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Electrochemical performance of Li-rich $Li[Li_{0.2}Mn_{0.56}Ni_{0.17}Co_{0.07}]O_2$ cathode stabilized by metastable Li_2SiO_3 surface modification for advanced Li-ion batteries

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ABSTRACT

With the desirable energy densities, Li-rich layered cathodes have attracted great attention as potential candidates for next generation Li-ion batteries (LIBs). In this context, the Li-rich layered cathode $Li[Li_{0.2}Mn_{0.56}Ni_{0.17}Co_{0.07}]O_2$ (LMNCO) is prepared and surface modified homogeneously with Li-conductive Li_2SiO_3 layer via a facile co-precipitation process. It is found that the 3 wt% Li_2SiO_3 modified Li-rich cathode delivers a specific capacity as high as 207 mAh g^{-1} after 50 cycles, which results from the interplay among the electrode, Li_2SiO_3 coating layer and the electrolyte. Further analysis indicates that the Li_2SiO_3 layer could effectively balance the exfoliation of surface alkaline speciation and the dissolution of surface transition metal to generate the Li–Mn–Ni–Co–Si–O protection layer, which will beneficial to the Li surface diffusion kinetics and the electrochemical stability of Li-rich layered materials as well.

1. Introduction

Li-ion batteries (LIBs) have been widely applied in various portable electronic devices and large-scale energy storage as one of the most promising energy storage technologies [1,2]. In recent years, development of LIBs with high energy density, low cost and safety has drawn great attention worldwide. Although the popular layered $LiCoO_2$, spinel $LiMn_2O_4$, and olivine $LiFePO_4$ materials have been already investigated as promising cathode candidates [3–6], the low energy density of these available cathodes demonstrates the unsatisfied electrochemical performance as power sources for next-generation battery technologies. Therefore, developing better electrode materials with higher energy densities seems to be the focus of present battery research [7]. In this regard, the Li-rich layer structured materials, referring to the composites of Li_2MnO_3 ($C2/m$) and $LiMO_2$ ($R\bar{3}m$) (M = Mn, Co, Ni, or combinations) have been considered as one type of attractive candidates upon their high energy density. It is reported that the Li_2MnO_3 component in the composite plays a role in stabilizing the electrode structure, which accounts for the increased charge capacity at high voltages between 4.4 and 4.6 V (versus Li/Li^+) [8–10]. While to date, several drawbacks are still needed to be solved, *viz.* the low initial coulombic efficiency, poor rate capability and capacity retention for LIBs.

In the past few decades, numerous effective strategies have been advertised, *e.g.* surface modification, cation/anion doping and hierarchical electrode structure to overcome the disadvantages as aforementioned in Li-rich layered cathodes. Many materials, such as the nitrogen-doped carbon, metal oxides, metal fluorides and metal phosphates have been proposed so far as effective surface coating intermediates to stabilize the electrode/electrolyte interfaces and thus ameliorate the electrochemical performance [8,11–13]. As a matter of fact, most of the present surface modification materials have rather poor ionic conductivity that does no good on the Li ion surface diffusion kinetics. While recently, the Li-ion conductors, which could allow the fast Li^+ diffusion during the charge/discharge, such as Li_2ZrO_3 [14–16], $LiAlO_2$ [17], Li_2SiO_3 [18–20], have been employed as coating layers to enhance the

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electrochemical performance for Li-rich cathode materials. Among them, the Li_2SiO_3 shows not only the similar crystal structure to well match the Li-rich electrode, but also the pathway with low energy barriers for the Li^+ diffusion [21]. Therefore, the Li_2SiO_3 is potentially regarded as an ideal coating material for Li-rich material [19].

In this work, a systematical investigation on the interactions between the coated Li_2SiO_3 and the $Li[Li_{0.2}Mn_{0.56}Ni_{0.17}Co_{0.07}]O_2$ (LMNCO) electrode was conducted to reveal the underlying mechanism for the good electrochemical performance. As a feature of this work, it is found that the superior electrochemical performance could be essentially ascribed to the introduced Li−Mn−Ni−Co−Si−O surface solid solution region after the Li_2SiO_3 coating, which facilitates the surface kinetics behavior of LMNCO electrode.

2. Experimental section

2.1. Synthesis of the pristine LMNCO

LMNCO sample was synthesized by a regular sol-gel method. Stoichiometric ratio of $CH_3COOLi\cdot 2H_2O$, $Mn(CH_3COO)_2\cdot 4H_2O$, $Co(CH_3COO)_2\cdot 4H_2O$, and $Ni(CH_3COO)_2\cdot 4H_2O$ precursors were separately dissolved in ethyl alcohol (C_2H_6O). With vigorous stirring, the acquired solutions were mixed with the citric acid solution ($C_6H_8O_7$) in a certain molar ratio (metal cations: $C_6H_8O_7 = 2:3$). The obtained solution was evaporated at 80 °C until the formation of the sol sample. Then it is transferred into a crucible and dried for 12 h to acquire the corresponding gel. Next, the gel sample was ground and preheated at 450 °C for 10 h in a chamber furnace to remove organic contents. Finally, the precursor was collected and ground carefully before it was further calcined at 900 °C for 12 h to obtain the pristine material.

