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Electrochemical behavior and cyclic fading mechanism of $LiNi_{0.5}Mn_{0.5}O_2$ electrode in $LiNO_3$ electrolyte

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Abstract: Electrochemical behavior of layered $LiNi_{0.5}Mn_{0.5}O_2$ in $LiNO_3$ aqueous solution and its cyclic fading mechanism in electrolytes with different pH values were investigated. CV results show that $LiNi_{0.5}Mn_{0.5}O_2$ has good electrochemical reversible behaviors in 5 mol/L $LiNO_3$ solution. Meanwhile, the electrode in 5 mol/L $LiNO_3$ with pH value of 12 demonstrates the best electrochemical stability. Based on the electrochemical impedance spectroscopy (EIS), X-ray diffraction (XRD) and scanning electron microscopy (SEM) results, it is proposed that suppressed charge-transfer resistance is the major reason, which is probably ascribed to the more stable electrode surface and less structure change.

Key words: lithium ion battery; $LiNi_{0.5}Mn_{0.5}O_2$; cyclic fading mechanism; cyclic voltammetry; $LiNO_3$ solution

1 Introduction

Aqueous lithium ion battery (ALIB) first reported by LI et al [1] has received considerable attention for fundamental studies as well as probable extensive applications owing to its low cost, intrinsic safety, environmental friendliness and easy operation [1−13]. During the low voltage power supplies, it is well proved that energy density of ALIB is of competition with those of Pd−acid and Ni−Cd batteries. However, in comparison with the corresponding lithium ion battery with non-aqueous electrolyte, it is still much lower for the limited stable electrochemical window of aqueous solution. Moreover, cyclic life of ALIB is much poorer.

It is well known that selection of appropriate intercalation cathode and anode materials with proper Li-ion insertion/extraction potential and high discharge capacity as well as long cyclic performance is a key access to ALIB with high energy density and excellent cyclic stability. Up to now, electrochemical properties of $LiMn_2O_4$ [1,2,5,13], $LiCoO_2$ [8,12], $LiNi_{0.81}Co_{0.19}O_2$ [14], $LiFePO_4$ [15,16], $LiMn_{0.05}Ni_{0.55}Fe_{0.9}PO_4$ [17], $LiMnPO_4$ [18], $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ [7,10,11] as cathode materials and VO_2(B) [1,2], $Li_xV_2O_5$ [9,11], LiV_3O_8 [8,10,12,14], PPy coated MoO_3 [19], TiP_2O_7 [20], $LiTi_2(PO_4)_3$ [17,20], $Na_2V_6O_{16}{\cdot}xH_2O$ [21], $H_2V_3O_8$ [22] as anode materials in different lithium aqueous electrolytes have been reported. It has been found that electrochemical performance of such materials strongly depends on the pH value of the used aqueous electrolyte [7,9]. Unfortunately, electrochemical stable window of the electrolyte reduces with increasing the content of OH^- in electrolyte, which is not conducive to enough release of lithium ion from bulk material. Thus, detailed studies of electrochemical behavior of electrode materials in aqueous electrolytes, especially the effects of pH value on electrochemical stability are essential. Our group [11] studied the effect of pH value on electrochemical stability of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ in $LiNO_3$ solution and chose 5 mol/L $LiNO_3$ with pH 11 as electrolyte for aqueous lithium ion battery. WANG et al [7] investigated the capacity fade mechanism of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ at Li_2SO_4 solution and found that the electrode was more stability in electrolyte with pH 13 than that with pH 11. Meantime, they considered that capacity fading of the electrode was attributed to H^+ intercalation when cycling in neutral electrolyte. On the basis of previous reports, it

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is still very necessary to find proper aqueous electrolyte with the best pH value for various cathode materials and further investigate the cycling fading mechanism, which would favor the best electrochemical behavior of electrode in aqueous solution.

Layered $LiNi_{0.5}Mn_{0.5}O_2$ is successively proposed by SPAHR et al [23], and MAKIMURA and OHZUKU [24] as a promising positive material for lithium ion battery. It has a reversible capacity as high as 200 mA·h/g in the voltage range of 2.5−4.5 V, good cyclic ability and excellent thermal stability. However, there is no study involving its electrochemical properties in aqueous electrolyte. In this work, layered $LiNi_{0.5}Mn_{0.5}O_2$ was prepared and proposed to be cathode material for aqueous lithium ion battery, and the cyclic fading mechanism of electrode in $LiNO_3$ solutions with different pH values was further discussed.

