

Cyclic voltammetry studies on 4 V and 5 V plateaus of non-stoichiometric spinel $\text{Li}_{1+x}\text{Mn}_{2-y}\text{O}_4$

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Abstract: $\text{Li}_{1+x}\text{Mn}_{2-y}\text{O}_4$ spinels with various Li/Mn ratios were synthesized by a solid-state reaction. By X-ray diffraction analysis, Li_2MnO_3 was detected as a second phase with increasing the Li/Mn ratio; and the role of Li_2MnO_3 in $\text{Li}_{1+x}\text{Mn}_{2-y}\text{O}_4$ spinel was discussed. A slow scanning cyclic voltammetry(CV) at the rate of 0.1 mV/s was adopted to characterize the evolutions of 4 V and 5 V plateaus of $\text{Li}_{1+x}\text{Mn}_{2-y}\text{O}_4$ spinels. An additional Li^+ insertion in 4 V region was observed in both Li-lack and Li-rich spinels at 3.95 V, which is different from the general Li^+ insertion with weak Li-Li interaction and strong Li-Li interaction; and this plateau disappeared in the subsequent cycles. The 4.4 V/3.8 V plateaus correspondent to Li^+ insertion and extraction of Li_2MnO_3 were discussed, and these plateaus have a high reversibility with cycling. The 5 V plateau was found only in the Li-rich samples, and this plateau has a tendency to emerge at higher voltage region with increasing Li/Mn ratio.

Key words: lithium manganese oxides; spinel; LiMn_2O_4 ; Li_2MnO_3 ; cyclic voltammetry

1 Introduction

As one of the most promising cathode materials for lithium ion batteries, spinel LiMn_2O_4 has received much attention in recent years. This material has reversible capacities at both 3 V and 4 V plateaus[1]. However, the Li^+ insertion and extraction at 3 V regions are two phase reactions representing the structural evolution of LiMn_2O_4 to $\text{Li}_2\text{Mn}_2\text{O}_4$, and $\text{Li}_2\text{Mn}_2\text{O}_4$ back to LiMn_2O_4 . This evolution is correspondent to a phase transition between cubic symmetry and tetragonal symmetry, causing a Jahn-Teller effect in the lattice, and leading to a serious capacity fading with cycling[2]. Therefore, most of the studies on spinel LiMn_2O_4 were concerning with the structures and the electrochemical performances in 4 V regions. The typical 4 V plateaus of LiMn_2O_4 are 4.0 V and 4.1 V plateaus. Since the structures of spinel Li-Mn-O compounds are sensitive to the synthesis conditions, Li/Mn ratios, and cation or anion dopants, some other plateaus such as 3.3 V/3.95 V and 4.5 V plateaus have been observed in some LiMn_2O_4 -based spinels[3–7].

More recently, many groups pay more and more

attentions to the transition metal substituted spinel LiMn_2O_4 , which exhibit high voltage plateaus at around 5 V[8–11]. Therefore, the studies on the structural and electrochemical properties of LiMn_2O_4 and its derivatives at 5 V region are of interest. Actually, the 5 V plateaus were observed in the LiMn_2O_4 spinels synthesized by melt-impregnation method[12], electron-beam evaporation or radio-frequency sputtering[13].

In this study, a slow scanning cyclic voltammetry is employed to analysis the evolutions of 4 V and 5 V plateaus in a series of $\text{Li}_{1+x}\text{Mn}_{2-y}\text{O}_4$ spinels with $-0.03 \leq x \leq 0.27$ and $2.12 \geq 2-y \geq 1.75$, namely, with the Li/Mn ratio from 0.46 to 0.72. The changes of spinel structure, average Mn valence, and Li^+ insertion and extraction with increasing Li/Mn ratio are discussed.

