Synthesize Li$_{2}$Mn$_{0.8}$Co$_{0.13}$Ni$_{0.13}$O$_{2}$ Cathode Materials for Li-ion Batteries by One-Step Co-precipitation Method

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Introduction
Transportable devices driven by Li-ion cells such as cell phones and laptop computers, and uninterrupted power supplies (UPS) have become indispensable parts in our daily life for the past decade. To satisfy the needs of wider applications in electrical vehicles, high performance cathode materials are required to build advanced Li-ion batteries with low mass, reliable safety, high energy density and durable cyclacity. Li-rich layered cathode materials (M=Mn, Ni, Co, etc.), because of the higher reversible capacity (~250 mAh g$^{-1}$), lower cost and better environmental friendliness than commercially used LiCoO$_2$, have been extensively studied as new generation of promising cathode materials for advanced Li-ion batteries [1-9]. The synthetic route of Li-rich layered cathode materials is various, such as sol-gel, solid-phase reaction, hydrothermal and co-precipitation [7-8]. In our previous research [9], ammonium oxalate was applied to serve as the precipitator to sublime transition-metal in the weak-acidic ammonium oxalate was applied to serve as the precipitator to sublime transition-metal in the weak-acidic aqueous solution. In the ammonium oxalate co-precipitation method, we heat treated the mixture of the precipitated precursor and LiNO$_3$ to obtain the high electrochemical active Li-rich layered materials. However, the co-precipitation method is a complex process and is time consuming. In present work, we synthesize Li$_{2}$Mn$_{0.8}$Co$_{0.13}$Ni$_{0.13}$O$_{2}$ cathode materials by one-step co-precipitation (replacing ammonium oxalate by oxalic acid to precipitate Mn$^{2+}$, Ni$^{2+}$, Co$^{3+}$ as well as Li$^{+}$ in ethanol solution) combining high-temperature calcination. The as-prepared cathode materials present homogeneous particles, ideal lattice parameters, a high initial discharge capacity, a small irreversible capacity loss and a good cycle performance.

Experimental
The pristine sample, Li$_{2}$Mn$_{0.8}$Co$_{0.13}$Ni$_{0.13}$O$_{2}$, was prepared by one-step co-precipitation method. Li(NO)$_3$ (Aladdin), Ni(NO)$_3$ (Aladdin), Co(NO)$_3$ (Aladdin), and Mn(NO)$_3$ (Aladdin, 50 % aqueous solution) were all dissolved in ethanol with the mole ratio of 9.23:1:1:4.15. Then, stoichiometric amount of H$_2$O was prepared by one-step co-precipitation method. Li$_{2}$Mn$_{0.8}$Co$_{0.13}$Ni$_{0.13}$O$_{2}$ cathode materials by one-step co-precipitation (replacing ammonium oxalate by oxalic acid to precipitate Mn$^{2+}$, Ni$^{2+}$, Co$^{3+}$ as well as Li$^{+}$ in ethanol solution) combining high-temperature calcination. The as-prepared cathode materials present homogeneous particles, ideal lattice parameters, a high initial discharge capacity, a small irreversible capacity loss and a good cycle performance.

Results and Discussion

As shown in Fig.1 (a), the has a The XRD patterns of the as-prepared sample is well fitted to the hexagonal α-NaFeO$_2$ structure (R-3m) with small extra peaks at 2θ of 20°-23°, which are typically caused by the super-lattice ordering of Li$^{+}$ and Mn$^{2+}$ in transition metal layer corresponding to Li$_x$MnO$_y$ phase [3]. At the same time, the ratio of c/a and $\alpha$ decreases with increased crystallite size and less cation disorder [9]. Fig.1 (b) shows that the materials is quite homogeneous in particle sizes with intricate bulk morphology. Fig. 1 (c) shows the voltage profiles of the initial charge/discharge cycle of the as-prepared sample at the current density of 20 mA g$^{-1}$ (C/10 rate). On the initial charge, there are two main charge areas: a sloping platform at 3.9-4.5 V, which is associated with the oxidation of Ni$^{2+}$ to Ni$^{3+}$ and Co$^{3+}$ to Co$^{4+}$; and another platform nearby 4.5 V, corresponding to the simultaneous removal of Li$^+$ and O$_2$ (as Li$_2$O) from the lattice of Li$_x$MnO$_y$ [3-5]. Fig. 1 (d) exhibits the cycle performance of the as-prepared sample. After 50 cycles at 40 mA g$^{-1}$ (C/5 rate), the discharge capacity decreases from 270.8 to 234.5 mAh g$^{-1}$, with a high retention of 86.6 %.

References