

Effect of High Levels of Impurity Calcium on the Electrochemical Performance of Spinel LiMn_2O_4

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Abstract: Spinel LiMn_2O_4 was synthesized by solid-state method, using Mn_2O_3 as manganese source. By X-ray diffraction, scanning electron microscope and electrochemical performance test, effects of impurity calcium from manganese source, i.e. MnCO_3 on the electrochemical properties of spinel LiMn_2O_4 were systematically studied. The results showed that all samples with different contents of impurity calcium were indexed to spinel phase with the cubic space of $Fd\bar{3}m$, and no impurity phase was detected; the particle size and morphology of samples were not obviously different; when the contents of impurity were low, the first charge-discharge capacity remained almost unchanged with the increase of calcium; and in contrast, it distinctly decreased. The results also showed that the cycle-stability of LiMn_2O_4 was improved collaboratively.

With the rapid development of the global economy, it is bound to increase consumption such as the oil and other fossil fuel resources. The lithium-ion secondary battery, called "green power", has attracted much more attention due to the most prominent features such as its small, lightweight, long working hours, long cycle life, no memory effect, fast charge and discharge, low self-discharge and environmental friendly etc.[1,2]. Owing to the serious attenuation of charge-discharge reversible capacity, instability and other shortcomings on electrochemical properties of the spinel LiMn_2O_4 , its development is facing with lots of restriction [3, 4, 5]. Much work has been done in an effort to improve the electrochemical performance of the spinel LiMn_2O_4 by suppressing Jahn-Teller distortion. Ma[6] studied the influence of different manganese sources on the performance of spinel LiMn_2O_4 , finding that the spinel LiMn_2O_4 synthesized by Mn_2O_3 exhibited dense particles, uniform distribution and the most excellent electrochemical performance. The price of high-purity Mn_2O_3 is significantly higher than electrolytic manganese dioxide (EMD), but the value of the industrial-grade Mn_2O_3 is lower than EMD. Industrial-grade Mn_2O_3 contains large amounts of impurities such as Ca^{2+} , Mg^{2+} , SiO_3^{2-} , SO_4^{2-} , K^+ , Na^+ . Peng[7] discussed the electrochemical properties of the spinel LiMn_2O_4 prepared by Mn_2O_3 that containing K^+ , showing that its first charge-discharge capacity drastically decreased and the capacity retention also declined with the increase of K^+ . Xie[8] researched the electrochemical properties of the spinel LiMn_2O_4 that containing Ca^{2+} and Mg^{2+} , illustrating that morphology of the samples was improved and cycle performance was enhanced with the increase of Ca^{2+} and Mg^{2+} . However, no relevant literatures are reported on the effects of Mn_2O_3 that containing high contents of impurity calcium on the electrochemical properties of the spinel LiMn_2O_4 . In this paper, spinel LiMn_2O_4 is synthesized by solid-state method, using Mn_2O_3 that containing high contents of impurity calcium as manganese source, and the electrochemical properties of the batteries and the microscopic appearance of the spinel LiMn_2O_4 will be studied.

1 Experiment

1.1 Preparation of Spinel LiMn_2O_4 and Battery

All the manganese sources were prepared in laboratory. LiCO_3 is produced by Shanghai Li Industrial Company Limited. Different manganese sources and LiCO_3 were weighed in Li/Mn at molar ratios of 1:2 and then completely mixed in an agate mortar for grinding. Then took the

mixture into a corundum crucible and heated to 560 °C at 3 °C/min in air, 5h later raised to 780 °C at the same heating rate, after 48 hours heat preservation, the raw materials were cooled down to room temperature, then passed through 200 mesh sieve, finally achieved the spinel LiMn_2O_4 as cathode material. The cathode material, the conductive agent (acetylene black) and the polytetrafluoroethylene (PTFE) emulsion were uniformly mixed according to the mass ratio of 85:10:5 accurately, and dried in an oven for 24h at 110°C. Subsequently the mixture was pressed into 5~10mg weight, 0.1mm thick slices, and then it was rushed into a wafer with a $\phi 8$ punch, thus the positive films were obtained. The lithium tablets were used as anode materials and 1.0M commercial LiPF_6 in DMC: EC: DEC (1:1:1 in volume) as the electrolyte. And then they are assembled the CR2032 button-type batteries in an argon-filled glove-box.