2 Experimental

2.1 Material synthesis and characterization

$\text{Li}_{1+x}\text{Mn}_{2-y}\text{O}_4$ spinels were synthesized by a solid-state reaction as described previously[14]. Lithium hydroxide (LiOH) and chemical manganese dioxide (MnO_2) served as the raw materials. On preparing Li-doped spinels, raw materials with various nominal

Li/Mn ratios (0.45 to 0.70) were mixed and ground carefully, then preheated at 480 °C for 6 to 8 h. Subsequently, they were reground and pressed into pellets, sintered at 750 °C for 24 h before being cooled down for about 12 h in air. The $\text{Li}_{1+x}\text{Mn}_{2-y}\text{O}_4$ spinels with various Li/Mn ratios were obtained by this way.

The real stoichiometry of lithium and manganese was determined on an ICP spectrometer (IRIS/AP, Thermo Jarrell Ash), while the oxygen stoichiometry was estimated from those of Li and Mn. Powder XRD patterns were recorded with a Rigaku B/max-2400 X-ray diffractometer with $\text{Cu K}\alpha$ radiation at 40 kV and 120 mA.

2.2 Cyclic voltammetry investigation

The cyclic voltammograms of the $\text{Li}_{1+x}\text{Mn}_{2-y}\text{O}_4$ spinels were investigated in typical Swagelok two-electrode cells, which adopt metal lithium foils as counter electrodes, and 1mol/L LiPF_6 in a 1 : 1 (volume ratio) mixture of ethylene carbonate(EC) and dimethyl carbonate(DMC) as electrolyte. A sheet of Celgard® 2300 was used as a separator. The cathodes were prepared by coating slurries of $\text{Li}_{1+x}\text{Mn}_{2-y}\text{O}_4$ powder, carbon black and cyclopentanone-dissolved polyvinylidene fluoride(PVDF) onto aluminum foils. Subsequently, the films were vacuum-dried at 55 °C for 24 h, compressed at 1 MPa between two stainless steel plates, and cut into sheets with an area of 0.5 cm². The resultant mass ratio of $\text{Li}_{1+x}\text{Mn}_{2-y}\text{O}_4$, carbon black, and PVDF was 85 : 10 : 5. All the tested cells were assembled in an argon-filled glove box (MBRAUN).

After a 12 h aging, the as-assembled cells were investigated. The cyclic voltammograms were performed on a CHI 660A electrochemical workstation in the voltage range from 3.0 to 5.2 V at a scanning rate of 0.1 mV/s.

3 Results and discussion

3.1 Structural characterization

Fig.1 shows the X-ray diffraction patterns of $\text{Li}_{1+x}\text{Mn}_{2-y}\text{O}_4$ spinels. Though all the samples show a spinel phase with the structure of $\text{Fd}\bar{3}\text{m}$ space group, the emergency of Li_2MnO_3 is observed with increasing Li/Mn ratio. According to the Li-Mn-O and Li_2MnO_3 - MnO - λ - MnO_2 ternary phase diagrams[2], Li-substituted spinel LiMn_2O_4 has a tendency to generate a stable rock-salt phased Li_2MnO_3 . In this study, when the Li/Mn ratio is 0.61, a new diffraction peak implying rock-salt Li_2MnO_3 emerges around the (311) diffraction of LiMn_2O_4 ; and the shoulder of (400) diffraction shows asymmetry, as shown in Fig.2. When the Li/Mn ratio is increased to 0.67, the (400) shoulder grows evidently. As the Li/Mn ratio is further increased to 0.72, the

diffraction peaks of Li_2MnO_3 are distinct. The second phase in a spinel cathode may have effects on the cation valences[15], and Li_2MnO_3 here in $\text{Li}_{1+x}\text{Mn}_{2-y}\text{O}_4$ spinels doesn't make an exception.

