Int. J. Electrochem. Sci., 9 **(2014)** 8182 - 8188

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Synthesis and Electrochemical Study of Co-doped $LiMn_2O_4$ at Room Temperature and High Temperature

Zhang Hai-Lang[1,*], *Zhang Lei*[1], *Yang Shi-Wan*[2]

[1]School of Chemical and Material Engineering, Jiangnan University,Wuxi 214122, Jiangsu Province, P. R. China
[2]Xinyang Vacational & Technical College , Xinyang 464000, Henan Province, P. R. China
[*]E-mail: zhl8868@vip.163.com

Received: 10 September 2014 / *Accepted:* 18 October 2014 / *Published:* 28 October 2014

Cathode material Li-Mn spinel materials $LiMn_2O_4$, $LiAl_{0.05}Mn_{1.95}O_{3.95}F_{0.05}$ and $LiCo_{0.01}Al_{0.05}Mn_{1.94}O_{3.95}F_{0.05}$ for Li-ion battrry have been successfully synthsized by a citric acid sol-gel method. The crystalline structures of as-prepared cathode materials were characterized by XRD. The electrochemical performances of the materials were tested by constant-current cyclic testing and cyclic voltammogram. The results showed that the materials possessed pure spinel structure . By multiple co-doping with Al,Co and F elements, $LiCo_{0.01}Al_{0.05}Mn_{1.94}O_{3.95}F_{0.05}$ exhibited very good electrochemical performance. Its initial specific discharge capacities were 122.9 mAh/g and 120.8 mAh/g at the room temperature (25 ^oC) and the high temperature (55 ^oC) , respectively. Its capacity retentions were 96.8% and 92.5% after 40 cycles，respectively. It has been confirmed that multiple doping could improve the stability of spinel structure and cycle performance greatly.

Keywords: Lithium-ion battery, Li-Mn spinel ,synthesis, multiple co-doping, improvement

1. INTRODUCTION

Because Li-Mn spinel $LiMn_2O_4$ has many advantages as one of the most promising cathode materials for Li-ion battery , it has been widely studied as a promising cathode material for lithium-ion batteries [1-12].. Also this kind of material has been systemically investigated in our laboratory over more than 10 years[1-5]. However, its low specific discharge capacity, specially 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 to claim for the capacity fading: (1) manganese dissolution from $LiMn_2O_4$ into electrolyte solution, [6,7]; (2) the decomposition of electrolyte solution in the higher voltage region [8];(3) the Jahn-Teller effect[9,11,12] out of the deep

discharging to distort the crystal lattice by more Mn^{3+}. Especially, the Jahn-Teller effect is the most prominent factor to reduce the electrochemical performance for Li-Mn spinel . Doped by metal element (Li,Mg,Co,Ni,Al,Cr,Fe, and so on) or by anion ions (Cl and F) has been proved to be one very good method to improve the cycling stability of $LiMn_2O_4$ [10,11, 13-32]. Especially ,many experiments have confirmed that Al doping[14-18] or Co doping[13,19-20] could improve the cycling stability of Li-Mn spinel . The F element doping has been proved to be favourable for the cycling stability of Li-Mn spinel[2,23,27,31]. Co-doping $LiMn_2O_4$ by metal element and anion ion would be more effective in improving the stability of $LiMn_2O_4$. Also in consideration of that the element Al is both cheaper and lighter than the Mn element. So in this work, mutiple co-doping Li-Mn spinel materials， $LiMn_2O_4$， $LiAl_{0.05}Mn_{1.95}O_{3.95}F_{0.05}$ and $LiCo_xAl_{0.05}Mn_{1.95-x}O_{3.95}F_{0.05}$ have been synthesized and investigated. All the materials have been synthesized by a citric acid sol-gel method at a lower temperature.

2. EXPERIMENTAL

2.1 Preparation of materials

The stoichiometrical reagents $LiNO_3$ (A.R grade), $Mn(CH_3COO)_2{\cdot}4H_2O$ (A.R. grade), $Co(NO_3)_2{\cdot}6H_2O$ (A.R. grade) , $Al(NO_3)_3{\cdot}9H_2O$ and LiF were dissolved into deion water. The resulting solution was heated to 80 ^oC, 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 3-5 h, the sol-gel was formed. After the sol-gel was dried in a dessicator at 85 ^oC for 8 h , it was heated at 300 ^oC for 6 h and 500 ^oC for 6 h. Then the sample was calcined at 700 ^oC for 12h. Finally, the pure spinel $LiMn_2O_4$ and the doped spinel cathode materials , $LiAl_{0.05}Mn_{1.95}O_{3.95}F_{0.05}$ and $LiCo_{0.01}Al_{0.05}Mn_{1.94}O_{3.95}F_{0.05}$ were obtained. Their compositions were confirmed by AAS and ICP measurements.

