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Synthesis and Electrochemical Performance of Nanosized Multiple-doped $LiMn_2O_4$ Prepared at Low Temperature for Li-ion Battery

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Undoped and multiple doped Li-Mn spinel cathode materials for Li-ion battrry have been successfully synthsized by citric acid sol-gel method at a lower temperature 600 ^oC. The micro-structures for the materials were charactered by X-ray diffraction (XRD) and scanning electron microscope (SEM). All the synthesized materials are pure spinel phase with cubic structure and nano-sized. Their electrochemical properties were tested by galvanostatic charge-discharge cycling for the half-cells at at the current density 0.2 $mA \cdot cm^{-2}$(equal to about C/3) between 3.0~4.5V (versus. Li/Li^+) at room temperature. The undoped $LiMn_2O_4$ spinel has a high initial discharge specific capacity of 122.5 $mAh.g^{-1}$ and a very high capacity retention of 92.4% after 40 cycles. The good result could be ascribed to its nano-scale size synthesized in lower temperature in a large part. By multiple doping, pure phase spinel $Li_{1.03}M_{0.06}Mn_{1.91}O_4$ (M= $Zn_{0.03}Mg_{0.03}$,$Al_{0.03}Zn_{0.03}$, $Al_{0.03}Mg_{0.03}$,$Al_{0.03}Mg_{0.015}Zn_{0.015}$) were obtained. Multiple doping could improve the Li-Mn spinel Li-ion battrry cathode materials furthermore. Among the synthesized materials, $Li_{1.03}Zn_{0.03}Mg_{0.03}Mn_{1.91}O_4$ has the highest capacity retention of 97.4% after 40 cycles with an initial discharge specific capacity of 107.5$mAh.g^{-1}$.

Keywords: Li-Mn Spinel, multiple doping, cathode material, nano material, lithium-ion battery

1. INTRODUCTION

For almost more than 20 years, spinel $LiMn_2O_4$ has been widely studied as a promising cathode material for lithium-ion batteries [1-26]. On one aspect, because it has many advantages in view of low

cost, low toxicity, high working voltage and high safety; on another aspect, it is hard to overcome its some drawbacks such as severe capacity fading during charge–discharge cycles and low specific capacity. Also it has other advantages, such as high-rate capability, higher thermal stability and high power density. These have made it a hot topic of research as a very hopeful cathode material in large-scale lithium-ion batteries for electric vehicles (EV) or hybrid electric vehicles (HEV)in recent years [23-26]. However its low specific discharge capacity, especially its fast capacity fading at high temperature limits its application in large scale. Although the fading mechanism is not yet very clear, it has been agreed that there are three main reasons for the capacity fading: (1) manganese dissolution from $LiMn_20_4$ into electrolyte solution, (2) the Jahn-Teller effect out of the deep discharging to distort the crystal lattice, and (3) the decomposition of electrolyte solution in the higher voltage region. It has been verified by many researchers that single metal element doping is one good way to improve the cycling performance of $LiMn_2O_4$. There has been much work on single metal element doping by such as Li[7], Al[5,27-30], Co[1,31-33], Cr[13,15,26,33], Fe[8,20], Mg[14,34-37,], Ni[10,33,38], Sc[39], Zn[10,25],and some rare earth elements [40-42]. Dual metal element doping has also been found effective in improving the cycling performances of $LiMn_2O_4$ [17, 22, 23, 26, 43-45]. These include Li+Ni [43, 44], Li+Al [44, 45], Li+Co [45], Li+Cr [26, 45], Li+Mg [17, 44], Co+Gd [22], and Ce+Zn [23] et.al. The functions of $LiMn_2O_4$ could also be enhanced by co-substitution [4, 5, 28,] i.e., by one metal element and one non-metal element, especiallly the F element.

It has been demonstrated by some authors that doping Al element could improve the crystallinity, rate capacity and the coulombic efficiency of $LiMn_2O_4$ very well . Locati et al. have found that doping Mg element could increase crystallinity and decrease charge transfer resistance. Takahashi et al [14] have proved that doping Mg could decresses the oxygen deficiency of $LiMn_2O_4$ and the Li-Mn spinel's performance has been improved at a high temperature. Many years ago, Ito et al [10]. found that doping Zn could improve the cycle performance. Arumugam et al.[25] have verified that Zn doped $LiMn_2O_4$ cathode materials have the excellent capacity retention, high rate capability, high reversible capacity and good reversibility. Therefore in this paper, multiple doping has been made by the combination of Li^+, Mg^{2+}, Zn^{2+} and Al^{3+} to dope into $LiMn_2O_4$. To effectivly check the doping effect, the advanced synthesis method, i.e. the citric acid sol-gel method was used [26]. In this work, a series of cathode materials $Li_{1.03}M_{0.06}Mn_{1.91}O_4$ （ M=$Zn_{0.03}Mg_{0.03}$, $Al_{0.03}Zn_{0.03}$, $Al_{0.03}Mg_{0.03}$, $Al_{0.03}Mg_{0.015}Zn_{0.015}$）have been prepared at a low temperature of 600℃. To our knoweledge, although dual doping and even triple doping researching have been found in in recent years literatures, almost no report has been found on doping more than three metal elements.

