

## Synthesis and characterization of multidoped lithium manganese oxide spinel $\text{LiCo}_{0.02}\text{La}_{0.01}\text{Mn}_{1.97}\text{O}_{3.98}\text{Cl}_{0.02}$

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**Abstract:** Multidoped spinel  $\text{LiCo}_{0.02}\text{La}_{0.01}\text{Mn}_{1.97}\text{O}_{3.98}\text{Cl}_{0.02}$  was synthesized by solid-state method. The structure and electrochemical performance were characterized by XRD, ESEM, particle size distribution analysis, specific surface area testing, galvanostatic cycling and electrochemical impedance spectroscopy. The XRD analysis shows that the sample exhibits pure spinel phase. The substitution of Co, La for Mn and Cl for O in the  $\text{LiMn}_2\text{O}_4$  stabilizes the structural integrity of the spinel host, which in turn increases the electrochemical cycleability. The electrochemical experiments confirm that the capacity of the  $\text{LiCo}_{0.02}\text{La}_{0.01}\text{Mn}_{1.97}\text{O}_{3.98}\text{Cl}_{0.02}$  electrode maintains 90.6% of the initial capacity at 180th cycle.

**Key words:** lithium ion batteries;  $\text{LiMn}_2\text{O}_4$ ; lithium manganese oxide spinel; multidoped; electrochemical properties

### 1 Introduction

The cathode material plays an important role in the performance of lithium ion batteries. Lithium transition metal compounds with layered and spinel structure are favourites among cathode materials for lithium rechargeable batteries. In this group of materials with high energy capacity, lithium-manganese spinel  $\text{LiMn}_2\text{O}_4$  is the most promising one because it is cheaper and less toxic[1–3].

It is well known that manganese ions in  $\text{LiMn}_2\text{O}_4$  are in two oxidation states. The increasing  $\text{Mn}^{3+}$  content during the intercalation process brings Jahn-Teller distortion. The asymmetric changing of cell parameters (ratio of  $c$  to  $a$  changing from 10% to 16%) is followed by destruction of spinel structure. Therefore, most research to stabilize cubic spinel structure in recent years has been directed toward the preparation of nonstoichiometric Li-Mn spinels, Mn-substituted stoichiometric  $\text{LiMn}_2\text{O}_4$  by low valence cations (<4) [4–8], O-substituted spinel by anions F and S[9], and surface passivation treatment of  $\text{LiMn}_2\text{O}_4$ [10].

Spinel  $\text{LiMn}_2\text{O}_4$  doped with single metal ions either offers a high capacity similar to the practical capacity obtained from undoped spinel cathode[11], but with limited cycleability upon cycling, or offers relatively

stable cycle-life but low initial capacity[12]. In this work, our intention is to synthesize a multidoped spinel material that exhibits the beneficial features of both single-doped spinels[13]. For this purpose, we synthesized a multidoped spinel  $\text{LiCo}_{0.02}\text{La}_{0.01}\text{Mn}_{1.97}\text{O}_{3.98}\text{Cl}_{0.02}$  and discussed the productions by substitution of Co, La and Cl for Mn and O, respectively, in both crystal structure and electrochemical properties.

### 2 Experimental

Both of the samples,  $\text{LiMn}_2\text{O}_4$  and  $\text{LiCo}_{0.02}\text{La}_{0.01}\text{Mn}_{1.97}\text{O}_{3.98}\text{Cl}_{0.02}$ , were synthesized by solid-state reaction of stoichiometric amounts of  $\text{LiOH}\cdot\text{H}_2\text{O}$ ,  $\text{Mn}_3\text{O}_4$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{La}_2\text{O}_3$  and  $\text{LiCl}$ . Well ground of the starting mixtures were preheated at 470 °C for 10 h, then ground and calcined at 750 °C for 36 h under air flow.

Powder X-ray diffraction(XRD) analyses were carried out on a D/max-2500 XRD diffractometer (Japan) with  $\text{Cu K}_\alpha$  radiation at 40 kV and 100 mA. Rietveld refinement was then performed on the XRD data to obtain the lattice constants. The scanning electron microscope(SEM) photos were gained on XL 30 ESEM surroundings scanning electron microscope(PHILIPS, Netherlands). The particle distribution for each as-prepared compound were analyzed with MASTERSIZER 2000 laser particle size analyzer

(Marlwin Apparatus Company, England). The specific surface area was inspected on CHEMBET300 specific surface area analyzer (QUANTA CHROM, USA).