1.2 Characterization and Electrochemical Measurements

The crystal structure of the materials was analyzed by an X-ray diffraction operated at 40KV and 150mA from 10° to 90° (Rigaku, D/Max-RB, Japan) with a wavelength of Cu K_α ($\lambda = 0.15406\text{nm}$). Scanning electron microscopy (SEM) was obtained through a spectrometer (SEM, Hitachi S-3400N Japan). Electrical performance test was carried out using a NEWARE tester, Charge-discharge cycles were carried out at 0.1C in CR2023 coin cells, with a potential range between 3.0 and 4.3V at room temperature.

2 Results and Discussion

2.1 Effect of Manganese Source with Low Levels of Calcium on the Performance of Spinel $\text{Li}_{1.06}\text{Mn}_2\text{O}_4$

Table 1 The contents of calcium in Mn_2O_3 and corresponding electrical properties of $\text{Li}_{1.06}\text{Mn}_2\text{O}_4$ as cathode materials

Samples	Ca^{2+} ($\mu\text{g}\cdot\text{g}^{-1}$)	The first charge capacity of $\text{Li}_{1.06}\text{Mn}_2\text{O}_4$ ($\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$)	The first discharge capacity of $\text{Li}_{1.06}\text{Mn}_2\text{O}_4$ ($\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$)	Discharge capacity retention rate after 50 cycles (%)
High purity	49	133.910	128.487	89.15
1-1	492	133.229	127.065	88.95
1-2	2240	132.483	126.902	90.68
1-3	4560	131.271	126.191	92.17
1-4	7747	129.825	125.035	92.93

Samples with low contents of Ca^{2+} are listed in Table 1.

Figure 1 shows the first charge-discharge curves of $\text{Li}_{1.06}\text{Mn}_2\text{O}_4$ containing Ca^{2+} at lower range. As shown in the figure, all the curves have two distinct charge-discharge platforms at 4.0V and 4.1V, illustrating that all the samples undergo two reversible electrochemical reactions in the vicinity of the two electrodes, the former corresponds to the escape of lithium-ions from the tetrahedral 8a position, the latter corresponds to the intercalation of lithium-ions from the empty octahedral 16c position. The first charge-discharge capacities of $\text{Li}_{1.06}\text{Mn}_2\text{O}_4$ remain almost unchanged with the increase of Ca^{2+} .

Figure 2(a) reveals cycling-curves of discharge-capacity of spinel $\text{Li}_{1.06}\text{Mn}_2\text{O}_4$ after 50 cycles. It can be seen from the figure that cyclic stability of lithium-rich $\text{Li}_{1.06}\text{Mn}_2\text{O}_4$ is improved with the increase of impurity Ca^{2+} , it is the reason that impurity Ca^{2+} replaces part of Mn^{3+} (16d) which results in improvement of morphology and more dispersion of the particles. So the electrolyte keeps in contact with the active materials more fully.