Nano-sized materials could show special properties. Nano-sized cathode material has been proved to be able to drain high capacity at high currents, because diffusion path of Li^+ in the solid is significantly smaller than in electrodes of the same kind of materials with higher particle size [45]. Arumugam et al [25] have successfully synthesized nano-scaled Zn doped spinel with high reversible capacity and excellent electrochemical performance. It has been demonstrated by Subramannia et al [32] that nano-scaled $LiMn_2O_4$ may be synthesized at low temperature with enhanced cyclicity. Iqbal and Ahmad [42] considered that nano-sized cathode materials would take an important role in lithium-ion batteries and proved that the sol-gel method is suitable for the synthesis of nanosized $LiMn_2O_4$ spinel and its derivatives. Nanocrystalline $LiMn_2O_4$ spinel was obtained at as low temperature as 200

^{o}C. Nano-crystalline pure $LiMn_2O_4$ powders have been synthesized by Subramania et al [47] as low temperature and the work revealed that smaller nanoparticles better electrochemical performance. Raja et al [48] also gave a work on low-temperature synthesis of nanocrystalline $LiMn_2O_4$ spinel. Phase pure $LiMn_2O_4$ spinel nanoparticles were obtained with rather good capacity and cycle performance,and an especially excellent high rete capability by Jiang et al[49]. One good method for synthesizing smaller nanocrystalline powders at low temperature has been found by Vivekanandhan et al [50].Kamarulzaman et al [51] have presented a good discussion on the structure properties and electrochemical behavior of $LiMn_2O_4$ nano powders.

Based on above information, multiple doping nano-sized $LiMn_2O_4$ spinel has been synthesized by traditional citric acid sol-gel method at low-temperature 600 ^{o}C. This is for one purpose to get excellent $LiMn_2O_4$ spinel cathode materials for lithium-ion batteries.

2. EXPERIMENTAL

2.1 Preparation of materials

The synthesis process is similar to our previous work[26]. The stoichiometrical reagents $LiNO_3$ (A.R grade), $Mn(CH_3COO)_2 \cdot 4H_2O$ (A.R. grade), or/and $Al(NO_3)_3 \cdot 9H_2O$ (A.R. grade) , or/and $Mg(NO_3)_3 \cdot 6H_2O$ (A.R. grade) or/and $Zn(NO_3)_3 \cdot 6H_2O$ (A.R. grade) were dissolved into deionized water. The resulting solution was heated to 80 ^{o}C, then a proper amount of citric acid (A.R grade) was dissolved into it. The pH value of the solution was adjusted to about 7.0 by adding concentrated $NH_3 \cdot H_2O$. After continous stirring for 3–5 h, the sol–gel was formed. Then, the gel was dried in vacuum drying oven for 12 h at 120 ^{o}C. In order to remove the organic contents, the dry gel was heated at 500 ^{o}C for 5 h in air. Then, the resulting precursor was ground to fine powders and calcined at 600 ^{o}C in air for 12 h to obtain the final spinel powders.

2.2 Materials characterization-diffraction methods and Materials morphogical studies

X-ray diffraction (XRD) for the materials were measured by the instrument Bruker D-8 with Cu Kα radiation at 4 °/min in $2\theta = 10 \sim 90°$. The morphology of the as-prepared materials were measured by scanning electron microscope (Hitachi S4800).

2.3 Cell Fabrication and electrochemical characterization

The cathode was prepared as following. The as-synthesized spinel materials were mixed with acetylene black and poly-vinylidene fluoride (PVDF) in the ratio of 80: 12: 8 using 1-methyl-2-pyrrolydon (NMP) as the solvent. The resulting slurry was coated on the Al foil by the Doctor-Blade technique. Then the film was dried in a vacuum oven at 120 ^{o}C for 12h followed by pressing. The working electrode was made by cutting the film into circle of 14 mm diameter. CR2032 coin cells were prepared in one Ar-filled glove box (H_2O < 1 ppm) with the lithium foil as the counter electrode..

The separator is Celgard 2325. The electrolyte is LB-315 (1M $LiPF_6$ in m(DMC) : m(EMC) : m(EC) = 1: 1:1). Constant current charge-discharge was made for the cells at the current density 0.2 $mA \cdot cm^{-2}$ (equal to about C/3) between 3.0~4.5V (versus. Li/Li^+) at room temperature. The measuring instrument is Land battery testing instrument made in China.

