Journal of Power Sources 275 (2015) 64-72

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Facile synthesis of spherical $xLi_2MnO_3 \cdot (1-x)Li(Mn_{0.33}Co_{0.33}Ni_{0.33})O_2$ as cathode materials for lithium-ion batteries with improved electrochemical performance



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HIGHLIGHTS

• Novel synthesis route for the spherical Li₂MnO₃-stabilized cathode which is time-efficient.

• CuO coating layer is prepared by spray drying for the first time.

• CuO-coated cathode possess excellent electrochemistry performance.

ARTICLE INFO

Article history: Received 24 July 2014 Received in revised form 3 November 2014 Accepted 5 November 2014 Available online 6 November 2014

Keywords: Layered lithium-rich Fast co-precipitation Spherical CuO-coated

ABSTRACT

The $xLi_2MnO_3 \cdot (1-x)Li(Mn_{0.33}Co_{0.33}Ni_{0.33})O_2$ (x = 0.3, 0.5, 0.7) cathode material with uniform spherical morphology has been successfully prepared by a facile carbonate co-precipitation method. These cathode materials are characterized by X-ray powder diffractometry (XRD), scanning electron microscopy (SEM), and inductively coupled plasma emission spectrometry (ICP-AES). The electrochemical properties of these cathode materials have been studied by charge/discharge cycling at various current rates. The results of these studies suggest that among these materials, the composite cathode with x = 0.5 (Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O₂) exhibiting the better electrochemistry performances than those with x = 0.3 and 0.7. Correspondingly, 2 wt% CuO-coated Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O₂ possess better cycling stability (173.9 mAh g⁻¹ after 50 cycles at 1C rate and 50 cycles at 2C rate) and rate capability than the pristine one. Meanwhile, the CuO-coating layer of the material has a contribution to improve its thermal stability. We believe it is a promising cathode for the high energy lithium batteries.

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1. Introduction

Rechargeable lithium-ion batteries (LIBs) are one of the most promising energy storage devices for electric vehicles (EV) and hybrid electric vehicles (HEV), because of their high energy density, high power density, low cost, superior safety, stable charge/ discharge cycling and long lifespan [1]. The most commonly used cathode material in high energy lithium batteries is layered LiCoO₂, which is expensive and is not friendly to the earth. The olivine LiFePO₄ and spinel LiMn₂O₄ have been regarded as the alternatives to LiCoO₂. However, the low electronic conductivity and poor

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capacity retention limit their application in LIB. Recently, many research groups studied the solid solutions of layered transition metal oxides with composition of $xLi_2MnO_3 \cdot (1-x)LiMO_2$ (M = Mn, Co, Ni), due to their high discharge capacity, low cost and good safety [2–5].

In general, $xLi_2MnO_3 \cdot (1-x)LiMn_{0.33}Co_{0.33}Ni_{0.33}O_2$ (0 < x < 1) cathode materials can deliver specific discharge capacity of 260 mAh g⁻¹ in the voltage range of 2–4.8 V with very good cycling performance [6], but its performance depends heavily upon the synthetic methods employed. So far, there are many synthetic methods are reported, for example, sol–gel [7], sucrose-combustion [8], molten salt [9,10], template-free [11] and coprecipitation [12–14] and so on. Among the methods, the coprecipitation method was widely chosen because it can generally produce uniform small spherical particles. As a rule of thumb, the powders composed of spherical particles can be processed easily to







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form an electrode with higher density [15] and also show better electrochemical properties [16–20] than the powders composed of irregular particles. However, such a slow co-precipitation procedure was usually carried out in a complicated continuous-stirred tank reactor (CSTR) and required precise control of the reaction conditions, such as the pH value, temperature, oxygen level, and the speed of mixing [21]. Therefore, it is necessary to find a simpler route to prepare this class of cathode materials with good performance.