2 Experimental

Precursor $[Ni_{0.5}Mn_{0.5}](OH)_2$ was synthesized by surfactant (sodium dodecyl sulfonate, SDS) assisted co-precipitation method. The appropriate amounts of $NiSO_4$ and $MnSO_4$ (cationic ratio of Ni:Mn=1:1) and surfactant SDS (the mass concentration of 0.056 g/L) were dissolved and then poured into a round-bottomed flask with long neck. The solution (about 150 mL) was stirred for 2 h by magnetic stirring apparatus, with the reaction temperature of 45 °C. After that, the appropriate alkaline solution consisted of NaOH and ammonia (molar ratio=4:1) was added drop-wise into round-bottomed flask under vigorous stirring. The hydroxide precipitation was then filtered, washed, and dried overnight at 110 °C. After being simply ground by hand, the powder was mixed with required amount of LiOH (cationic ratio of Li:Ni=2.1:1). Then the mixed powder was ground for 5 h by ball milling and calcined at 800 °C for 12 h.

Crystal structure was identified by X-ray diffractometer (Rigaku D/MAX2500, Japan) with a Cu K_α radiation in the angular range of 10°−80° (2θ). The surface morphology was observed by scanning electron microscope (SEM, JSM6430F).

A three-electrode electrochemical cell was employed for the measurement of cyclic voltammetry (CV) in $LiNO_3$ aqueous electrolyte. Saturated calomel electrode (SCE) and platinum (Pt) electrode were used as the reference and the counter electrodes, respectively. The positive electrode was constituted 85% active material as cathode material, 10% black as conducting additive, and 5% polytetrafluoroethylene (PTFE) as binder. It was pressed onto a 100 mm^2 stainless steel mesh used as the current collector at 300 kg/cm^2 and then dried at 110 °C for 8 h in a vacuum oven in order to remove moisture. CV test was carried out at different scanning rates in electrochemical station (Shanghai Chenhua, China) at room temperature. Electrochemical impedance spectroscopy (EIS) was also performed in the same electrochemical station. The frequency range was from 100 kHz to 10 mHz and the amplitude voltage was 5 mV. Before the EIS test, each cell was charged to 0.5 V and then the voltage was kept stable for 2 h.

3 Results and discussion

Figure 1 shows the X-ray diffraction pattern of as-prepared $LiNi_{0.5}Mn_{0.5}O_2$ powder. Obviously, all the peaks can be well indexed to $LiNi_{0.5}Mn_{0.5}O_2$ phase with the space group of $R\bar{3}m$ and there is no impurity phase. As mentioned, it is hard to synthesize the pure phase of $LiNi_{0.5}Mn_{0.5}O_2$ by solid state method [24]. However, the XRD pattern indicates that well crystallized pure $LiNi_{0.5}Mn_{0.5}O_2$ can be obtained through a co-precipitation method combined with the solid state process.

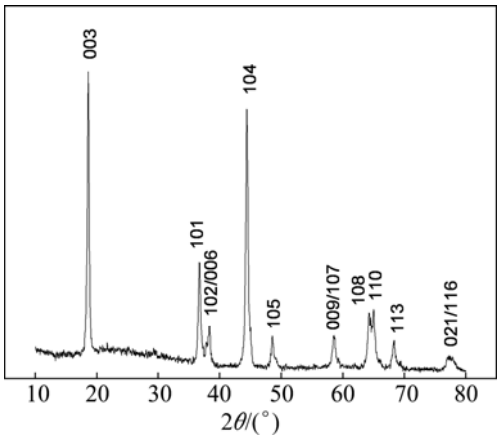

Fig. 1 X-ray diffraction pattern of as-prepared material by co-precipitation method

The morphology of $LiNi_{0.5}Mn_{0.5}O_2$ particles was observed by SEM (Fig. 2). It can be seen clearly that the $LiNi_{0.5}Mn_{0.5}O_2$ powder is composed of particles. The particle size covers a narrow distribution range from 100 nm to 200 nm.