3. RESULTS AND DISCUSSION

3.1. X-ray diffraction analys

The X-ray diffraction patterns of undoped and doped Li-Mn oxide samples are presented in Fig. 1. It could be seen that all the materials show single phase diffraction patterns. This could be indexed on the basis of the cubic spinel structure. It was demonstrated that pure cubic spinel phase Li-Mn oxides could be obtained at lower temperature 600 ^oC by traditional citric acid sol-gel method. After doping the structures are still typical of pure spinel phase,which shows that doped metal ions have been occupued the 16 sites for Mn. So the spinel's strcuture has been enhanced.

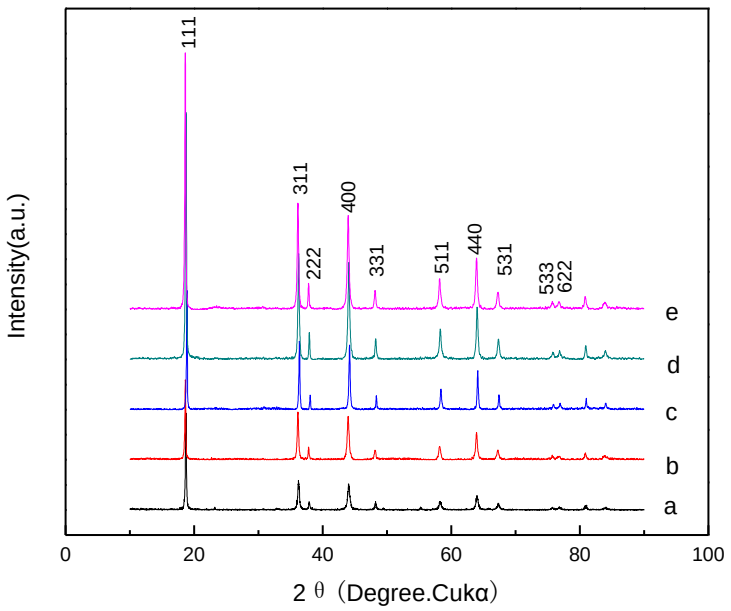


Figure 1. XRD Patterns of the as-prepared samples:(a)pristine $LiMn_2O_4$,(b)$Li_{1.03}$ $Zn_{0.03}Mg_{0.03}Mn_{1.91}O_4$, (c) $Li_{1.03}$ $Al_{0.03}Zn_{0.03}Mn_{1.91}O_4$,(d) $Li_{1.03}$ $Al_{0.03}Mg_{0.03}Mn_{1.91}O_4$,(e) $Li_{1.03}Al_{0.03}Mg_{0.015}Zn_{0.015}Mn_{1.91}O_4$

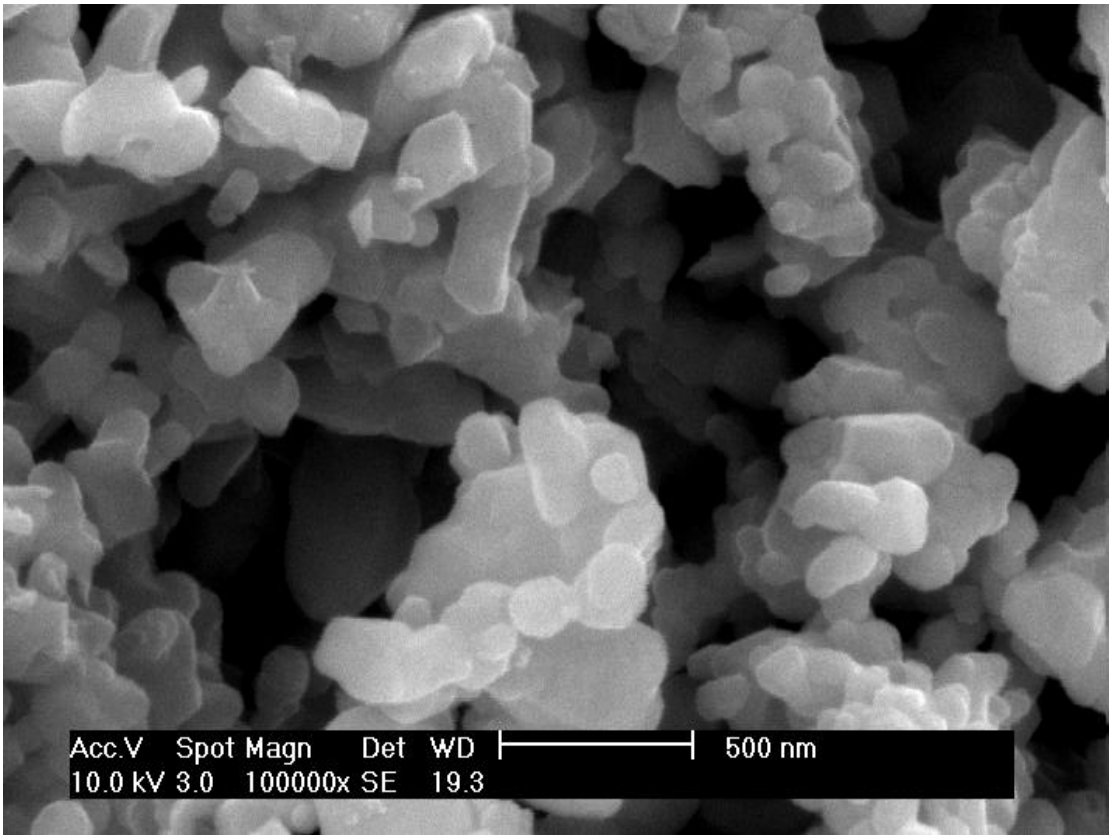
From the X-ray diffraction patterns it could be seen that the main diffraction peaks are not only strong and very sharp, but also very symmtrical, which shows that the synthesized samples have complete crystal structures and the arrangements of of the internal sites are more regular and almost no cation mixing happens. Some crystal structure parameters for the materials are presented in Table 1.

