

Insertion/removal kinetics of lithium ion in spinel $\text{LiCu}_x\text{Mn}_{2-x}\text{O}_4$

ZENG Rong-hua(曾荣华), LI Wei-shan(李伟善), LÜ Dong-sheng(吕东生),
HUANG Qi-ming(黄启明), ZHAO Ling-zhi(赵灵智)

School of Chemistry and Environment, South China Normal University, Guangzhou 510006, China

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Abstract: The insertion/removal processes of lithium ion in spinel lithium manganese oxide (LiMn_2O_4) and copper doped spinel lithium manganese oxide ($\text{LiCu}_x\text{Mn}_{2-x}\text{O}_4$) on a powder microelectrode were studied by electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and X-ray diffractometry (XRD). The insertion/removal process of lithium ion in the spinel oxides consists of three steps: charge transfer of lithium ion on the surface of the spinel oxides, diffusion and occupation of lithium ion in the lattice of the spinel oxide. Similar to chromium, the doping of copper in spinel lithium manganese oxide results in the increase of the charge transfer resistance and the double layer capacitance for lithium insertion or removal, and the decrease of the diffusion coefficient of lithium ion in the lattice of spinel oxide. However, the insertion capacitance, a parameter reflecting the occupation of lithium ion in the lattice of the spinel oxide, is hardly influenced by the doping of copper. The influence of the doped copper on the kinetic process of lithium insertion/removal in spinel lithium manganese oxide is related to the contraction of spinel lattice.

Key words: insertion and removal kinetics; spinel lithium manganese dioxide; doping; copper

1 Introduction

Manganese oxides are good cathode materials for primary and secondary batteries, because they are less toxic and abundant in nature[1–2]. The most important manganese oxide is spinel lithium manganese oxide, LiMn_2O_4 , used as the cathode materials for lithium ion battery, which is easy to prepare and has high capacity density[3–5]. However, its application is limited by its instability due to Jahn-Teller effect and dissolution of manganese into electrolyte during cycling of charging and discharging[6–8]. This problem can be solved to a great extent by substitution of other elements such as copper, cobalt and chromium for a small fraction of manganese atoms in spinel lattice[9–15].

The stability of spinel lithium manganese oxide is related to the insertion/removal kinetics of lithium ion in the spinel. Unfortunately, less knowledge is available on the effect of doped elements on the kinetics of lithium insertion and removal in the spinel oxide, which is essential for the understanding of stability improvement

and for the better application of doped lithium manganese oxide. In our previous study, the effect of chromium on the insertion/removal kinetics of lithium in the spinel has been understood by using powder microelectrode[16]. The effect of copper was considered with the same method in this work.

2 Experimental

Three samples, LiMn_2O_4 , $\text{LiCu}_{0.05}\text{Mn}_{1.95}\text{O}_4$ and $\text{LiCu}_{0.16}\text{Mn}_{1.84}\text{O}_4$, were synthesized by sol-gel method with $\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$, $\text{Mn}(\text{CH}_3\text{COO})_2$, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, and $\text{C}_6\text{H}_8\text{O}_7 \cdot 7\text{H}_2\text{O}$ in the ratios of 1:2:0:3, 1:1.95:0.05:3 and 1:1.84:0.16:3, respectively. Aqueous solution with $\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$ and $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ was added into $\text{Mn}(\text{CH}_3\text{COO})_2$ saturated solution under stirring. Then $\text{C}_6\text{H}_8\text{O}_7 \cdot 7\text{H}_2\text{O}$ solution was added to obtain a mixture solution containing lithium, manganese and copper. The mixture solution was mediated with aqueous concentrated NH_3 solution to pH=6.3 and kept at 80 °C under stirring until a dry precursor was obtained. The precursor was heated to 500 °C with 1 °C/min and kept

at 500 °C for 12 h to remove organic compounds and then heated to 750 °C with 1 °C/min and kept at 750 °C for 72 h to obtain the samples. All the chemicals were in analytic grade.

