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$LiMnPO_4$ surface coating on $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ by a simple sol-gel method and improving electrochemical properties

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ABSTRACT

Recently, cathode materials based on $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ are being widely investigated for application in lithium ion batteries (LIB). However, the cycle performance of this material needs to be enhanced. The surface coating modification is a feasible option to further improve the electrochemical properties of the material. In this paper, a simple sol-gel method was used to prepare a $LiMnPO_4$ (LMP) coating with a thickness of about 25 nm on the surface of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (denoted as NCM523-LMP). As a cathode material for lithium ion batteries, NCM523 coated with 3 wt% LMP showed good cycle performance as well as improved thermal stability. The coated sample exhibited improved cycle stability (200 cycles, 136.8 mAh g^{-1}) and high temperature cycle performance (55 °C, 200 cycles, and 125.2 mAh g^{-1}). This significant enhancement can be attributed to the strengthening of surface structure and effective isolation from harmful side reactions between the material and electrolyte. The LMP coating modified NCM523 shows potential as a high-performance cathode material for LIB.

1. Introduction

With the increasing demand for electric vehicles, hybrid electric vehicles and large capacity energy storage devices, it is necessary to develop lithium-ion batteries (LIB) with high energy and high power densities [1–7]. The commercial lithium-ion battery materials on the market, such as the layered oxides $LiCoO_2$ [8] and $LiNiO_2$ [9], have poor electrochemical stability in their highly oxidized states [10], which limits their widespread applications. Among the new generation electrode materials, three-component layered $LiNi_{1-x-y}Co_xMn_yO_2$, especially $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (NCM523) [11–13] has become one of the most promising cathode materials for Li-ion batteries because of its advantages such as source abundance, easy preparation, environmental friendliness and high capacity [1, 14]. However, these materials are susceptible to structure deterioration and side reactions between the material and electrolyte [15, 16]. Therefore, there would be rapid decay of capacity and poor stability when NCM523 is cycled at high rate or high temperature [17, 18].

In literature, much effort has been devoted to improve the electrochemical properties of NCM523 materials. Modifying the surface of cathode materials with suitable materials (MgO [19], TiO_2 [20], C [21],etc.) is an efficient method to improve their electrochemical properties. One approach is coating NCM523 materials with different metal oxides. Chen et al. [22] reported that TiO_2 coating could protect the cathode material from the electrolyte and improve the surface structure of the material. Likewise, AlF_3 coating was investigated for the suppression of oxygen release from the active material. Myung et al. [23] reported that an AlF_3 surface coating played a significant role in depressing the HF concentration in the electrolyte solution and thus improved the electrochemical performance and thermal stability. In addition, NCM523 materials coated with Li^+ conducting Li_2TiO_3 layer showed an enhanced reversible capacity of 200 mAh g^{-1} at 1C [24]. However, it still remains a challenge to apply these materials for high-temperature batteries. Currently, the phospho-olivines $LiMnPO_4$ (LMP) [25–27] with an open three-dimensional frame network are deemed as attractive cathode materials, because of their strong P-O covalent bonds [28] as well as high structural stability, low toxicity, low cost, and excellent thermal stability [29]. However, the intrinsic high ionic and electronic resistance of these materials restrict their activity [30]. There are few literature reports on the use of $LiMnPO_4$ as a coating material to obtain a new material with superior performance in kinetics, energetics, and stability.

In this work, we have investigated the design and synthesis of NCM523-LMP material to combine the advantages of both layered structure and phosphate group. It is expected that this material would have both the thermal stability of the phosphate structure and high Li^+ storage capacity of the layered structure. Due to the low electronic and ionic conductivity of LMP, the coating should be as thin as possible.

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Therefore, a simple sol-gel method was used for the coating process and LMP coatings with mass fractions of 1 wt%, 3 wt% and 5 wt% were coated on the pristine NCM523 surface, respectively. The electrochemical performances of the LMP coated NCM523 samples were investigated. As expected, the capacity retention was enhanced significantly because of the stabilization of the interface between cathode and electrolyte. Since the safety issue is emerging as a serious concern regarding the cathode materials for Li-ion batteries, we also investigated the effect of LMP-coating on the cycling stability of NCM523 at high temperature (55 °C).

2. Experimental

2.1. Preparation of the materials

$Ni_{0.5}Co_{0.2}Mn_{0.3}O_2(OH)_2$ synthesized by co-precipitation was used as the precursor in this experiment. $Ni_{0.5}Co_{0.2}Mn_{0.3}O_2(OH)_2$ was first mixed with 105% (stoichiometry) of $LiOH{\cdot}H_2O$, and then calcined in air at 480 °C for 6 h and then further calcined at 900 °C for 12 h to produce pristine NCM523.

LMP with different mass fractions (1 wt%, 3 wt%, and 5 wt%) was coated on the surface of NCM523 via sol-gel method. The main starting materials including lithium acetate dihydrate $CH_3COOLi{\cdot}2H_2O$, manganese acetate tetrahydrate $Mn(CH3COO)_2{\cdot}4H_2O$ and ammonium dihydrogen phosphate $NH_4H_2PO_4$ were dissolved in an appropriate amount of distilled water at room temperature. Then, a certain amount of citric acid monohydrate was added as a chelating agent to form a sol gradually. The prepared NCM523 was dispersed in a sol with stirring and heated in an oil bath at 80 °C to rapidly evaporate the solution. As a result, a gel containing metal ions (Mn^{2+} and Li^+) trapped by citric ions and $PO_4{}^{3-}$ ions was deposited on the surface of the NCM particles. After completion of the reaction, the product was ground and heated in air at 400 °C for 4 h (heating rate 5 °C min^{-1}) to obtain the coated samples (denoted as NCM-LMP 1 wt%, 3 wt%, and 5 wt%). For comparison, the pristine NCM523 was also sintered with the same heat treatment procedure.