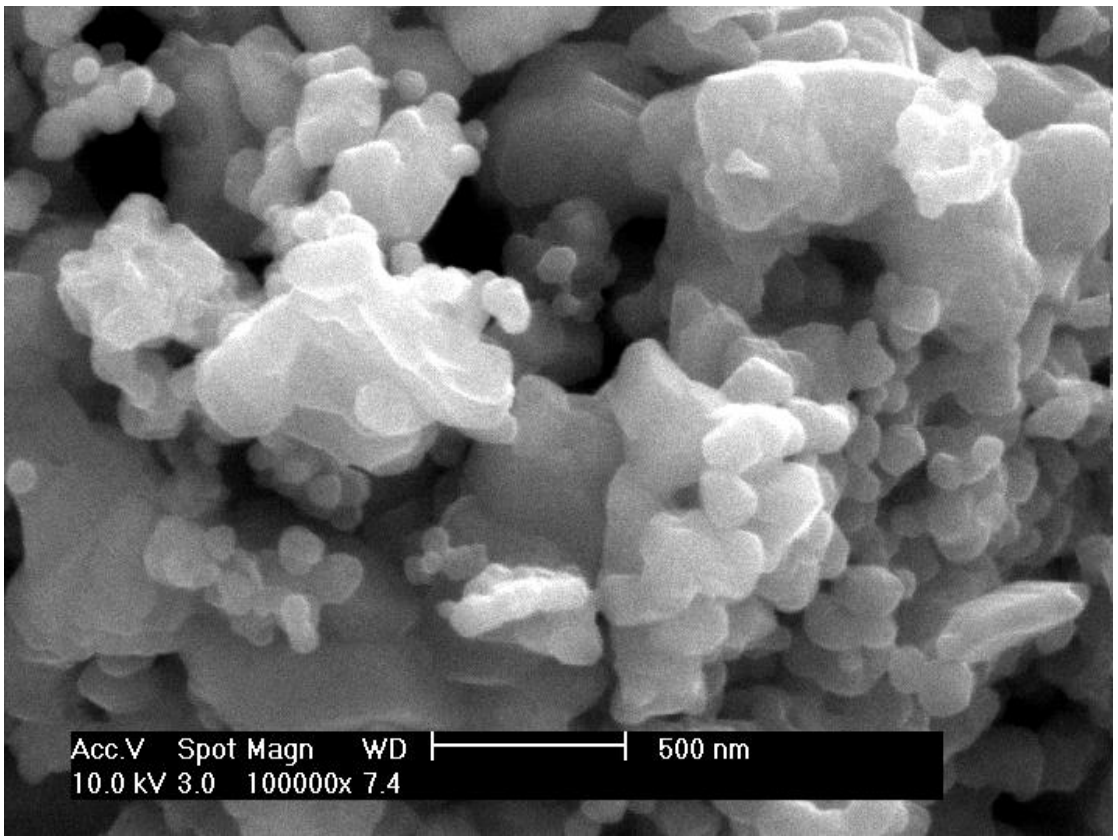
Table 1. Lattice parameters and crystallite sizes of the as-prepared samples

No.	Samples	Lattice parameter(Å)	Cell size(Å^3)	Crystallite size(nm)
A	$LiMn_2O_4$	8.2230	557.3738	89.8
B	$Li_{1.03}\ Zn_{0.03}Mg_{0.03}Mn_{1.91}O_4$	8.2306	557.5636	87.6
C	$Li_{1.03}\ Al_{0.03}Zn_{0.03}Mn_{1.91}O_4$	8.2213	554.5949	62.1
D	$Li_{1.03}\ Al_{0.03}Mg_{0.03}Mn_{1.91}O_4$	8.2199	555.3920	71.9
E	$Li_{1.03}Al_{0.03}Mg_{0.015}Zn_{0.015}Mn_{1.91}O_4$	8.2304	557.5230	93.3

