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Mo-doping for improving the ZrF_4 coated-$Li[Li_{0.20}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ as high performance cathode materials in lithium-ion batteries

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ABSTRACT

The different amounts of Mo^{6+} and the 2 wt% ZrF_4 coating layer have been co-modified the $Li[Li_{0.20}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ cathode material via using the carbonate co-precipitation method and wet coating process. And the influences of Mo^{6+} doping and ZrF_4 surface coating on the cathode crystal structure, morphology and electrochemical properties were investigated by X-ray diffraction (XRD), scanning electron microscope (SEM), Transmission Electron Microscope (TEM) and galvanostatic charge–discharge tests. The 2 wt% ZrF_4 coated-$Li[Li_{0.20}Mn_{0.52}Ni_{0.13}Co_{0.13}Mo_{0.02}]O_2$ demonstrated the lower cation mixing and a thickness of 15–35 nm film coated on the surface of cathode particles. Compared with the pristine cathode, the samples after ZrF_4 coating and Mo^{6+} doping exhibited the less irreversible capacity loss, better high rate capability and superior cyclic performance owing to the lower impedance for Li^+ migration across the SEI film and the faster Li^+ migration speed in the cathode bulk. Among all samples, the 2 wt% ZrF_4 coated-$Li[Li_{0.20}Mn_{0.52}Ni_{0.13}Co_{0.13}Mo_{0.02}]O_2$ showed the optimum electrochemical properties, with a high capacity retention of 88.7% after 100 cycles at 55 °C, much higher than that (82.9%) of the pristine cathode. Besides, when the electric current increased to 5C high rate, the pristine $Li[Li_{0.20}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ delivered a discharge capacity of 21.9 mAh g^{-1} lower than that of 2 wt% ZrF_4 coated-$Li[Li_{0.20}Mn_{0.52}Ni_{0.13}Co_{0.13}Mo_{0.02}]O_2$.

1. Introduction

Nowadays, the Lithium-ion batteries (LIB) have been extensively used in energy storage equipment, consumer electronics products, military and other fields owing to the Green & Environmental protection [1–3]. However, with the fast development of New Energy Vehicles, the conventional positive materials, such as $LiCoO_2$ [4], $LiMn_2O_4$ [5], $LiFePO_4$ [6] and $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ [7], cannot satisfy the demand of the high-energy density, which have hindered the popularity of new energy vehicles. Currently, the Li-rich Mn-based positive material $Li[Li_{0.20}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ has attracted much attention by the researchers due to the high specific discharge capacity of 250 mAh g^{-1}, which will be a competitive candidate as cathode materials when applied to the high power output equipment [8,9]. However, the cathodes have suffered from some blocks, such as the large initial irreversible capacity loss, severe capacity degradation at high rate, and unstable structure at high temperature, which has limited the commercial applications [10,11].

To improve the abovementioned problems, considerable effort has been made by the scientists from different countries. Many investigations have indicated that the surface coating modification can effectively protect the cathode from reacting with the electrolyte and restrain the occurrence of side effects [12,13]. And the ion doping modification can stabilize the cathode crystal structure and suppress the layer structural damage [14,15]. For example, the ordinary metal oxides, such as Al_2O_3 [16], ZnO [17], MgO [18], ZrO_2 [19], have been used as coating materials to enhance the electrochemical properties of the Li-rich Mn-based positive material. Among these metal oxides, ZrO_2 delivers the highest fracture toughness, and when it was used as coating material, it can form a fracture-toughened thin film adhered to the cathode particle

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surface for protecting the cathode from reacting with the electrolyte [19]. The metal cations, such as, Mg^{2+} [20], Al^{3+} [21], Zr^{4+} [22], and Mo^{6+} [23,24] have been used as substitute elements to stabilize layered structure and retard the phase transformation during cycling. Thereinto, Mo^{6+} doping modification has attracted extensively studies owing to the remarkable effect. Yuan et al. have synthesized the Mo-doped $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ by a facile and novel organic co-precipitation process, and found that the Mo-doped $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ demonstrated the faster Li^+ migration rate and better thermodynamic properties than those of the un-doped sample [23]. In addition, when Mo^{6+} was doped into the $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ cathode, the $Li[Li_{0.2}Mn_{0.54\text{-}x/3}Ni_{0.13\text{-}x/3}Co_{0.13\text{-}x/3}Mo_x]O_2$ ($x = 0.007$) delivered a high discharge capacity of 181 mAh g^{-1} after 200 cycles at 1 C rate, corresponding to the high capacity retention of 81.8%, while the $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ only retained 144 mAh g^{-1} with a capacity retention of 75.4% [24].

Therefore, based on the above analysis, the surface coating with ZrO_2 and the ion doping with Mo^{6+} have been both adopted to co-modify the $Li[Li_{0.20}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$, which not only protect the cathode from reacting with the electrolyte, but also stabilize the cathode crystal structure during cycling. However the hydrolysis of electrolyte with a trace amount of water in cells will generate the aggressive HF species, where the ordinary metal oxides served as coating materials can not suffer from the erosion effect and finally decomposed [25]. Research has indicated the fluorides demonstrate the high structure stability and potent erosion resistance in the HF environment [26,27]. Therefore, combined with the ZrO_2 characteristic, the ZrF_4 will be a superior candidate to coat on the surface of $Li[Li_{0.20}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$.