XRD was conducted on a D/MAX-3A/Rigaku diffractometer with Cu K α radiation of 30 kV, 30 mA at 12 (°)/min. The cell constant a of the spinel oxide was obtained by

$$a = d / (h^2 + k^2 + l^2)^{-0.5} \quad (1)$$

where h , k and l are the indexes of crystal plane and d the distance between crystal planes. The volume of the spinel cell V was obtained:

$$V = a^3 \quad (2)$$

The length $R/\text{\AA}$ of Mn—O and Mn—Mn was obtained with

$$R_{\text{Mn—Mn}} = 2^{0.5} a / 4 \quad (3)$$

$$R_{\text{Mn—O}} = a(3u^2 - 2u + 0.375)^{0.5} \quad (4)$$

where u is position constant of oxygen in the spinel lattice and equals 0.265.

Electrochemical experiments were performed with PGSTAT-30 (Autolab) in a two-electrode cell with powder microelectrode as the working electrode and metal lithium as the counter electrode and the reference electrode. The electrolyte was 1 mol/L LiPF $_6$ -EC+EMC+DMC ($m_{\text{EC}}:m_{\text{EMC}}:m_{\text{DMC}}=1:1:1$, Merck). The electrolyte cell was set up in a glove box under argon atmosphere. The powder microelectrode was prepared as follows [17–19]. A platinum (99.995%) wire with a diameter of 100 μm was sealed in a glass tube to obtain a platinum microdisk electrode. The microdisk electrode was etched in a mixed concentrated acid solution for 30 min to obtain a microcavity electrode. The cavity electrode was ground on a glass plate with the mixture powder of sample and graphite (1:1, in mass fraction) to obtain the powder microelectrode.

3 Results and discussion

3.1 XRD pattern

Fig.1 shows the XRD pattern of three samples. It can be found that the diffraction patterns of three samples have characteristic of spinel crystal structure, in which lithium ions occupy the 16a positions of tetrahedra, manganese ions (Mn $^{3+}$ and Mn $^{4+}$) occupy the 16d positions of octahedra and oxygen ions occupy the 32e positions, the vertices of tetrahedral and octahedra. The similar diffraction patterns of spinel structure for the samples with and without doping indicate that the doped copper has entered the lattice of 16d positions to replace manganese. However, the samples with doping have MnO $_x$ and Li $_2$ MnO $_3$ intermediate phase[9–10].

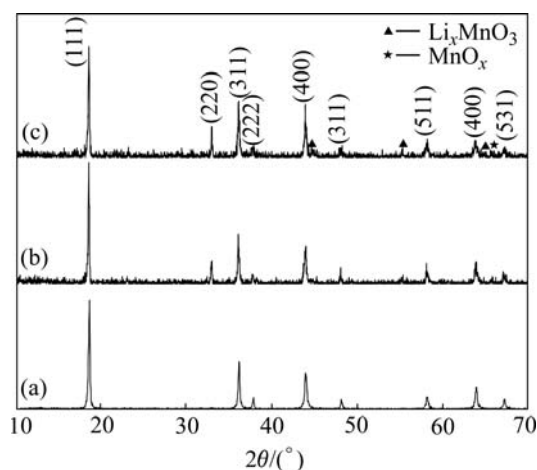


Fig.1 XRD patterns of samples: (a) LiMn $_2$ O $_4$; (b) LiCu $_{0.05}$ Mn $_{1.95}$ O $_4$; (c) LiCu $_{0.16}$ Mn $_{1.84}$ O $_4$

The cell parameters calculated with Eqns.(1)–(4) based on the diffraction peaks of Fig.1 are listed in Table 1. It can be seen from Table 1 that the cell constant, the volume and the bond length of spinel lithium manganese oxide become small due to the doping of copper and decrease as the copper contents increase, indicating that spinel cell of lithium manganese oxide is contracted due to the doping of copper. This effect can be ascribed to the stronger bond of Cu—O than that of Mn—O.