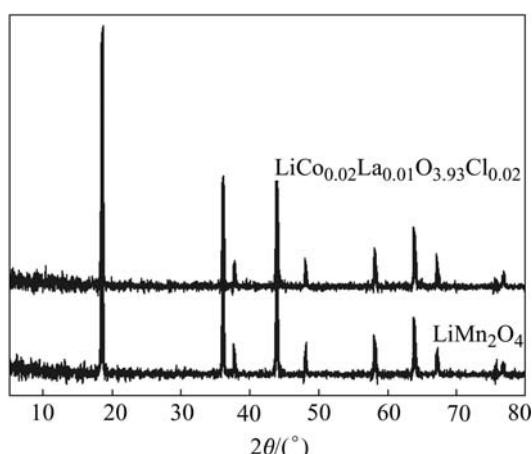
Electrochemical experiments were performed using coin-type cells. The cathode was prepared by spreading the mixture of 85% active material, 10% acetylene black as conductive additives and 5% polytetrafluoroethylene as binder on to aluminum foil. The prepared electrode was dried in vacuum oven at 120 °C for 12 h. The cell was assembled in an argon-filled. The cell consisted of a cathode and lithium metal anode separated by American Celgard2300 membrane, using 1 mol/L LiPF<sub>6</sub> in a mixture of EC and DMC in mass ratio of 1 : 1 as electrolyte. The charge and discharge cycles were carried out with a LandCT2001 battery program-control test system at current of 0.2C rate over a potential range between 3.0 and 4.3 V.

The AC impedance measurement was performed using CHI660B electrochemical interface. Before AC impedance measurements, the cell was pre-cycled between 3.0 and 4.3 V for five cycles to establish and stabilize the solid electrolyte interface(SEI) between the electrolyte and electrodes. The cell was then potentiostatically conditioned to a potential and equilibrated for 2 h, then, AC impedance spectra were obtained by applying a sine wave of 5 mV amplitude over the frequency range of 100 kHz to 10 mHz.

### 3 Results and discussion

#### 3.1 Structure and physical characterization

The structure of the as-prepared powders of undoped spinel and (Co, La, Cl)-doped spinel were characterized by XRD. Their XRD patterns are shown in Fig.1. Both of the samples were identified as a single phase of cubic spinel with a space group Fd3m. The cubic lattice parameters were listed in Table 1. As compared with that of LiMn<sub>2</sub>O<sub>4</sub>, the doped spinel



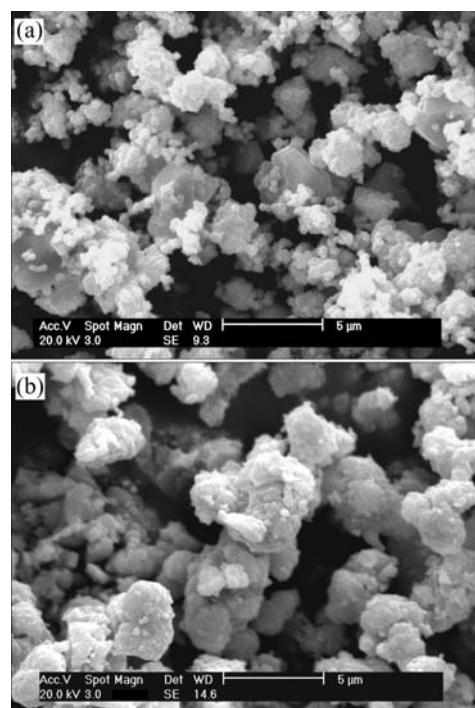
**Fig.1** XRD patterns of LiMn<sub>2</sub>O<sub>4</sub> and LiCo<sub>0.02</sub>La<sub>0.01</sub>Mn<sub>1.97</sub>O<sub>3.98</sub>Cl<sub>0.02</sub> powders

**Table 1** Lattice parameters of as-prepared spinels

Sample	<i>a</i> /nm	<i>V</i> /nm <sup>3</sup>
LiMn <sub>2</sub> O <sub>4</sub>	0.824 02	0.008 236 4
LiCo <sub>0.02</sub> La <sub>0.01</sub> Mn <sub>1.97</sub> O <sub>3.98</sub> Cl <sub>0.02</sub>	0.559 517 0	0.558 743 3

indicates smaller lattice parameters with the doping of Co, La, Cl ions in the spinel structure.