Figure 3 displays the CV curve of $LiNi_{0.5}Mn_{0.5}O_2$ electrode in neutral 5 mol/L $LiNO_3$ solution at −0.1 to 1.4 V. The scannig rate is 0.6 mV/s. As can be seen, a pair of redox peaks, with the anodic peak at about 0.71 V and cathodic peak at about 0.49 V, are observed obviously. Based on previous reports [9,10], appearance of redox peak indicates a reversible intercalation and de-intercalation of Li ions in solid phase with charge transfer at the electrode/electrolyte interface. The corresponding equations for the redox reaction can be written as follows:

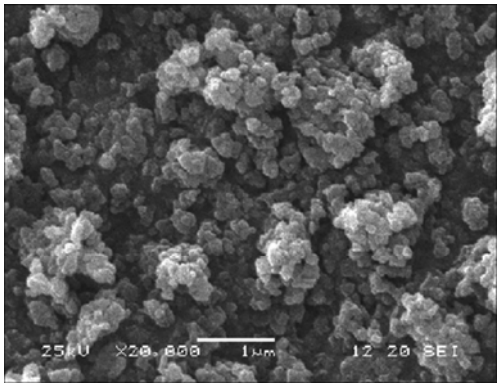

Fig. 2 SEM image of $LiNi_{0.5}Mn_{0.5}O_2$ powder

In oxidation process,

$$LiNi_{0.5}Mn_{0.5}O_2 \rightarrow xLi^+ + xe + Li_{1-x}Ni_{0.5}Mn_{0.5}O_2 \quad (1)$$

In reduction process,

$$xLi^+ + xe + Li_{1-x}Ni_{0.5}Mn_{0.5}O_2 \rightarrow LiNi_{0.5}Mn_{0.5}O_2 \quad (2)$$

It is interesting to note that the potentials of Li^+ ion intercalation and de-intercalation of $LiNi_{0.5}Mn_{0.5}O_2$ electrode in aqueous $LiNO_3$ solutions are within the safety range of water decomposition. Accordingly, $LiNi_{0.5}Mn_{0.5}O_2$ could be proposed as one kind of promising cathode materials for aqueous lithium ion battery. When the scanning voltage is more than 1.2 V, a large irreversible peak appears, which is probably due to the oxygen evolution [7,9,20]. As seen by results above, $LiNi_{0.5}Mn_{0.5}O_2$ electrode shows good electrochemical reversible behaviors in $LiNO_3$ aqueous electrolyte.

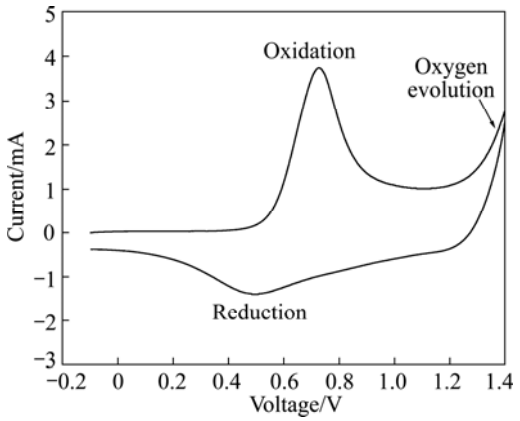

Fig. 3 CV curve of $LiNi_{0.5}Mn_{0.5}O_2$ electrode in neutral 5 mol/L $LiNO_3$ solution at −0.1 to 1.4 V with scanning rate of 0.6 mV/s

The pH value of the solution electrolyte has been proved as a very important factor to the electrochemical performance [25]. Therefore, effect of 5 mol/L $LiNO_3$ electrolytes with different pH values (7, 11, 12, 13) to electrochemical behavior is further studied in details. Related results are shown in Fig. 4. The scanning voltage

