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Novel Gel-like Process for Synthesizing Submicron $Li_aNi_{0.8}Co_{0.2}O_2$ Powders Used in Lithium Ion Batteries

Rong Zhong YUAN, Zuo Long YU*, Mei Zhen QU

Chengdu Institute of Organic Chemistry, the Chinese Academy of Sciences, Chengdu 610041

Abstract: A novel gel-like process has been developed for synthesizing $Li_aNi_{0.8}Co_{0.2}O_2$ powders, using citric acid as a chelating agent. This process improves the homogeneity of constituent cation and enhances their reactivity in the obtained precursor. The results of electrochemical test demonstrated that these materials exhibited excellent electrochemical properties. Its initial capacity reached 181.6 mAh/g and reversible efficiency at the first cycle is about 88.6%.

Keywords: Lithium ion batteries, cathode material, $Li_aNi_{0.8}Co_{0.2}O_2$, gel-like process.

In recent years, research and development of lithium nickel cobalt mixed oxides have become a subject of utmost importance in the field of lithium ion batteries. $LiNi_{0.8}Co_{0.2}O_2$, one of the promising nickel rich phases of $LiNi_{1-y}Co_yO_2$ solid solutions has been synthesized by various methods from the conventional solid state method to the sol-gel and colloidal precipitation techniques[1]. Sol-gel methods have some advantages over conventional solid state methods, but the application of the true sol-gel process involving metal alkoxides for the synthesis of $LiMO_2$ (M = Ni, Co, Mn) is quite difficult owing to the insolubility of the polymeric alkoxides, not withstanding the cost of these metal-organics. Hence, a modification of the sol-gel approach is necessary[2]. In the present study, a modified route called the gel-like process has been developed for synthesizing $LiNi_{0.8}Co_{0.2}O_2$. It exhibited excellent electrochemical properties.

$Li_aNi_{0.8}Co_{0.2}O_2$ powders were synthesized by a novel gel-like method with citric acid as a chelating agent. At first, the mixture of $LiOH{\cdot}H_2O$, Ni acetate, Co acetate salts and citric acid in a mol ratio of 1.15:0.8:0.2:1 was ground. Water (or ethanol) was added for dispersing to form coordination precursor slurry and then the slurry was ball-milled overnight in a planetary micro miller with stainless steel balls. After milling, the precursor was subsequently dried at 90-100°C, then precalcined at 400°C for 6 h in air in order to eliminate organic contents. Finally, The decomposed powders were subjected to further heat treatment at 800°C for 2 h and then 720°C for 10 h under a flowing oxygen stream. For comparison, the conventional solid state method was also used to synthesize $Li_aNi_{0.8}Co_{0.2}O_2$ powders. The mixture of $LiOH{\cdot}H_2O$, $Ni(OH)_2$, Co acetate were calcined at 630°C for 8 h and then at 750°Cfor 16 h.

The positive electrode consisted of 85 wt% $Li_aNi_{0.8}Co_{0.2}O_2$ and 10 wt% acetylene

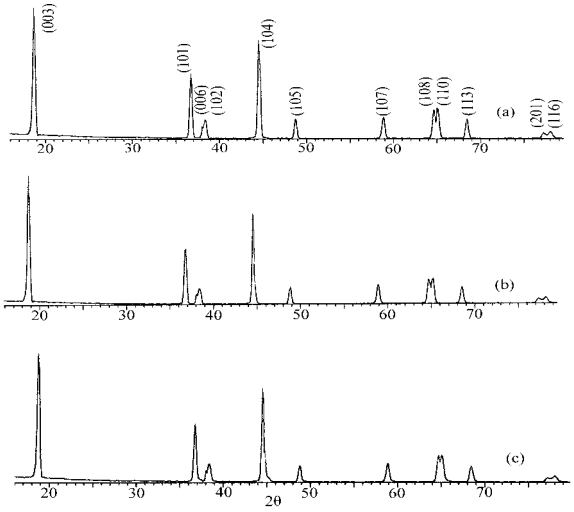
*E-mail: yrzchem@sina.com

black and 5 wt% polytetrafluoroethylene (PTFE) as a binder, and metal Al was used as collector. The electrolyte solution consists of ethylene carbonate + diethylene carbonate (1:1) + 1 mol/L $LiClO_4$. Lithium metal foil was used as the counter electrode during the electrochemical measurements. All cell assemblies were put in a dry box filled with argon gas. All electrochemical tests were carried out in a DC-5 fully automatic program test instrument, with constant current.

Power X-ray diffraction (XRD) was performed by means of a Rigaku D/max-ra with Cu K α radiation and a graphite monochromator. Scanning electron microscope (SEM) was carried out using JEOL JSM-35 microscope.

