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Short Communication

Synthesis and Electrochemical Performance of Li-rich Cathode Material $Li[Li_{0.2}Ni_{0.16}Mn_{0.56}Co_{0.06}Al_{0.02}]O_2$ in the Lithium-Ion Battery

Zhang Hai-Lang[*], *Ye Yan-Yan*

School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, China
[*]E-mail: ZHL8868@vip.163.com

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The layered Li-rich cathode material $Li[Li_{0.2}Ni_{0.16}Mn_{0.56}Co_{0.06}Al_{0.02}]O_2$, which is a solid solution between $Li[Li1/3Mn_{2/3}]O_2$ and $LiNi_{0.4}Mn_{0.4}Co_{0.15}Al_{0.05}O_2$ has been synthesized firstly by a sol–gel process. X-ray diffraction (XRD) identified that the material has layered α-NaFeO2 structure, and images of scanning electron microscopy (SEM) showed the material particles are about 100nm. Electrochemical measurements showed that in the range of 2.0–4.8V at a rate of 0.1C, the initial discharge capacity at 20 °C is 221.8mAh/g with the irreversible capacity loss of 38.2mAh/g, and the initial discharge capacity at 55 °C is 281.7mAh/g with the irreversible capacity loss of 21.1mAh/g. The material also exhibits good cycleability and rate capability. The cyclic voltammetry data are reflected in the charge–discharge studies.

Keywords: lithium-ion battery, $Li[Li_{0.2}Ni_{0.16}Mn_{0.56}Co_{0.06}Al_{0.02}]O_2$, cathode, high capacity, electrochemical performance

1. INTRODUCTION

Lithium ion batteries (LIBs) have been widely used for electronic devices, hybrid electric vehicles, portable power tools and many other power supplies owing to their high energy and power density. The price and performance of one Li-ion battery is mainly based on its cathoe material . The layered lithium transition metal oxide $LiCoO_2$ has been used as the cathode material for Li-ion battery for a long time and still used. However , its high cost,toxicity and unsatisfactory thermal stability seriously limit its use[1-3]. Other cathode materials such as spinel $LiMn_2O_4$ [4] and olivine $LiFePO_4$[5]have been successfully applied in lithium ion batteries, but they typically have very low capacities and also usually do not performe very well . Among all the cathode materials of LIBs, the $xLi[Li_{1/3}Mn_{2/3}]O_2 \cdot (1-x)LiMO_2$ (M= Mn, Co, Ni, etc.) is a promising material because of its high reversible capacity following an "activation" process[6]. This family of cathode materials are also called Li-rich layered materials. Because Li-rich layered materials could deliver a very high discharge capacity of about 235mAhg^{-1} at room temperatue and of over 285 mAhg^{-1} at 55℃, they have been investigated intensively in recent years[7-28]. Although this kind of cathode material has many attracting advantages, it has a poor rate performance and is subject to voltage decay after long cycling. Doping one or more metal elements have been demonstrated to be one effective method to improve one cathode material[29-31]. Doping has also successfully been used for improving Li-rich layered materials[16,18,22]. Surface modification, i.e. coating , is also one useful method for improving one cathode material. In recent years,many researchers have employed this method to improving Li-rich layered material [11,13,15,16,6,19-21].

In the group of Li-rich layered cathode materials, $Li[Li_{0.2}Mn_{0.6}Ni_{0.2}]O_2$ and $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ have been widely investigated already[7,12,14-18,20 , 24-27]. Between them, $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ always shows better performance[7], because of that the presence of cobalt reduces the electrode polarization significantly and improves the activation of the Li_2MnO_3 component[7], but it still contains 13 mol% of Co which certainly represents an issue with regard to cost, and the effect of the cobalt seems to deteriorate the high-potential cycling performances of the materials[8,28].