Table 1 Cell parameters of spinel samples with and without doping

Samples	$a/\text{\AA}$	$V/\text{\AA}^3$	$R_{\text{Mn—Mn}}/\text{\AA}$	$R_{\text{Mn—O}}/\text{\AA}$
LiMn $_2$ O $_4$	8.227 5	556.93	2.908 9	1.941 3
LiCu $_{0.05}$ Mn $_{1.95}$ O $_4$	8.220 0	555.41	2.906 2	1.939 6
LiCu $_{0.16}$ Mn $_{1.84}$ O $_4$	8.215 1	554.42	2.904 5	1.938 4

3.2 Cyclic voltammogram

Fig.2 shows the voltammograms of three samples obtained with slow potential sweep during the first cycle. It can be seen that two steps for lithium insertion and removal in the spinel oxide can be separated significantly for the sample with and without the doping of copper. However, there are differences in the voltammograms between the samples with and without the doping of copper.

Firstly, the charging efficient and discharging efficiency are different. Charging and discharging efficiencies, the ratios of electric quantity of charging and discharging obtained by integrating forward or backward scan voltammogram, are 95%, 97%, 100% for the samples LiMn $_2$ O $_4$, LiCu $_{0.05}$ Mn $_{1.95}$ O $_4$ and LiCu $_{0.16}$ Mn $_{1.84}$ O $_4$, respectively. The charging and discharge effi-

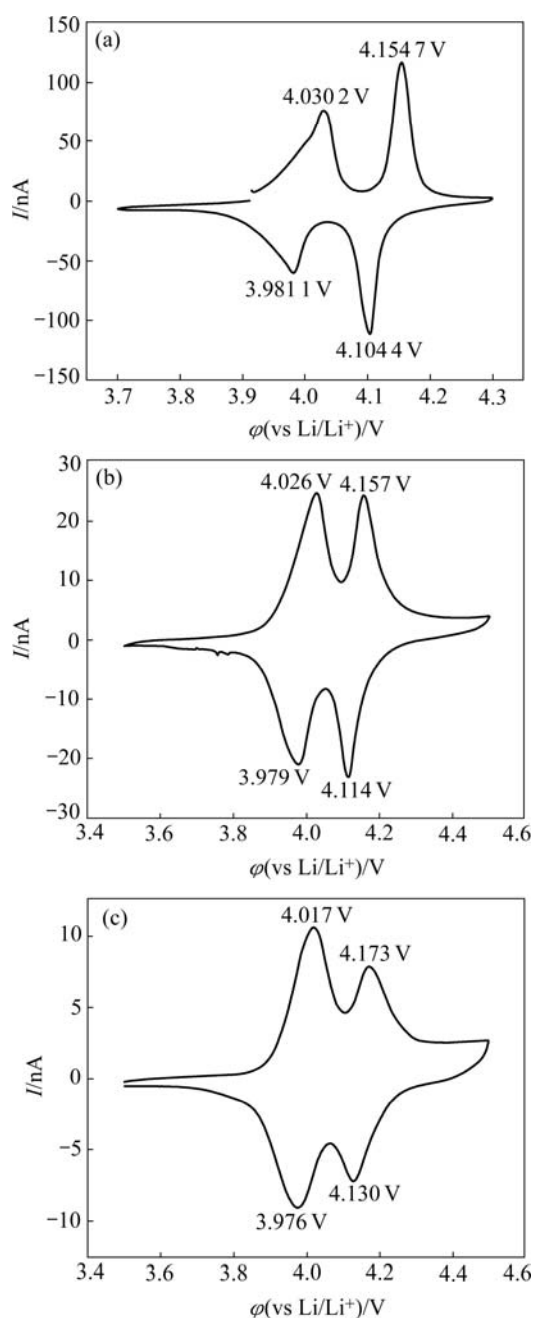


Fig.2 Cyclic voltammograms of samples on powder microelectrode (scan rate: 80 μ V/s): (a) LiMn_2O_4 ; (b) $\text{LiCu}_{0.05}\text{Mn}_{1.95}\text{O}_4$; (c) $\text{LiCu}_{0.16}\text{Mn}_{1.84}\text{O}_4$

ciencies increase with increasing copper content in the spinel oxide, indicating that irreversible capacity loss of spinel lithium manganese oxide is reduced by the doping of copper.