2.2. Material characterization

The crystal structure of NCM and NCM-LMP was characterized by X-ray diffraction (XRD, Bruker AXS D2 PHASER) under Cu-Kα radiation in the 2θ range of 10°–80°. The microstructures and morphology of the samples were analyzed by scanning electron microscopy (SEM, Phenom ProX) and transmission electron microscopy (TEM, Tecnai G2 F30, S-TWIN). The elemental distribution was characterized by energy dispersive X-ray spectroscopy (EDS). Raman spectra for samples were recorded using a Raman spectrometer (Raman, Thermo Fisher DXRxi) with a 532.00 nm laser as the excitation source.

2.3. Electrochemical characterization

The electrochemical performance of a CR2025 type half-cell consisting of lithium metal as anode and active material as cathode was measured. The preparation procedure for the cathode material is as follows. First, the active material powder, polyvinylidene fluoride (PVDF) and Ketjen Black, were mixed in the weight ratio of 8:1:1, and then an appropriate amount of N-methyl-2-pyrrolidine (NMP) was added as the dispersant. The prepared viscous liquid was uniformly coated on the surface of an aluminum foil. After drying at 80 °C for 6 h, the aluminum foil was punched into a 10-mm diameter wafer. The content of each piece of aluminum foil on the active material was 2.4–3.5 $mg{\cdot}cm^{-2}$. Finally, the sample was dried for 12 h under vacuum at 120 °C. The dry electrode was used as the working electrode, and the battery was assembled in the Ar glove box. The charge–discharge cycle test was carried out on a LAND CT-2001A system at constant temperature. The battery was cycled at a constant current charge/discharge test of 2.8–4.4 V versus Li^+/Li on a LAND. The electrochemical impedance spectroscopy (EIS) was performed on a biological electrochemical workstation (Bio Logic VSP-300). The EIS measurement was carried out in a fully charged state in the frequency range of 100 kHz to 0.1 Hz with an amplitude voltage of 5 mV.

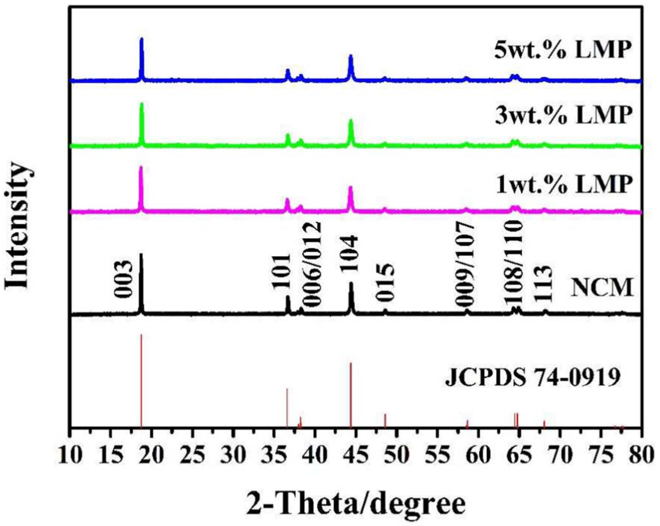

Fig. 1. XRD patterns of pristine NCM523 and NCM-LMP (1 wt%, 3 wt% and 5 wt%) samples.

3. Results and discussion

3.1. Crystal structure and particle morphology

Fig. 1 shows the XRD patterns of pristine NCM523 [31] and NCM-LMP (1 wt%, 3 wt% and 5 wt%) powders. All the diffraction peaks of the prepared pristine NCM523 powder matched exactly with the layered alpha-$NaFeO_2$ structure with space group $R\bar{3}m$ (JCPDS no. 74-0919). Moreover, the diffraction peaks (006 and 102) and (108 and 110) were distinctly split, which is characteristic of ordered layered hexagonal structure. All diffraction peaks of the three LMP coated samples were almost identical to those of the pristine NCM523 sample. This indicates that the coating modification of LMP has no significant effect on the crystal structure of NCM523. Also, due to the low content of LMP ($\leq$5 wt%), the diffraction characteristic peaks of the olivine phosphate structure were not observed in the XRD patterns of the coated samples. XRD results show that there is only strong interface interaction between the pristine NCM pure phase and the coated LMP, and no new compounds are generated. Therefore, the pristine host structure is not altered.

Fig. 2 shows the SEM images of the pristine NCM523 sample and LMP coated modified sample. It shows that both samples have secondary spherical particles with a diameter of about 10 μm, which consist of a number of primary particles of size 0.2–0.5 μm. The tiny primary particles are favorable for the diffusion of lithium ions. The surface of the pristine NCM523 sample is relatively smooth and clean. SEM image of the non-calcined LMP-coated sample is shown in the Fig. 2b, which indicates that many nanoparticles are distributed on the surface of the sphere. In addition to a slight increment in roughness, these nanoparticles did not change the morphology of primary particles. This indicates that there are many LMP nanoparticles attached to the NCM523 surface, and no agglomeration occurs. Furthermore, Fig. 2c shows the SEM image of the calcined LMP-coated sample. After the sample was sintered, the surface roughness decreased obviously, and the coating was denser and complete, without pores, and the structural stability was improved. The surface element distribution of the LMP coated sample is revealed by the mapping diagram in Fig. 3. It