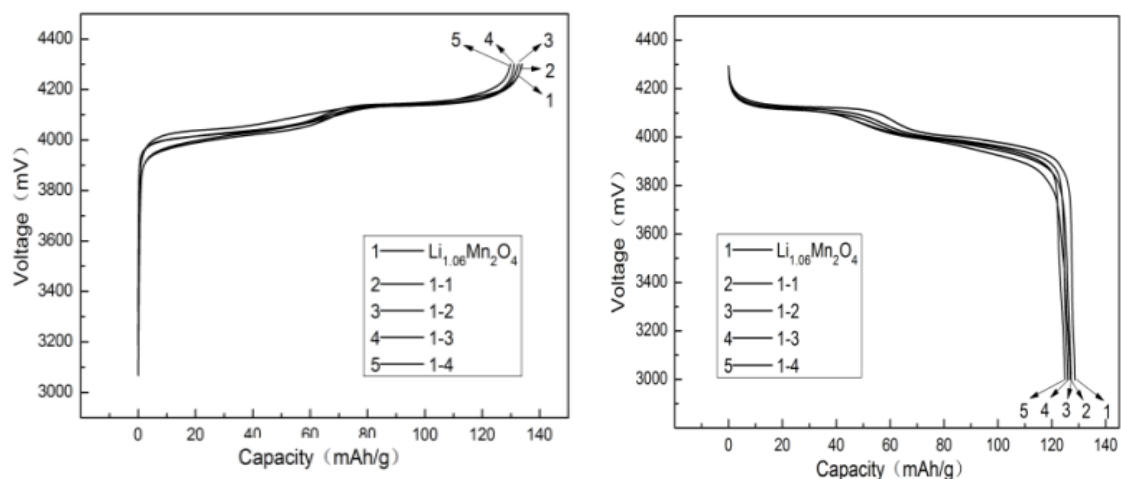


Figure 1 The initial charge-discharge curves of synthetic $\text{Li}_{1.06}\text{Mn}_2\text{O}_4$ with low levels of calcium

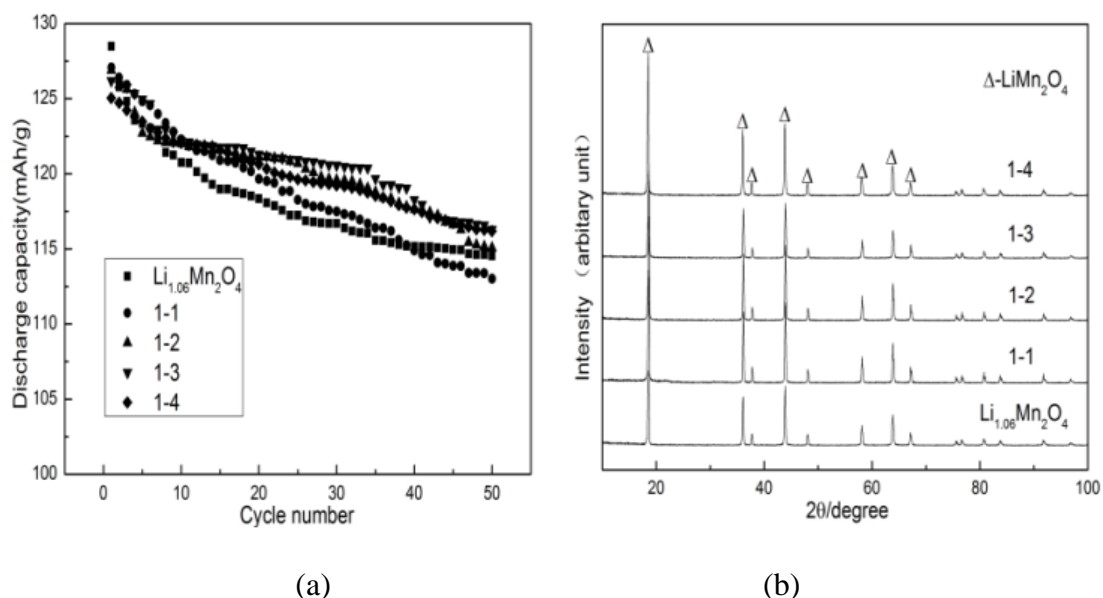


Figure 2 The discharge-cycle characteristics (a) and XRD patterns (b) of synthetic $\text{Li}_{1.06}\text{Mn}_2\text{O}_4$ with low levels of calcium

Figure 2(b) is the XRD patterns of synthetic lithium-rich $\text{Li}_{1.06}\text{Mn}_2\text{O}_4$ with low contents of calcium. All synthetic samples are indexed to spinel phase with the cubic space of $\text{Fd}3\text{m}$, which are in agreement with that of standard spinel LiMn_2O_4 . No peaks of calcium compounds are detected in each sample with the increase of calcium, which may be related to the fact that the content of impurity calcium is small. Additionally, the spinel lattice sizes of the as-prepared samples calculated according to the XRD patterns are from 0.8249 nm to 0.8245 nm, their changes are not obvious.