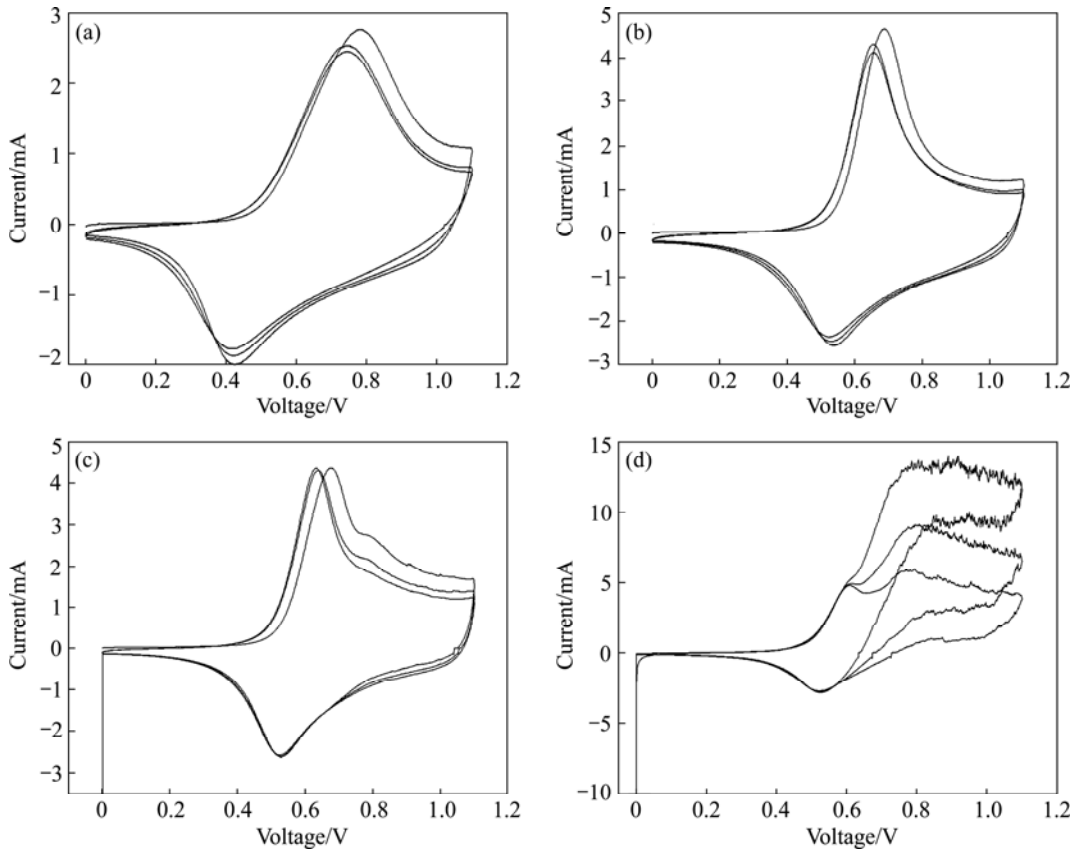

Fig. 4 CV comparison of $LiNi_{0.5}Mn_{0.5}O_2$ electrodes in 5 mol/L $LiNO_3$ solution with various pH values between 0 and 1.1 V (vs SCE) at 0.6 mV/s: (a) pH=7; (b) pH=11; (c) pH=12; (d) pH=13

range is from 0 to 1.1 V and the scanning rate is 0.6 mV/s. As observed, the potential of oxidation peak in $LiNO_3$ electrolytes (pH=11, 12, 13) shifts backward and that of reduction peak moves forward in comparison with that in neutral electrolyte, suggesting that the reversibility of redox reaction could be improved while increasing the pH of solution electrolyte. In this work, there is no oxygen evolution at oxidation curves in electrolyte with pH 7 and 11. Surprisingly, when the pH is increased to 13, large second irreversible reaction happens with the oxygen release. As shown in Fig. 4, it is concluded that it will lead to oxygen release in a lower decomposition potential when excessively increasing the pH of $LiNO_3$ electrolyte. That is to say, adding too much amount of OH^- into the electrolyte would result in inferior cyclic stability of electrode. According to the difference of CV curves in $LiNO_3$ with various pH values, it is clearly discovered that reduction process becomes more and more stable with increasing pH value. At the same time, a little oxygen evolution happens in oxidation curve of that with pH 12. After three cycles, the oxygen evolution process in Fig. 4(c) seems so small that it is hard to see. From the results above, it can not be distinguished easily that either electrolyte with pH value of 11 or 12 is the best choice to improve the electrochemical behavior of $LiNi_{0.5}Mn_{0.5}O_2$. For $LiNi_{0.5}Mn_{0.5}O_2$ in electrolyte with pH 12, obviously, the pH of electrolyte decreases a little with the oxygen release and then seems stably after several CV curves. Herein, long cyclic test will be carried out to compare the electrochemical stability of electrode in electrolyte with different pH values (11 and 12). Considering the complicate effect if the aqueous lithium ion battery with anode material is built, the three-electrode cell is still used to evaluate the electrochemical stability of $LiNi_{0.5}Mn_{0.5}O_2$ electrode.

