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Synthesis and Characterization of $0.5Li_2MnO_3$-$0.5LiNi_{1/4}Mn_{1/4}Co_{1/2}O_2$/C Composite with Improved Performance for Lithium Ion Battery

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$0.5Li_2MnO_3$-$0.5LiNi_{1/4}Mn_{1/4}Co_{1/2}O_2$/C composite is prepared by coprecipitation method followed by sintering with sucrose in the air. The $0.5Li_2MnO_3$-$0.5LiNi_{1/4}Mn_{1/4}Co_{1/2}O_2$/C composite is characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electroscopy (TEM) and electrochemical tests. The effects of carbon coating on the morphology, structure and electrochemical properties of the lithium and manganese-rich materials are investigated. Based on the morphological results, a thin layer of residual carbon is observed on the surface of the $0.5Li_2MnO_3$-$0.5LiNi_{1/4}Mn_{1/4}Co_{1/2}O_2$ particle. Electrochemical and structural results demonstrate that the carbon coating greatly improves the electrochemical property and rate capability of $0.5Li_2MnO_3$-$0.5LiNi_{1/4}Mn_{1/4}Co_{1/2}O_2$ without destroying its crystal structure. The improvements of the carbon coated material can be attributed to its enhanced conductivity and electrochemical kinetic.

Keywords: lithium-rich oxide; carbon coating; electrochemical property; lithium ion battery

1. INTRODUCTION

The expanding demand for high-power and high-energy batteries has motivated the continuous research on large-scale lithium-ion batteries with high energy density. Recently, one novel lithium and manganese-rich layered cathode material, i.e. yLi_2MnO_3-$(1-y)LiNi_{0.5-x}Mn_{0.5-x}Co_{2x}O_2$ has draw much attention for large scale batteries [1-3]. This material can be considered as solid solutions between Li_2MnO_3 and $LiNi_{0.5-x}Mn_{0.5-x}Co_{2x}O_2$, and it exhibits many advantages such as high capacity, good cycling performance, low cost and high safety [4-7]. Therefore, it has been considered as the most promising cathode materials for next-generation lithium ion batteries.

Many techniques including optimization synthetic method [8], surface modification [9-11] and ion doping [12] have been employed to improve the electrochemical performance of lithium and manganese rich materials. S. H. Kang et al prepared the lithium manganese oxide by a sol-gel method using glycolic acid and tartaric acid as chelating agent, and they demonstrate the participation of the manganese ions in the electrochemical reaction [8]. C. S. Johnson et al treated the surface of $0.3Li_2MnO_3$-$0.7LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ with 0.1 M HNO_3, and the first cycle capacity loss was eliminated [9]. L. Y. Yu et al synthesized $0.65Li_2MnO_3$-$0.35LiMO_2$ (M=Co, $Ni_{1/2}Mn_{1/2}$, $Mn_{1/3}Ni_{1/3}Co_{1/3}$) by a low-heating solid state reaction, and good cycle performance were obtained [12].

Carbon coating is an effective surface modification method that is widely used to enhance the electrochemical performance of electrode materials in lithium ion batteries [13-16]. In this study, we employed the carbon coating on the lithium and manganese-rich material and synthesized $0.5Li_2MnO_3$-$0.5LiNi_{1/4}Mn_{1/4}Co_{1/2}O_2$/C composite. The impacts of carbon coating on the physical and electrochemical characteristics of $0.5Li_2MnO_3$-$0.5LiNi_{1/4}Mn_{1/4}Co_{1/2}O_2$ were investigated. The possible mechanism of the improvements was discussed.

2. EXPERIMENTAL

2.1 Sample synthesis

The pristine $0.5Li_2MnO_3$-$0.5LiNi_{1/4}Mn_{1/4}Co_{1/2}O_2$ was synthesized by a co-precipitation method. Stoichiometric solutions of $NiSO_4$, $MnSO_4$ and $CoSO_4$ were mixed with the solution of Na_2CO_3 under magnetic stirring at 40 ^{o}C. The precipitated powders were carefully filtered and washed, and then they were dried in a vacuum oven at 100 ^{o}C overnight. The obtained precursors were pressed into pellets. The pellets were sintered at 500 ^{o}C for 5 h and were subsequently ground. The obtained material was then mixed with stoichiometric amount of $LiOH \cdot H_2O$. After careful grinding, the mixture was calcined at 850 ^{o}C for 12 h.