The ESEM of the synthesized LiMn<sub>2</sub>O<sub>4</sub> and LiCo<sub>0.02</sub>La<sub>0.01</sub>Mn<sub>1.97</sub>O<sub>3.98</sub>Cl<sub>0.02</sub> powders were observed by scanning electron microscopy, the results are shown in Fig.2. Both LiMn<sub>2</sub>O<sub>4</sub> and LiCo<sub>0.02</sub>La<sub>0.01</sub>Mn<sub>1.97</sub>O<sub>3.98</sub>Cl<sub>0.02</sub> exhibit similar particle shape. Despite the sample process condition, the spinel powder shows a relatively smooth surface appearance and large particle size by multi-doping with Co, La and Cl ions.



**Fig.2** ESEM images of LiMn<sub>2</sub>O<sub>4</sub>(a) and LiCo<sub>0.02</sub>La<sub>0.01</sub>Mn<sub>1.97</sub>O<sub>3.98</sub>Cl<sub>0.02</sub>(b)

The particle sizes of LiMn<sub>2</sub>O<sub>4</sub> and LiCo<sub>0.02</sub>La<sub>0.01</sub>Mn<sub>1.97</sub>O<sub>3.98</sub>Cl<sub>0.02</sub> powders were also measured. The particle properties of LiMn<sub>2</sub>O<sub>4</sub> and LiCo<sub>0.02</sub>La<sub>0.01</sub>Mn<sub>1.97</sub>O<sub>3.98</sub>Cl<sub>0.02</sub> are listed in Table 2. It can be seen that the mean particle size of the two samples are 4.034 and 5.628 μm. Compared with the substituted sample, LiMn<sub>2</sub>O<sub>4</sub> shows a slightly larger particle size value, which is consistent with the ESEM results. The corresponding data of specific area of the two samples are also summarized in Table 2, which shows that the specific surface area of LiCo<sub>0.02</sub>La<sub>0.01</sub>Mn<sub>1.97</sub>O<sub>3.98</sub>Cl<sub>0.02</sub> is lower than the one for LiMn<sub>2</sub>O<sub>4</sub> due to the smooth surface and the larger particle size.

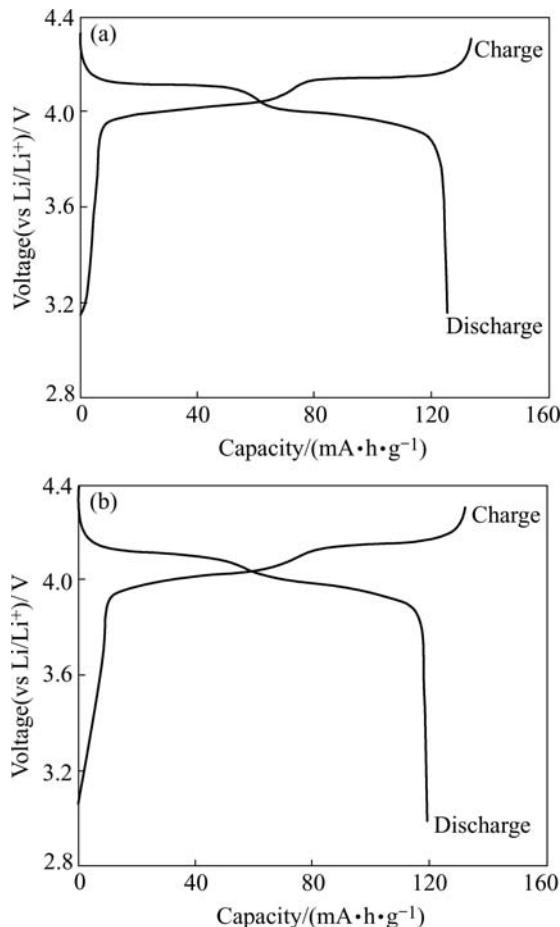
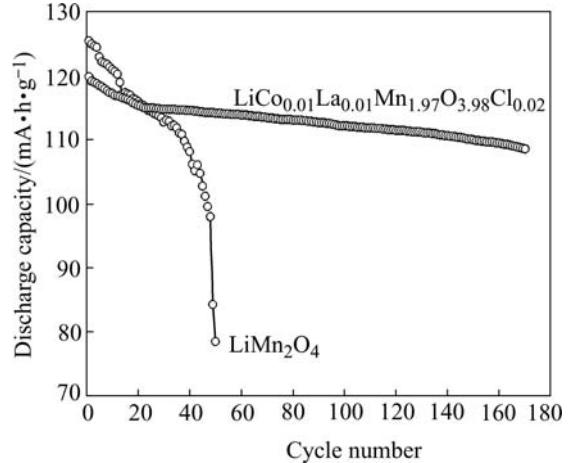
Fig.3 shows the first charge-discharge curves of