From the above information, the electrodes which have been cycled three CV curves in Fig. 4 are carried out another 17 CV curves in the same condition, respectively. The following 17 CV curves are compared in Fig. 5. From CV curves with pH 7, the couple of redox peak corresponding to the intercalation and de-intercalation of lithium ion disappears nearly after cycles, revealing the poor cyclic stability. As we know, bulk cathode materials for aqueous lithium ion battery such as $LiMn_2O_4$ [2,9] and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ [7,11] without any modification in neutral aqueous electrolyte show poor cyclic performance. When the pH is increased to 11, the cyclic stability is somewhat enhanced. Not like that in neutral solution, there is still an obvious pair of redox peak located at 0.87 V and 0.36 V, respectively, after 20 CV curves. To our surprise, CV curves with pH 12 indicate a couple of better defined and reversible redox peak and much less fading with increasing cycle,

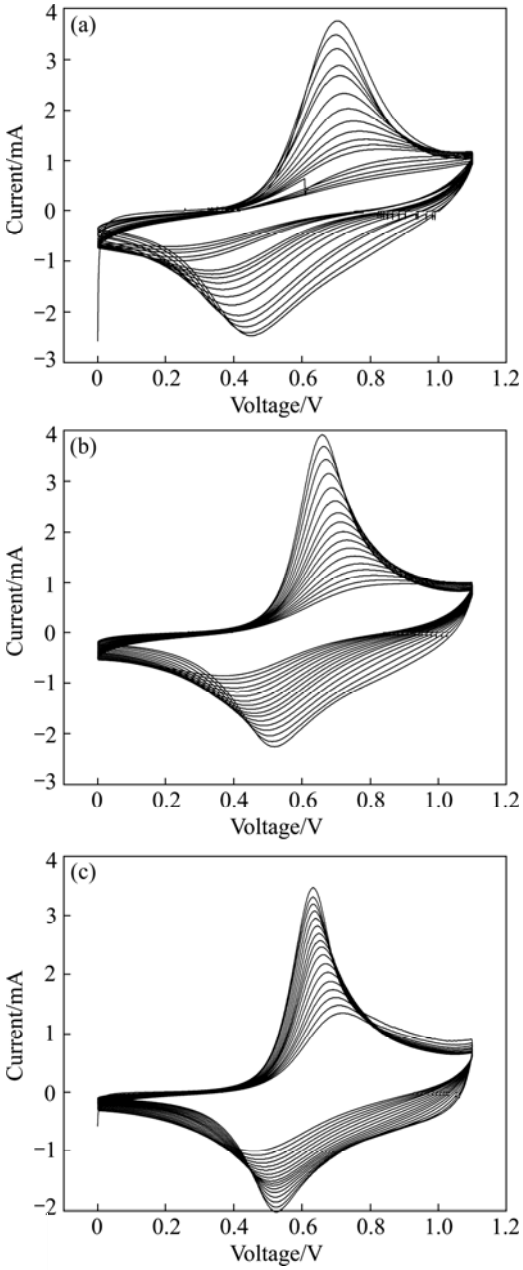

Fig. 5 Next 17 CV curves of $LiNi_{0.5}Mn_{0.5}O_2$ electrodes in 5 mol/L $LiNO_3$ solution between 0 and 1.1 V (vs SCE) at 0.6 mV/s with various pH values: (a) pH=7; (b) pH=11; (c) pH=12

compared with those in electrolyte with pH 7 and 11. The potentials of such redox peaks after 20 CV curves are about 0.7 and 0.46 V, respectively. In addition, no oxygen evolution exists in oxidation curves in electrolyte with pH 12. It is further confirmed the pH of that electrolyte lowers a little with the oxygen release and then becomes stable after some CV curves. Hereby, it is concluded that 5 mol/L $LiNO_3$ with pH 12 is the most suitable for $LiNi_{0.5}Mn_{0.5}O_2$ cycling in $LiNO_3$ aqueous solution.