The carbon coated sample was prepared by mixing the pristine $0.5Li_2MnO_3$-$0.5LiNi_{1/4}Mn_{1/4}Co_{1/2}O_2$ with desired amount of sucrose, and then the mixture was calcinated at 500 °C for 30 min in the air to synthesize the composite.

2.2 Characterization

Powder X-ray diffraction (XRD, Rigaku D/max-IIB) employing Cu Kα radiation was used to identify the crystalline phase of the prepared powders in the 2θ range of 10°~80°. The morphological features of the powders were observed with a scanning electron microscope (SEM, HITACHI S-4700). The surface layer was observed with a transmission electron microscope (TEM, JEOS-2010). The electrochemical measurements of all the cathode materials were carried out in CR2032 coin-type half-cells. The cells were composed of a solid solution cathode and a lithium metal anode separated by a

Celgard 2400 polypropylene film. The cathode contains a mixture of the cathode material, polyvinylidene fluoride and conductive carbon black in a weight ratio of 80:10:10. N-Methyl pyrrolidone was used to make the slurry of the mixture. The mixture was cast onto an aluminum foil and dried in vacuum at 100 ℃ for 5 h. Disks were punched out of the foil. The coin cell was assembled in an argon filled glove box. The electrolyte was 1M $LiPF_6$ in ethylene carbonate/dimethyl carbonate (EC/DMC, 1:2 by volume). The electrochemical properties were measured with a BTS-2000 Neware Battery Testing System.

3. RESULTS AND DISCUSSION

The XRD patterns of both the pristine and the carbon coated materials are shown in Figure 1. Both samples have a layered α-$NaFeO_2$ structure in space group $R\bar{3}m$. Weak superstructure reflections around 20-25° are observed for both samples, which is associated with the ordering of the Li^+/M ($M=Ni^{2+}$, Mn^{4+}) in the transition metal layer [17]. There is no peaks indexed to carbon was observed for $Li_3V_2(PO_4)_3/C$, which may be attributed to the amorphous state of carbon coating. All these results indicate that the structure of $0.5Li_2MnO_3$-$0.5LiNi_{1/4}Mn_{1/4}Co_{1/2}O_2$ was not destroyed by carbon coating.

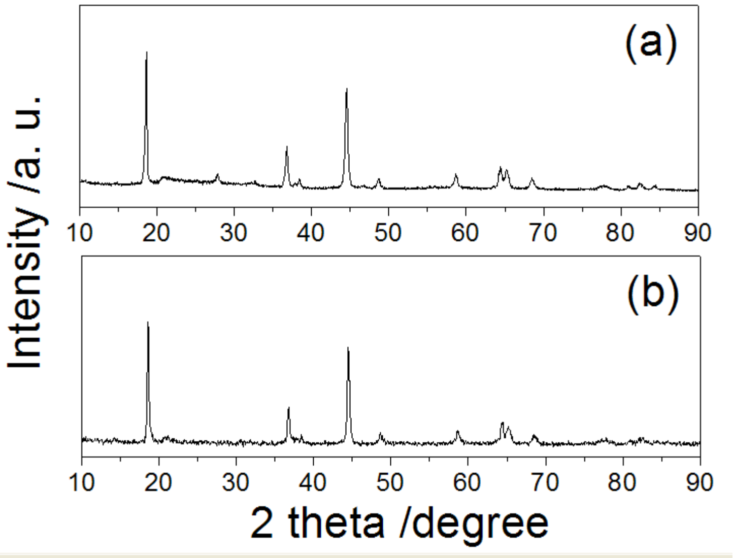

Figure 1. XRD patterns of the (a) pristine and (b) carbon coated sample

The SEM images of both the pristine and carbon coated samples were shown in Figure 2. Large aggregates of about 5~10 μm are observed for both the materials, and they are composed of small primary particles with the size of 100~200 nm. Compared with the pristine sample, the carbon coated sample exhibits more coarse surface and seriously agglomeration. The TEM observation was carried out on the carbon coated sample to clarify its surface state. As shown in Figure 3, a surface layer is observed, which confirms the presence of carbon layer on the surface of particles for the $0.5Li_2MnO_3$-$0.5LiNi_{1/4}Mn_{1/4}Co_{1/2}O_2$/C composite.