On the other hands, how to improve the electrochemistry performance is also an important issue for this class of the materials. Many attempts such as modification of the surface of layered—layered composite by coating with different electrochemically inactive oxides/phosphates have been done [22–24]. In particular, CuO-coated composite cathode has shown good discharge capacity, cycling performance, and rate capability relative to the uncoated materials [25–27]. The enhanced performance is attributed to the surface property by inhibiting formation of SEI layer and thereby improving fast charge transfer reaction kinetics. Until now, the concerns with Li₂MnO₃–LiMO₂ composite cathodes such as high irreversible capacity and poor rate performance remain to be the main obstacle to the commercialization.

In this paper, a facile carbonate co-precipitation method to produce a family of the cathode material, $xLi_2MnO_3 \cdot (1-x)$ Li(Mn_{0.33}Co_{0.33}Ni_{0.33})O₂ (x = 0.3, 0.5, 0.7), with uniform spherical morphology was reported. In this method, instead of using CSTR, we employed an easy and manipulable process. The electrochemical properties of these materials were also thoroughly investigated and compared with the same class of cathode materials prepared by other methods mentioned above [28,29]. In order to further improve the electrochemical performance of Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O₂, the CuO-coated Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O₂ material was prepared for the first time. Owing to the coated CuO layer decreasing the contact the between the electrode and electrolyte, the CuO-coated Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O₂ shows enhanced rate capability, cycling stability performance and thermal stability.

2. Experimental

2.1. Material synthesis

Preparation of metal carbonate $(Mn_{1-2y}Co_yNi_y)CO_3$ (y = 0.23, 0.17, 0.10): 0.03 mol $MnSO_4 \cdot H_2O$ (>99%), $CoSO_4 \cdot 7H_2O$ (>99.5%), $NiSO_4 \cdot 6H_2O$ (>99.5%) were mixed in de-ionized water. After mixing a required amount ethanol with the aqueous solution for 30 min, NH_4HCO_3 solution was added quickly. The precipitates were collected after one hour at 10 °C, and then washed with de-ionized water several times, dried in the air.

Preparation of solid solutions of metal oxides: the obtained carbonate compounds with mixed metal cations were then heated at 500 °C for 5 h to obtain the solid solutions of transition metal oxides with spherical morphology.

Preparation of $xLi_2MnO_3 \cdot (1-x)LiMn_{0.33}Co_{0.33}Ni_{0.33}O_2$ (x = 0.3, 0.5, 0.7): the metal oxides were mechanically mixed well with LiOH \cdot H₂O (3 wt% excess). Then the mixture was heated at 480 °C for 4 h in air, and further calcined at 800 °C for 10 h. The heating rates for these three samples were all maintained at 5 °C min⁻¹.

Preparation of CuO-coated $Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$ samples: 10 g of $Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$ and 0.5 g of Cu(CH₃COO)₂·H₂O (which is equivalent to 0.1992 g of CuO after calcination were dispersed and mixed in 500 ml distilled water with vigorous stirring. So the initial mass fraction of CuO in the CuO-coated $Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$ samples is about 2 wt%. After treated ultrasonically for 2 h, the obtained suspension was dried directly by spray drying process (B-290, Buchi, Switzerland) to form a kind of powder with uniform size. Then, the powder was heat-treated at 500 °C in air for 4 h to obtain the 2 wt% CuO-coated $Li_{1.2}Mn_{0.54-}$ Co_{0.13}Ni_{0.13}O₂, which was marked as sample CuO-coated.

2.2. Physical characterization

Crystal characterization of the materials was performed with a Rigaku Ultima IV (Rigaku Corporation) using K α radiation operated at 40 kV and 30 mA. Data were collected over the range of $10^{\circ} \leq 2\theta \leq 90^{\circ}$ and analysed using PDXL-2 analysis software (Rigaku Corporation).

Scanning electron microscopy (SEM) was performed on S-4800 (Hitachi Corporation). Transmission electron microscope (TEM) was carried out on JEM-1400 (JEOL). The elementary composition of the materials were determined by inductive coupled plasmaatomic emission spectroscopy (ICP-AES), carried out on IRIS intrepid II XSP (Thermo Electron).

