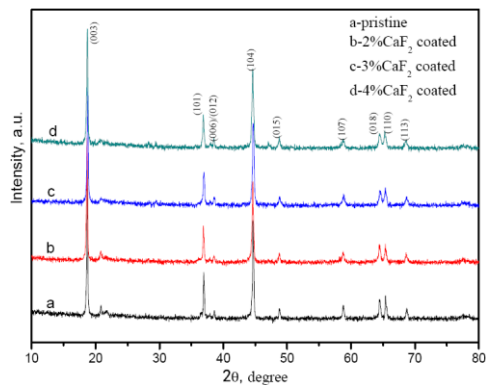


Fig. 1. XRD patterns of pristine and various CaF_2 coated $\text{Li}_{1.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}\text{O}_2$

XRD patterns of pristine and various CaF_2 coated $\text{Li}_{1.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}\text{O}_2$ are revealed in Fig. 1. Each sample is the layered α - NaFeO_2 structure belonging to the space group of R-3m. The peak intensity ratio of (003) to (104) in Fig. 1 a can be calculated as 1.25, bigger than the critical value of 1.20, indicating the pristine sample has low cation mixing [15, 16]. Also, the well splitting of (006)/(012) and (018)/(110) diffraction peaks suggest as-prepared samples possess excellent layered structure. Especially, a weak diffraction nearby 2θ degree of 23° can be observed for each sample, indicating the co-existence of Li_2MnO_3 component in the $\text{Li}_{1.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}\text{O}_2$, which is the key evidence that the formation of lithium rich layered oxides [7–9]. As for the CaF_2 coated sample, the

XRD patterns are consisting with the pristine $\text{Li}_{1.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}\text{O}_2$, suggesting the structure of lithium rich layered oxides can be well kept after a coated and calcination process. The diffraction characteristic of CaF_2 has not been found due to low content or its amorphous structure.

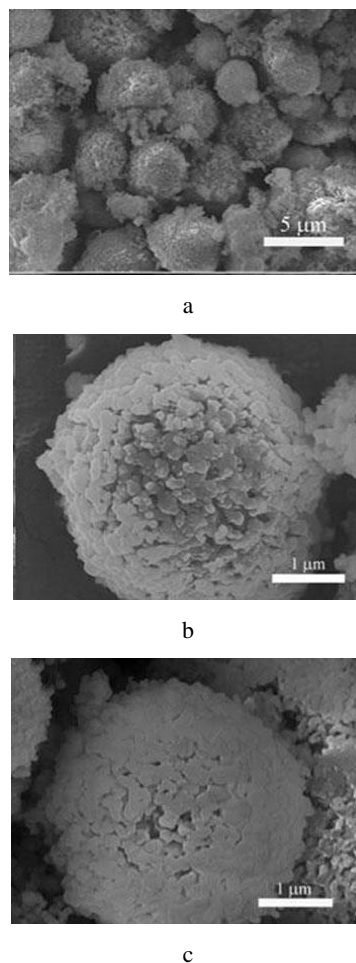


Fig. 2. SEM images of the pristine: a–low magnification; b–high magnification; c–2 wt.% CaF_2 -coated $\text{Li}_{1.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}\text{O}_2$

SEM images of pristine and CaF_2 coated $\text{Li}_{1.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}\text{O}_2$ are revealed in Fig. 2. The pristine sample presents morphology of porous microspheres, and its diameter can come to 1 – 10 μm . In a high magnification view, the porous microspheres are composed of numerous nanoparticles (Fig. 2 b). Generally speaking, the microspheres are suitable as lithium ion battery due to their stable structure upon cycling, and the nanoparticles can provide short lithium ion pathway for charge discharge process [17, 18]. After coated by 2 wt.% CaF_2 , the SEM image is shown in Fig. 2 c. It can be found that the porous nature and the voids among nanoparticles are not obvious in comparison with the pristine sample (Fig. 2 b), which may be attributed to the uniform and effective coating of 2 wt.% CaF_2 , suggesting the formation of coated layer.

3.2. Electrochemical performance

Fig. 3 reveals the initial charge/discharge curves the pristine, 2 wt.%, 3 wt.% and 4 wt.% CaF_2 -coated electrodes within 2.0 – 4.7 V. Each curve presents a typical

electrochemical behavior of lithium rich layered oxide with a voltage plateau of 4.6 V in initial charge [7–9].