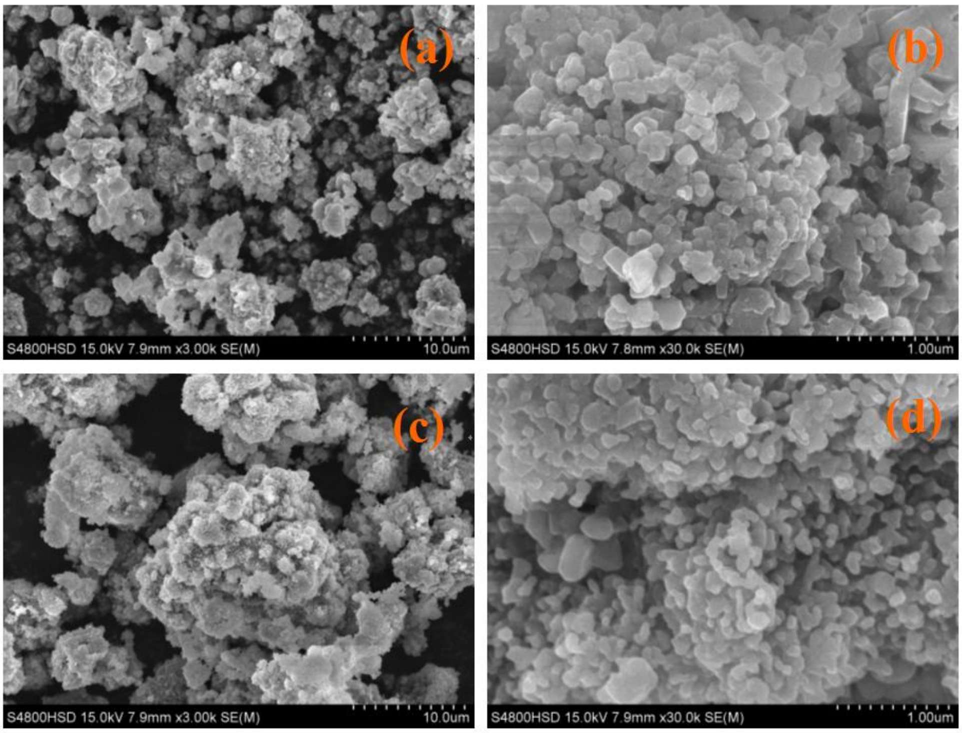

Figure 2. SEM images of the pristine (a,b) and carbon coated (c,d) sample

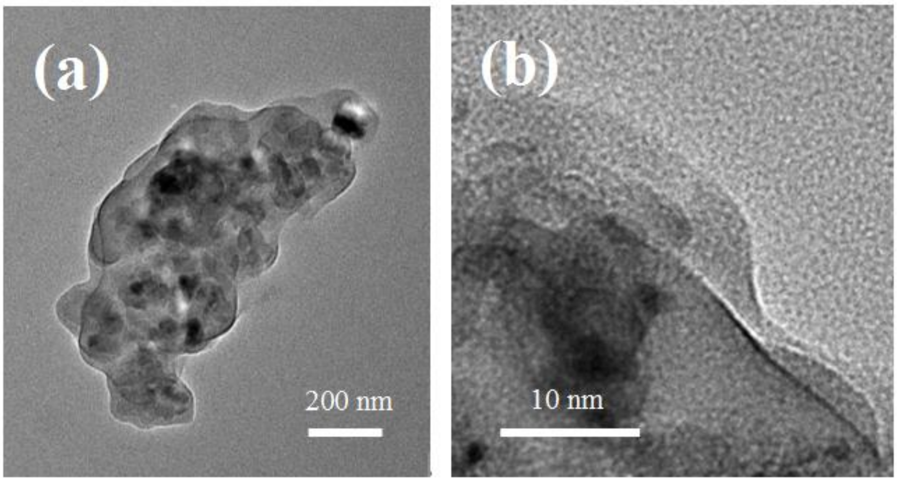

Figure 3. TEM images of the carbon coated $0.5Li_2MnO_3$-$0.5LiNi_{1/4}Mn_{1/4}Co_{1/2}O_2$

The first charge/discharge curves of the pristine and carbon coated $0.5Li_2MnO_3$-$0.5LiNi_{1/4}Mn_{1/4}Co_{1/2}O_2$ materials compared in Figure 4. The charge/discharge measurements were carried out at the current density of 20 mA g^{-1} in the voltage range of 2.0-4.8 V. All the samples show two different regions in the first charge curve. The initial sloping region A below 4.5 V corresponds to the oxidation of the transition metal ions, which is similar to that in $LiMO_2$ (M=Co, Ni). The following plateau region B around 4.5 V corresponds to an oxidation of O^{2-} ions and loss of oxygen from the lattice, which is similar to that in Li_2MnO_3 [18]. Compared with the pristine sample, the carbon coated sample exhibited large discharge capacity and less irreversible capacity in the initial cycle. The result indicates that carbon coating effectively improved the electrochemical performance of $0.5Li_2MnO_3$-$0.5LiNi_{1/4}Mn_{1/4}Co_{1/2}O_2$ in the initial cycle.