2.3. Electrochemical measurements

The electrochemical characteristics of these solid solution cathode materials were tested using CR2016 coin cells with 1.0 M LiPF₆ in mixed organic solvents of ethylene carbonate (EC), diethyl and carbonate (DEC), dimethyl carbonate (DMC)(EC:DEC:DMC = 1:1:1, volume) as electrolyte and the porous polypropylene film as separator. The active materials, acetylene black, and polyvinylidene fluoride (PVDF) were mixed in a weight ratio of 85:10:5 in N-methyl-2-pyrrolidene (NMP). The slurry was coated onto a 20 µm Al foil and dried at 80 °C to obtain an electrode sheet. The sheet was punched into round discs (12 mm in diameter) and pressed at 16 MPa before drying for 4 h at 120 °C. A metallic lithium foil was served as the anode. All cells were fabricated in an argon-filled glove box (Mbraun, Germany). The charge and discharge tests were performed galvanostatically between 2.0 and 4.8 V using a Landian CT2001A (Wuhan, China) battery testing system at room temperature. All the capacity was calculated based on weight of the active material in the electrode.

The initial charge–discharge test was studied at 0.1C and the cycling test was measured at 1C after the first cycle at 0.1C. The rate performance was carried out at different discharge rates between 2.0 and 4.8 V. The electrochemical impedance spectroscopy (EIS) of the cells was conducted on an electrochemical workstation (Autolab PGSTA T302 N) with an amplitude voltage of 10 mV and frequency range of 0.01 Hz–10 kHz.

The DSC/TG (STA 449 F3 Jupiter Netzsch) was used to measure the thermal stability of electrodes in 1 M LiPF6 EC-DMC electrolyte from 100 °C to 300 °C at a heating rate of 5 °C/min. Firstly, cell was charged to 4.8 V at 1C and then kept them at 4.8 V for 2 h, then the cell was taken apart to get electrode materials film in an Ar-filled glove box. Secondly, the film was washed several times by dimethyl carbonate (DMC) and naturally dried. Thirdly, the electrode materials scraped from film and electrolyte were sealed together in a gold-plated stainless steel crucible in the glove box. The ratio of electrolyte to electrode materials was 10 μ L of electrolyte per milligram of electrode materials.

Table 1	
Compositions of $xLi_2MnO_3 \cdot (1-x)Li(Mn_{0.33}Co_{0.33}Ni_{0.33})O_2$ Electrode	Materials.

x	Targeted Mn/Co/ Ni ratio	Li/Mn/Co/Ni ratio expected(with 5 wt% Li evaporative)	Li/Mn/Co/Ni ratio experimental (AES-ICP)
0.3	0.53:0.23:0.23	1.30:0.53:0.23:0.23	1.35:0.53:0.22:0.23
0.5	0.66:0.17:0.17	1.50:0.66:0.17:0.17	1.54:0.66:0.16:0.17
0.7	0.80:0.10:0.10	1.70:0.80:0.10:0.10	1.75:0.80:0.10:0.10

3. Result and discussion

3.1. Elementary analysis

The compositions of three materials of $xLi_2MnO_3 \cdot (1-x)$ Li(Mn_{0.33}Co_{0.33}Ni_{0.33})O₂ (x = 0.3, 0.5, 0.7) are experimentally determined by ICP and were shown in Table 1. The elemental ratios of Mn/Co/Ni are in excellent agreement with the targeted stoichiometries, whereas the lithium values are higher than the anticipated quantity due to the 3 wt% excess lithium that was used to compensate the evaporative loss of lithium during calcination.

3.2. Morphological studies of $xLi_2MnO_3 \cdot (1-x)Li(Mn_{0.33}Co_{0.33}Ni_{0.33})$ $O_2 (x = 0.3, 0.5, 0.7)$

The SEM images of carbonate precipitates with x = 0.3, 0.5 or 0.7 are shown in Fig. 1A–C. All these particles are spherical and uniform in size. However, their particles sizes depend strongly on their stoichiometries of compositions. As *x* increases, the diameter of the spheres decreases (x = 0.7, 2 µm; x = 0.5, 3 µm; x = 0.3, 4 µm). According to the report [30], when x = 1, the diameter of the sphere is even smaller. After heat-treated at 800 °C, all three samples retain their spherical structures (shown in Fig. 1a–c). The diameter