In the present work, we synthesized a novel Li-rich cathode material with a substantially lower Co content. The material has a general formula of $Li[Li_{0.2}Mn_{0.56}Ni_{0.16}Co_{0.06}Al_{0.02}]O_2$,which can also be indicated as $Li[Li_{1/3}Mn_{2/3}]O_2 \cdot 0.4LiNi_{0.4}Mn_{0.4}Co_{0.15}Al_{0.05}O_2$. The Al element is much more cheaper and also environment friendly. And also the Al element has been demonstrated to improve Li-ion cathode materials[31]. So the Al element has been selected to replace the Co element a little. This The structure, electrochemical properties are reported in this paper. The as-synthesized sample exhibits both high capacity and cycling stability.

2. EXPERIMENTAL

2.1. Preparation of materials

$Li[Li_{0.2}Mn_{0.56}Ni_{0.16}Co_{0.06}Al_{0.02}]O_2$ powder was synthesized by a sol–gel process in which citric acid was used as a chelating agent as the synthesis method in our labarotory[29-31]. Stoichiometric amounts of $LiNO_3$, $Mn(CH_3COO)_2 \cdot 4H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ and $Co(NO_3)_2 \cdot 4H_2O$ were used as starting chemicals and dissolved in distilled water, and added to a continuously stirred aqueous solution of citric acid. The molar ratio of citric acid to total metal ions was unity. The pH of the solution was adjusted in the range 7–8 by adding aqueous ammonium hydroxide. The resultant solution was evaporated at 80 ^{o}C until a transparent sol-gel was obtained. The gel was dried at 120 ^{o}C for 15 h. The resulting gel precursor was decomposed at 500 ^{o}C for 5 h in air to eliminate the organic substances. The decomposed powders were pressed into pellets, heated at 750 ^{o}C for 6 h, and then 950 ^{o}C for 6h in air, The final material was obtained by quenching the pellet in air to room temperature.

2.2. Measurements

The crystal structure of the as-prepared $Li[Li_{0.2}Mn_{0.56}Ni_{0.16}Co_{0.06}Al_{0.02}]O2$ powder was characterized by XRD with a D8 ADVANCE diffractometer using Cu Kα radiation. The diffraction angle was scanned from 2θ =10° to 80° at the scanning speed of 3°/min. The size and morphology of the sample was visualized using SEM performed on S4800 microscope with 3 kV.

Electrochemical experiments were performed using two-electrode coin cells[29-31]. The composite cathodes were made by dispersing active material (80 wt.%), acetylene black (12 wt.%), and PVDF (8 wt.%) to form a slurry, The slurry was pasted onto Al foil ,then pressed at 10MPa and dried at 120°C for 10h in a vacuum oven. The CR2032 coin cells were assembled in an argon-filled glove box using lithium metal as the counter electrode, Celgard 2325 as the separator, and 1 M LiPF6 in 1:1 EC:DEC solution as the electrolyte. Charge–discharge performance of the cells was evaluated within different cut-off voltages and at different discharge rates at 20 °C and 55 °C using LAND BT1210 electrochemical test instrument(Made in China).