2.2. The Li_2SiO_3 coating

To prepare the Li_2SiO_3-coated LMNCO samples, first the tetraethyl orthosilicate ($(C_2H_5O)_4Si$) was dissolved in the distilled water with continuous stirring. Then the as-prepared LMNCO power was dispersed in the solution. Next, the $LiOH\cdot H_2O$ solution was slowly added into the mixture with vigorous stirring, which was dried afterwards at 100 °C for 10 h. The molar ratio of Li to Si was adjusted to be 2:1 and the amounts of Li_2SiO_3 in the solution varied from 2 wt% , 3 wt% and 4 wt%. Finally, the dried powers were calcined at 500 °C for 6 h at a rate of 5 °C min^{-1} to obtain the target materials.

2.3. Physical characterizations

The X-ray diffraction (XRD) patterns were collected on the Bruker D8 Advance diffractometer (Bruker, Germany) with slit size of 0.6 mm and Cu Kα radiation of $\lambda \sim 0.15418$ nm between 10° and 80° (2θ) at a scanning rate of 0.03° s^{-1}. Surface morphologies of the materials were observed using a field emission scanning electron microscope (FE-SEM, JEOL 7001F) equipped with electron dispersive spectroscopy (EDS) to determine the element compositions. The high-resolution transmission electron microscopy (HRTEM) was used to investigate the microstructure of the as prepared materials on the FEI Tecnai F20 equipment. The inductively coupled plasma (ICP) analysis was performed on the Perkin Elmer Optima 2100DV. The X-ray photoelectron spectroscopy (XPS) was performed on the Thermo Electron Corporation spectrometer with an Al Kα (1486.6 eV) radiation. Differential scanning calorimetry (DSC) analysis was carried out on the TA Q600 by sealing the charged cathode (4.8 V at galvanostatic 0.1 C) in an Al crucible in dry Ar and heated from room temperature to 400 °C at a rate of 5 °C min^{-1}. The Raman spectra were collected on a laser Raman spectrometer (Renishaw RM-1000) with 633 nm He−Ne laser. Fourier transformed infrared (FTIR) measurements were performed on the Nicolet AVATAR360 Fourier-transformed infrared spectrometer. The cycled cells were disassembled carefully in glove box and the electrodes were washed with dimethyl carbonate (DMC) solution.

2.4. Electrochemical measurements

The working electrodes were fabricated by mixing active materials, acetylene black and binder (PVDF dissolved in N-methyl-2-pyrrolidone (NMP)) with mass ratio of 8:1:1 to form a homogeneous slurry, which was then spread onto an aluminum foil and dried in a vacuum oven at 120 °C for 12 h. The dried electrodes were cut into sheets (8 mm × 8 mm). Then the cells were assembled in an argon-filled glove box with lithium foil as counter electrode and porous polypropylene film (Celgard 2400) as separator. The electrolyte was 1 **M** $LiPF_6$ in a mixture of ethylene carbonate/diethyl carbonate (EC/DMC) with volume ratio of 1:1. The galvanostatic cycling of the cells was performed on the NEWARE program-controlled test system (Shenzhen, CT-2001A, China) between 2.0 and 4.8 V (vs. Li/Li^+) with a current density of 0.1 C ($1\,C = 378\,mA\,g^{-1}$) at room temperature. The electrochemical impedance spectroscopy (EIS) investigations were performed on an electrochemical workstation (CHI660D, Shanghai Chenhua) with three-electrode system over a frequency range from 100 kHz to 5 mHz in the charged state of 4.8 V after aging for two days.

2.5. Material soaking experiments

The electrode materials are thoroughly dried before being soaked into the polytetrafluoroethylene (PTFE) containers to avoid any possible contaminations from the adsorbed water. To verify the influence of Li_2SiO_3 coating layer, the pristine LMNCO, the Li_2SiO_3 modified LMNCO samples are added to 50 ml electrolyte in tetrafluoroethylene containers, respectively. Then they were carefully sealed with magnetic stirring at 50 °C for aging. In a typical experiment, 0.1 g pristine LMNCO material and 20 wt% Li_2SiO_3-coated LMNCO (such a high ratio of Li_2SiO_3 is helpful to characterize the interplay between the Li_2SiO_3 and LMNCO sample) were added into 50 mL electrolyte (1 **M** $LiPF_6$ in EC:DMC solution with volume ratio of 1:1) in two separate PTFE containers with continuous stirring. After 1, 2, 3 and 4 weeks, the mixed solutions were taken out for characterizations. The electrochemical titration test was carried out at 0 °C to suppress the decomposition of $LiPF_6$ in water. Two drops of bromthymol blue was added into the mixture as an indicator. Then NaOH solution (0.01 **M**) was added into the electrolyte dropwise. The titration stopped when the color of the electrolyte converted from yellow to blue. The content of the consumed NaOH and the weight of the tested electrolyte were carefully recorded. The acidity (supposed to be HF) of the electrolyte can be calculated as $\text{Acidity} = V_{(NaOH)} \times C_{(NaOH)} \times M_{(HF)} \times 10^6/$ Weight (electrolyte) (*ppm*).

3. Results and discussion

3.1. Structural characterizations

The Rietveld refinement on the X-ray diffraction patterns of the pristine and Li_2SiO_3-coated LMNCO samples is performed carefully as shown in Fig. 1a and Figures S1a1-a3. All the main diffraction peaks could be indexed unambiguously into the hexagonal α-$NaFeO_2$ type structure with the space group of $R\overline{3}m$ [22]. The peak pairs of (006)/(012) and (018)/(110) around 38° and 65° could be easily discernible in all the samples, implying the well-developed