of sphere of each sample does not shrink but slightly increase. The surfaces of all oxide solid solution particles are rough which could be attributed to the CO₂ evolution from the carbonate precipitate decomposition after the heating process. The detailed structural evolution of x = 0.5 sample upon these treatments is shown in Fig. 2. The sphere of the x = 0.5 sample after final calcination actually expands to nearly about 5 µm probably due to the crystal growth, and its surface becomes rougher. Higher magnification does show that it is composed of nanoscale primary particles, shown in Fig. 2d. The tap-density of the powder obtained was 1.6 g cm⁻³.

The morphologies of the Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O₂ powers with and without CuO coating are shown in Fig. 3. The pristine Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O₂ particles are about 200 nm in sizes, and distinct grain of the particles can be observed clearly. For the 2 wt% CuO-coated sample, the distinct of the particles can also be seen clearly due to the low quantity of CuO and a thin coating on the surface of the particles. EDS was conducted to check the CuO coating layer on the surface of 2 wt% CuO-Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O₂. As shown in Fig. 3 and Fig. S1, all the elements especially Cu are distributed homogeneously on the surface of the particles. These data are well consistent with the TEM (shown in Fig. 4) results. The details of TEM and EDS images are shown in Fig. S2.



Fig. 1. SEM images of the carbonate precipitate and $xLi_2MnO_3 \cdot (1-x)Li(Mn_{0.33}Co_{0.33}Ni_{0.33})O_2$: A and a, x = 0.3; B and b, x = 0.5; C and c, x = 0.7.



Fig. 2. SEM images of 0.5Li₂MnO₃·0.5Li(M

3.3. Structural characterization

Fig. 5 shows the XRD patterns of spherical $xLi_2MnO_3 \cdot (1-x)$ $Li(Mn_{0.33}Co_{0.33}Ni_{0.33})O_2$ (x = 0.3, x = 0.5, x = 0.7) after final calcination. The diffraction peaks of all samples are the same and can be indexed as a hexagonal α-NaFeO₂ structure (space group: 166, R-3m), with a few broad peaks between $2\theta = 20^{\circ}$ and 25° (Fig. 5B). Several features of these XRD data are worthy of mentioning. Firstly, the diffraction peaks between $2\theta=20^\circ$ and 25° are known to be caused by the superlattice ordering of Li and Mn in the transition metal layers in the Li-rich layered oxides, which confirms the existence of Li₂MnO₃ [2]. Secondly, the formation of ordered lamellar structures in the hexagonal structure can be indicated by the (018)/(110) peaks splitting [31]. In these samples, the (018)/ (110) doublets are well separated, indicating the formation of highly ordered lamellar structures. The last important feature is the ratio of the intensities of (003)/(104) peaks. A well-ordered sample should have a much bigger value than 1.2, while a heavily ionmixed sample should have a value much smaller than 1.2 [32]. The ratios for these three materials are 1.43 (x = 0.3), 1.46 (x = 0.5), 1.48 (x = 0.7), respectively, all bigger than 1.2, suggesting these samples should be considered as free of cation-mixing or at very low level mixing if it exists.

Fig. 6 shows the XRD patterns of CuO-coated and the pristine sample. Except for the super-lattice peaks between 20° and 25° , the other peaks of the XRD patterns can be indexed to the α -NaFeO₂ structure with space group R-3m. It reveals that no other impurities are formed after the coating process. In addition, there is no shift of peaks and no evident change for the values of the lattice constant a and b before and after coating (shown in Table 2), indicating that Cu-doping does not happen during the calcination process. However, the slightly decrease of the lattice constant c probably attributes to the H⁺/Li⁺ exchanged reaction generated during coating process which shorten the distance between oxygen layers [33].

Although, the host structure of $Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$ was not influenced by CuO coating.