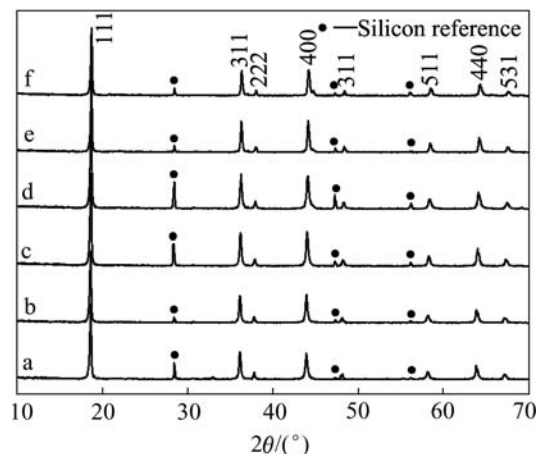


Fig.1 Powder XRD patterns of $\text{Li}_{1+x}\text{Mn}_{2-y}\text{O}_4$ spinels synthesized by solid state reaction: (a) Sample H09, Li/Mn ratio=0.46; (b) Sample H10, Li/Mn ratio=0.50; (c) Sample H11, Li/Mn ratio=0.54; (d) Sample H12, Li/Mn ratio=0.61; (e) Sample H13, Li/Mn ratio=0.67; (f) Sample H14, Li/Mn ratio=0.72.

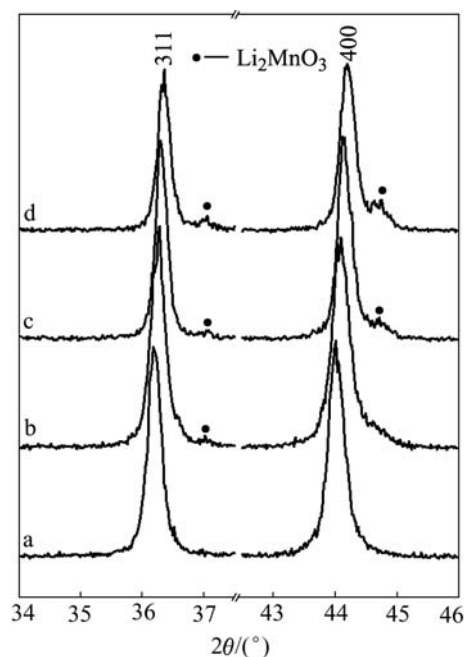


Fig.2 Evolution of (311) and (400) diffraction peaks of $\text{Li}_{1+x}\text{Mn}_{2-y}\text{O}_4$ spinels, in which Li/Mn ratios are 0.54(a), 0.61(b), 0.67(c) and 0.72(d), respectively

The real stoichiometry and average Mn valences of the samples are listed in Table 1. The average Mn valences are calculated from the real stoichiometry of the samples based on charge balance. Obviously, the average Mn valences of the Li-rich samples are higher than 3.5, which is the critical of Jahn-Teller effect. The increase of

the valence is due to two factors. On one hand, the excessive Li^+ ions have inserted into 16d sites of MnO_6 octahedron to replace Mn^{3+} ions; therefore, some of the rest Mn^{3+} ions have to convert to Mn^{4+} ions in order to keep the charge balance. On the other hand, the growth of the second phase Li_2MnO_3 , which has no Mn^{3+} ions but Mn^{4+} ions, increases the relative content of Mn^{4+} ions in manganese ion species, and upgrades the average Mn valence.

Table 1 Real stoichiometry and general structural parameters of $\text{Li}_{1+x}\text{Mn}_{2-y}\text{O}_4$ spinels

Sample	Real stoichiometry		Li/Mn ratio	Mn average valence
	x	$2-y$		
H09	-0.03	2.12	0.46	3.32
H10	0.01	2.03	0.50	3.44
H11	0.05	1.96	0.54	3.55
H12	0.16	1.91	0.61	3.58
H13	0.20	1.78	0.67	3.82
H14	0.27	1.75	0.72	3.85

The evolutions of lattice parameter with various Li/Mn ratios for $\text{Li}_{1+x}\text{Mn}_{2-y}\text{O}_4$ spinels are shown in Fig.3. It is evident that the lattice of $\text{Li}_{1+x}\text{Mn}_{2-y}\text{O}_4$ shrinks with increasing the Li/Mn ratio. The higher the Li/Mn ratio is, the higher the Mn^{4+} content is. Thus, the Mn—O bonds in spinel lattice are enhanced, which results in smaller lattice parameter. This phenomenon is correspondent with the average Mn valences listed in Table 1.