2.2. Structure characterization

X-ray diffraction (XRD) for the materials were measured by the instrument Bruker D-8 with Cu Kα radiation at 3 °/min in $2\theta = 10 \sim 90°$ with the step 0.02°.

2.3. Electrochemical measurements

After mixing the active material (80 wt%) with acetyleneblack (12 wt%) and polyvinylidene fluoride (PVDF) binder (8 wt%) in N-methylpyrrolidinone (NMP) solvent, the mixed slurry was obtained. The slurry was coated on an aluminum foil by a Doctor-blade technique, followed by drying in a vacuum oven at 100 ^oC overnight. The cells were assembled in in an Ar-filled glove box. The complete cell comprises a cathode, a Celgard (2325) separator, and a Li-foil anode. The electrolyte used is LB-315 (1M $LiPF_6$ in m(DMC):m(EMC):m(EC)=1:1:1).

Then some CR2032 coin cells were made. Charge-discharge characteristics were tested galvanostatically on a Land CT2001A (Wuhan, China) between 3.0 and 4.5V (versus Li/Li^+) with a current density of 0.2 mA/cm^2 (corresponding C/3) at 25 ^oC and 55 ^oC , respectively. Cyclic voltammetry (CV) measurements of the prepared powders were performed in the voltage range 3.0-4.5V at a scan rate of 0.1mV s^{-1}. The CV measurements were by one ZAHNER-IM6 instrument made in Germany.

3. RESULTS AND DISCUSSION

3.1. X-ray diffraction

Fig.1 presents the XRD patterns of $LiMn_2O_4$, $LiAl_{0.05}Mn_{1.95}O_{3.95}F_{0.05}$ and $LiCo_{0.01}Al_{0.05}Mn_{1.94}O_{3.95}F_{0.05}$. It can be seen that all the XRD patterns of all the materials show typical spinel phase. Their structures still have space Fd3m group. So it could be considered that the doped metal elements occupy some 16d positions of Mn in the crystals. And in the Fd3m group, Li^+ occupys 8a position, O^2 and F^- occupy 32e posions. In the $LiCo_{0.01}Al_{0.05}Mn_{1.94}O_{3.95}F_{0.05}$ sample, the radius of Co^{3+} or Al^{3+} is almost equal to that of Mn^{3+} , so Co^{3+} and Al^{3+} could easily occupy the 16d positions in $LiMn_2O_4$ crystal. Also the Mn-F bonding is stronger than the Mn-O bonding, so the F doping would enhance the crystal stability.

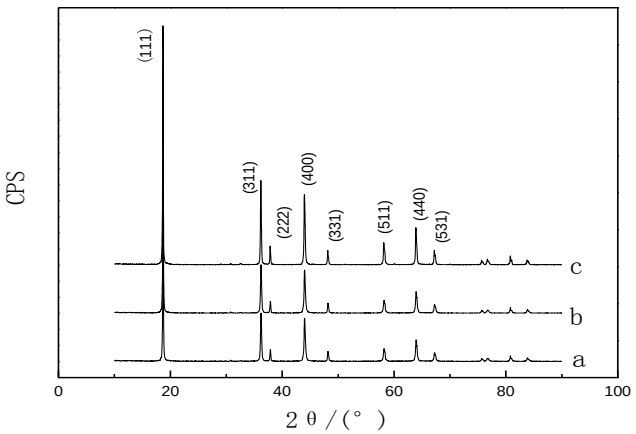

Figure 1. XRD patterns of the as-prepared materials (a) $LiMn_2O_4$; (b)$LiAl_{0.05}Mn_{1.95}O_{3.95}F_{0.05}$; (c)$LiCo_{0.01}Al_{0.05}Mn_{1.94}O_{3.95}F_{0.05}$

3.2. Charge-Discharge Characteristics

Fig.2 shows the initial charge-discharge curves of the prepared samples at room temperature and a constant current density of 0.2mA/cm^2 in the potential range from 3.0 to 4.5V. It can obviously be seen that the charge-discharge curves of all the samples have two distinctive voltage plateaus, characteristic of the well-defined spinel $LiMn_2O_4$ cathode, which implies that there are two steps for

lithium intercalating and deintercalating into the material. The charging voltage plateau appears in 4.0V~4.2V and discharging voltage plateau appears in 4.12V~3.98V.