Figure 3 is the SEM of the $\text{Li}_{1.06}\text{Mn}_2\text{O}_4$ containing low levels of Ca^{2+} . It can be seen from the figure that all samples display dense spherical particles. The cathode materials synthesized by MnCO_3 also exhibit fine and evenly distributed particles, but there is a certain amount of agglomeration. Particles progressively become much larger, agglomeration is improved with the increase of Ca^{2+} . That is especially obvious for sample 1-4, the particles become more dispersed and the agglomeration is improved more distinctly.

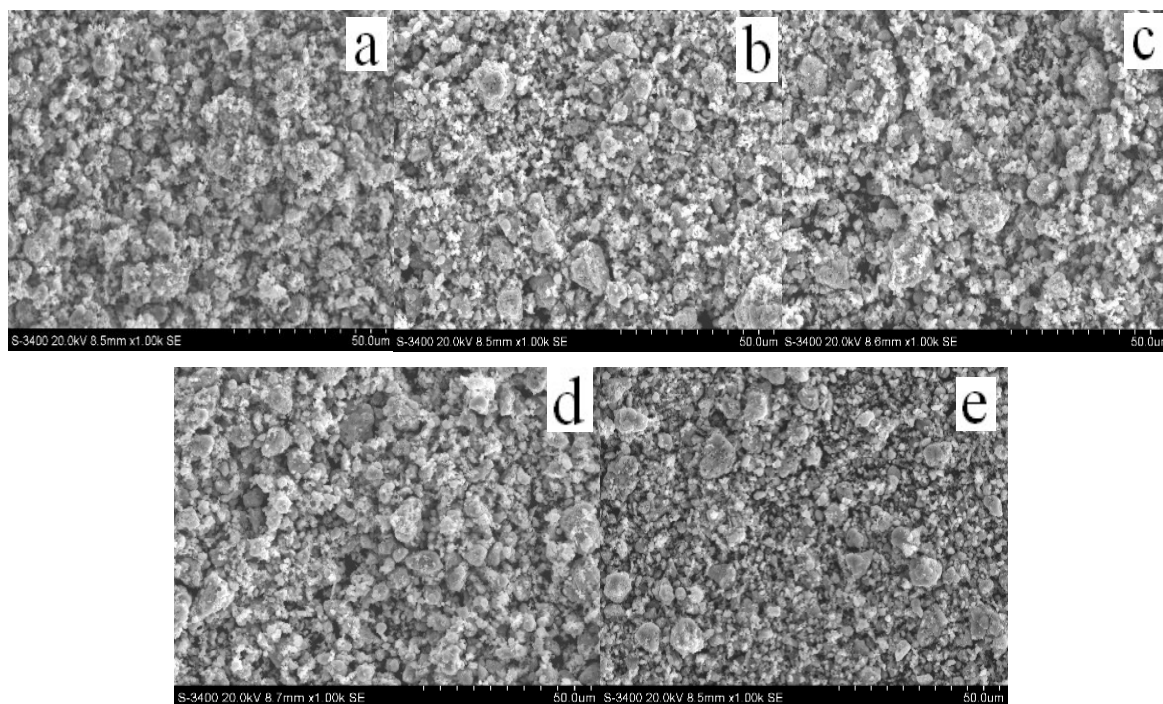


Figure 3 The SEM of synthetic $\text{Li}_{1.06}\text{Mn}_2\text{O}_4$ with low levels of calcium

(a: $\text{Li}_{1.06}\text{Mn}_2\text{O}_4$, b: 1-1, c: 1-2, d: 1-3, e: 1-4)

2.2 Effect of Manganese Source with High Levels of Calcium on the Performance of Spinel LiMn_2O_4

Table 2 The contents of calcium in Mn_2O_3 and corresponding electrical properties of LiMn_2O_4 as cathode materials

Samples	Ca^{2+} ($\mu\text{g}\cdot\text{g}^{-1}$)	The first charge capacity of LiMn_2O_4 ($\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$)	The first discharge capacity of LiMn_2O_4 ($\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$)	Discharge capacity retention rate after 50 cycles (%)
High purity	20.85	137.939	126.856	69.47
2-1	7640.99	122.035	115.900	72.38
2-2	8659.93	120.805	114.276	82.42
2-3	11336.00	104.561	101.130	84.64
2-4	15103.58	98.300	97.179	86.89

Samples with high contents of Ca^{2+} are listed in Table 2.