To understand the possible reason of improved cyclic stability of $LiNi_{0.5}Mn_{0.5}O_2$ in electrolyte with pH

12, EIS results for electrodes after 20 CV curves in 5 mol/L $LiNO_3$ electrolytes with pH 7 and 12 are measured at the charged state of 0.5 V (vs SCE), as shown in Fig. 6. Both AC impedance spectra of electrodes in $LiNO_3$ electrolytes with different pH values consist of a high-frequency arc and a low-frequency line. It has been confirmed that the high frequency contribution is due to the charge-transfer process and the low-frequency line corresponds to diffusion process of lithium ion in electrode solid [26,27]. Apparently, after 20 CV curves, high-frequency arc of electrode in aqueous electrolyte with pH 7 is much larger than that electrode in with pH 12. In another word, charge-transfer resistance of $LiNi_{0.5}Mn_{0.5}O_2$ in 5 mol/L $LiNO_3$ with pH 12 after 20 CV curves is suppressed effectively. Using the equivalent circuit (inset of Fig. 6), the charge-transfer resistances of $LiNi_{0.5}Mn_{0.5}O_2$ in 5 mol/L $LiNO_3$ with pH 7 and 12 are calculated to be 79.5 and 11.7 Ω, respectively. In some previous reports, change of charge-transfer resistance was considered the important factor to capacity fading for cathode materials [27−30]. SUN et al [27] considered that the improved electrochemical performance of AlF_3-coated $LiCoO_2$ could be explained by the lower charge transfer resistance (R_{ct}) and reduced Co dissolution of the coated electrode. LI et al [29] deduced that $LiNi_{0.5}Mn_{0.4}Co_{0.1}O_2$ with upgraded rate capabilities, compared with non-doped $LiNi_{0.5}Mn_{0.5}O_2$, was attributed to the decrease in charge-transfer resistance. In brief, suppressed charge-transfer resistance is the major cause why electrochemical stability of $LiNi_{0.5}Mn_{0.5}O_2$ electrode in electrolyte with pH 12 improves remarkably. It is well known that charge transfer resistance involves many factors such as electronic conductivity, crystal structure, and the inter-particle contacts (active particle−active particle, carbon−active particle, and carbon−carbon grain contracts) [31]. For that reason, the electrodes after cycling are further characterized by XRD and SEM to explain the origin of change in charge transfer resistance.

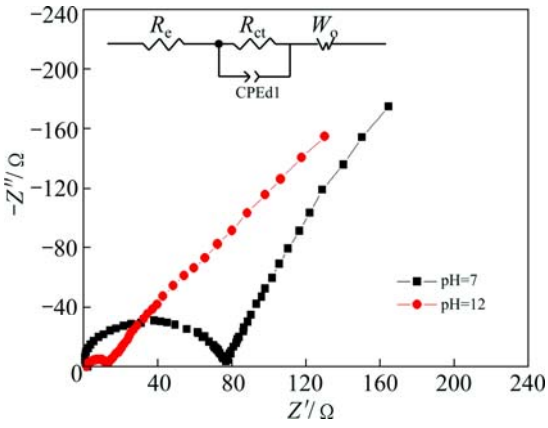

Fig. 6 AC impedance spectra of $LiNi_{0.5}Mn_{0.5}O_2$ electrodes at 0.5 V (vs SCE) after 20 CV curves in 5 mol/L $LiNO_3$ solution with pH 7 and 12, respectively, associated with equivalent circuit inset

With regard to the poor cyclic stability of cathode material in neutral aqueous solution, probable capacity fade mechanisms of aqueous lithium ion battery have been proposed by some research groups and are mainly focused on the transition metal ion dissolution in aqueous solution, structural changes of electrode materials, as well as the decomposition of water [2,13,30]. In this work, structural change of $LiNi_{0.5}Mn_{0.5}O_2$ electrodes in electrolyte with different pH values should be considered. Figure 7 shows the XRD patterns of $LiNi_{0.5}Mn_{0.5}O_2$ electrodes after 20 CV curves in 5 mol/L $LiNO_3$ solution with various pH values (7, 12) between 0 and 1.1 V (vs SCE). With the exception of those diffraction peaks marked with *, which are due to the stainless steel mesh, the other lines in Fig. 7 are attributed to $LiNi_{0.5}Mn_{0.5}O_2$. Evidently, both samples keep good α-$NaFeO_2$-type structure and no impurity phases are detected. The lattice constants of $LiNi_{0.5}Mn_{0.5}O_2$ electrodes are recorded in Table 1. It needs to note that the lattice constants of the electrode after cycling in the aqueous electrolyte with pH 12 agree well with those of pristine $LiNi_{0.5}Mn_{0.5}O_2$ powder. When cycling in neutral electrolyte, the electrode shows the large change with the crystallite volume from 120.068 to 120.266 Å^3. It is well known that the intensity ratio of I_{003}/I_{104} in XRD line depends on the degree of displacement between the cations located at 3*a* and 3*b*