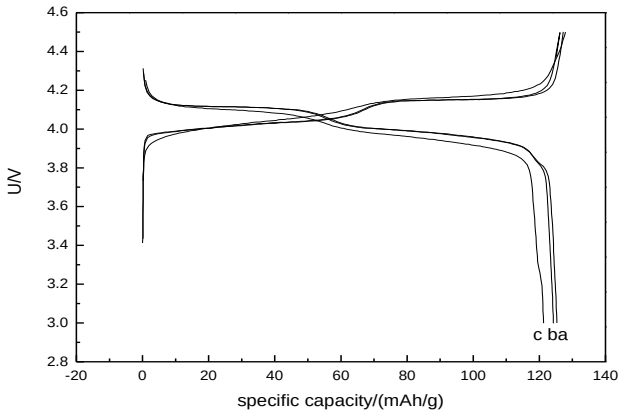

Figure 2. Initial charge /discharge curves of the as-prepared materials, (a): $LiMn_2O_4$; (b)$LiAl_{0.05}Mn_{1.95}O_{3.95}F_{0.05}$; (c)$LiCo_{0.01}Al_{0.05}Mn_{1.94}O_{3.95}F_{0.05}$

3.3 Cycling Performance at Differen Temperatures

Fig.3 shows the cycling performance of the three materials at C/3 rate in voltage range of 3.0-4.5V at 25 ^oC.

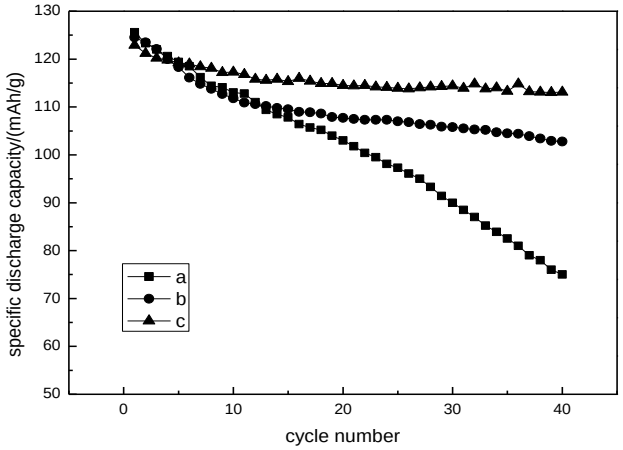

Figure 3. Cycle performance of the as-prepared materials, (a)$LiMn_2O_4$; (b) $LiAl_{0.05}Mn_{1.95}O_{3.95}F_{0.05}$; (c) $LiCo_{0.01}Al_{0.05}Mn_{1.94}O_{3.95}F_{0.05}$; at 25 ^oC

Fig.4 shows the cycling performance of the three materials at C/3 rate in voltage range of 3.0-4.5V at 55 ^oC. From Fig.3 and Fig.4 ,it could be found that co-doping may increase the cycling stabllity at both room temperature and high temperature with a great deal. Among the three materials,

$LiCo_{0.01}Al_{0.05}Mn_{1.94}O_{3.95}F_{0.05}$ has the best cycling stabllity. The doping by Co^{3+} and Al^{3+} could increase the average valence of Mn so as to reduce the unfavourable Jahn-Teller effect. The stronger Co-O or Al-O bonding also enhance the spinel crystal stability. Further co-doping by F could increase the ability of spinel material against HF attack in electrolyte solution[14] . So it is not surprising that $LiCo_{0.01}Al_{0.05}Mn_{1.94}O_{3.95}F_{0.05}$ has displayed the best cycling stability not only at room temperature , but also at high temperature.