3. RESULTS AND DISCUSSION

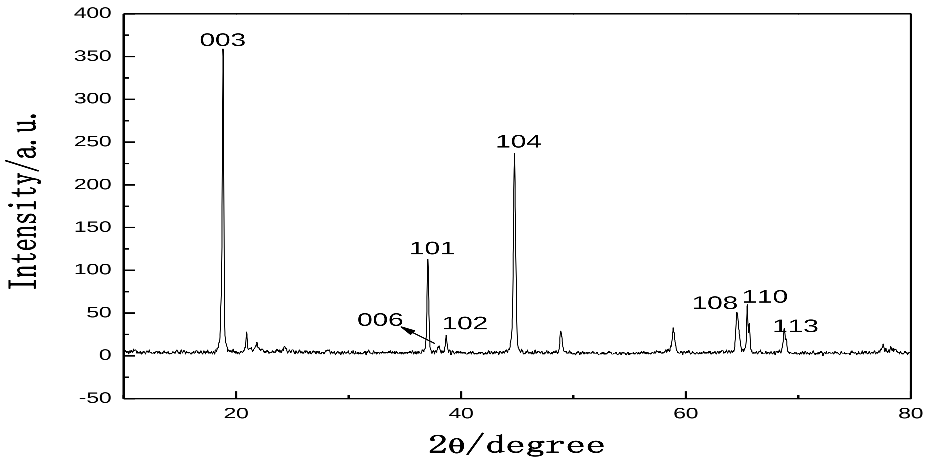

Figure 1. XRD patterns of $Li[Li_{0.2}Mn_{0.56}Ni_{0.16}Co_{0.06}Al_{0.02}]O_2$

The XRD pattern of $Li[Li_{0.2}Mn_{0.56}Ni_{0.16}Co_{0.06}Al_{0.02}]O_2$ is shown in Fig. 1.The XRD patterns are indexed in α-$NaFeO_2$ type structure, space group $R\bar{3}m$. It exhibits a well defined diffractogram that contains sharp and highly intense peaks. The weak reflections at 2θ =21°–25° are known to originate from the monoclinic Li_2MnO_3-like (C2/m) super lattice, which correspond to the ordering of the Li^+ and transition metal ions in the transition metal layer of the layered lattice[32]. The significantly split (006), (102) and (108), (110) peak pairs in the XRD patterns and the *c*/*a* ratio of 4.99, confirm that the synthesized $Li[Li_{0.2}Ni_{0.16}Mn_{0.56}Co_{0.06}Al_{0.02}]O_2$ compound has a high degree of crystallinity and good layered characteristics[9,33]. The integrated intensity ratio '*R*' of the (003) to (104) line was found to be 1.52, which is an indication that the compound has good cation ordering[34].

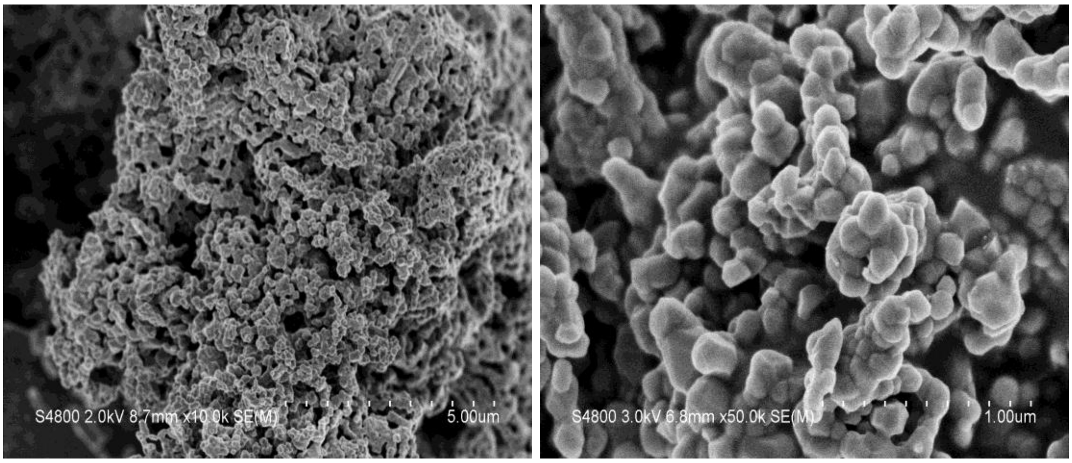

Figure 2. SEM images of $Li[Li_{0.2}Mn_{0.56}Ni_{0.16}Co_{0.06}Al_{0.02}]O_2$

The morphological features of $Li[Li_{0.2}Mn_{0.56}Ni_{0.16}Co_{0.06}Al_{0.02}]O_2$ were characterized by scanning electron microscopy and the results are shown in Fig. 2. It can be seen that the as-prepared particles have a nearly spherical morphology with an average diameter of approximately 100nm, almost a nano-material. Since small particles present shorter diffusion path for Li ions[7], the insertion and de-insertion of the Li^+ in this material are expected to be faster, thus enhancing the electrochemical performance of this material[35].