From the data in Table1, it can be proposed that the distances between different facets increase due to the increase of crystal cell parameters for B and E samples compared to the undoped sample and this is favourable for the quick and easy insertation-deinsertation for Li^+ . This is also due to that either the radius of Mg^{2+}(r_{Mg2+}=0.074nm) or the radius of Zn^{2+} (r_{Zn2+}=0.072nm) is larger than that of Mn^{4+}(r_{Mn4+}=0.065nm). For the sample C and D, their structure parameters change a little due to containing Al^{3+} which radius (r_{Al3+} = 0.0535nm) is smaller than that of Mn^{4+}(r_{Mn4+}=0.065nm) apart from containing either larger Mg^{2+} or larger Zn^{2+} [36] .The crystallite sizes have been obtained by Scherrer equation.

3.2. Surface morphology and particle size analysis

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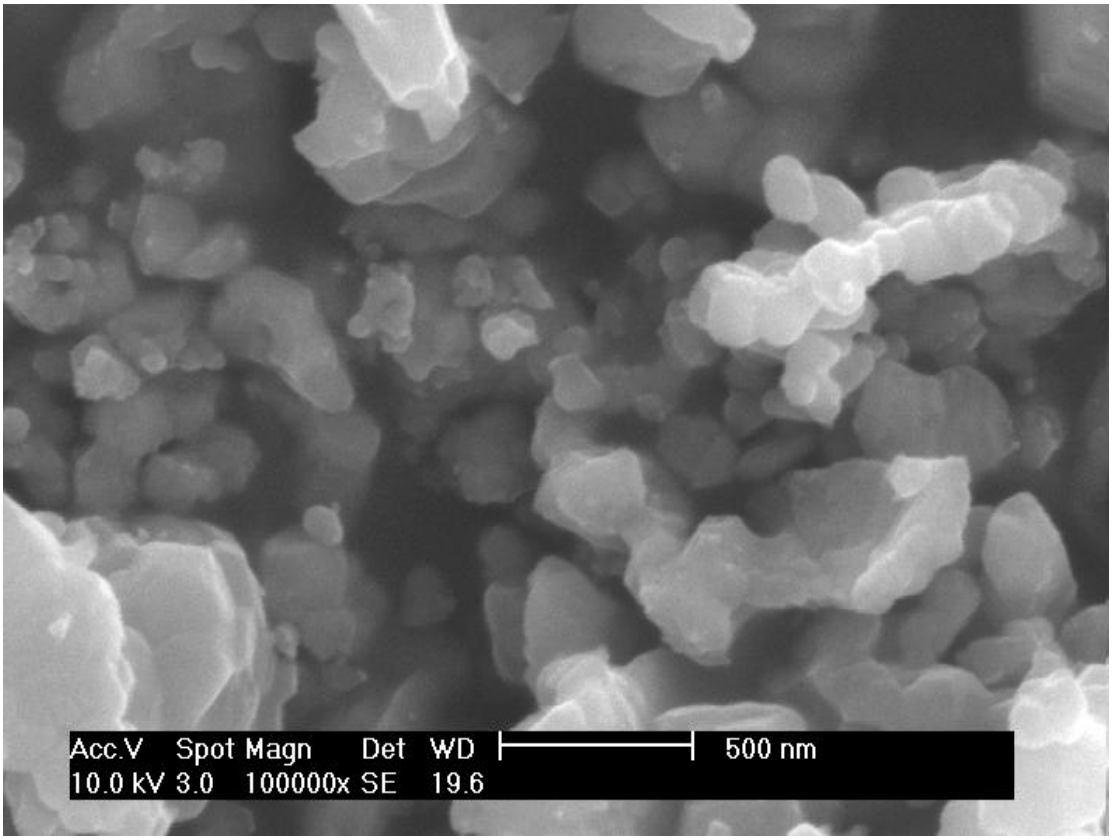
Acc.V Spot Magn Det WD 500 nm
10.0 kV 3.0 100000x SE 19.6