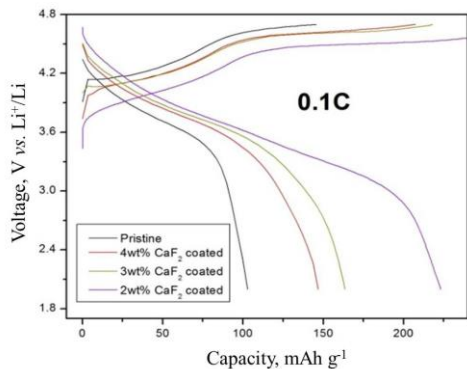


Fig. 3. Initial charge/discharge curves of the pristine, 2 wt.%, 3 wt.% and 4 wt.% CaF_2 -coated electrodes within 2.0–4.7 V at 0.1 C

The charge/discharge capacity of pristine, 2 wt.%, 3 wt.% and 4 wt.% CaF_2 -coated electrode is 145/103, 277/223, 218/163 or 230/157 $\text{mAh}\cdot\text{g}^{-1}$, correspondingly giving an initial Coulombic efficiency of 71.03 %, 80.51 %, 74.77 %, 68.26 %, respectively. Among all samples, the 2 wt.% coated sample shows the highest discharge capacity and Coulombic efficiency. In comparison with the pristine sample, the initial irreversible capacity ratio decreases from $\sim 29\%$ to $\sim 19.5\%$, suggesting the CaF_2 can effectively improve the surface structure of pristine sample upon initial charge discharge process. However, an excessive coating of CaF_2 may be unfavorable to the electrochemical performance due to the inhibit of diffusion of electron and connection with electrolyte [12–14].

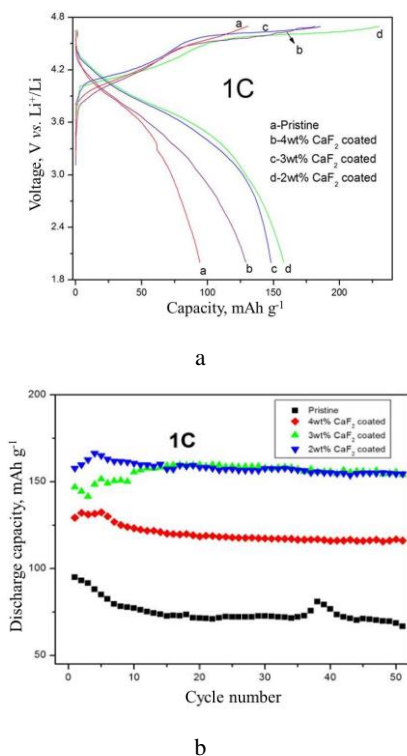


Fig. 4. a–initial charge discharge curves; b–cycle performance of pristine, 2 wt.%, 3 wt.% and 4 wt.% CaF_2 -coated electrodes within 2.0–4.7 V at 1 C

Initial charge discharge curves and cycle performance of various samples at the rate of 1 C are revealed in Fig. 4. An initial discharge capacity of Coulombic efficiency of 2 wt.% coated sample can reach $157.8\text{mAh}\cdot\text{g}^{-1}$ and 78.5 %, much better than three other samples, consisting with the results in Fig. 3. In Fig. 4 b, the 2 wt.% coated sample can retain a discharge capacity of $\sim 151\text{mAh}\cdot\text{g}^{-1}$ after 50 cycles, and the capacity retention above 95 % can be reached. In contrast, the residual discharge or capacity retention of pristine sample is poor, and the improved electrochemical performance of 2 wt.% coated sample may attributed to the porous microspheres, and especially appropriate coated amount [12–18].