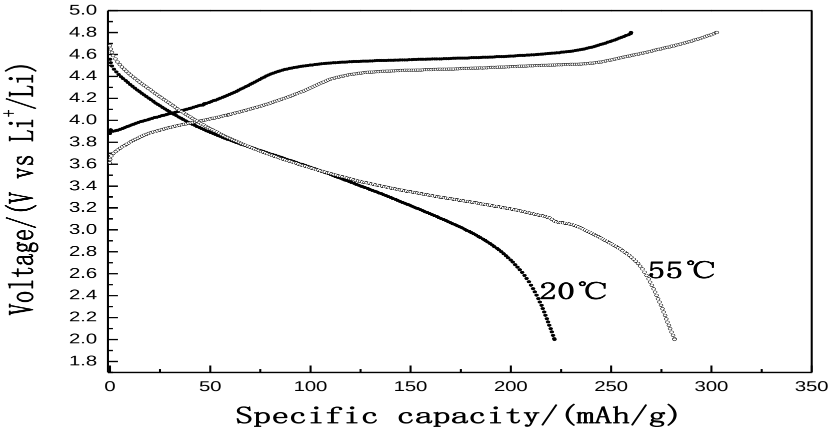

Figure 3. Discharge curves of $Li[Li_{0.2}Ni_{0.16}Mn_{0.56}Co_{0.06}Al_{0.02}]O_2$ at a rate of 0.1C

Fig. 3 shows the first charge–discharge profiles of $Li[Li_{0.2}Ni_{0.16}Mn_{0.56}Co_{0.06}Al_{0.02}]O_2$ in the range of 2.0–4.8V at a rate of 0.1C at room temperature and high temperature, recpectively.. $Li[Li_{0.2}Ni_{0.16}Mn_{0.56}Co_{0.06}Al_{0.02}]O_2$ exhibits charge and discharge capacity values of260mAh/g and 221.8mAh/g , respectively, with a small irreversible capacity loss of 38.2mAh/g at 20 °C. The discharge capacity at 55 ^{o}C increases to 281.7mAh/g and the irreversible capacity loss decreases to 21.1mAh/g. It is important to notice that the first columbic efficient delivered by our material is larger than that of the Al_2O_3 coated $Li[Li_{0.2}Ni_{0.17}Mn_{0.56}Co_{0.07}]O_2$ which is reported to have a larger irreversible capacity loss of 58mAh/g[36]. This may predict that doping is more effective than coating.

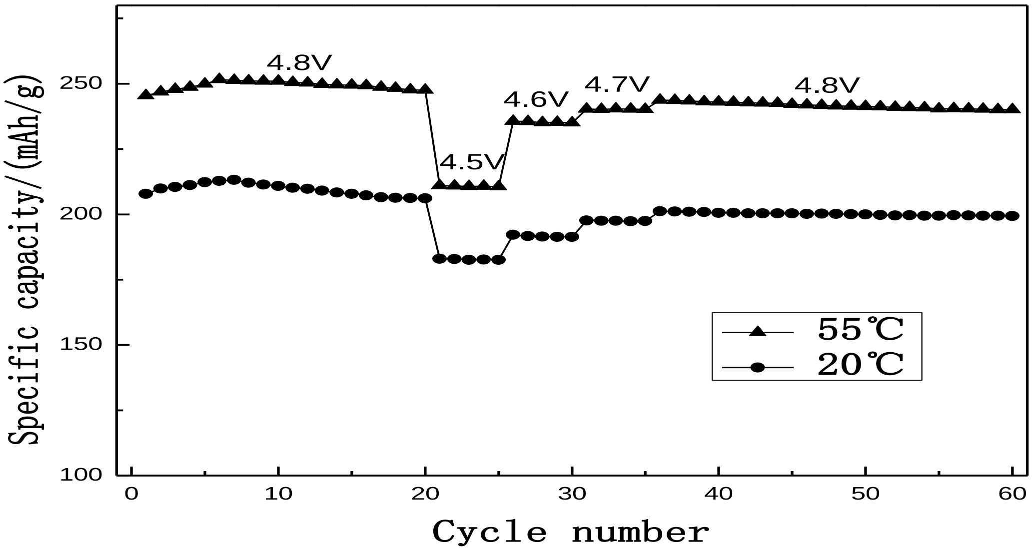

Figure 4. Cycling performance of $Li[Li_{0.2}Ni_{0.16}Mn_{0.56}Co_{0.06}Al_{0.02}]O_2$ within different cut-off voltages