Figure 4(a) is the first charge-discharge curves of LiMn_2O_4 with high contents of Ca^{2+} . It can be seen from the figure that all the charge-discharge curves have two obvious platforms, corresponding to the insertion and prolapse of lithium-ions respectively. With the increase of calcium, it appears seriously damped for the first charge-discharge capacity of LiMn_2O_4 . Especially, first charge-discharge capacity decays obviously for sample 2-4. The severe capacity loss is mainly due to the decrease of active substance Mn^{3+} of the spinel material. Replacement of Mn^{3+} -ions by Ca^{2+} -ions forms $\text{LiMn}_{2-x}\text{Ca}_x\text{O}_4$, which results in decrease of active-ions Mn^{3+} and obstacle of Li^+ diffusion in the process of charge-discharge. To reach the charge balance, the amount of Mn^{4+} -ion inevitably increases in the spinel structure. The increased Li/Mn ratio suggests the Li^+ -ions would diffuse into the octahedral sites to occupy the Mn sites to form $\text{LiMn}_{2-y}\text{Li}_y\text{O}_4$ ^[9]. And the increase of the ratio of $\text{Mn}^{4+}/\text{Mn}^{3+}$ in the spinel LiMn_2O_4 would reduce the spinel lattice size because the radius of Mn^{3+} -ion is larger than that of Mn^{4+} -ion. As a result, the charge-discharge capacity decreases

along with it.

Figure 4(b) is the cyclic performance-curves of LiMn_2O_4 containing high levels of Ca^{2+} at room temperature. It can be obtained from figure that the samples with high levels of Ca^{2+} -ion exhibit more excellent cycle stability than the sample without Ca^{2+} -ion (high-purity). This is mainly because the discharge capacity can be affected by the relative crystallinity of synthesized samples, while the Ca^{2+} -ion will have a large impact on the crystallization quality. The adjunction of Ca^{2+} -ion reduces the unit cell volume of the spinel LiMn_2O_4 , and bond length of Ca-O is stronger than Mn-O on the basis of standard Gibbs energies, thereby the crystal structure is enhanced and Jahn-Teller is effectively suppressed. As a result, it is more conducive to deintercalation of the lithium-ions and the improvement of cycling performance of the samples.

Figure 5 is the XRD spectra of LiMn_2O_4 with high contents of calcium. It can be seen from the figure that all the diffraction peaks completely match with the cubic spinel structure with space group of $\text{Fd}\bar{3}\text{m}$, indicating that the calcium substitution does not change the intrinsic spinel structure of LiMn_2O_4 (Joint Committee on Powder Diffraction Standards (JCPDS) no. 18-0736), in which lithium ions occupy the tetrahedral 8a sites, manganese ions occupy the octahedral 16d sites, and oxygen ions occupy the 32e sites [11]. X-ray diffraction patterns also reveal that the materials are good crystallinity and no diffraction peak of impurity can be discovered. It is believed that Ca^{2+} -ion completely occupies the Mn^{3+} -ion (16d) site in $\text{LiMn}_{2-x}\text{Ca}_x\text{O}_4$, which stabilizes the structures of the materials.