Secondly, the amounts of lithium insertion and removal for each of two steps, which can be obtained from the integration of the oxidation or reduction peak, are different. As shown in Fig.2(a), the amount of lithium insertion and removal at low potential is almost equal to that at high potential. However, the amount of lithium insertion and removal increases at low potential and

decreases at high potential due to the doping of copper, as shown in Figs.2(b) and (c). This suggests that the doping of copper in the spinel lithium manganese oxide changes the amount of lithium insertion and removal for each of two steps.

To understand the cyclic stability of the doped lithium manganese oxide, cyclic voltammograms of three samples were measured on powder microelectrodes with a faster scan rate. The voltammograms of the first and the 100th cycles are shown in Fig.3. It can be

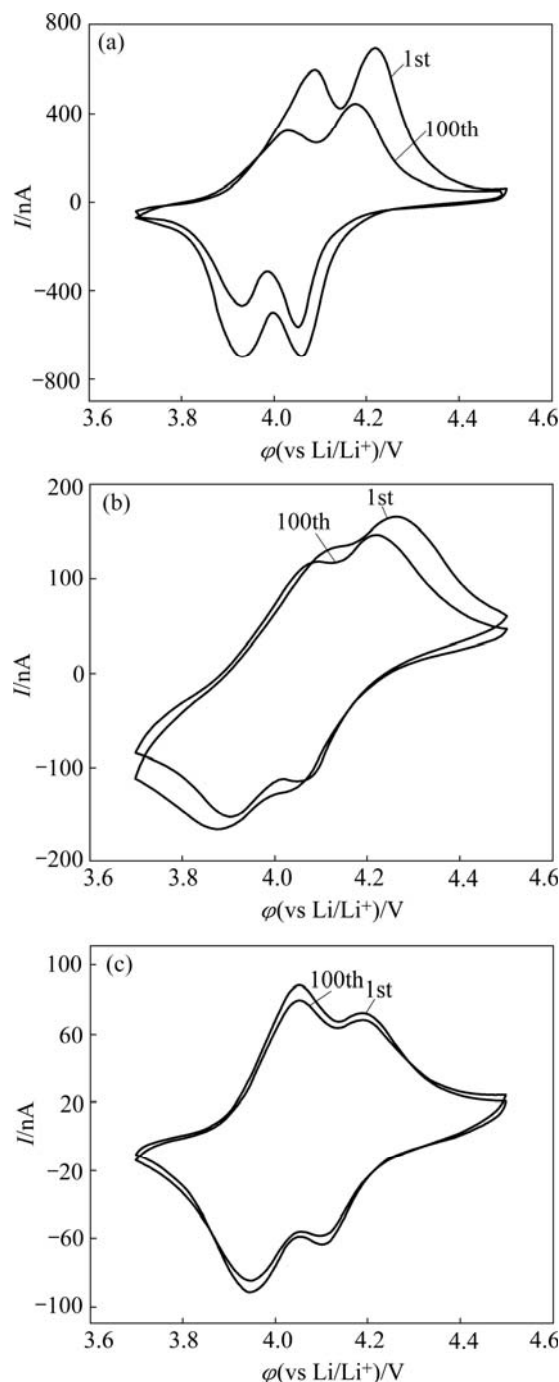


Fig.3 Cyclic voltammograms of samples on powder microelectrode (scan rate: 2 mV/s): (a) LiMn_2O_4 ; (b) $\text{LiCu}_{0.05}\text{Mn}_{1.95}\text{O}_4$; (c) $\text{LiCu}_{0.16}\text{Mn}_{1.84}\text{O}_4$