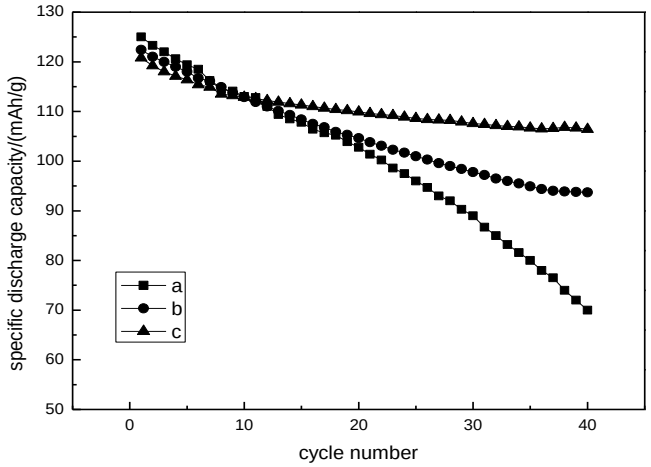

Figure 4. Cycle performance of the as-prepared materials, (a)$LiMn_2O_4$; (b) $LiAl_{0.05}Mn_{1.95}O_{3.95}F_{0.05}$; (c) $LiCo_{0.01}Al_{0.05}Mn_{1.94}O_{3.95}F_{0.05}$; at 55 ^oC

3.4. Cyclic Voltammetry

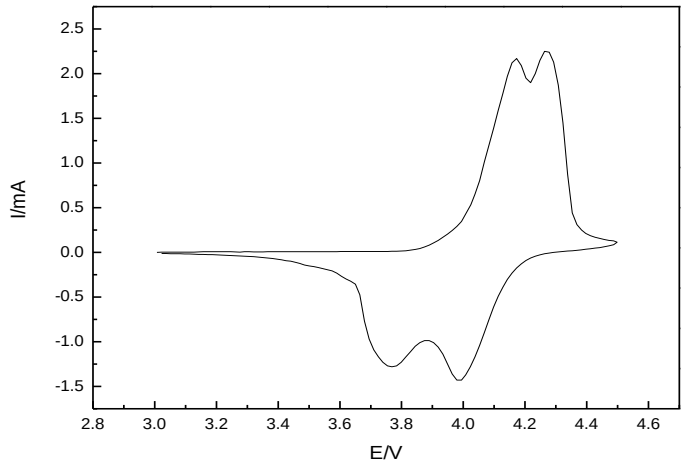

Figure 5. Cyclic voltammetric curve of the $LiCo_{0.01}Al_{0.05}Mn_{1.94}O_{3.95}F_{0.05}$ sample

The cycle voltammogram properties of the best sample $LiCo_{0.01}Al_{0.05}Mn_{1.94}O_{3.95}F_{0.05}$ was tested. Cyclic voltammogram (sweep rate: 0.1mV s^{-1}) in the potential region of 3.0-4.5 V is presented

in Fig. 5. For the cyclic voltagram curve, there are two pairs of reversible peaks, oxidation and reduction peaks corresponding to Li^+ extraction and insertion, which reflect the typical Mn^{3+}/Mn^{4+} redox process of the spinel structure in the 4V domain. That all the peaks are sharp shows that this spinel material has excellent lattice structur [33,34].

4. CONCLUSIONS

The Al^{3+}, Co^{3+}, and F^- co-doped Li-Mn spinel cathode materials $LiMn_2O_4$, $LiAl_{0.05}Mn_{1.95}O_{3.95}F_{0.05}$ and $LiCo_{0.01}Al_{0.05}Mn_{1.94}O_{3.95}F_{0.05}$ have been successfully synthesized by a sol-gel method calcined at 700 ^oC. The co-doping materials present very good cycling stability. Among all the materials synthesized in this work, $LiCo_{0.01}Al_{0.05}Mn_{1.94}O_{3.95}F_{0.05}$ shows the best electrochemical performance. At room temperature, it has a very high initial discharge capacity of 122.9 $mAh \cdot g^{-1}$ and a high capacity retention of 96.8% after 40 cycles . At high temperature 55 ^oC , it still has a very high initial discharge capacity of 120.8 $mAh \cdot g^{-1}$ and a high capacity retention of 92.5% after 40 cycles . It could be concluded that co-doping is a good way to improve the stability of Li-Mn spinel $LiMn_2O_4$. The spinel $LiCo_{0.01}Al_{0.05}Mn_{1.94}O_{3.95}F_{0.05}$ is one promising cathode material for Li-ion battery.