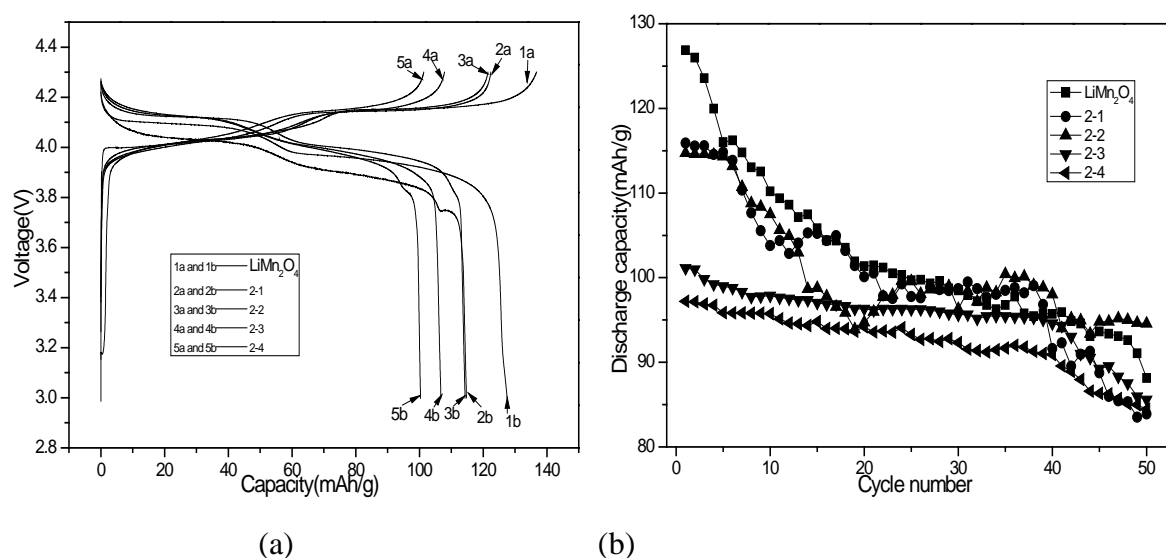


Figure 4 The initial charge-discharge curves (a) and cycle-stability curves (b) of LiMn_2O_4 with high levels of calcium