found from Fig.3 that the peak currents of the spinel oxide without doping decrease more quickly than those of the spinel oxides with doping. After 100 cycles, the discharge capacities, obtained by integrating the backward scanning voltammogram, become 37.7%, 13.7% and 4.4% of those at the first cycle for the samples LiMn_2O_4 , $\text{LiCu}_{0.05}\text{Mn}_{1.95}\text{O}_4$ and $\text{LiCu}_{0.16}\text{Mn}_{1.84}\text{O}_4$, respectively. It is apparent that the cyclic stability of spinel lithium manganese oxide can be improved by the doping of copper. Similar results have been obtained for the doping of elements other than copper and this effect can be ascribed to the stability improvement of the spinel oxide by the doping of elements.

3.3 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy was used to understand the kinetic process of lithium ion in samples. Before the EIS measurement, the powder microelectrode was charged with a constant current of 15 nA to 4.3 V and kept at 4.3 V until the current was lower than 10 pA. The measurement begun after potentiostat at each measured potential for 30 min. The frequency range used was from 100 kHz to 10 mHz with an amplitude of 5 mV.

Fig.4 shows the Nyquist plot of the sample without the doping of copper. It can be found that the Nyquist plot is composed of three part: semicircle at high frequency, straight line with a smaller slope at middle frequency and straight line with a bigger slope at low frequency. The semicircle at high frequency corresponds to a charge transfer step, which should be ascribed to the charge transfer of lithium ion on the surface of spinel oxide because there are no other electrode reactions during lithium insertion and removal in the spinel oxide. The straight line at middle frequency corresponds to a diffusion step, which can be ascribed to the diffusion of lithium in the lattice of the spinel oxide because the diffusion of lithium ion in electrolyte is fast and can be

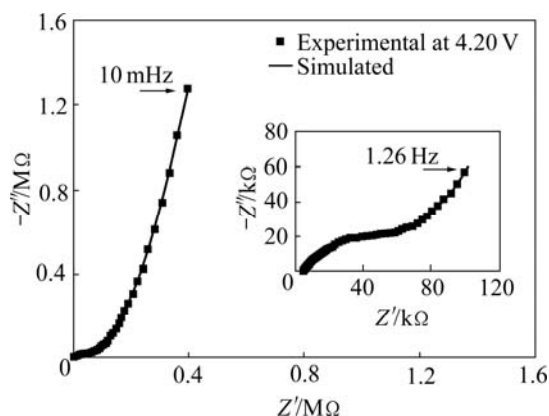


Fig.4 Nyquist plot of sample LiMn_2O_4 on powder micro-electrode

neglected in EIS compared with the diffusion of lithium in the lattice of the spinel. The straight line with higher slope at low frequency belongs to a capacitance behavior and it should be ascribed to the insertion/removal capacitance of lithium in the lattice of the spinel oxide. Based on these considerations, the equivalent circuit of Fig.5 can be used to describe the kinetic process of lithium in the spinel oxide.

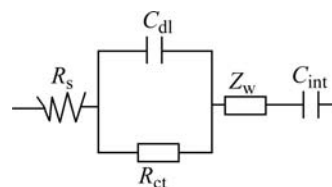


Fig.5 Equivalent circuit describing kinetic process of lithium in spinel lithium manganese oxide on powder microelectrode

In Fig.5, R_s represents the solution resistance, C_{dl} the double layer capacitance, R_{ct} the resistance of charge transfer, Z_w Warburg impedance reflecting the diffusion process of lithium in the lattice of the spinel oxide and C_{int} insertion or desertion capacitance reflecting the occupation process of lithium in lattice of the spinel oxide. The solid line in Fig.4 is the result obtained by simulating the experimental result with the equivalent circuit of Fig.5. It can be found that the experimental result can be well fitted and thus the kinetic parameters can be easily obtained by simulation.