Fig. 4 shows the Cycling performance of $Li[Li_{0.2}Ni_{0.16}Mn_{0.56}Co_{0.06}Al_{0.02}]O_2$ electrodes subjected to continuous cycling within different cut-off voltages at a rate of 0.2C. It can be seen from the figure that the discharge capacity of the cell $Li[Li_{2/10}Ni_{1/10}Co_{2/10}Mn_{5/10}]O_2$/Li increases with the increase of cycle number initially then slightly decreases afterwards and finally becomes stable up to 60 cycles both at 20 ^{o}C and 55 ^{o}C, respectively.The $Li[Li_{0.2}Ni_{0.16}Mn_{0.56}Co_{0.06}Al_{0.02}]O_2$ electrode delivers 245.8mAh/g at the beginning and its discharge capacity reaches the maximum of 251.6mAh/g at the 6th cycle which means that the electrochemical properties have been fully activated, and then its discharge capacity decreases to 240.1mAh/g at the 60th cycle when the upper cut-off voltage is 4.8V at 55 ^{o}C. The excellent cycling characteristics of $Li[Li_{0.2}Ni_{0.16}Mn_{0.56}Co_{0.06}Al_{0.02}]O_2$ electrode can be attributed to the enhanced structural stability reflected by high degree of crystallinity shown in Fig. 1 and the small crystallite size shown in Fig. 2 [37].

As can be seen in the Fig. 4, the discharge capacities of $Li[Li_{2/10}Ni_{1/10}Co_{2/10}Mn_{5/10}]O_2$ at 20 ^{o}C are 183mAh/g in 4.5–2.0 V, 192.2mAh/g in 4.6–2.0 V and 197.6mAh/g in 4.7–2.0 V, respectively. The discharge capacities of $Li[Li_{2/10}Ni_{1/10}Co_{2/10}Mn_{5/10}]O_2$ at 55 ^{o}C are 211mAh/g in 4.5–2.0 V, 235.6mAh/g in 4.6–2.0 V and 240.3mAh/g in 4.7–2.0 V, respectively. We can notice that the discharge capacities increase slightly when the upper cut-off voltage is above 4.6V. It may be proposed that once the material activation has been finished, the cell could be cycled at a little lower up-cut voltage of 4.6 V to avoid electrolyte decomposition.

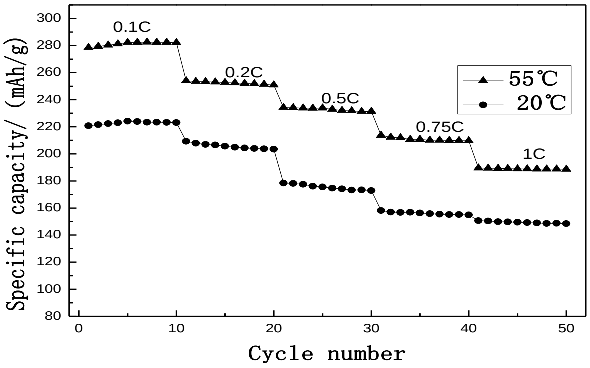

Figure 5. Cycling and rate performances of Li[$Li_{0.2}Ni_{0.16}Mn_{0.56}Co_{0.06}Al_{0.02}$]$O_2$

Fig. 5 shows the discharge curves and cycling performance of Li[$Li_{0.2}Ni_{0.16}Mn_{0.56}Co_{0.06}Al_{0.02}$]$O_2$ in the range of 2.0–4.8V at various rates from 0.1 C to 1C. As can be seen, the electrodes are able to deliver capacities of 223.1mAh/g and 282.1mAh/g at 0.1C after 10 cycles at 20 °C and 55 °C, respectively. Very interestingly, at 1C rate, the electrodes are still able to deliver 148.5mAh/g and 188.6mAh/g after 50 cycles at 20 °C and 55 °C, respectively, which correspond to 66.6% and 66.9% of the 0.1C delivered capacity. This comparison clearly indicates the excellent cycling characteristics and promising good rate capability of the material, especially at 50 °C. But compared to other materials from the same family, the Li[$Li_{0.2}Mn_{0.56}Ni_{0.16}Co_{0.08}$]$O_2$ material reported by Klopsch still has the better rate capability at high rate at 20 °C[35]. Therefore, a further study is necessary to improve its rate capability at low temperature.