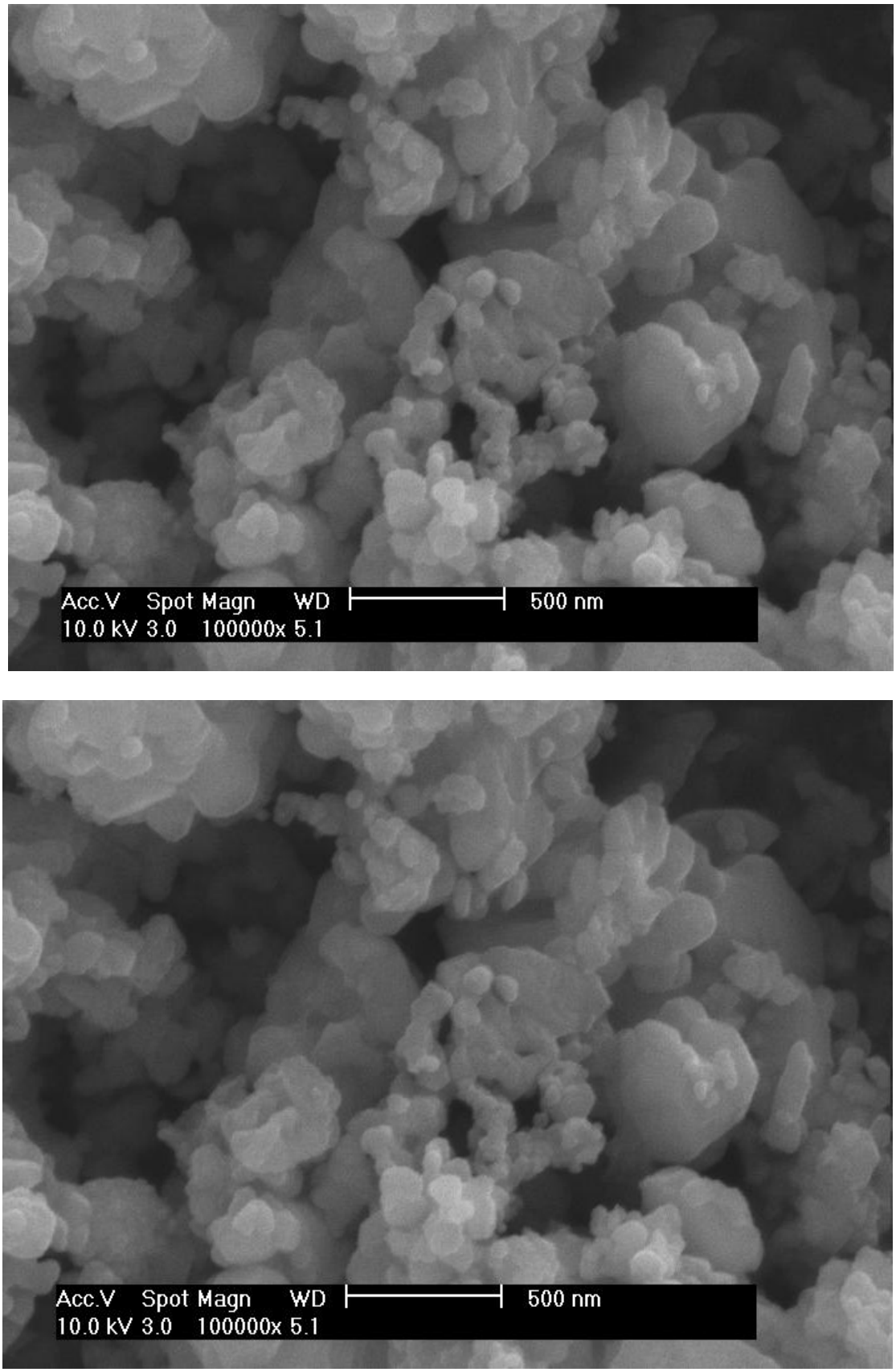

Figure 2. SEM of the as-prepared samples:(a)pristine$LiMn_2O_4$,(b)$Li_{1.03}Zn_{0.03}Mg_{0.03}Mn_{1.91}O_4$, (c)$Li_{1.03}Al_{0.03}Zn_{0.03}Mn_{1.91}O_4$,(d)$Li_{1.03}Al_{0.03}Mg_{0.03}Mn_{1.91}O_4$, (e) $Li_{1.03}Al_{0.03}Mg_{0.015}$ $Zn_{0.015}$ $Mn_{1.91}O_4$

SEM photoes are presented in Figure 2. From the figures, it could be seen that all the samples heve good morphologies, even particle sizes. The average diameter for each sample is smaller 100 nm, which indicats that the materials could be considered to be nano-materials. This can also be verified by the results in Table1 obtained from Scherrer equation. But agglomeration appeares in some samples. Based on the particle size and morphology results, the as-prepared materials should have better electrochemical performances.