Structure studies

Figure 1 XRD patterns of $Li_aNi_{0.8}Co_{0.2}O_2$ compounds synthesized by different methods



The gel-like method using (a) water and (b) ethanol as a solvent; (c) the solid state method.

The X-ray diffractograms recorded for the $Li_aNi_{0.8}Co_{0.2}O_2$ compounds synthesized by different methods are shown in **Figure 1**. All the synthesized compounds show sharp peaks indicating a high degree of crystallinity. All the Bragg peaks could be indexed to the hexagonal lattice in the R3-m space group. The splittings of the (006)/(012) and (018)/(011) peaks are prominent, indicating perfect hexagonal ordering for all the compounds synthesized. The structural data calculated from the XRD data are summarized in **Table 1**. The R-factor, which was defined by Reimers *et al.*[3], should be at minimum in a system with good hexagonal ordering. Hence, the $Li_aNi_{0.8}Co_{0.2}O_2$ compound synthesized using water as a solvent showed the lower R-factor than those synthesized by solid state reaction, indicating better hexagonal ordering of the system. However, the $I_{(003)}/I_{(104)}$ peak intensity ratio (only 1.12) decreased when ethanol was used as the solvent. This result indicated that the $Li_aNi_{0.8}Co_{0.2}O_2$ using ethanol leads to a

deviation from hexagonal ordering, which obviously has adverse effects on capacity and cyclability of the materials.

Table 1 Structural parameters, discharge capacities Coulomb efficiency at the first cycle and capacity retention at the 15th cycle for $Li_aNi_{0.8}Co_{0.2}O_2$ synthesized using different method

Methods		R-factor= $(I_{006}+I_{102})/I_{101}$	I_{003}/I_{104}	Discharge capacity (mAh/g)[a]	Coulomb efficiency at the first cycle (%)	Capacity retention rate at the 15th cycle[b] (%)
Gel-like method	Ethanol	0.37	1.12	171.1	86.2	92.0
	Water	0.38	1.33	181.6	88.6	94.1
Solid state method		0.46	1.43	176.0	85.5	90.8

[a] Data at a 0.5C rate, cycled between 2.7 and 4.25V a discharge capacity at the 4th cycle was taken as the discharge capacity

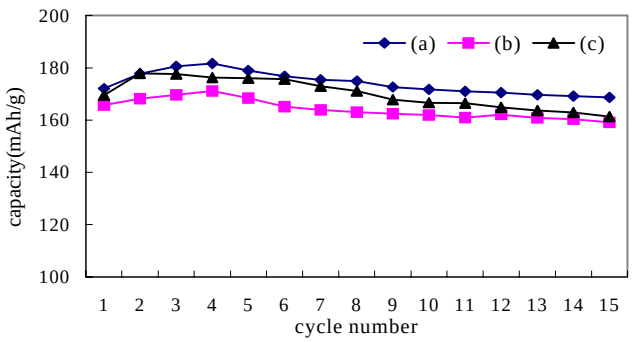
[b] Capacity retention rate obtained by dividing the discharge capacity at the 15th cycle by that at the the 4th cycle

Electrochemical studies

Table 1 shows the initial discharge capacity, Coulomb efficiency at the first cycle and capacity retention rate at the 15th cycle of the $Li_aNi_{0.8}Co_{0.2}O_2$ compounds. Among these compounds, the compound synthesized using water exhibited the highest capacity and the best cyclability. The discharge capacity was 181.6 mAh/g and the Coulomb efficiency at the first cycle was around 88.6%.

Figure 2 shows the cycling performance of the materials synthesized by different methods. At the initial cycles, the capacity gradually increases, and then slowly reduced. We can find that the compound synthesized using water as a solvent showed the best cycling performance. After 15 continuous cycles, it has exhibited the least loss. The capacity still has around 169 mAh/g and the capacity retention was 94.1%. But the compound synthesized by the solid state method has the worst cycling property, and the capacity retention was only 90.5%.

Figure 2 Cycling performance of the materials synthesized by different methods



the gel-like method using (a) water and (b) ethanol as a solvent; (c) the solid state method.

From above results, we can draw the conclusion that polycrystalline $Li_aNi_{0.8}Co_{0.2}O_2$ synthesized by soft chemistry with citric acid as a chelating agent and water as a solvent had excellent layered structure, and exhibited the best capacity and cycling performance. The main reason may be the initial formation of a chelation complex, which decides the homogeneity of the final compound. The complex formation reaction of the compound was more facilitated in a water medium than in the ethanol medium. Formation of a stable chelation complex will lead to the formation of homogeneous and uniform oxide particles. It proved that this method not only provided a simple practicable and effective route for the synthesis of the $LiNi_{1-y}Co_yO_2$ solid solution, but also had many advantages over the traditional solid state method.

Acknowledgment

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