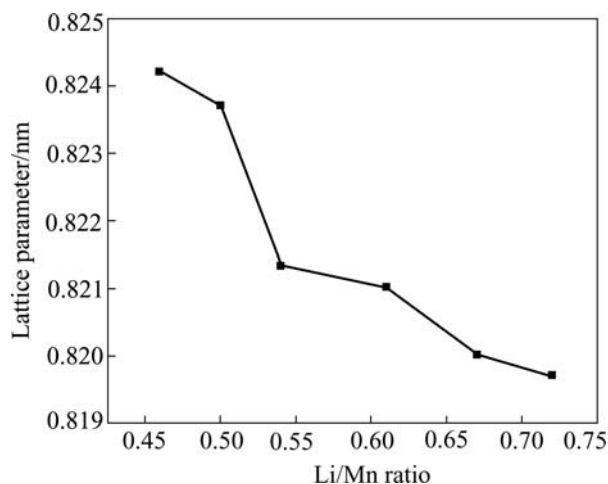


Fig.3 Lattice parameter vs Li/Mn ratio plot for $\text{Li}_{1+x}\text{Mn}_{2-y}\text{O}_4$ spinels

3.2 Cyclic voltammogram

3.2.1 Li^+ extraction in 4.05 V to 4.15 V plateaus

The insertion and extraction of lithium ions were investigated via a slow cyclic voltammetry, as shown in Fig.4 and Fig.5. When concerning with the 4V plateau of spinel LiMn_2O_4 , the split phenomena of the redox peaks are generally interpreted as two-step insertion and

extraction. Namely, during the charge process, the Li^+ ions with strong Li-Li interaction are removed from half of the tetrahedral positions at lower potential, and some of the Mn^{3+} ions are converted to Mn^{4+} ions. As the content of Mn^{4+} increases, the second half of Li^+ ions with weak Li-Li interaction is extracted at higher potential. The two binary equilibrium systems during Li extraction and insertion are considered LiMn_2O_4 - $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$ and $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$ - λ - MnO_2 [16]. Since the two steps for Li^+ insertion or extraction can not be separated distinctly, the reductive peaks may overlap with each other in some case, as well as the oxidative peaks.

Here we found the overlap of 4.05 V and 4.15 V plateaus with each other (see Fig.4). In the initial cycle, the two plateaus in 4 V regions can be identified distinctly when the Li/Mn ratio is in the range of 0.46-0.54. However, these plateaus are gradually combined to one plateau when the Li/Mn ratio exceeds 0.61. This phenomenon may be related to the increase of average Mn valence. With increasing the Li/Mn ratio, the average Mn valence increases as well. This results in a high proportion of Mn^{4+} in 16d sites, enhancing the Mn—O bonds, and weakening the Li-O interaction. Thus, the Li^+ ions with weak Li-Li interaction can also be extracted out of the spinel lattice at a relative low voltage region, in company with those having strong Li-Li interaction.

3.2.2 Li^+ insertion in 4.1 V to 3.8 V plateaus

Even though all the cells have gone through a 12 h aging, there are still kinetic polarizations found in the initial cycling. In the initial cycle, the second reductive peak that implies the insertion of Li^+ ions into spinel lattice, which should be located around 3.90 V (see Fig.5), is located in 3.80–3.85 V (see Fig.4).

Unlike the common Li^+ insertion in LiMn_2O_4 spinel, an additional Li^+ insertion plateau at 3.95V is found in this study, as shown in Figs.4(a) and (c). This plateau is different from the 3.95 V Li^+ extraction observed by PALACÍN et al[7], which corresponds to a 3.3 V Li^+ insertion step. Since there is no corresponding extraction plateau for the 3.95 V plateau observed here, it is reasonable to consider this plateau as a third kind of insertion, which differs from the Li^+ insertion with weak Li-Li interaction and with strong Li-Li interaction in the 8a sites. For the Li-lack spinel H09, Li^+ ions occupy less than 1/2 of the tetrahedral 8a sites; the 3.95 V plateau may be correspondent to the Li^+ insertion to fill the 8a vacancies, until the Li^+ occupation achieves 1/2.

