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Simultaneous surface coating and chemical activation of the Li-rich solid solution lithium rechargeable cathode and its improved performance

Yingqiang Wu[a,b,c], Jun Ming[a,b], Linhai Zhuo[a,b,*], Yancun Yu[a,b], Fengyu Zhao[a,b,*]

[a] State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China
[b] Laboratory of Green Chemistry and Process, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China
[c] University of Chinese Academy of Science, Beijing 100049, PR China

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ABSTRACT

In this study, highly dispersive spherical Li-rich solid solution ($Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$) particles are successfully synthesized by a co-precipitation method. Then these particles are treated with aluminum nitrates ethanol solution at 80 °C. The treatment can extract lithium (Li_2O) from the Li_2MnO_3 component in the composite of $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$. Simultaneously, a thin layer of Al_2O_3 can be precipitated on the surface of the electrode particles via direct thermal decomposition of aluminum nitrates. After treatment, the first-cycle coulombic efficiency of the electrode increases from 72.1% to 93.6%, meanwhile it shows a superior cycling stability at 100 mA g^{-1} with a discharge capacity of around 220 mAh g^{-1} and retention of 92.5% after 100 cycles, which is much higher than that of the pristine electrode (83.2%). Even at a high current density of 2 A g^{-1} (10 C), the discharge capacity could still achieve and well maintain as high as 140 mAh g^{-1}.

1. Introduction

Lithium-rich layered solid solution oxide composites represented by a chemical formula of $x Li_2MnO_3 \cdot (1-x) LiMeO_2$ (Me = Mn, Ni and Co) are considered to be one of the most promising cathode materials for high performance lithium ion batteries (LIBs), because they can deliver an exceptionally high capacity of above 250 mAh g^{-1} between 2.0 and 4.6 V [1–15]. However, the materials are still suffering from several fatal limitations: (i) a lower tap density near 1.5 g cm^{-3}; (ii) a relatively poor cycle stability and rate capability (e.g., below 200 mAh g^{-1} at 1 C); (iii) a high, first-cycle irreversible capacity (C_{ir}) loss of 40–100 mAh g^{-1} [16]. The high C_{ir} can be attributed to the especial mechanism of electrochemical activation of $x Li_2MnO_3 \cdot (1-x) LiMeO_2$. Generally in the first cycle, two lithium ions can be extracted electrochemically as Li_2O above 4.5 V from the Li_2MnO_3 ($Li_2O \cdot MnO_2$) component to yield an active MnO_2, while only one lithium ion can be re-inserted into the MnO_2 component in the following discharge [17]. In addition, the lost of oxygen from the electrode is irreversible, resulting in yield a lot of oxide ion vacancies on the surface of particle. The elimination of oxide ion vacancies from the layered lattice in cycling should damage the discharge capacity and cycle stability [18,19].

To date, an effective strategy to eliminate the C_{ir} is to blend the layered oxide with a lithium insertion host such as V_2O_5 [20], VO_2 [21], LiV_3O_8 and $Li_4Mn_5O_{12}$ [22]. This kind of compound can act as a host to accept the extracted lithium ions which could not be inserted back into the layered lattice, thereby eliminating the C_{ir}. However, these “Li-rich layered oxide/Li-insertion host” composites cannot suppress the elimination of oxide ion vacancies from the layered lattice during the first charge and also are hard to ameliorate the surface structure characteristic of the Li-rich layered oxides, which always result in a large capacity fade in the cycling [22]. Another strategy to reduce the C_{ir} is aforehand chemical activation of the Li_2MnO_3 component in $x Li_2MnO_3 \cdot (1-x) LiMeO_2$ materials by surface treatment, such as treating with HNO_3 [23–25], $(NH_4)_2SO_4$ [16] and $Na_2S_2O_8$ [26], etc. The chemical pre-treatment can remove lithium ions from the Li_2MnO_3 ($Li_2O \cdot MnO_2$) component and then increase the first-cycle coulombic efficiency to almost 100%. However, the treatment could damage the long-term cycling stability and rate capability of the electrodes, because the surface damage and/or H^+-ion exchange occurred in the treating process [23]. Beside the above methods, surface coating of the cathodes with inert materials such as Al_2O_3 or $AlPO_4$ can also reduce the C_{ir} [27,28]. Other inert materials, such as AlF_3 [29,30], Li-Ni-PO_4 [31,32], aluminum [33] and double-layer