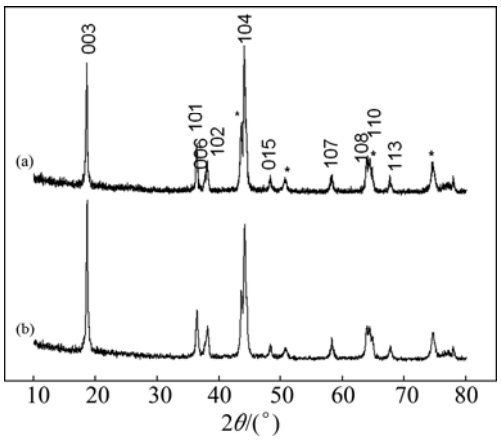

Fig. 7 XRD patterns of $LiNi_{0.5}Mn_{0.5}O_2$ electrodes after 20 CV curves in 5 mol/L $LiNO_3$ solution between 0 and 1.1 V (vs SCE) with different pH values: (a) pH 7; (b) pH 12

Table 1 Crystallographic data of $LiNi_{0.5}Mn_{0.5}O_2$ after CV curves in electrolyte with different pH values

State	*a*/Å	*c*/Å	*c*/*a*	*V*/Å^3
$LiNi_{0.5}Mn_{0.5}O_2$ powder	2.8933	14.343	4.957	120.068
$LiNi_{0.5}Mn_{0.5}O_2$ (pH 7)	2.8955	14.345	4.954	120.266
$LiNi_{0.5}Mn_{0.5}O_2$ (pH 12)	2.8938	14.344	4.957	120.128

sites [32]. The higher the ratio is, the less the cationic disorder in the α-$NaFeO_2$-type structure is. As shown in Fig. 7, the degree of cationic disorder is greatly reduced in $LiNi_{0.5}Mn_{0.5}O_2$ that cycling in electrolyte with pH 12, compared with that in neutral electrolyte. The structure change of $LiNi_{0.5}Mn_{0.5}O_2$ cycling in neutral aqueous electrolyte could probably be resulted from the H^+ intercalation and exchange [7].

The morphology comparison (Fig. 8) of $LiNi_{0.5}Mn_{0.5}O_2$ electrodes after 20 CV curves in 5 mol/L $LiNO_3$ electrolyte with different pH values highlights the difference between the two materials. In the case of $LiNi_{0.5}Mn_{0.5}O_2$ after cycling in neutral electrolyte, the particles seem to be self-aggregated, and their contact with binder (PTFE) and acetylene black becomes poor because of the presence of many large voids, which may be attributed to the attack of H_2O [13,29]. As demonstrated in Fig. 8, PTFE binder is apparently observed. On the other hand, $LiNi_{0.5}Mn_{0.5}O_2$ electrode in electrolyte with pH 12 shows excellent particle distribution and better surface smoothness. Besides, no obvious crack is observed on the surface of $LiNi_{0.5}Mn_{0.5}O_2$ electrode. Results above suggest that electrode surface after cycling in electrolyte with pH 12 is more stable than that in neutral electrolyte, which agrees well with the suppressed charge transfer resistance, thus resulting in improved cyclic stability. In other words, the attack of H_2O in electrolyte with pH 12 is probably greatly suppressed. According to results above, it is believed that the mechanism of suppressed charge transfer resistance should be originated from the less change in the electrode surface and structure. It should be pointed out that WANG et al [7] once found that capacity fading of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ was attributed to H^+ intercalation when cycling in neutral Li_2SO_4 electrolyte; however, no study mentioned the change of electrode surface.

4 Conclusions

1) $LiNi_{0.5}Mn_{0.5}O_2$ was prepared by surfactant assisted co-precipitation method.

2) XRD and SEM results indicate that $LiNi_{0.5}Mn_{0.5}O_2$ is pure phase and covers a narrow distribution range from 100 to 200 nm.

3) The as-prepared $LiNi_{0.5}Mn_{0.5}O_2$ exhibits good electrochemical reversible behavior in 5 mol/L $LiNO_3$ solution electrolyte. Meantime, the electrode in $LiNO_3$ electrolyte with pH value of 12 has the best electrochemical cyclic stability.

4) EIS result indicates that the improved cyclic stability of $LiNi_{0.5}Mn_{0.5}O_2$ in aqueous electrolyte with pH 12 could be explained by the suppressed charge-transfer resistance, which is probably ascribed to the more stable electrode surface morphology and less structure change according to SEM and XRD results.