Fig.4(c) shows that the slight Li-rich sample H11 also has a 3.95 V plateau. Since the 16c octahedral shares faces with the 8a tetrahedral, the excess Li^+ ions may be crowded into the neighboring vacant 16c octahedral. In the spinel LiMn_2O_4 phase, the tetrahedral 8a sites are of lower energy than the octahedral 16c sites.

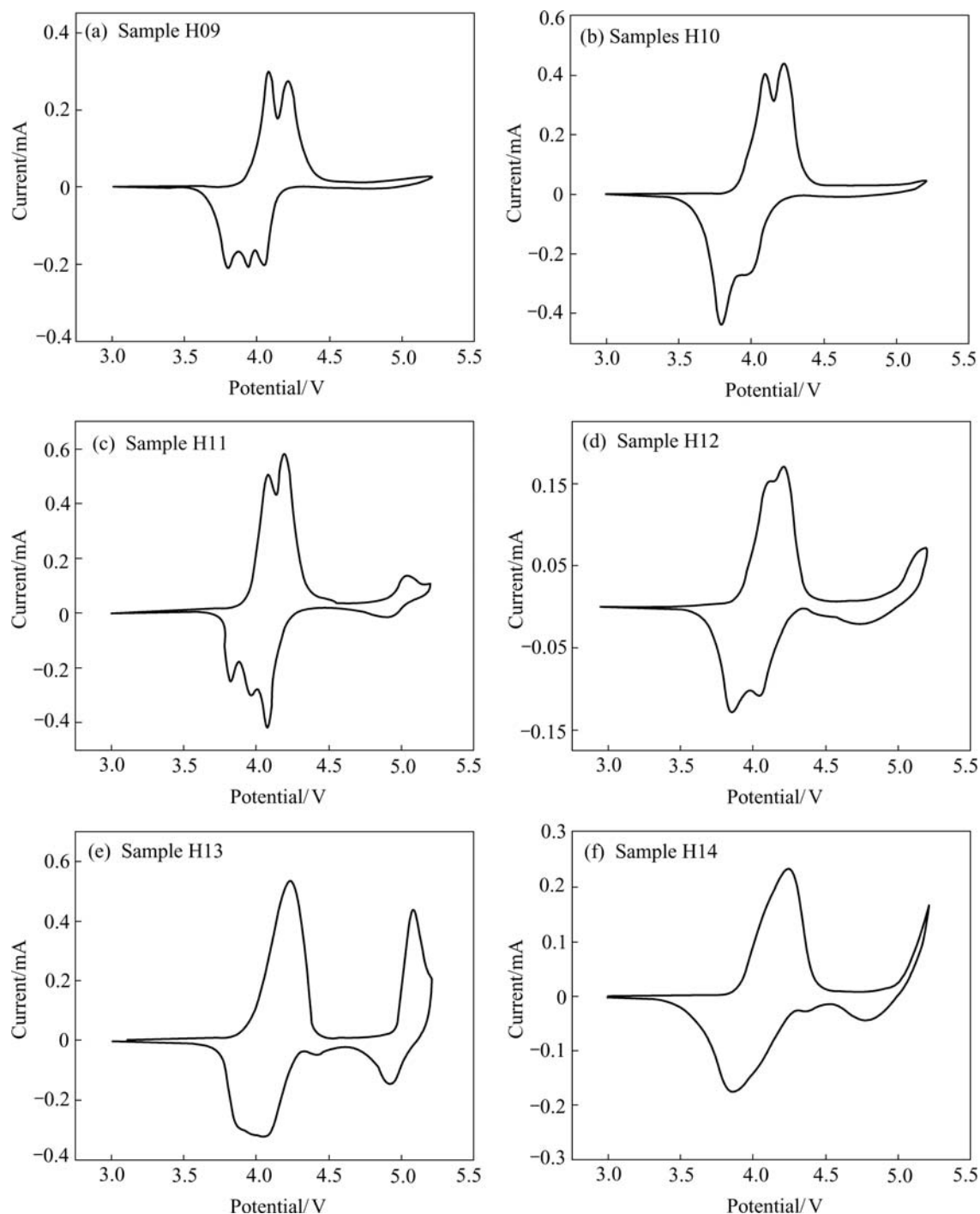


Fig.4 Initial cyclic voltammograms of $\text{Li}_{1+x}\text{Mn}_{2-y}\text{O}_4$ spinels at scanning rate of 0.1 mV/s in voltage range from 3.0 to 5.2 V

Therefore, in the 4 V plateau region, some of the Li^+ ions extracted from octahedral 16c sites are preferable to insert tetrahedral 8a sites, rather than inserting back to 16c octahedral sites; and the 3.95 V plateau may imply this Li^+ insertion process.

