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Enhanced electrochemical performance of Lithium Metasilicate-coated $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ Ni-rich cathode for Li-ion batteries at high cutoff voltage

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A B S T R A C T

Li_2SiO_3-coated $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ cathode material has been synthesized and exhibit much better electrochemical performance than pristine $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ at cut-off voltage 4.6 V. The as-prepared samples are characterized by X-ray diffraction, field emission scanning electron microscopy, field emission transmission electron microscope, and X-ray photoelectron spectroscopic. The results show that the coating-layer Li_2SiO_3 is not incorporated into the $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ host structure and coated well on the surface of the active material. The sample coated with 3 mol. % Li_2SiO_3 delivers a capacity of 168 mAh g^{-1} at 0.2 C after 100 cycles, and remains 85.5% of the first discharge capacity. The capacity retention at 1 C is 73.6% after 100 cycles and the first discharge capacity reaches 158 mAh g^{-1} at 10 C. This superior performance is attributed to the coating layer which restrains the side reactions at electrode/electrolyte interface and enhances structure stability, meanwhile, it can decrease the electrode polarization because it is an excellent Li^+-ion conductor.

1. Introduction

Currently, lithium-ion batteries (LIBs) have been used in both electric vehicles (EVs) and grid energy storage systems because their high voltage and energy density [1–4]. However, with the rapid development of EVs, higher requirements for the LIBs energy density are brought forward. Therefore, developing the high performance cathode material is critical.

As a promising Ni-rich layered cathode material, $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NCM622) shows comparatively better comprehensive electrochemical properties [5–7]. To gain higher specific capacity, increasing the operation voltage is an effective way [8,9]. Unfortunately, the fade of structural, cycle and thermal stability are inevitably accompanied by the high-voltage operation (>4.3 V) [9–13]. The problem is the surface irreversible structural degradation due to the dissolution of transition metal ions and the reaction between the cathode material and the electrolyte, leading to the increase of the interfacial impedence and the worse of interfacial stability [14,15].

Surface modification is a very simple and effective method to solve those problems by avoiding the reaction between the cathode material and the electrolyte. The coating materials such as Al_2O_3 [16], AlF_3 [17], MgO [18], TiO_2 [19] and ZrO_2 [20,21] have been reported in the surface modification. However, most of these coating materials are insulators for Li^+ conduction. So a fast ionic conductor for Li^+ as coating material has important implications. Li_2SiO_3 is such a kind of excellent coating material with 2.5×10^{-8} S cm^{-1} [22], which has a three-dimensional path for Li^+-ion diffusion through the (010) and (001) planes [23]. As far as we know, there are no reports about the effect of the Li_2SiO_3 coating on the $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ layered cathode material yet.

In this paper, the surface of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ cathode material was coated by a fast ionic conductor of Li_2SiO_3 via a

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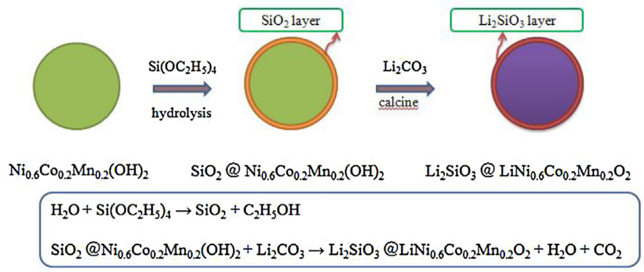

Fig. 1. Schematic illustration of the preparation process and reaction equation for Li_2SiO_3@$LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$.

hydrolyzation method. By the simple method, the cathode material with the coating Li_2SiO_3 can be obtained by one step calcination. The surface modification of the $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ cathode material with the Li_2SiO_3 was demonstrated to be effect in improving its cycling stability and high rate performance, especially in the high cutoff voltage (4.6 V).

2. Experimental section

The Li_2SiO_3-coated $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ material was prepared by means of a combination of hydrothermal method and subsequent calcination. A schematic illustration of the synthesis is shown in Fig. 1. Firstly, the SiO_2-coated $Ni_{0.6}Co_{0.2}Mn_{0.2}(OH)_2$ precursor was prepared by hydrolysis method. The precalculated Si $(OC_2H_5)_4$ was dissolved in a mixed solution of ethanol and water with a volume ratio of 50: 1. Then, the pristine $Ni_{0.6}Co_{0.2}Mn_{0.2}$ $(OH)_2$ precursor (HEC Institute) power was added to the mixed solution. After that, the mixture was stirred at 30 °C for 5 h and continuously stirred at 50 °C to vaporize the solvent completely to gain the product of SiO_2@$Ni_{0.6}Co_{0.2}Mn_{0.2}$ $(OH)_2$. Finally, the SiO_2-coated $Ni_{0.6}Co_{0.2}Mn_{0.2}(OH)_2$ (SiO_2@$Ni_{0.6}Co_{0.2}Mn_{0.2}$ $(OH)_2$) was grinded with stoichiometric amounts of Li_2CO_3 following the equation: $nLi_2CO_3 = 1.05*[n(Ni+Co+Mn)+2n(Si)]/2$, then calcinated at 450 °C for 4 h, and 850 °C for 12 h in air with a 5 °C min-1 heating rate. The amounts of the coated Li_2SiO_3 were 0.0, 1.0, 3.0, and 5.0 mol.% of the $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ powders, marked as LS0, LS1, LS3, LS5, respectively. The pure Li_2SiO_3 material was prepared referring to the process above except the $Ni_{0.6}Co_{0.2}Mn_{0.2}$ $(OH)_2$ precursor.