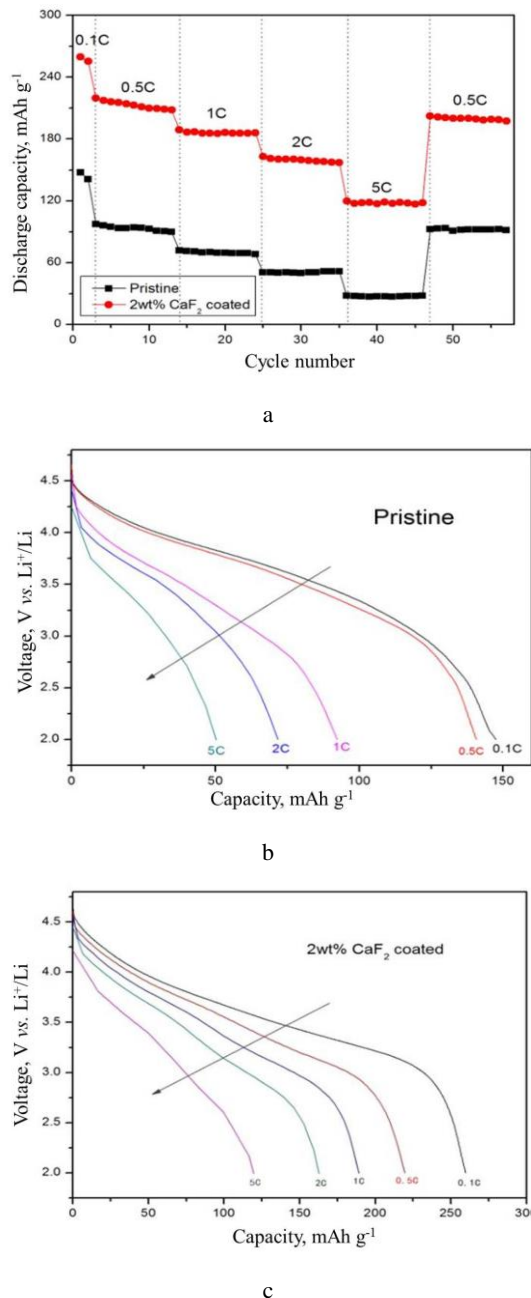


Fig. 5. a–rate capability of the pristine and 2 wt.% CaF_2 -coated electrodes; b–typical pristine discharge profile; c–2wt% CaF_2 -coated sample at different current densities

Rate capability is other important parameter to weigh the electrochemical performance. Fig. 5 a reveals the discharge

capacity of pristine and 2 wt.% CaF₂-coated electrodes at different current densities. Each sample experiences the decrease of discharge capacity with the increased current densities, and the 2 wt.% CaF₂-coated sample has a better rate capability. It delivers a discharge capacity of 259.8, 189.0, 162.9 mAh·g⁻¹ at a current density of 0.1, 1 and 2 C, respectively. Even at a high rate of 5 C, this electrode also keep a stable capacity value of 119.8 mAh·g⁻¹. Interestingly, when the current density goes back to 0.5 C, a stable discharge capacity of 197.7 mAh·g⁻¹ can be recovered. By comparison, the pristine only delivers a discharge capacity of 92.5 and 51.5 mAh·g⁻¹ at rate of 2 C and 5 C. Fig. 5 b and c are the typical discharge profiles of pristine and 2 wt.% CaF₂-coated sample at different current densities. As shown by the arrow, the voltage decay upon increased rate is very obvious for pristine sample. However, this decay can be effectively inhibited by CaF₂-coated sample, suggesting the surface modification can help to improve the electrochemical conductivity. According to above data, the CaF₂ may play a role as fast Li ion conductor, as well as induce the formation of surface Li-Ni-Mn-O spinel structure, which can accelerate the diffusion of Li ion and protect the etch of electrolyte.

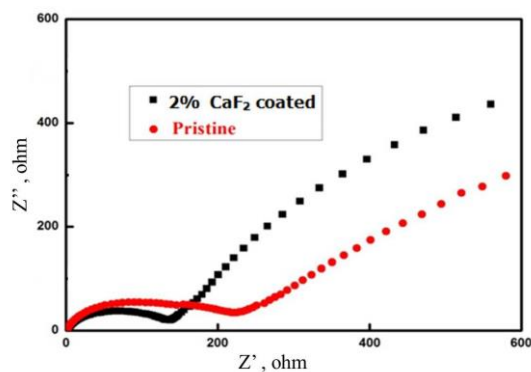


Fig. 6. Electrochemical impedance spectroscopy of pristine and 2 wt.% CaF₂-coated sample after 3 cycles at a discharge state

AC EIS measurement of pristine and 2 wt.% CaF₂-coated sample are studied after 3 cycles, as shown in Fig. 6. Both the Nyquist plots give a high-frequency semicircle and a low-frequency slope line, corresponding to an electrolyte–electrode interfacial resistance of charge transfer (R_{ct}) and a Warburg impedance of lithium diffusion within the electrode [16, 17]. Generally speaking, a smaller radii of high-frequency semicircle means a lower charge transfer resistance, indicating the CaF₂-coated sample should possess a lower resistance in Fig. 6. In previous literatures [12, 14], a metal fluorine-contained compound has been regarded as fast Li ion conductor, and the interfaced CaF₂ may elevate the diffusion rate of Li ion, resulting to an enhanced charge transfer process.

4. CONCLUSIONS

A facile and effective surface coating of CaF₂ has been used to improve the electrochemical performance of Li_{1.2}Mn_{0.56}Ni_{0.16}Co_{0.08}O₂. The coating can't change the structure of pristine sample, but affect the surface microstructure. As cathode material of LIBs, the 2 wt.%

CaF₂-coated sample presents a high discharge capacity (223 mAh·g⁻¹, 0.1 C), good cycling performance (95 %, 50 cycles) and rate capability (119 mAh·g⁻¹, 5 C). The improved performance may be beneficial from effective coating of CaF₂.

Acknowledgments

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