In a word, the 3.95 V plateau may represent a further Li^+ insertion in tetrahedral 8a sites of the $\text{Li}_{1+x}\text{Mn}_{2-y}\text{O}_4$ spinels, which have some phase defections. After the initial cycle, the spinel phases are activated to more perfect structures, and the 3.95 V plateau is no longer existent in the subsequent cycles, see Figs.5(a)

and (c).

3.2.3 Additional 4.4 V insertion and 3.8 V extraction plateaus

With increasing the Li/Mn ratio, a pair of additional redox plateaus is observed at 4.4/3.8 V more and more evidently, as shown in Fig.5. These plateaus are highly reversible, but have much less capacities than other plateaus.

According to previous studies[3], the 4.5 V plateau has been considered as a result of the co-occupation of lithium and manganese ions in the tetrahedral 8a sites.

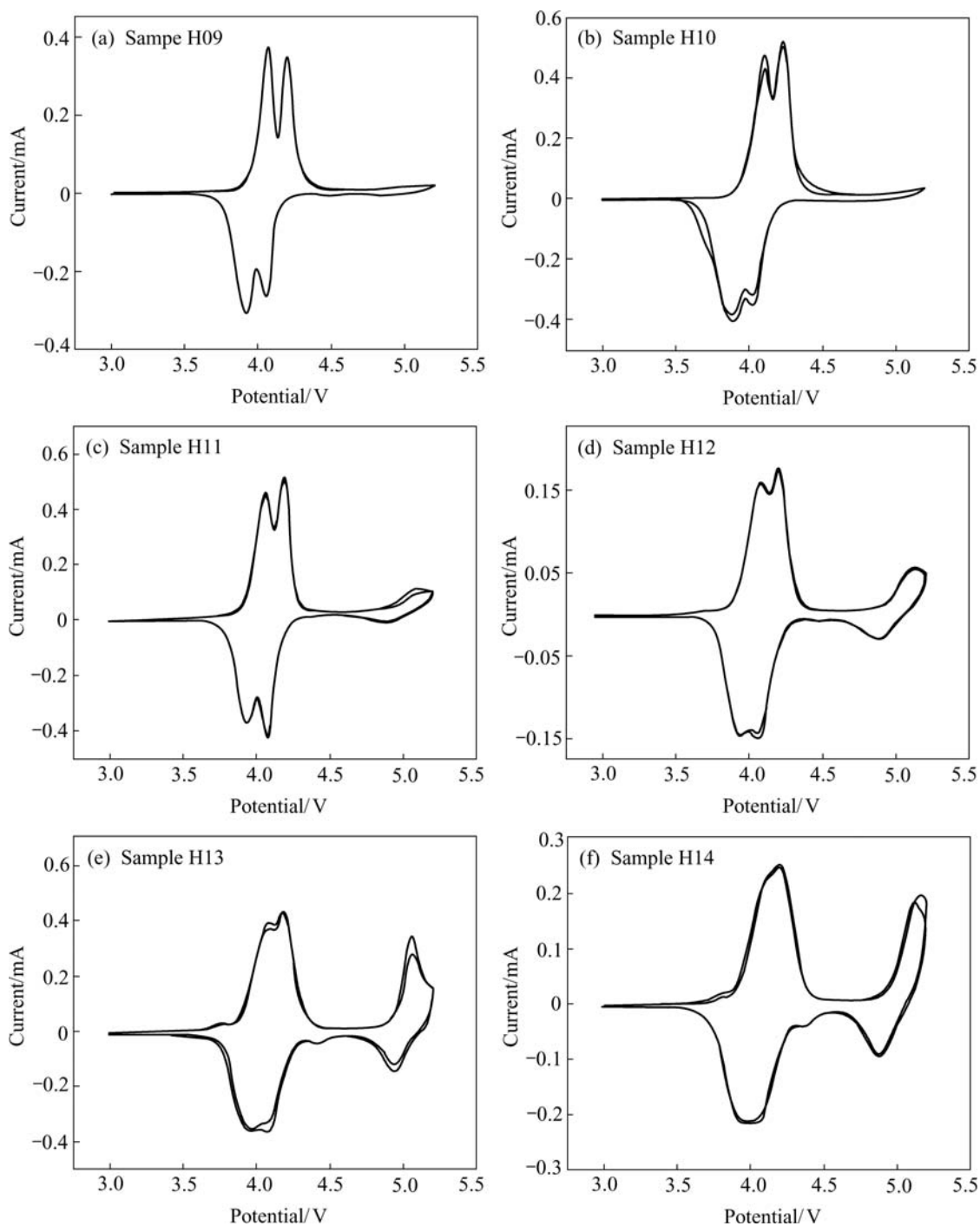


Fig.5 Second and third cyclic voltammograms of $\text{Li}_{1+x}\text{Mn}_{2-y}\text{O}_4$ spinels at scanning rate of 0.1 mV/s in voltage range from 3.0 to 5.2 V

However, from the analysis of powder X-ray diffraction and Rietveld refinement[3], GAO et al hypothesized oxygen defect as the inducement of the additional reduction process. Subsequently, AMATUCCI et al[5] and TABUCHI et al[6] reported respectively that the 4.5 and 3.3 V plateaus are relative to low average Mn valence, which leads to Jahn-Teller effect during cooling process. More recently, PALACÍN et al[7] detected that the origin of these peaks is the formation of double hexagonal-type layers in the spinel.

In this paper, the 4.4/3.8 V plateaus are also relative