Possible oxidation states of transition metal ions in the layered composite material were checked using XPS, and the corresponding spectra in the narrow binding energy range for Mn, Co, Ni, and Cu are presented in Fig. 7. Binding energies observed for the elements were in good agreement with the values reported for similar oxide cathode materials [34]. The major peaks at binding energies of ca. 642, 780, and 855 eV are attributed to Mn^{4+} , Co^{3+} , and Ni^{2+} . There are distinct Cu 2p peaks in the spectra for the coated sample (Fig. 7D). The binding energy obtained here is 952.5 eV for Cu $2p_{1/2}$, and 932.7 eV for Cu $2p_{3/2}$, which are consistent with the value reported for CuO [35].

3.4. Electrochemical results

The initial charge–discharge curves of x = 0.3, x = 0.5, x = 0.7are shown in Fig. 8A, in the voltage range of 2–4.8 V under gravimetric current density of 0.1C (20 mA g^{-1}). It is clearly shown that the first charge at 4.4-4.6 V for oxidation beyond the formal oxidation potential of Ni^{2+} to Ni^{4+} and Co^{3+} to Co^{4+} [33]. The materials can deliver specific discharge capacities of 203.6 mAh g^{-1} , 252.7 mAh g^{-1} , 158.2 mAh g^{-1} , respectively. The data show that the x = 0.5 sample has the highest specific discharge capacity agrees well with the one reported by Kim, Guyeon and coworkers [5]. The capacity retention data shown in Fig. 8B also show that the x = 0.5sample has the highest capacity retention. In the capacity retention test, all the samples were firstly cycled at 0.1C rate, and secondly, cycled at 1C rate. The gradual increase of the specific discharge capacity of x = 0.7 sample with at an early cycling stage (Fig. 8B) is attributed to the appearance the Mn^{3+}/Mn^{4+} redox couple as the cycling progresses and this phenomenon becomes more evident [36].

In spite of the $Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$ (x = 0.5) sample exhibits good electrochemical performance, it still could be improved by



Fig. 3. SEM images of Li12Mn0.54Ni0.13C00.13O2: A and B, the pristine; C and D, CuO-coated. EDS dot-mapping for element of the 2% CuO-coated.

surface modification, especially in amending the thermal stability and electrochemical impedance [23,37,38]. Based on this consideration, we had prepared the 2 wt% CuO-coated $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Co}_{0.13-}$ $\text{Ni}_{0.13}\text{O}_2$ sample and investigated its electrochemical performance for the first time.

Fig. 9A shows the cyclic performance of the pristine and the CuO-coated $\rm Li_{1,2}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$ at a charge–discharge density of 200 (from 1st to 51st cycle) and 400 (from 52nd to 100th cycle) mA g⁻¹ between 2.0 V and 4.8 V at room temperature. It is obvious that the cycling properties of the Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O₂ cathode powders were affected by the CuO coating layer. The discharge capacities of the pristine sample were 212.7, 199.9, and 157.2 mAh g⁻¹ at the 1st, 50th, and 100th cycle. The discharge capacities of the CuO-coated cathode powders were 234.3, 215.2, and 183.7 mAh g⁻¹ at the 1st, 50th, and 100th cycle. As the current

density increases, the CuO-coated cathode powders can deliver much higher discharge capacities than the pristine sample, due to the CuO coating layer could restrain the reaction between the metal oxide cathode and the electrolyte. To further demonstrate this conclusion, we had tested the rate capability of the Li_{1.2}Mn_{0.54}-Co_{0.13}Ni_{0.13}O₂ with and without CuO coating layer, the cells made from these samples were first charged and discharged at 0.1C for activation, then charged and discharged at 20 mA g⁻¹, 100 mA g⁻¹, 200 mA g⁻¹, 400 mA g⁻¹, and 20 mA g⁻¹ (20 mA g⁻¹ = 0.1C) between 2 and 4.8 V vs. Li⁺/Li, respectively. The results are shown in Fig. 9B.