3.3 Galvanostatic charge/discharge studies

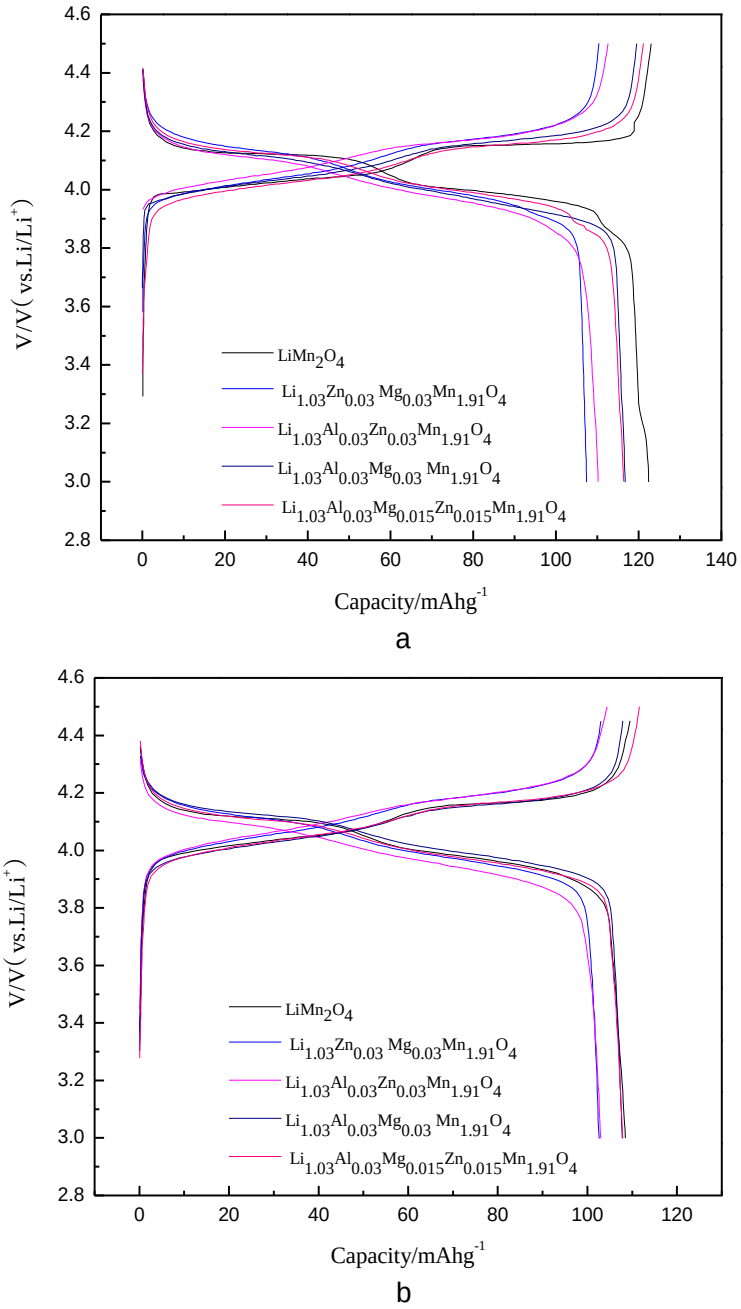

Figure 3. (a)First charge/discharge curves of the samples，(b)the 40th cycle charge/discharge curves of the samples

In Figure 3 the initial charge/discharge curves are for the materials at the current density of 0.2mA/cm^2 in the voltage cut-off 3.0-4.5 V. From (a) It could be found that the curves show two distinct voltage plateaus with the charging voltage plateaus of 4.15V and 4.05V and the discharging plateaus of 4.10V and 3.92 V, which is typical of the plateaus of undoped $LiMn_2O_4$. This indicates that doping does not destroy the spinel strcucture[14,44], which is consistant with the XRD results. In Figure 3 charge/discharge curves for the 40th cycle are also presented. The voltage plateaus are still well, which means that the cycled cells have reached stable states. Also from a and b in Fig.3 it could be found that the couloumic efficencies for the materials are still very high in the 40th cycle. Perhaps the nano-effect could also play an important part in improving the performance.

3.4 Cycling performances

The cycling curves for the synthesized spinel cathode materials are presented in Fig.4. The initial discharge specific capacities and the discharge specific capacities in 10th, 20th,30th and 40th are listed in Table 2. So the capacity retentions can also be presented in Table 4 for detailed comparisons. It could be happily found that the undoped has a relatively very high capacity retention of 92.4% after 40 cycles. By our knowledge this could be the highest capacity retention for undoped $LiMn_2O_4$. In consideration of its high initial discharge specific capacity of 122.5 mAh.g^{-1}, so good undoped $LiMn_2O_4$ spinel could be ascribed to its nano-scale sizes synthesized in lower temperature in a large part. After multiple doping, the capacity retentions for the doped $LiMn_2O_4$ become even larger than the undoped $LiMn_2O_4$. Especially for the material $Li_{1.03}Zn_{0.03}Mg_{0.03}Mn_{1.91}O_4$, it has a very high capacity retention of 97.3% after 40 cycles. It could be demonstrated that multiple doping can improve the electrochemical performance of $LiMn_2O_4$ in a great degree.