to phase transition. However, they are not correspondent to the transition of spinel phase, but that of the second phase, Li_2MnO_3 . Since the manganese ions in rock-salt phased Li_2MnO_3 are at a high oxidation state, namely, Mn(IV), it is difficult for the spinels to get a charge compensation, which allows Li^+ ions to be extracted out of the lattice. KALYANI et al[17] reported that only after several cycles, the typical discharge-charge curves of Li_2MnO_3 could be obtained. Hence, there is no plateau for Li^+ extraction from the lattice of Li_2MnO_3 observed in the initial cycle, see Fig.4.

In the 4 V insertion plateau region, Li^+ insertion of Li_2MnO_3 is prior to that of $\text{Li}_{1+x}\text{Mn}_{2-y}\text{O}_4$ spinels, for the average Mn valence of the former is higher than that of the later, and has a priority to be reduced at 4.4 V, whereas the reduction of $\text{Li}_{1+x}\text{Mn}_{2-y}\text{O}_4$ is around 4 V, see Figs.3(d), (e) and (f). In the subsequent cycles, the extraction plateau correspondent to the 4.4 V insertion plateau emerges at 3.8 V, and this pair of plateaus show a high reversibility, see Figs.4(d), (e) and (f). In addition, since the Li^+ insertion of Li_2MnO_3 is located at 4.4 V, the effect of Li_2MnO_3 on the charge-discharge capacity is in dependence on the cut-off charging voltage of the cathode.

3.2.4 Li^+ insertion and extraction at 5 V plateaus

Reversible 5 V plateaus are observed in Li-rich samples, see Figs.4(c)–(f) and Figs.5(c)–(f). When studying the capacity fading of 4 V $\text{Li}/\text{LiMn}_2\text{O}_4$ batteries, XIA et al[12] had found a 5 V plateau during cycling. They took this plateau for electrolyte decomposition or Mn(IV) oxidation to higher valence. In this paper, on one hand, the electrolyte adopted in the batteries is 1mol/L $\text{LiPF}_6\text{-EC/DMC}$ (1 : 1), which is stable to 5.2 V; on the other hand, samples H09 and H10, which are cycled under the same conditions as the other spinels, have no 5 V plateau. Therefore, the 5 V plateau here is not implying the decomposition of electrolyte, but the evolution of spinel structure with increasing Li/Mn ratio.