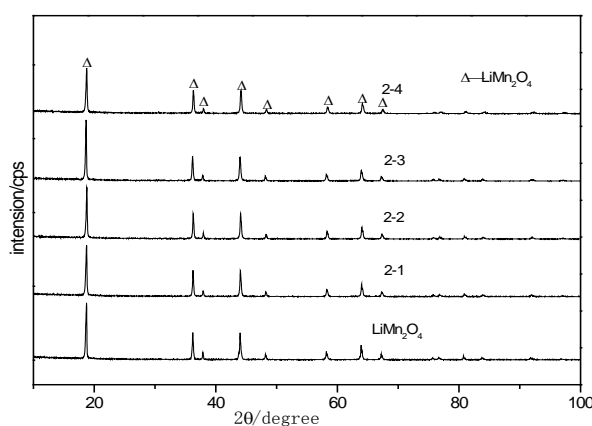


Figure 5 The XRD pattern of synthetic LiMn_2O_4 with high levels of calcium

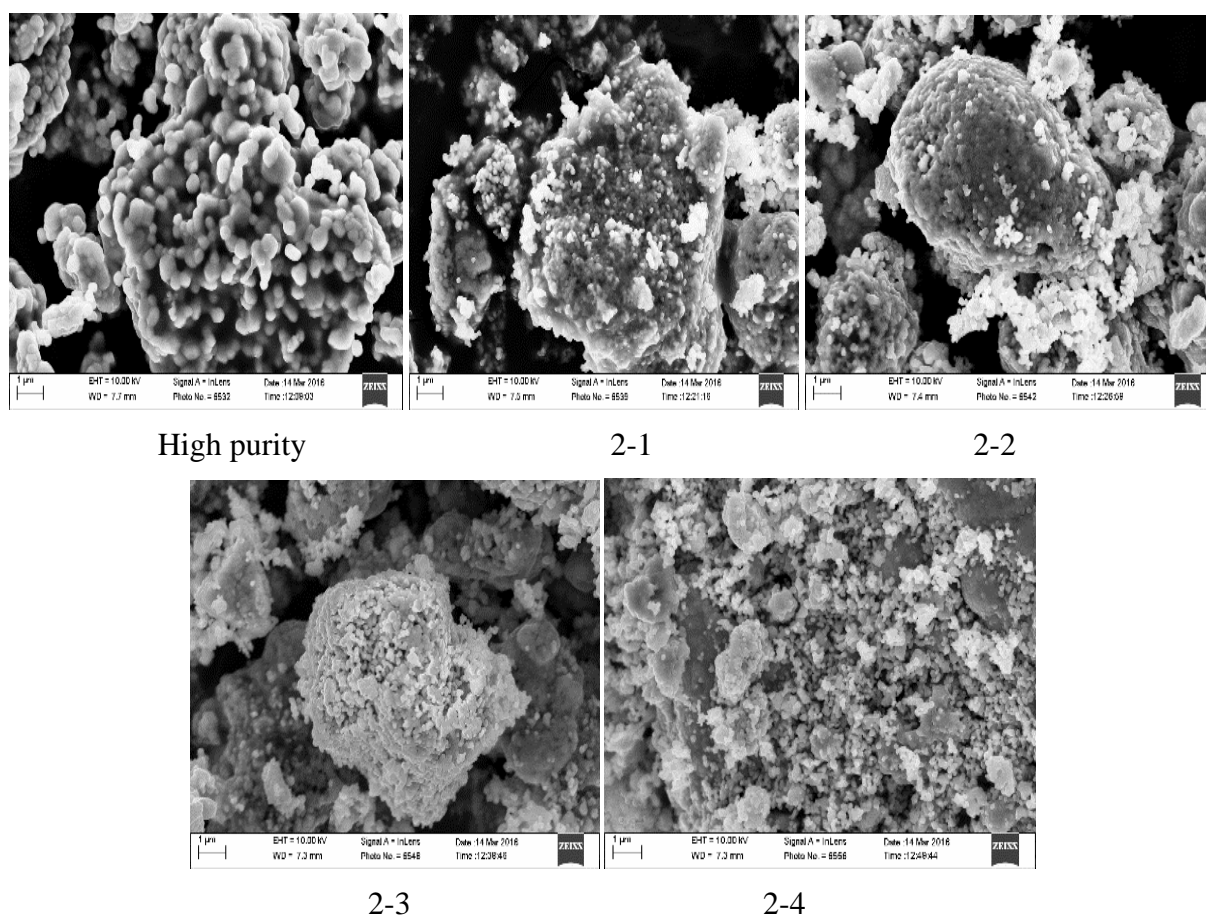


Figure 6 The SEM of synthetic LiMn_2O_4 with high levels of calcium

Figure 6 is SEM images of the LiMn_2O_4 containing high levels of Ca^{2+} . From the view of microstructure, all cathode materials present irregular-shaped particles and uneven particle size distribution. Furthermore, it is important to note that the substitution of Ca^{2+} -ion contributes to improving the crystallization and decrease of the average microscopic particle size of obtained products. That is especially obvious for sample 2-4, the particles with good crystallization have more regular morphology, which leads to shortening the paths of prolapse-embedded of the lithium-ions and decrease of polarization effects of Li^+ -ions. Simultaneously, agglomeration of the electrode materials is improved and the particles become more small dense with the increase of Ca^{2+} -ion. Additionally, the increase of specific surface area results in the more sufficient contact between the cathode material and the electrolyte.

Conclusions

(1) The $\text{Li}_{1.06}\text{Mn}_2\text{O}_4$ samples containing low contents of calcium are synthesized by solid-state method, using Mn_2O_3 as manganese source. The samples are indexed to spinel phase with the cubic space of $\text{Fd}3\text{m}$, small and distributed particles and no agglomeration. Particles become more dispersed with the increase of calcium. The first charge and discharge capacities of assembled batteries remain almost unchanged, and the efficiency of the first charge-discharge and the retention rate of 50 cycles are improved.

(2) The LiMn_2O_4 samples containing high contents of calcium are synthesized by solid-state method, using Mn_2O_3 as manganese source. The samples completely match with the cubic spinel structure with space group of $\text{Fd}3\text{m}$, particle size distribution is more discrete and there is a certain amount of agglomeration. The initial charge-discharge capacities emerge seriously attenuated with the increase of calcium, but stability of 50-cycles is significantly improved.

(3) Comprehensive results show that effects of manganese source with low contents of calcium on the electrochemical properties of lithium manganese oxide are beneficial. Only when the content

of calcium is higher, it is obviously adverse to electrochemical properties of lithium manganese oxide.

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