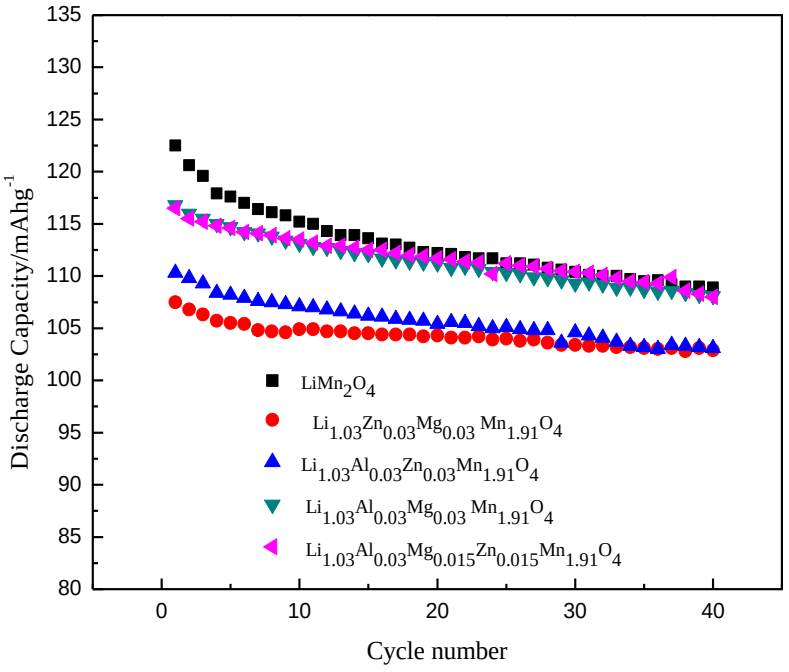

Figure 4. The discharge capacity vs. cycle number of the samples

Table 2. Discharge Capacity and Capacity retention data of $Li_{1.03}M_{0.06}Mn_{1.91}O_4$(M= $Zn_{0.03}Mg_{0.03}$, $Al_{0.03}Zn_{0.03}$,$Al_{0.03}Mg_{0.03}$,$Al_{0.03}Mg_{0.015}Zn_{0.015}$)

	first specific discharge	capacity rentention(%)			
	capacity $mAh.g^{-1}$	after 10 cycles	after 20 cycles	after 30 cycles	after 40 cycles
$LiMn_2O_4$	122.5	97.7	95.2	93.6	92.4
$Li_{1.03}Zn_{0.03}Mg_{0.03}Mn_{1.91}O_4$	107.5	99.2	98.7	97.8	97.4
$Li_{1.03}Al_{0.03}Zn_{0.03}Mn_{1.91}O_4$	110.3	98.8	97.2	96.5	95.1
$Li_{1.03}Al_{0.03}Mg_{0.03}Mn_{1.91}O_4$	116.8	98.3	96.7	95.0	94.0
$Li_{1.03}Al_{0.03}Mg_{0.015}Zn_{0.015}Mn_{1.91}O_4$	116.5	98.9	97.3	96.2	94.1

For the $Li_{1.03}Al_{0.03}Mg_{0.03}$ $Mn_{1.91}O_4$ cathode material, doped Al could promote and stability the crystal structure of spinel. Meanwhile the amount of Mn^{4+} relative to Mn^{3+} is increased and cation disoder around has been reduced [36]. Mg doping can increase the average valence of Mn.

From Table 2 it can also be found that the cycling retentions for the Zn-doped materials are a little larger than those for spinel materials containing no Zn, but the previous capacites are slightly smaller than the later. This is most possibly due to that the radius of Zn^{2+} is larger than that of either Mg^{2+} or Al^{3+} and that there is no Jahn-Teller effect because of its $3d^{10}$ structure.

4. CONCLUSIONS

Nano-size Li-Mn spinel cathode materials have been successfully synthsized by citric acid sol-gel method at a lower temperature 600 ^oC . The undoped $LiMn_2O_4$ spinel has a high initial discharge specific capacity of 122.5 $mAh.g^{-1}$ and a very high capacity retention of 92.4% after 40 cycles at a lower current density. To our knowledge this could be the best pure $LiMn_2O_4$ synthesized by common synthesis methods at lower temperatures. This good result could be ascribed to its nano-scale size synthesized in lower temperature in a large part. By multiple doping, pure phase spinel $Li_{1.03}M_{0.06}Mn_{1.91}O_4$(M= $Zn_{0.03}Mg_{0.03}$,$Al_{0.03}Zn_{0.03}$,$Al_{0.03}Mg_{0.03}$,$Al_{0.03}Mg_{0.015}Zn_{0.015}$) have been obtained by the method mentioned above, All the doped materials are nano-scale. By multlple doping, their electrochemical performances become better. Among the synthesized materials, $Li_{1.03}Zn_{0.03}Mg_{0.03}Mn_{1.91}O_4$ has the highest capacity retention of 97.4% after 40 cycles.

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