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[*] Corresponding authors at: State Key Laboratory of Electroanalytical Chemistry, Laboratory of Green Chemistry and Process, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China. Fax: +86 431 8526 2410.
E-mail addresses: lhzhuo@ciac.ac.cn (L. Zhuo), zhaofy@ciac.ac.cn (F. Zhao).

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Table 1
Relative amounts of Li, Mn, Ni, and Co (normalized to the Mn content) in a fired sample (SL) for the target stoichiometry $Li(Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13})O_2$ and the content of metallic ions in the supernatant solution (mol% of corresponding metallic ions) after the treatment process (SL-2h, SL-4h and SL-8h) (ICP data).

Samples	Elements				
	Li	Mn	Ni	Co	Al
SL	1.226	0.540	0.128	0.129	/
SL-2h	15.7	0[a]	0	0	1.1[b]
SL-4h	16.5	0	0	0	0.12
SL-8h	16.8	0	0	0	0

[a] The content of transition metal ions in the solution was quite small.
[b] The originally total Al^{3+} ions was 0.294 mmol.

coating ($AlPO_4$-Al_2O_3, $CoPO_4$-Al_2O_3, etc.) [19] were also reported to decrease the C_{ir} and increase the cycle stability and rate capability. The decrease of C_{ir} in this way could be ascribed to the decreasing of elimination of oxide ion vacancies at the end of first charge. However, these surface coating methods generally include multiple step operations and/or use precipitant in the coating process.

In this work, we prepared highly dispersive spherical $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$ particles to improve the tap density of the materials first. And then the cathode material was coated with Al_2O_3 and activated simultaneously in ethanol solution of aluminum nitrate at 80 °C. The ethanol solution of aluminum nitrate can not only provide a weak acidic condition to activate the $Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$ cathode materials, but also can easily deposit of Al_2O_3 on the surface of the particles via direct thermal decomposition of aluminum nitrate. After the treatment, the first-cycle coulombic efficiency, cycle stability and rate capability of the cathode material were improved greatly. Particularly, the simple operation, low cost and little pollution of this presented method could be easily large-scalable for the application.

2. Experiment

2.1. Synthesis spherical $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$

The spherical $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$ was synthesized by a co-precipitation method [34,35]. A 2.0 mol L^{-1} of $MnSO_4{\cdot}H_2O$, $NiSO_4{\cdot}6H_2O$ and $CoSO_4{\cdot}7H_2O$ solution (cationic ratio of Mn:Ni:Co = 0.675:0.1625:0.1625) were used as the starting materials to fabricate the carbonate precursors. They were pumped into a 2 L of three-neck flask under stir at 60 °C. At the same time, a solution (aq.) content of 2.0 mol L^{-1} Na_2CO_3 and 0.2 mol L^{-1} $NH_3{\cdot}H_2O$ were also fed into the reactor. The pH value of the solution was controlled at 8.3 in the process of the precipitation. The as-prepared spherical carbonate precursors were first heated at 500 °C for 5 h to convert to oxides, then these oxides were thoroughly mixed with $LiOH{\cdot}H_2O$ and heated at 700 °C for 5 h then 800 °C for 12 h in air.