**Table 2** Particle properties of  $\text{LiMn}_2\text{O}_4$  and  $\text{LiCo}_{0.02}\text{La}_{0.01}\text{Mn}_{1.97}\text{O}_{3.98}\text{Cl}_{0.02}$ 

Sample	$d_{0.1}/\mu\text{m}$	$d_{0.5}/\mu\text{m}$	$d_{0.9}/\mu\text{m}$	Specific surface area/ $(\text{m}^2\cdot\text{g}^{-1})$
$\text{LiMn}_2\text{O}_4$	1.921	4.034	12.767	2.35
$\text{LiCo}_{0.02}\text{La}_{0.01}\text{Mn}_{1.97}\text{O}_{3.98}\text{Cl}_{0.02}$	2.547	5.628	15.311	1.75

$\text{LiMn}_2\text{O}_4$  and  $\text{LiCo}_{0.02}\text{La}_{0.01}\text{Mn}_{1.97}\text{O}_{3.98}\text{Cl}_{0.02}$  cathodes. It can be obviously seen that the charge-discharge curves of the two samples have two voltage plateaus at approximately 4.05 and 4.15 V, which is a remarkable characteristic of well-defined  $\text{LiMn}_2\text{O}_4$  spinel. From charge-discharge curves, it is found that lithium ion is reversibly lithiated/delithiated through  $\text{LiMn}_2\text{O}_4$  spinel framework. The initial capacity of  $\text{LiMn}_2\text{O}_4$  obtained in this work is 125.9  $\text{mA}\cdot\text{h/g}$  (theoretical capacity of  $\text{LiMn}_2\text{O}_4$  is 148  $\text{mA}\cdot\text{h/g}$ ). By doping with Co, La and Cl, the initial capacity decreased to 119.9  $\text{mA}\cdot\text{h/g}$ . This is due to Co, La substitutions for Mn to decrease of  $\text{Mn}^{3+}$  amount in the substituted spinel phase since during the intercalation/deintercalation of  $\text{Li}^+$  in the  $\text{LiMn}_2\text{O}_4$  matrix only the amount of  $\text{Mn}^{3+}$  contributes to the charge/discharge capacity.

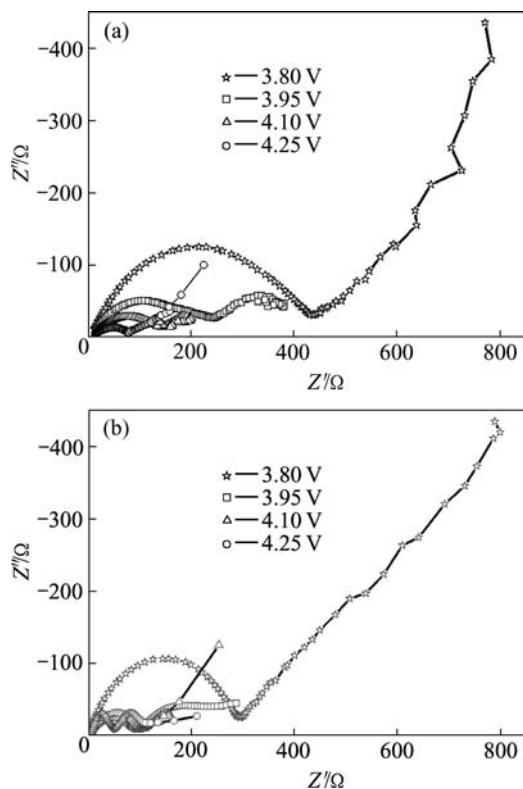
Fig.4 shows the comparison of the cycle performance of  $\text{LiMn}_2\text{O}_4$  and  $\text{LiCo}_{0.02}\text{La}_{0.01}\text{Mn}_{1.97}\text{O}_{3.98}\text{Cl}_{0.02}$  powders.

