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High-voltage electrochemical performance of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode materials via Al concentration gradient modification

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ABSTRACT

Al_2O_3-modified $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode material is successfully synthesized via a facile carboxymethyl cellulose (CMC)-assisted wet method followed by a high-temperature calcination process. Al concentration gradient doping and accompanying formation of Al-coating are simultaneously accomplished in the modified samples. XRD and EDS analysis demonstrate that Al element is successfully doped into the crystal lattice with concentration gradient distribution inside the particles, reducing the Li/Ni cation mixing and stabilizing the layered structure. The compact distribution of Al on the surface forms a protective layer between the electrodes and the electrolyte, prohibiting the harmful side reactions and phase transition on the interphase. Compared with the pristine, the modified material with 2000 ppm Al_2O_3 (Al-2000) shows the best high-voltage performance with the capacity retention increased by ~13.3% from 138.3 to 163.0 mAh g^{-1} at 1 C in 3.0–4.6 V after 100 cycles. Even under the high current rate of 8 C (1240 mAh g^{-1}) after 200 cycles, the Al-2000 still exhibits a capacity retention of 88.6%, greater than 80.3% for the pristine. Furthermore, results from the cyclic voltammetry (CV) and the electrochemical impedance spectroscopy (EIS) measurements confirm the roles of the Al_2O_3 modification in decreasing polarization and electrochemical resistances, contributing to the kinetic process of electrodes.

1. Introduction

Since its commercial use as cathodes in Lithium ion batteries (LIBs) by Sony in 1990s, $LiCoO_2$ is widely applied in the mobile phone, laptop, cameras and other portable electronic equipment [1–4]. However, there are several shortcomings of $LiCoO_2$ including high cost, safety concerns and relatively low practical capacity of approximately 160mAh g^{-1} (less than 60% lithium utilization in the structure). In addition, with the rapid development of electric devices ranging from portable electronics to electrical vehicles, many efforts have been made to find substitutions for $LiCoO_2$ [5–8]. The layered nickel-cobalt-manganese composites (NCM) are commonly recognized as the most promising candidates for replacing $LiCoO_2$, among which $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (NCM523) is one of the most widely used nickel-rich layered oxides [9]. Compared with nickel-poor materials such as $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, NCM523 has relatively higher capacity and costs less. In addition, NCM523 shows better cycling performance and higher thermal stability than nickel-rich cathode materials such as $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$. Because of its excellent comprehensive properties, NCM523 is playing an important role in the main or auxiliary power source for new-energy vehicles, such as hybrid electric vehicles (HEVs), plug-in hybrid vehicles (PHEVs) and electric vehicles (EVs) [10,11].

Generally speaking, working at a wider electrochemical window by pushing the limits of cutoff potentials allows more lithium ions insertion/extraction, meaning the higher capacity and energy density [12,13]. However, the issues of rapid capacity decay and voltage plateau fading come forth especially when the voltage threshold increases up to 4.4 V [14]. Materials in the charged state, especially under high potential, are thermally and chemically unstable because of the release of O_2 [14]. The highly reactive Ni^{4+} at the interface of electrode-electrolyte could aggravate the electrolyte decomposition [15,16]. Therefore, a stable interface between electrodes and electrolyte is necessary for long-life batteries. Such interface layers, including ZrO_2, Al_2O_3, ZnO, MoO_3, have been used for improving the materials' structural stability and electrochemical performance through surface coating [17–20]. The coating layers, to some extent, can keep electrodes away

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from electrolyte, suppressing the harmful side reaction and phase transition at the interface. In addition, Ni^{2+} ions at transition-metal 3a sites can easily move to the 3b lithium sites, exacerbating the Li/Ni cation mixing since Ni^{2+} ions hold the similar ionic radius (0.069 nm) to that (0.076 nm) of Li^+ ions [21]. Ni^{2+} ions in the 3b lithium sites give rise to the hindrance of lithium diffusivity, concurrently causing the low capacity and poor rate capability [5]. Lattice doping method is considered as one of the most prevailing strategies to improve the cycling performance by stabilizing the layered structure. Doping ions including Mg^{2+}, Al^{3+}, Zr^{4+},Na^+, are common choices [21–24]. Hua et. al [24] demonstrated in their research that Na-doped NCM523 materials hold the superior electrochemical performance for the broadened lithium ion slab spacing, the decreased cation mixing, and the increased Li^+ diffusion coefficient compared to the bare one.

On the basis of the strong Al-O bond due to a significant Al(s)-O(p) overlap, the impressive charge transfer capabilities of Al, and the inert chemical properties of Al_2O_3, Al-doping and Al-coating strategies are frequently applied for the enhancement of electrochemical performances [23,25,26]. However, there are rare reports on the synergistic effects of NCM type cathodes simultaneously with Al-coating and Al-doping. In this sturdy, the Al-doped and Al-coated $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode material has been successfully prepared via a facile CMC-assisted wet process followed by a high-temperature calcination. Not only does the Al_2O_3 form a transition layer at the cathode surface, but also Al element intercalates into the bulk lattice, enabling the improvement of rate capability and long cycle property simultaneously. In this paper, we put the emphasis on the effects of Al concentration gradient modification on the structural stability and the improvements of electrochemical performance. Served with the analysis of XRD, SEM, EDS, EIS, CV, etc., the improved electrochemical performances are exhibited and discussed in detail.