In the work, the Mo^{6+} doping and ZrF_4 surface coating have been adopted to co-modify the $Li[Li_{0.20}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ cathode materials. The different amounts of Mo^{6+} have been doped into the $[Mn_{0.54}Ni_{0.13}Co_{0.13}](CO_3)_{0.8}$ via using the carbonate co-precipitation method. And the 2 wt% ZrF_4 has been covered on the surface of $Li[Li_{0.20}Mn_{0.54\text{-}x}Ni_{0.13}Co_{0.13}Mo_x]O_2$ ($x = 0$, 0.01, 0.02, 0.03). The surface morphology, microstructural, and electrochemical properties were investigated deeply to evaluate the influences of the Mo^{6+} doping and ZrF_4 surface coating.

2. Experimental details

2.1. Preparation of samples

The pristine $Li[Li_{0.20}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ powders and the Mo^{6+} doping with ZrF_4 coating co-modified samples were synthesized by the representative co-precipitation and wet coating process, as is shown in Fig. 1. For the preparation of the $[Mn_{0.54\text{-}x}Ni_{0.13}Co_{0.13\text{-}}Mo_x](CO_3)_{0.8}$ ($x = 0$, 0.01, 0.02, 0.03) carbonate precursors, firstly, the stoichiometric amounts of $MnSO_4 \cdot H_2O$, $NiSO_4 \cdot 6H_2O$, $CoSO_4 \cdot 7H_2O$ and $((NH_4)_6Mo_7O_{24} \cdot 4H_2O$ were dissolved in distilled water to form a transparent solution. Then the $NH_3 \cdot H_2O$ (chelating agent) and Na_2CO_3 (precipitant) both with appropriate amount were pumped into the above reactor container under continuous stirring to form the $[Mn_{0.54\text{-}x}Ni_{0.13}Co_{0.13}Mo_x](CO_3)_{0.8}$ ($x = 0$, 0.01, 0.02, 0.03) carbonate precursors, followed by separating and filtrating with deionized water. Finally, the dried $[Mn_{0.54\text{-}x}Ni_{0.13\text{-}}Co_{0.13}Mo_x](CO_3)_{0.8}$ ($x = 0$, 0.01, 0.02, 0.03) powders mixed with an excess 3 wt% amount of $LiOH \cdot H_2O$ powder were pre-heated at 450 °C for 6 h and then calcined at 900 °C for 10 h in tube furnace to get the $Li[Li_{0.20}Mn_{0.54\text{-}x}Ni_{0.13}Co_{0.13}Mo_x]O_2$ ($x = 0$, 0.01, 0.02, 0.03) samples.

To obtain the 2 wt% ZrF_4 coated-$Li[Li_{0.20}Mn_{0.54\text{-}x}Ni_{0.13}Co_{0.13}Mo_x]O_2$ ($x = 0$, 0.01, 0.02, 0.03) samples, the typical wet coating process was adopted as follows: (1) the quantitative $Zr(NO_3)_4$ and NH_4F with the corresponding molar ratio of 1:4 were dissolved in the deionized water; (2) the appropriate amount of $Li[Li_{0.20}Mn_{0.54\text{-}x}Ni_{0.13}Co_{0.13}Mo_x]O_2$ ($x = 0$, 0.01, 0.02, 0.03) powders were immersed into the above mixed solution, followed by continuous stirring under the 85 °C water bath; (3) the obtained dried cathode materials were sintered at 450 °C for 6 h in air to form the 2 wt% ZrF_4 coated-$Li[Li_{0.20}Mn_{0.54\text{-}x}Ni_{0.13}Co_{0.13}Mo_x]O_2$ ($x = 0$, 0.01, 0.02, 0.03).

2.2. Material characterizations

The relative contents of Mn, Ni, Co, and Mo in the prepared $[Mn_{0.54\text{-}x}Ni_{0.13}Co_{0.13}Mo_x](CO_3)_{0.8}$ ($x = 0$, 0.01, 0.02, 0.03) carbonate precursors was determined by ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometer, iCAP 6000). Prior to ICP-OES

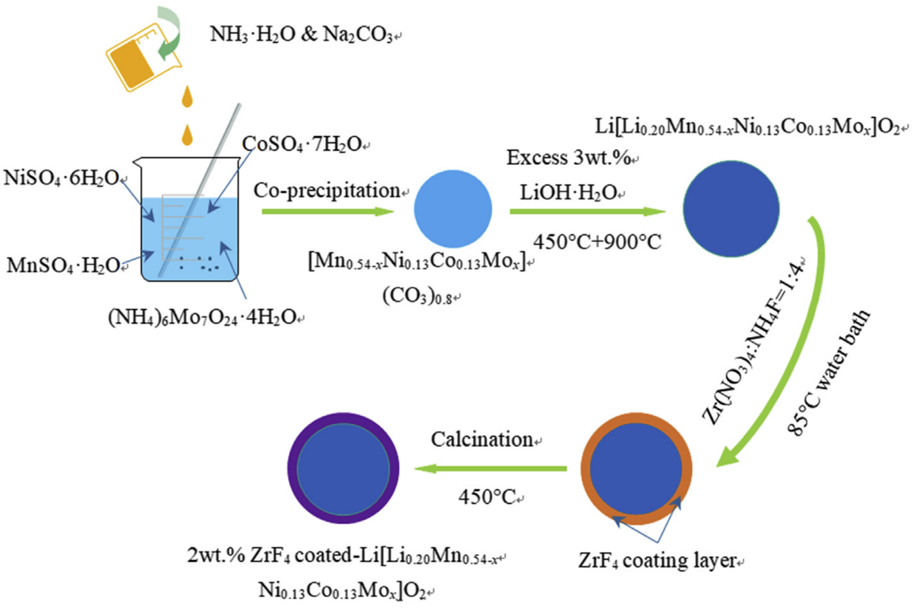

Fig. 1. The schematic presentation of the synthesis procedure.