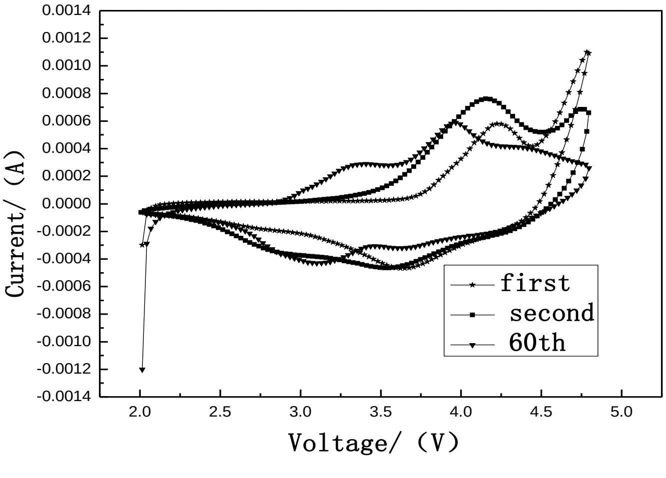

Figure 6. Cyclic voltammograms of Li[$Li_{0.2}Ni_{0.16}Mn_{0.56}Co_{0.06}Al_{0.02}$]$O_2$

In order to further understand the electrochemical properties of Li[$Li_{0.2}Ni_{0.16}Mn_{0.56}Co_{0.06}Al_{0.02}$]$O_2$, cyclic voltammetry was carried out in the range 2.0–4.8V with a scanning rate of 0.1 mV/s. As shown in Fig.6, there are two peaks during the first charging, the first one is below 4.5 V, and it is due to the oxidation of Ni^{2+} to Ni^{4+} and Co^{3+} to Co^{4+}. The second peak which is above 4.5 V is the irreversible reaction in which the lithium is extracted from the removed from $Li[Li_{1/3}Mn_{2/3}]O_2$ component with the simultaneous release of oxygen[8]. In the first charge curve, there are no peaks below 3.5 V that corresponds to Mn^{3+}/Mn^{4+} redox-reaction in CV. The absence of the Mn^{3+}/Mn^{4+} peaks indicates that Mn^{4+} ions are electrochemically inactive, so it is presumed that Mn in our sample synthesized is in the valence of Mn^{4+} [10,38]. In the second charge curve, the Mn^{3+}/Mn^{4+} peaks around 3.0V appear, which proves that part of Mn^{4+} has been reduced to Mn^{3+}. As the cycling progresses, the Mn^{3+}/Mn^{4+} peaks become more evident which results in the increase of the capacities at the beginning as shown in Fig. 4.

4. CONCLUSION

In this paper, $Li[Li_{0.2}Ni_{0.16}Mn_{0.56}Co_{0.06}Al_{0.02}]O_2$ has been succeedly synthesized by a sol–gel method. The material shows the single phase layered with the super lattice structure originating from the monoclinic Li_2MnO_3, and the as-prepared particles have a nearly spherical morphology with an average diameter of approximately 100nm. The electrochemical properties were analyzed by charge–discharge and CV studies. The highlights of this material are its high first columbic efficient, excellent cycling characteristics and good rate capability. Electrochemical measurements show that the irreversible capacity loss of the compound is 38.2mAh/g and 21.1mAh/g at 20 °C and 55 °C, respectively, in the range of 2.0–4.8V at a rate of 0.1C. The electrodes are still able to deliver 148.5mAh/g and 188.6mAh/g after 50 cycles at 1C rate at 20 °C and 55 °C, respectively. All those demonstrate that $Li[Li_{0.2}Ni_{0.16}Mn_{0.56}Co_{0.06}Al_{0.02}]O_2$ is a promising cathode material for next-generation Li-ion battery. The Al element is an ideal element to replace the expensive and toxic element Co in this kind of cathode material.

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