The electrochemical impedance of the samples with and without the doping of copper was measured under the potentials every 50 mV from 4.3 to 3.90 V. Fig.6 shows the results of three samples under 4.15, 4.10 and 4.05 V. The dots and the lines in Fig.6 represent the experimental and simulated results, respectively. It can be found that the Nyquist plots are similar for the samples with and without the doping of copper and can be well fitted by the equivalent circuit of Fig.5. The parameters of three samples under different potentials, R_s , C_{dl} , R_{ct} , Z_w and C_{int} can be obtained by simulating the measured electrochemical impedance with the equivalent circuit of Fig.5.

Fig.7 shows the dependence of charge transfer resistance R_{ct} on the potential. It can be found that the charge transfer resistance for lithium insertion and removal in the samples with and without doping of copper is influenced by the potential and its dependence on potential is similar for the samples with and without the doping of copper. There is a minimum charge transfer resistance for all the samples, which is at the potential between the two peak potentials for two steps of lithium insertion and removal, about 4.05 V for the sample without the doping of copper and 4.1 V for the samples with the doping of copper. The charge transfer resistance

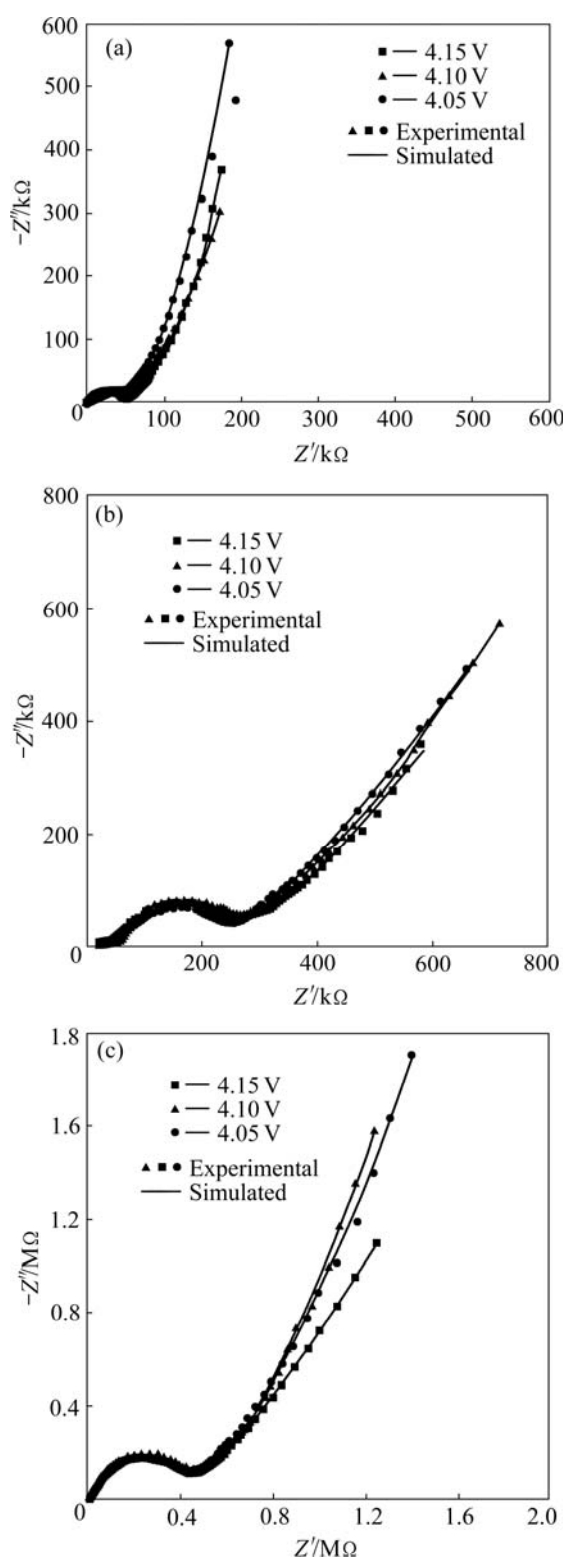


Fig.6 Nyquist plots of samples on powder microelectrode at some potential: (a) LiMn_2O_4 ; (b) $\text{LiCu}_{0.05}\text{Mn}_{1.95}\text{O}_4$; (c) $\text{LiCu}_{0.16}\text{Mn}_{1.84}\text{O}_4$

increases for all samples as the potential increases or decreases from the potential, where the charge transfer resistance is in its minimum value. By comparing the samples with and without doping of copper, it can be seen that the charge transfer resistance increases from the