At 20 mA g^{-1} charge current, the pristine and CuO-coated samples show the similar discharge capacity of about 252 mAh g^{-1} . However, there are obvious differences between the two samples with the charge current increase. The discharge



Fig. 4. TEM images of Li1.2Mn0.54Ni0.13Co0.13O2 with and without CuO-coated.

capacities of the pristine sample were 223.4 mAh g^{-1} , 202.6 mAh g^{-1} , and 159.6 mAh g^{-1} at the charge current of 100 mA g^{-1} , 200 mA g^{-1} , and 400 mA g^{-1} , while for the CuO-coated sample were 230.1 mAh g^{-1} ,220.3 mAh g^{-1} , and 179.8 mAh g^{-1} , respectively. It is worth noting that the capacity retention rate of the CuO-coated is 71.9% (compared to the value of 20 mA g^{-1} charge current), whereas the pristine is 63.8%. After charged and discharged at 400 mA g^{-1} , when the charge/discharge currents return to 20 mA g^{-1} , the specific capacity of the samples recovers almost to the same value of initial discharge capacity at 20 mA g^{-1} , indicating that the cathode material still retains its structural integrity. We believe that is the chemical reaction between the metal oxides and electrolyte becomes more strongly as the charge current increase, result in blocking up the Li⁺ transport and bringing down the discharge capacity. This chemical reaction was depressed by the CuO layer. It is reported that Li_xCuO₂ compounds in the coating layer can be formed with CuO and Li₂O and exhibit electrochemical activity during lithiation/delithiation cycling [39]. The good rate demonstrates that the CuO layer can effectively enhances the kinetics of Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O₂, which is further confirmed by the EIS data, as described in the next section.

3.5. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) experiments were performed to investigate the impedance change upon cycling of the cell prepared with pristine and coated Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O₂ at the cut-off voltage of 4.8 V at 2nd and 50th cycle. Nyquist plots of the Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O₂ are shown in Fig. 10. The semicircle at the higher frequency range reflects the resistance for Li⁺ ion migration through the surface films (R_{SEI}), the one at lower frequency is associated with the charge transfer (R_{CT}), and the slop line at low frequency range reflects Li⁺ diffusion in the particles of the electrode materials [40]. The cell impedance depends mostly on R_{SEI} and R_{CT} [41,42]. Therefore, we focused on the effect of CuO coating of surface film and charge transfer. The calculated values of the R_{SEI}, R_{CT} and R_{SEI} + R_{CT} of the cells are presented in Table 3. The fitting data were shown in the Supporting Information (Tables 1–4).

As the cycling goes on, the R_{SEI} for the pristine sample increase from 2.3 Ω cm² at 2nd cycle to 74.8 Ω cm² at 50th cycle, while, for the CuO-coated sample increase from 10.8 Ω cm² at 2nd cycle to 34.5 Ω cm² at 50th cycle. It is noticed that the value of R_{SEI} at 2nd cycle for the CuO-coated is slightly larger than that for the pristine one. We believe the probable reason for this phenomenon is that the coating layer does not be activated entirely. After 50th cycle, the value of R_{SEI} for the CuO-coated is much smaller. The above results indicate that 2 wt% CuO coating can effectively suppress the formation of the SEI layer and decrease the surface film resistance.

On the other hand, R_{CT} for the pristine sample decreases from 165.8 Ω cm² at 2nd cycle to 48.4 Ω cm² at 50th cycle, but for the CuO-coated sample decreases from 133.5 Ω cm² at 2nd cycle to 43.6 Ω cm² at 50th cycle. This result indicates that the a suitable amount of CuO coating has an effect on restraining the increase of



Fig. 5. XRD patterns of the $xLi_2MnO_3 \cdot (1-x)Li(Mn_{0.33}Co_{0.33}Ni_{0.33})O_2$.



Fig. 6. XRD patterns of the $Li_{1,2}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$ with and without CuO coating.

 Table 2

 The cell parameters summary of lattice constant values obtained from the XRD profiles.

	a/Å	b/Å	c/Å
Pristine	2.8571	2.8571	14.2412
CuO-coated	2.8569	2.8569	14.2418

charge transfer impedance (R_{CT}) and polarization, which can be considered as one of the possible reasons for the enhanced rate capability by CuO coating. We speculated that the electrochemical activity of Li₂MnO₃ in Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O₂ with the charge/ discharge cycles made the value of R_{ct} dropped.