**Fig.3** First charge-discharge curves of  $\text{Li/LiMn}_2\text{O}_4$ (a) and  $\text{Li/LiCo}_{0.02}\text{La}_{0.01}\text{Mn}_{1.97}\text{O}_{3.98}\text{Cl}_{0.02}$ (b) cells**Fig.4** Cycle performance of  $\text{Li/LiMn}_2\text{O}_4$  and  $\text{Li/LiCo}_{0.02}\text{La}_{0.01}\text{Mn}_{1.97}\text{O}_{3.98}\text{Cl}_{0.02}$  cells

Obviously, the substituted spinel phase is more stable than the  $\text{LiMn}_2\text{O}_4$  spinel phase, the effect of dopant incorporation is a subsequent improvement of  $\text{Li/LiMn}_2\text{O}_4$  cyclability. The electrode of  $\text{LiCo}_{0.02}\text{La}_{0.01}\text{Mn}_{1.97}\text{O}_{3.98}\text{Cl}_{0.02}$  retains 90.6% (108.6  $\text{mA}\cdot\text{h/g}$ ) of the initial capacity after 180 cycles at 0.2C rate. The electrochemical stability has been attributed to the stronger metal-oxygen bonding in substituted  $\text{LiCo}_{0.02}\text{La}_{0.01}\text{Mn}_{1.97}\text{O}_{3.98}\text{Cl}_{0.02}$  spinel phase and the substitution of Cl for O is very effective in hindering the formation of the tetragonal  $\text{Li}_2\text{Mn}_2\text{O}_4$  in the low voltage range[14].

Electrochemical impedance spectroscopy aids understanding the electrode kinetics by analyzing the variation in impedances associated with different processes during lithium intercalation/deintercalation reaction[15]. Fig.5 shows Nyquist plots of  $\text{LiMn}_2\text{O}_4$  and  $\text{LiCo}_{0.02}\text{La}_{0.01}\text{Mn}_{1.97}\text{O}_{3.98}\text{Cl}_{0.02}$  electrode at different charging voltages. All the impedance spectra show a high-frequency semicircle with a maximum at a frequency of a few kilohertz, a medium-frequency semicircle, which is evident at highly charged state and low frequencies, the typical behavior of a diffusion process inside the electrode materials. We ascribed the high-frequency semicircle to the charge of the external surface area of the lithium manganese oxide composite electrodes and the related resistance to both interparticle electronic contact and ionic migration through the passivation layer. The medium-frequency semicircle resistance is assigned to the Faradic charge process of lithium manganese oxide and the interfacial capacitance.

In the charge state the  $\text{Li}/\text{LiCo}_{0.02}\text{La}_{0.01}\text{Mn}_{1.97}\text{O}_{3.98}\text{Cl}_{0.02}$  system generates a lower cell impedance than that of  $\text{Li}/\text{LiMn}_2\text{O}_4$  system as a consequence of good thermodynamics and reasonable reaction kinetics. The impedance patterns further verify that the  $\text{LiCo}_{0.02}\text{La}_{0.01}\text{Mn}_{1.97}\text{O}_{3.98}\text{Cl}_{0.02}$  system has excellent electrochemical performance.



**Fig.5** Nyquist plots recorded for  $\text{Li}/\text{LiMn}_2\text{O}_4$ (a) and  $\text{Li}/\text{LiCo}_{0.02}\text{La}_{0.01}\text{Mn}_{1.97}\text{O}_{3.98}\text{Cl}_{0.02}$ (b) system at different charging voltages

#### 4 Conclusions

A new doped spinel  $\text{LiCo}_{0.02}\text{La}_{0.01}\text{Mn}_{1.97}\text{O}_{3.98}\text{Cl}_{0.02}$  was synthesized by a solid-state method. XRD result reveals that the structure of the substituted compound retains cubic spinel phase. The powder has similar morphology and particle size distribution with undoped  $\text{LiMn}_2\text{O}_4$ , but larger particle size and lower specific area. The good electrochemical performance of the  $\text{Li}/\text{LiCo}_{0.02}\text{La}_{0.01}\text{Mn}_{1.97}\text{O}_{3.98}\text{Cl}_{0.02}$  system is confirmed by the charge-discharge curve and the electrochemical impedance spectra. The  $\text{LiCo}_{0.02}\text{La}_{0.01}\text{Mn}_{1.97}\text{O}_{3.98}\text{Cl}_{0.02}$  electrode shows excellent cycleability, which retains

90.6% (108.6  $\text{mA}\cdot\text{h}/\text{g}$ ) of the initial capacity after 180 cycles at  $0.2C$  rate.

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