2. Experimental

2.1. Material synthesis

For the synthesis of NCM523 materials, the transition metal hydroxide precursor powders $Ni_{0.5}Co_{0.2}Mn_{0.3}(OH)_2$ (250 g, Hunan Brunep Recycling Corp., China) were blended thoroughly with Li_2CO_3 at the molar ratio of 1.06 (excess lithium for the compensation of lithium loss during the sintering process). The mixture was preheated at 500 °C for 4 h, then sintered at 750 °C for 4 h and at 920 °C for 8 h. The sample without Al modification is marked as pristine.

To obtain the quantitative Al_2O_3 modified NCM523 materials, 0.1 mol/L $Al(NO_3)_3$ solution was firstly prepared. Firstly, the ammonia solution was dropwise added into the continually stirred $Al(NO_3)_3$ solution, maintaining the pH in 6 ~ 8. The amount of $Al(NO_3)_3$ solution is based on the mass ratio of Al_2O_3/NCM523 (1000, 2000, 5000 and 8000 ppm). Secondly, the thickening additive, CMC was added and stirred for another 20 min to form a uniform mixed solution. Then, the obtained NCM-pristine was dispersed in that mixed solution with magnetic stirring for 2 h. After that, the slurry was aged at 90 °C for 12 h until desiccated, which is essential to ensure the slow evaporation of solvent and the homogenous distribution of the Al element. The mixtures were finally heated at 750 °C in air for 4 h. The modified materials with Al_2O_3 contents of 1000, 2000, 5000 and 8000 ppm are marked as Al-1000, Al-2000, Al-5000 and Al-8000.

2.2. Material characterization

The XRD patterns were obtained by powder X-ray diffraction(XRD, Rigaku, Rint-2000) with Cu Kα radiation in the 2 θ range of 10–70° at a scan rate of 6° min^{-1}. The micromorphology of the composite powders was observed by scanning electron microscope (SEM, JEOL JSM-6360LV, Japan) with an operating voltage of 20 kV.

2.3. Electrochemical measurements

The electrochemical performance of the cathode was evaluated by assembling CR2016-type coin cells with a working cathode (round slices with radius of 14 mm), a lithium metal anode and a Cegard 2340 microporous membrane in an argon-filled glove box (LS800S, DELLIS, Chengdu, China). The working cathode was fabricated using 80 wt% active materials, 10 wt% acetylene black and 10 wt% PVDF binder. A 1 M solution of $LiPF_6$ dissolved in DMC: EMC: EC (1:1:1 vol ratio) was employed as the electrolyte. The electrochemical performances were investigated by Land (CT2001A) cell systems at different rates (1 C = 155 mA g^{-1}). The cyclic voltammetry (CV) was carried out in the voltage range from 2.5 to 4.6 V at a scanning rate of 0.1 mV s^{-1}. The electrochemical impedance spectroscopy (EIS) measurements were performed over the frequency from 100 kHz to 0.01 Hz with an amplitude of 10 mV.

3. Results and discussion

3.1. Material characteriation

As shown in Fig. 1**(a)**, all diffraction patterns of the pristine and the modified materials can be indexed to the layered hexagonal α-$NaFeO_2$ structure with R-3 m space group. The exhibited narrow and sharp peaks indicate the excellent degree of crystallinity and the obvious splitting peaks of (006/012) and (018)/(110) present a highly ordered hexagonal structure [26]. No impurity phases are observed, indicating that the minor amounts of Al_2O_3 insignificantly disturb the intrinsic layered structure of the pristine.

The lattice parameters of the obtained samples are calculated and listed in Table 1. There is no obvious change of the lattice parameter *a* before and after Al_2O_3 modification while the lattice parameter *c* shows a slightly increasing trend, which indicates that Al_2O_3 modification has induced the structural transformation of the bulk lattice to some extent. This is consistent with some previous papers [27,28], presenting a primary evidence that Al^{3+} as a doping element has been successfully incorporated into crystal lattice. It's also reported that the increasing value of the parameter c means the wider layer slab, contributing to the increasing Li^+ diffusion coefficient and therefore facilitating the transportation of lithium ion [21]. Cation mixing leads to the discharge capacity loss and poor cyclic performance [29]. The intensity ratio of I (003)/I(104) is an important indicator for the extent of Li/Ni cation mixing; the higher the ratio I(003)/I(104), the lower the cationic mixing. Compared with the pristine, the ratios of I(003)/I(104) increase in all the modified samples, among which the Al-2000 has the biggest ratio I(003)/I(104), indicating the lowest extent of Li/Ni cation mixing and predicted to show the best electrochemical performance. In addition, the cross-section EDS analysis is conducted to further validate the existence of Al element inside the material particles. As seen in Fig. 1**(b) and (c)**, four dots (marked area 1–4, respectively) are chosen from core center to outer layer, showing the different Al contents of 0.35, 0.80, 0.94, 1.33%, respectively. Different from the doping and coating, the internal distribution of Al presents an alike linear relation, similar to the concentration gradient structure materials [30]. It is said that Al-O bond shows an strong iono-covalent nature with a significant charge transfer and considerable orbital overlap [31]. Such strong iono-covalent Al-O bonding is extremely beneficial for the structural stabilization of NCM lattice [25].

Fig. 2**(a) and (b)** present the similar morphologies of spherical secondary particles with approximate 10 μm diameter for the pristine and Al-2000, which are composed of numerous primary particles in the range of 200–500 nm. Fig. 2**(c)** shows the elemental mappings of energy dispersive spectrometer (EDS), which is applied to further investigate the distribution of Al on the surface of particles. The visible Al peaks declares the existence of Al element on the surface of particles. Furthermore, the EDS elemental mapping of Al is in accordance with