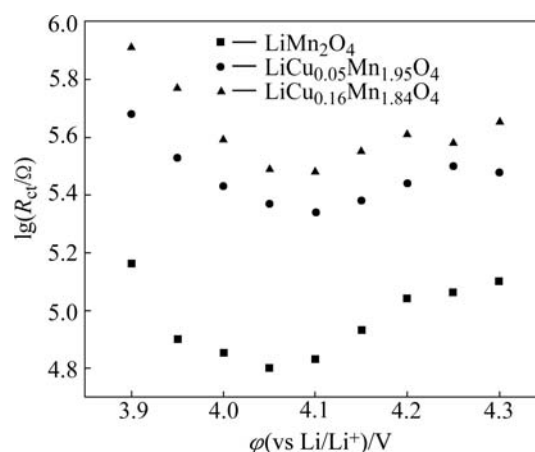


Fig.7 Dependence of charge transfer resistance on potential for lithium insertion and removal in samples

sample without doping to the sample with doping. The charge transfer resistance increases due to the doping of copper and as the content of doped copper in spinel oxide increases, the charge transfer resistance increases.

Fig.8 shows the dependence of double layer capacitance on the potential. It can be found that the double layer capacitance for lithium insertion and removal in the samples with and without the doping of copper is also influenced by the potential and its dependence on potential is similar for the samples with and without the doping of copper. Like the change of charge transfer resistance that has a minimum, there is a maximum double layer capacitance for all the samples, which is also at the potential between the two peak potentials for two steps of lithium insertion and removal, about 3.95 V for the sample without the doping of copper and 4.05 V for the samples with the doping of copper. The double layer capacitance decreases for all samples as the potential increases or decreases from the potential, where the double layer capacitance is in its maximum value. By comparing the samples with and without the

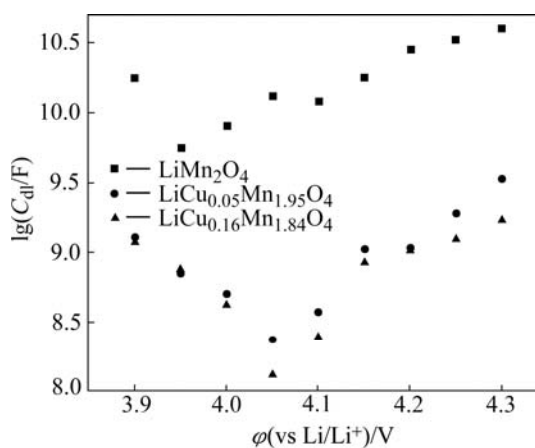


Fig.8 Dependence of double layer capacitance on potential for lithium insertion and removal in samples

doping of copper, it can be seen that the double layer capacitance also increases from the sample without doping to the sample with doping. There is about a decade of increase in double layer capacitance due to the doping of copper. Different from the effect of copper on the charge transfer resistance, however, the double layer capacitance of doped spinel oxide is almost independent of the content of doped copper.