References

1. J. F. Wang, H. L. Zhang，Funct. *Mater. Letters*, 3(2010)65
2. H. L. Zhang, N. Ch. Xiang, *Adv.in Mater. Sci. and Eng*., V2013(2013), ID137032,1
3. J. K. Tian, F. Ch. Wan, Vincent. S. Battaglia,, H. L. Zhang, *Int. J. Electrochem. Sci*., 9(2014)931
4. F. Ch. Wan, J. K. Tian, H. L. Zhang, *Int. J. Electrochem. Sci*., 9(2014)4627
5. H. L. Zhang, L. Zhang, L. Ye, *Int. J. Electrochem. Sci*., 9(2014)4635
6. S.-W. Lee, K-S. Kim, H.- S. Moon, J.-P. Lee, H.-J. Kim, B.-W. Cho, W.-I. Cho, J.-W. Park, *J Power Sources*, , 130(2004) 227
7. D. Shu, G. Kumar, K.B. Kim , K.S. Ryu, and S.H. Chang, Solid State Ionics, 160(2003) 227
8. G. G. Amatucci, C. N. Schmutz, and A. Blyr, C.Sigla,A.S.Gozdz, D.Larcher,and J.M. Tarascon, *J Power Sources*, 69(1997) 11
9. X. Li, Y. Xua, and C. Wang, *J. Alloys Compd*. 479 (2009) 310
10. H. J. Choi, K. M. Lee, and J. G. Lee, *J Power Sources*, 103(2001) 154
11. A. B. Yuan , L. Tian , and W. M. Xu , *J. Power Sources*, 195(2010)5032
12. C.Y. Ouyanga, S.Q. Shi, M.S Lei, *J. Alloys and Comp*., 474(2009)370
13. B. Banov, Y.Todorov , A. Trifonnova , A.Momchilov and V. Manev, *J.Power Sources*, 68 (1997) 578
14. G. G. Amatucc, N. Pereira, T. Zheng and J. M .Taraseon, *J. Electrochem. Soc.*, 148 (2001) A171
15. Y.-J. Kang, J.-H. Kim and Y.-K. Sun, *J Power Sources*, 146 (2005) 237
16. Sh.-J. Bao, Y.-Y. Liang, W.-J. Zhou, B-L.He and H.-L. Li, *J Colloid Interface Science*, 291 (2005) 433
17. W.-J. Zhou, Sh.-J. Bao, B.-L. He, Y.-Y. Li,H.-L. Li, *Electrochim. Acta*, 51 (2006) 4701
18. T. Kakuda, K. Uematsu, K. Toda and M. Sato, *J. Power Sources*, 167 (2007) 4 99
19. A. Subramania, N. Angayarkanni and T. Vasudevan, *Ionics*, 13 (2007) 61
20. M. J. Iqbal, Z. S. Zahoor, *J. Power Sources*, 165 (2007) 393
21. W. Lu, I. Belharouak, and S. H. Park, and K. Amine, *Electrochim. Acta*, 52(2007) 5837

22. K. Suryakala, G. P. Kalaignan, and T. Vasudevan, *Mater. Chem. and Phys*., 104(2007) 479
23. J. T. Son, H. G. Kim. *J Power Sources,* 147(2005) 220
24. T. F. George, C. Z. Lu, and T. P. Kumar, *J Power Sources,* 115(2003) 332
25. K. S. Lee, H. J. Bang, S. T. Myung, J. Prakash,K. Amine,and Y.-K. Sun, *J Power Sources,* 174(2007) 726
26. D. Arumugam , G. Paruthimal Kalaignana , K. Vediappanm , and C. W. Lee, *Electrochim. Acta* , 55(2010) 8439
27. J. T. Son , H. G. Kim, *J. Power Sources*, 147(2005)220
28. X. Q. Wang , O. Tanaike , M. Kodama, and H. Hatori, *J. Power Sources* , 168(2007) 282.
29. Ch. B. Wu , Y. Bai , F. Wu , *J. Power Sources*, 189(200)89
30. Y.-S. Lee ,N. Kumada ,M. Yoshio , *J. Power Sources* , 96(2001) 376
31. B. L. He , Sh. J. Bao , and Y. Y. Liang , W. J. Zhou, H. Li, and H. L. Li, J. Solid State Chem., 178(2005)897
32. J. M. Amarilla , K. Petrov ,F. Picó , G. Avdeev, J. M. Rojo, and R. M. Rojas, *J. Power Sources*, 191(2009)591
33. S. J. Bao, Y. Yu. Liang, W. J. Zhou, B. L. He, and H. L. Li, *J Power Sources,* 154(2006) 239
34. R. Thirunakaran, K.T. Kimb, Y. M. Kang, C.-Y. Seo, and. J. Y. Lee, *J Power Sources,* 137(2004) 100