2.2. Process of chemical activation and surface coating with Al_2O_3

The as-prepared spherical $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$ (0.50 g) were well dispersed in 8 mL ethanol solution of $Al(NO_3)_3{\cdot}9H_2O$ (110.4 mg) in a glass bottle by ultrasonic treatment for 10 min. Then the dense colloidal solution was transferred into an autoclave (50 mL) and treated at 80 °C under stir. The $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$ materials were treated with different time, while maintaining the weight ratio of $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$ to Al_2O_3 (100:3) (see in Table 1, the pristine $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$ material was labeled as SL and the sample treated with 2 h was labeled as SL-2h, by analogy for SL-4h and SL-8h). The resulting product was centrifuged washed repeatedly with ethanol, and then dried at 80 °C for 12 h. The samples were heat-treated at 400 °C for 5 h under air with a heating rate of 3 °C min^{-1}.

2.3. Characterization

The content of metallic ions in the supernatant solution after the treatment was measured by inductively coupled plasma atomic emission spectrometer (ICP-AES) (Thermo Scientific iCAP 6000 Series). The phase structures were characterized with X-ray diffraction [XRD, Bruker D8 Advance diffractometer using Cu Kα (λ = 1.5418 Å)]. The morphology of the materials was analyzed by the scanning electron microscope (SEM Hitachi S-4800).

2.4. Battery fabrication and electrochemical performances measurement

The cathode was constructed by mixing the cathode material with acetylene black and poly(vinylidene fluoride) powder in a weight ratio of 80:10:10. After being blended in N-methylpyrrolidinone, the slurry was spread uniformly on aluminum foil and dried at 100 °C for 12 h in vacuum. Electrode disks were prepared with an average loading of ∼4 mg of active material. Charge and discharge performances of the electrodes were evaluated using 2025 coin cells with a Celgard 2320 microporous separator membrane. The electrolyte (DCC120416-YH) was donated by Daikin Industries Ltd., Japan. The cells were assembled in an argon-filled glove box (O_2 and H_2O levels <1 ppm). The galvanostatic charge and discharge were controlled between 2.0 and 4.6 V on a LAND CT2001 (A cell test instrument, Wuhan Kingnuo Electronic Co., China).

3. Results and discussion

3.1. Characterizations

Fig. 1a shows SEM images of the as-prepared $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$ materials. With finely controlling the condition of co-precipitation and calcination, the $Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$ particles had a high dispersion and uniform spherical structure with an average diameter of 9.5 μm (Fig. 1a and b). The magnification SEM image (Fig. 1e) exhibits that the large spherical particle was composed of nanoscale primary particles. The XRD pattern of the pristine $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$ material is shown in Fig. 2a. It had all the peaks belonging to the layered character and Li_2MnO_3–like features as confirmed by the weak superlattice reflection peak around 21°, which was resulted from the ordering of Li and Mn in the transition-metal layer. Moreover, the Mn:Ni:Co ratio as measured by ICP was well consistent with the target stoichiometry of $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13})O_2$ (Table 1).

To activate and surface coat the $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$, the $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$ powders were treated with ethanol solution of $Al(NO_3)_3{\cdot}9H_2O$ (corresponding to 3 wt% Al_2O_3) at 80 °C for 2 h, 4 h and 8 h, respectively. In this way, the weak acidic condition of the solution (pH ≈ 3.5) could activate the $Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$ cathode materials. And simultaneously, a thin layer of Al_2O_3 could deposit on the surface of $Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$ due to its surface alkaline. After treatment, the characteristics of particles, including the morphology and particle size, were well persevered (Fig. 1c and d). Moreover, the rough surface of the spherical particles became rather smooth after the treatment (Fig. 1f). XRD patterns of the treated powders were unaltered beside the intensity reduction of the superlattice reflection peak around 21° (SL-8h vs. SL) and the peak ratio of $I_{(003)}/I_{(104)}$ (Fig. 2a). The decreasing of the peak intensity around 21° was due to the lithium extraction from the Li_2MnO_3 component [23]. The ratio of $I_{(003)}/I_{(104)}$ gradually decreased from 1.237 ± 0.02