In the study of thin-film LiMn_2O_4 electrodes, THACKERAY[13] discussed the 5 V plateaus observed with a small charge-discharge current of 0.2 μA . There were two kinds of spinel LiMn_2O_4 in the thin-film electrodes, which were described as $\text{Li}_{8a}[\text{Mn}_2]_{16d}\text{O}_4$ and $\text{Li}_{8b}[\text{Mn}_2]_{16c}\text{O}_4$. The presence of manganese ions on both sets of octahedral sites destabilizes the tetrahedral sites, and displaces some of the tetrahedral-site Li^+ into neighboring octahedral sites. The residual Li^+ ions in 16d octahedral sites must go through the energetically unfavorable 8b tetrahedral sites to be extracted out, and requiring more energy.

Here the samples H11, H12, H13 and H14 are all Li-rich spinels. The excess Li^+ ions substitute some Mn^{3+} ions in the octahedral 16d sites. At a high voltage around 5 V, the Li^+ ions begin to extract from spinel lattice, and form a 5 V plateau. When the Li/Mn ratio increases from 0.54 to 0.72, the relative capacity of 5 V plateau to 4 V plateau is increasing as well. Furthermore, the extraction of Li^+ in 16d sites has a tendency to a higher voltage with increasing Li/Mn ratio. An electrolyte stable to the voltage higher than 5.2 V is needed to further study the 5 V region activities. The further Li^+ extraction at 5 V plateau is inevitable to induce an increase of average Mn valence. According to BATES et al[18], the 5 V plateau might be correspondent to the converting of Mn^{4+} to Mn^{5+} . Actually, this plateau may not only be

assigned to $\text{Mn}^{4+} \rightarrow \text{Mn}^{5+}$, but also the converting of other Mn species, including the converting of the residual half of Mn^{3+} in 16d sites to Mn^{4+} . Namely, it should be considered as an average effect of the oxidations of all the Mn species. This is unlike nickel substitute spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, whose 5V plateau is resulted from $\text{Ni}^{2+}/\text{Ni}^{4+}$ redox[19, 20]. For samples H12, H13 and H14, which have a second phase Li_2MnO_3 , the 5 V plateaus might also comprise the Li^+ migrations in Li_2MnO_3 .

4 Conclusions

1) $\text{Li}_{1+x}\text{Mn}_{2-y}\text{O}_4$ spinels with various Li/Mn ratios were synthesized and characterized. Li_2MnO_3 was detected as a second phase by X-ray diffraction with increasing Li/Mn ratio. When the Li/Mn ratio exceeds 0.67, the diffraction peaks of Li_2MnO_3 are distinct.

2) Cyclic voltammetry was adopted to characterize the evolutions of 4 V and 5 V plateaus of $\text{Li}_{1+x}\text{Mn}_{2-y}\text{O}_4$ spinels. An additional Li^+ insertion plateau located at 3.95 V was observed in both Li-lack and Li-rich spinels. This plateau is different from the 3.95 V Li^+ extraction observed by PALACÍN et al, and may represent a further Li^+ insertion in tetrahedral 8a sites of the $\text{Li}_{1+x}\text{Mn}_{2-y}\text{O}_4$ spinels, which have some phase defections. After the initial cycle, the spinel phases are activated to more perfect structures, and the 3.95 V plateau is no longer existent in the subsequent cycles. The 4.4/3.8 V plateaus correspondent to Li^+ insertion and extraction of Li_2MnO_3 were detected, and these plateaus have a high reversibility in the following cycles. The presence of 5 V plateaus implies the existence of Li^+ ions in octahedral 16d sites, which need more energy to be removed from the lattice. The further Li^+ extraction at 5 V plateau is inevitable to induce an increase of average Mn valence, and has a tendency to emerge at higher voltage region with increasing Li/Mn ratio.

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