To obtain the diffusion parameter of lithium in the lattice of the samples, a simplified treatment is made. The diffusion coefficient D_{Li} of lithium in the lattice of spinel lattice can be expressed as

$$D_{\text{Li}} = \frac{1}{\sigma^4} \frac{R^4 T^4}{4A^4 n^8 F^8 c^2} = \kappa \frac{1}{\sigma^4} \quad (5)$$

where σ is obtained by simulating experimental electrochemical impedance with the equivalent circuit of Fig.5, A the surface area of the samples, n the electron number in the charge transfer step, T temperature, R gas constant and F Faradaic constant. Under the same temperature, A , n , T , R and F are considered to be constants and the same for all samples, thus they can be put together to be a constant κ .

The dependence of diffusion coefficients of lithium in lattice of three samples obtained from Eqn.(5) is shown in Fig.9. It can be found that the diffusion coefficients of lithium in lattice of the samples with and without the doping of copper increase with increasing potential when potential is lower than 4.0 V but is less dependent on the potential when potential is higher than 4.0 V. By comparing the samples with and without the doping of copper, it can be seen that the diffusion coefficient of spinel lithium manganese oxide becomes smaller due to the doping of copper.

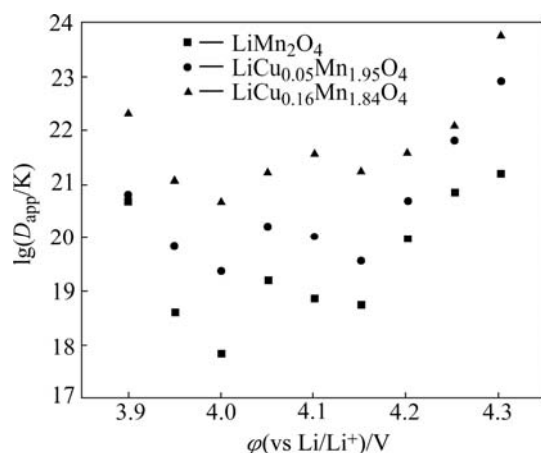


Fig.9 Dependence of diffusion coefficient on potential for lithium insertion and removal in samples

Fig.10 shows the dependence of insertion

capacitance on the potential. It can be found that the insertion capacitance for the occupation of lithium in the lattice of samples with and without the doping of copper is hardly influenced by potential except for the potentials between the two peak potentials for two steps of lithium insertion and removal, where the insertion capacitance reaches a higher value. Different from the behaviors of double layer capacitance behavior, the insertion capacitance is hardly influenced by the doping of copper.

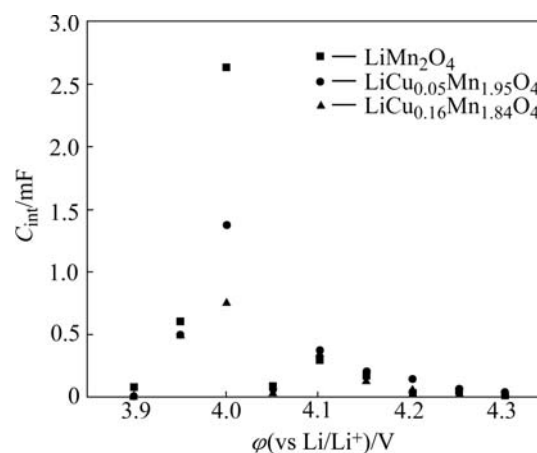


Fig.10 Dependence of insertion capacitance on potential for lithium insertion and removal in samples

The effect of doped copper on the charge transfer resistance, the double layer capacitance and the diffusion coefficient must be related to the lattice contraction of spinel lithium manganese oxide due to the doping. However, the lattice contraction of spinel lithium manganese oxide does not affect the occupation of lithium in the spinel lattice.

4 Conclusions

- 1) The charge transfer resistance and the double layer capacitance increase.
- 2) The diffusion coefficient of lithium in the lattice of spinel oxide decreases.
- 3) The insertion capacitance of lithium in the spinel lattice is hardly influenced by the doping of copper.

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