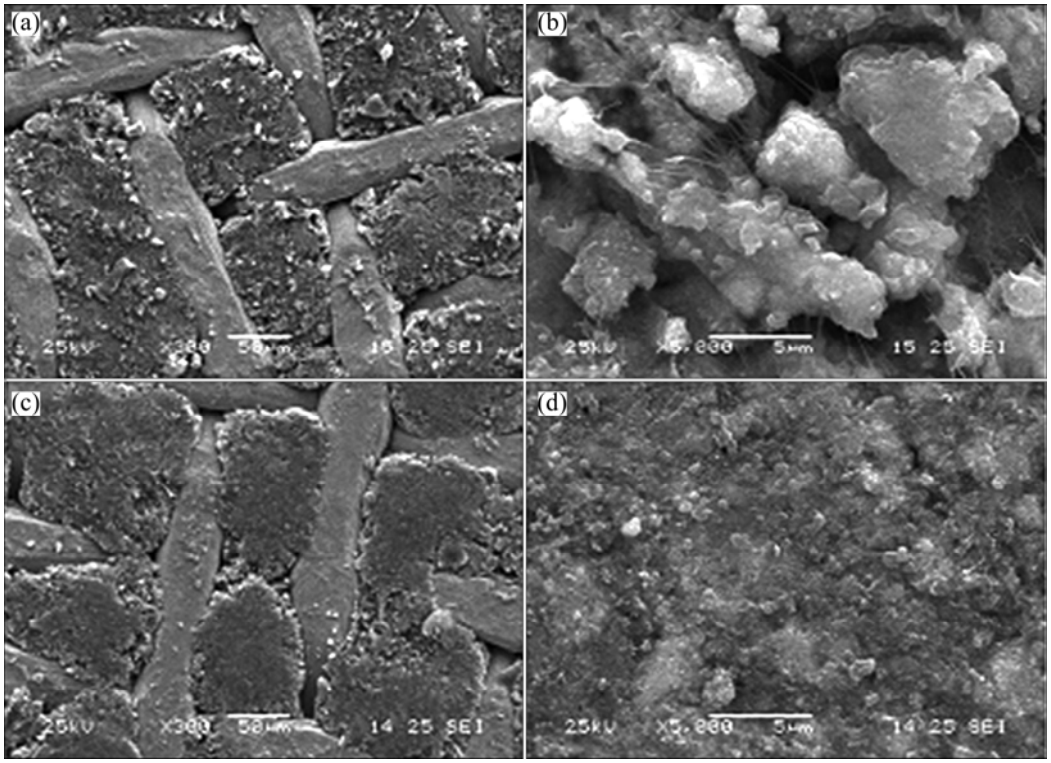

Fig. 8 SEM images of $LiNi_{0.5}Mn_{0.5}O_2$ electrodes after 20 CV curves in 5 mol/L $LiNO_3$ solution between 0 and 1.1 V (vs SCE) with various pH values: (a), (b) pH 7; (c), (d) pH 12

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$LiNi_{0.5}Mn_{0.5}O_2$ 电极在 $LiNO_3$ 电解液中的电化学性能及循环衰减机理

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摘 要：研究 $LiNi_{0.5}Mn_{0.5}O_2$ 电极在 $LiNO_3$ 水溶液中的电化学行为，同时分析该电极在不同 pH 值电解液中的循环衰减原因。循环伏安测试显示 $LiNi_{0.5}Mn_{0.5}O_2$ 在浓度为 5 mol/L 的 $LiNO_3$ 水溶液中具有较好的锂离子脱嵌能力。对比发现，$LiNi_{0.5}Mn_{0.5}O_2$ 电极在浓度为 5 mol/L，pH 值为 12 的 $LiNO_3$ 水溶液中具有最好的循环稳定性能。通过交流阻抗法、X 射线衍射分析及电极形貌的对比分析发现：电极在浓度为 5 mol/L，pH 值为 12 的 $LiNO_3$ 水溶液中循环时，电极的表面形貌和电极结构都能得到较好的保持，电极的电荷传递阻抗得到明显抑制，因此在该 pH 值电解液中的循环稳定性最好。

关键词：锂离子电池；$LiNi_{0.5}Mn_{0.5}O_2$；循环衰减机制；循环伏安法；$LiNO_3$ 溶液

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