Fig. 8. A: The initial charge/discharge plots of $xLi_2MnO_3 \cdot (1-x)Li(Mn_{0.33}Co_{0.33}Ni_{0.33})O_2$ under 0.1C in the voltage range of 2.0–4.8 V; B: The Cycle performance of $xLi_2MnO_3 \cdot (1-x)Li(Mn_{0.33}Co_{0.33}Ni_{0.33})O_2$.



Fig. 7. X-ray photoelectron (A) Ni 2p, (B) Co 2p, (C) Mn 2p, and (D) Cu 2p spectra recorded for the 2 wt % CuO-coated Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O₂.



Fig. 9. The cycle and rate performance of the $\rm Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$ with and without CuO coating.



Fig. 10. Impedance spectra of the $Li_{1,2}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$ with and without CuO coating electrodes after 2 cycles and 50 cycles.

Table 3

The impedance parameters of equipment circuits.

Samples	$R_{SEI}(\Omega \ cm^2)$		$R_{SEI}(\Omega \text{ cm}^2)$ $R_{CT}(\Omega \text{ cm}^2)$		$R_{SEI} + R_{CT}(\Omega \ cm^2)$	
	2	50	2	50	2	50
Pristine CuO-coated	2.3 10.8	74.8 34.5	165.8 133.5	48.4 43.6	168.1 144.3	123.2 78.1

3.6. Thermal stability

The thermal stability of cathode materials, especially in its highly delithiated state, is one of the important concerns in battery safety [24]. The thermal stability of the pristine and CuO-coated cathode powders was measured at 4.8 V after the 5th cycle at 1C, using differential scanning calorimetry (DSC) (Fig. 11). The area of the exothermic peak reveals the amount of heat releasing, which is generated from the decomposition of oxides and the reactions with the electrolyte [23]. The pristine sample shows an exothermal thermal peak at 246.1 °C with a thermal value of 59.2 J g⁻¹, while, the CuO-coated shows an exothermal thermal peak at 260.7 °C with a thermal value of 32.4 Jg^{-1} . It is obvious that the thermal stability is remarkably improved by CuO coating modification. The improved stability is attributed to the CuO-coated layer, which protects the highly oxidized cathode particles from direct contact with the electrolyte solution and reduces the exothermic reaction. Another possible reason for the enhanced thermal stability could be that the coating layer introduces strong Cu=0 bond onto the surface to lower the oxygen activity, which protects the surface of the active material and suppresses the generation of oxygen.

4. Conclusion

In summary, we have developed a facile carbonate coprecipitation method to prepare well-crystallized and spherical $xLi_2MnO_3 \cdot (1-x)Li(Mn_{0.33}Co_{0.33}Ni_{0.33})O_2$ (x = 0.3, 0.5, and 0.7) materials as high capacity and high power cathode for advanced lithium-ion batteries. The results suggest that in this family of cathode materials, spherical Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O₂ shows the good electrochemistry performance. Furthermore, it was found that 2 wt% of CuO-coating could improve the properties of this



Fig. 11. DSC profiles of the $Li_{1,2}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$ with and without CuO coating electrodes after the 2 cycle at 1C rate and charged to 4.8 V.

sample in discharge capacity, capacity retention rate and rate capability well. The improved discharge capacity and enhanced thermal stability are due to suppression of side reaction between active material and electrolyte at high potential and the high retention of oxide ion vacancies in the layered lattice after the first charge. The better rate capability is attributed to a fast charge transfer kinetics arising from the suppression of the undesired SEI layer and the growth of the charge transfer impedance. Therefore, the work reported herein offers a new way to prepare and improve various cathode materials in general formula of $xLi_2MnO_3 \cdot (1-x)$ LiMO₂ (0 < x < 1; M = Mn, Co, Ni et al.) for high-performance energy storage. The detailed mechanism for this synthesis process is still under research.

Acknowledgement

The authors gratefully acknowledge the financial supports from the National High Technology Research and Development Program of China (2012AA110204) and the Key Project of Science and Technology of Xiamen (2012S0504). The authors also wish to express their thanks to Dr. Dong Sun and Dr. Bo Liu of Xiamen University for his valuable suggestion.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2014.11.018.

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