Influence of Cu doping and high-pressure torsion on electrochemical performance of lithium-rich cathode material

Mingcai Wang1, Fan Zhang1*, Linfeng Chen1, Bin Xu1, Zhonglu Cui1 and Kaveh Edalati2

1 School of Materials Engineering, Shanghai University of Engineering Science, Shanghai, 201620, China
2 WPI, International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University, Fukuoka, 819-0395 Japan
fzhang@sues.edu.cn (F Zhang).

Abstract. Lithium-rich manganese based layered oxide yLi2MnO3∙(1-y)LiMO2 (M=Ni, Co and Mn) is one of the candidate materials for high-capacity cathodes in next-generation lithium-ion batteries. Ion doping with cation and introducing oxygen vacancy are regarded as two methods to change the electrochemical performance of Li-rich cathode materials. In this work, Li1.2Mn0.54Co0.13Ni0.13O2 was synthesized via one-step co-precipitation process, ion doping with low cost element Cu as well as high-pressure torsion were carried out to modify the Li-rich material. Results show that doping with Cu can slightly improve the specific discharge capacity as well as the coulombic efficiency which may be attributed to the lower cation mixing degree.

1. Introduction
Due to the advantages of high energy density, long cycle life and no memory effect, lithium-ion batteries (LIBs) are widely used in digital products, electric vehicles and hybrid electric vehicles. Compared with anode materials which generally have high specific capacity, low capacity of cathode material becomes the bottleneck which limit the further improving of the energy density of LIBs[1]. It is urgent to develop new type cathode material with higher capacity. Among the candidate cathode materials, Li1.2Mn0.54Co0.13Ni0.13O2 material can high discharge capacity due to its more active surfaces. However, some shortcomings such as the high irreversible capacity loss limit the further application of this material[2]. Controlling and improving the synthesis method is very effective to overcome these shortcomings and improve the electrochemical performance of lithium-rich manganese based cathode materials[3,4]. So far, many methods have been developed to prepare high-quality Li-rich materials, such as coprecipitation method, microwave heating process, sol-gel method, ion exchange reaction and solid phase method[3-6].

Among these preparation methods, coprecipitation can make all the transition metal ions be fully contacted in solution at the atomic level, thereby the morphology of the prepared sample is easy to form a regular spherical shape with uniformed particle size, so as to ensure the final product possessing a stable electrochemical performance[6]. To further enhance the electrochemical performance, ion doping and introducing oxygen vacancies into the material can be two effective ways[7-9]. From the economical point of view, the using of low cost element such as Cu and Mg might be desirable for commercial production[10,11]. High-pressure torsion (HPT) is a method of severe plastic deformation (SPD), in which the material is stretched between two rotating anvils under
high pressure, showing the potential to stabilize oxygen vacancies in different oxides such as BaTiO$_3$, TiO$_2$ and ZnO[12].

Therefore, in this work, Li$_{1.2}$Mn$_{0.54}$Co$_{0.13}$Ni$_{0.13}$O$_2$ was synthesized via one-step co-precipitation process using oxalic acid as precipitant. Ions doping with low cost element Cu as well as HPT processing were carried out to modify the Li-rich material. The microstructures of both the unmodified and modified materials were checked by X-ray diffraction. Their cycle performances were also investigated.

2. Materials and methods

Acetates of transition metals and lithium acetate were solved in 100 mL ethanol with stoichiometric ratio to form solution A and excess oxalic acid with 100ml ethanol was used as solution B. Solution A and solution B were then transferred to a 500mL beaker with a peristaltic pump and stirred continuously to form oxalate precipitates. After that, the solution was continuously stirred for 4 hours. The precipitates were filtered with 95% ethanol for 3-4 times and was subsequently placed in a drying oven at 80 °C for 12 hours the precursors and then sintered at 900 °C for 12 hours to finally achieve Li$_{1.2}$Mn$_{0.5}$Co$_{0.13}$Ni$_{0.13}$O$_2$ and Li$_{1.2}$Mn$_{0.5}$Co$_{0.1}$Ni$_{0.1}$Cu$_{0.1}$O$_2$. For Li$_{1.2}$Mn$_{0.54}$Co$_{0.13}$Ni$_{0.13}$O$_2$, powders were processed by HPT at room temperature under a pressure of $P = 6$ GPa. Shear strain was introduced through the rotation of the lower anvil with respect to the upper one for $N = 3$ turns with a rotation speed of 1 rpm.