The XRD patterns of the as prepared materials were measured using a Rigaku Ultima IV-185 (Japan) with Cu Ka radiation source from 10° to 80° at a scanning rate of 1° min^{-1}. The surface morphologies of the materials were observed using a field emission scanning electron microscopy (FESEM, FEI QUANTA250, USA), equipped with energy X-ray (EDX) analysis, and a field emission transmission electron microscope (FE-TEM, JEM 2010). The X-ray photoelectron spectroscopic (XPS) measurement was performed on an ESCALAB spectrometer (VG scientific) using a monochromic Al Ka light source. The obtained spectra were analyzed using XPSPEAK software.

The electrochemical properties of the material were tested using CR2025 coin-type cell. The positive electrode was fabricated by pasting N-methyl-2-pyrrolidone (NMP)-based slurry consisted of 80 wt.% of active material, 10 wt.% of Super P conductive carbon black and 10 wt.% of polyvinylidene difluoride (PVDF) binder on an aluminum foil followed by drying at 110 °C for 24 h in a vacuum oven. Then, the dried electrode was pressed with 10 MPa pressure and cut into a disk with a diameter of 11 mm, each disk is approximately 3.5 mg. The cells were assembled in a glove box filled with pure argon, consisting of the as-prepared electrode, a lithium metal anode, the electrolyte of 1 mol L^{-1} $LiPF_6$/EC-DMC (1:1 by volume) and the separator of Celgard 2400 microporous film. The charge/discharge tests of cells were galvanostatically performed on LAND system (Wuhan, China) within various cut-off voltages at 30 °C at different rates, where 1C was defined as 180 mA g^{-1}. The electrochemical impedance spectroscopy (EIS) tests were conducted on a CHI 660D electrochemical workstation with 5 mV perturbation over a frequency range from 0.1 Hz to 0.1 MHz. The electrode were disassembled from the cycled cells (0.2C after 100 times), and wished with pure DMC prior to XPS measurement.

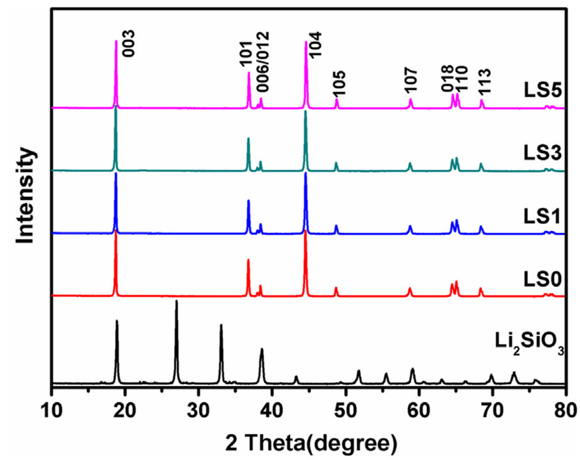

Fig. 2. XRD patterns of coating material of Li_2SiO_3 and Li_2SiO_3-coated $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$: LS0, LS1, LS3, LS5.

3. Results and discussion

The $Ni_{0.6}Co_{0.2}Mn_{0.2}$ $(OH)_2$ precursor is well coated by SiO_2, as analyzed in Fig. S1, which is contributed to the subsequent preparation of Li_2SiO_3@$LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ cathode material.

The XRD patterns of the bare, Li_2SiO_3-coated $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ and the as-prepared Li_2SiO_3 are shown in Fig. 2. The diffraction peaks of bare and Li_2SiO_3-coated samples can be indexed to a hexagonal α-$NaFeO_2$ layered structure (space group R3m) without obvious impurity phases and secondary phase. The obvious splitting of (006)/(012) and (018)/(110) peaks for the samples demonstrates that a well-defined layered structure of the NCM material [11,24]. The positions of diffraction peaks and the intensity characteristics of the as-prepared Li_2SiO_3 are very close to the orthorhombic structure of Li_2SiO_3 compound (JCPDS card 29-0829) [25,26], which indicates Li_2SiO_3 is synthesized by the calcination. Further, no peaks of Li_2SiO_3 can be found in the patterns of the coated samples, which may be due to the small amount of Li_2SiO_3 coating [19]. Despite a small amount of Li_2SiO_3, it might exist in the coated samples. To identify whether the Li_2SiO_3 affects the crystal structure of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$, the lattice parameters of related samples were calculated, as listed in Table 1. Obviously, the lattice parameters of the Li_2SiO_3-coated samples do not change. It is speculated that the Li_2SiO_3 is not incorporated into the $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ host structure.

The cycling performance and the initial charge/discharge curves of the samples are tested at 0.2C (36 mA g^{-1}) between

Table 1
The Lattice parameters of XRD data for the coated samples.

Samples	a/Å	c/Å	c/a	I_{003}/I_{104}
LS0	2.8650	14.2051	4.958	1.004
LS1	2.8634	14.2030	4.960	1.013
LS3	2.8636	14.2073	4.961	1.035
LS5	2.8603	14.1846	4.959	1.006