The crystal structures of the prepared samples were analyzed by an X-ray diffractometer (XRD, D2-PHASE, Bruker, Karlsruhe, Germany) at room temperature, with a scanning range of 5°-90°, a rate of 1°/min, using Cu-Kα radiation source ($\lambda = 0.1540560$ nm). The electrochemical tests were carried out with 2032 coin cells using lithium metal foil as the opposite electrode. The active material (Li$_{1.2}$Mn$_{0.5}$Co$_{0.13}$Ni$_{0.13}$O$_2$, Li$_{1.2}$Mn$_{0.5}$Co$_{0.1}$Ni$_{0.1}$Cu$_{0.1}$O$_2$, HPTed- Li$_{1.2}$Mn$_{0.54}$Co$_{0.13}$Ni$_{0.13}$O$_2$), the binder (PVDF) and carbon source acetylene black were mixed with a mass ratio of 8:1:1 in a high-speed vibrating ball milling machine (MSK-SFM-12M, HF-Kejing, China). After a few minutes of ball milling, a small amount of N-methyl-2-pyrrolidone (NMP) was added into the mixture and was kept stirring to form a slurry. The slurry was then well pasted on a Al foil with a diameter of 16 mm by a changer (MSK-AFA-III, HF-Kejing, China), which was subsequently dried in a vacuum oven at 60°C for 12 h, and finally a working electrode was obtained. Celgard 2300 polypropylene was used as separator, 1 M LiPF$_6$ was dissolved in the mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) with a volume ratio of 1:1. The 2032 coin cells were assembled in a glove box (Super 1220/750/900, Shanghai Mikrouna Electromechanical Technology Co., Ltd, Shanghai, China) with a built-in high-purity argon gas (99.999% purity). The water and oxygen level of the glove box were maintained below 1 ppm before the battery was assembled. The electrochemical performance tests of the 2032 button batteries were carried out in an electrochemical workstation (CT 4008, Neware Electronics Co., Ltd, China). The cycle stability test was carried out at a voltage of 1-3V and 1 C rate for 100 cycles at room temperature.

3. Results and discussion

Figure 1 illustrates the cycle performance of Li$_{1.2}$Mn$_{0.54}$Co$_{0.13}$Ni$_{0.13}$O$_2$ at 1 C rate for 100 cycles. The black line represents the specific discharge capacity against cycle numbers while the blue line represents the variation of coulombic efficiency during cycling. It can be observed that the initial specific discharge capacity for this matrix material can reach 172 mAh·g$^{-1}$ with an initial coulombic efficiency of about 80%.
The cycle performance of Cu doped material is shown in figure 2. After doping Cu ions into matrix material, the electrochemical performance is slightly improved. As can be seen from figure 2 that its initial specific discharge capacity increased to 174 mAh g⁻¹ with a higher initial coulombic efficiency of about 86%.

Figure 3 shows XRD profiles of unmodified and modified Li1.2Mn0.54Co0.13Ni0.13O2. It is clear that all the samples show two different kinds of peaks corresponding to LiMO₂ (M = Mn, Ni, Co, Cu) and Li₂MnO₃, respectively. This indicates that the modifications with doping Cu or by HPT-processing didn’t change the layered structure of α-NaFeO₂. However, when one calculate the intensity ratio of (003) plane and (104) plane, it can be found that the I(003)/I(104) value changed with preparation methods. Generally speaking, the higher the I(003)/I(104) value is, the lower the cation mixing degree will be and the more stable the layered structure will be. After Cu doping, the I(003)/I(104) value increased from 1.22 to 1.25 indicating a more stable layered structure is formed in Li1.2Mn0.5Co0.1Ni0.1Cu0.1O2, which may
be the reason of slight increase of the electrochemical performance. After HPT, however, this value decreased to lower than 1.2 which may cause the disruption of stable layered structure during charge/discharge process and finally result in a decrease of electrochemical performance. Moreover, an unknown phase also appeared around 36°after HPT, this phase may be also harmful to the electrochemical cycling.

Figure 4. XRD profiles of unmodified and modified Li$_{1.2}$Mn$_{0.54}$Co$_{0.13}$Ni$_{0.13}$O$_2$.

4. Conclusions
Li-rich layered Li$_{1.2}$Mn$_{0.54}$Co$_{0.13}$Ni$_{0.13}$O$_2$ was successfully obtained via one-step coprecipitation method using oxalic acid as precipitant. After doping with low cost element Cu, the layered structure became more stable and the electrochemical performance was slightly increased in the term of increased specific discharge capacity (174 mAh·g$^{-1}$) and higher coulombic efficiency (86%). However, HPT processing resulted in unknown phase in the structure which may be harmful to maintain the stable layered structure during charge/discharge cycling and finally led to a dramatic decrease in electrochemical performance.

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