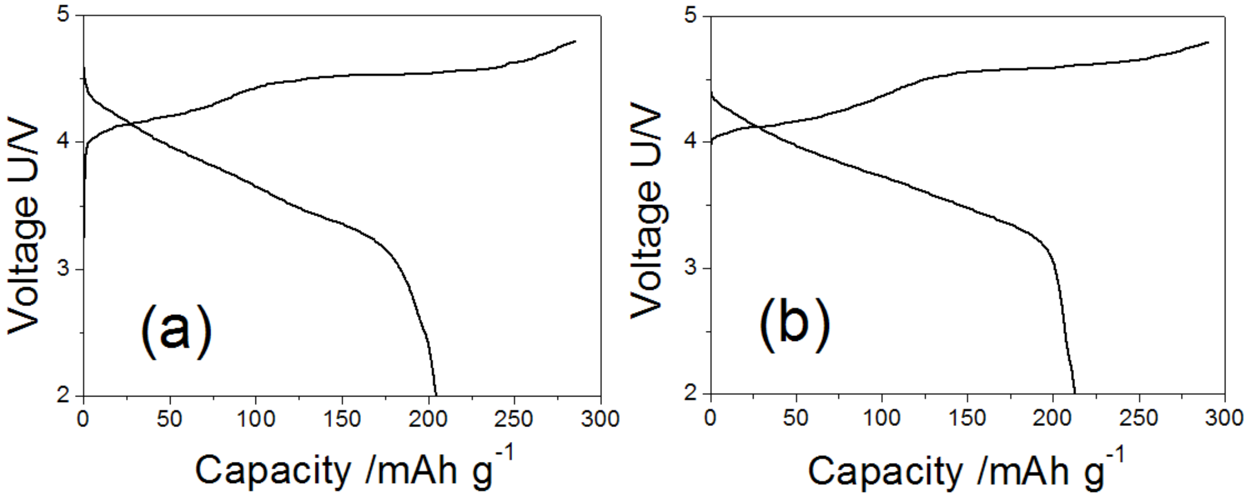

Figure 4. Initial charge/discharge curves of the pristine (a) and carbon coated (b) $0.5Li_2MnO_3$-$0.5LiNi_{1/4}Mn_{1/4}Co_{1/2}O_2$

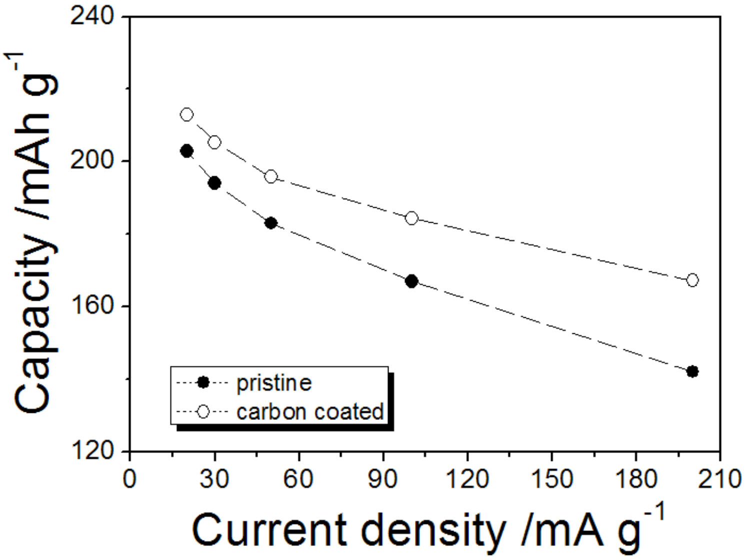

Figure 5. Rate capability of the pristine and carbon coated $0.5Li_2MnO_3$-$0.5LiNi_{1/4}Mn_{1/4}Co_{1/2}O_2$

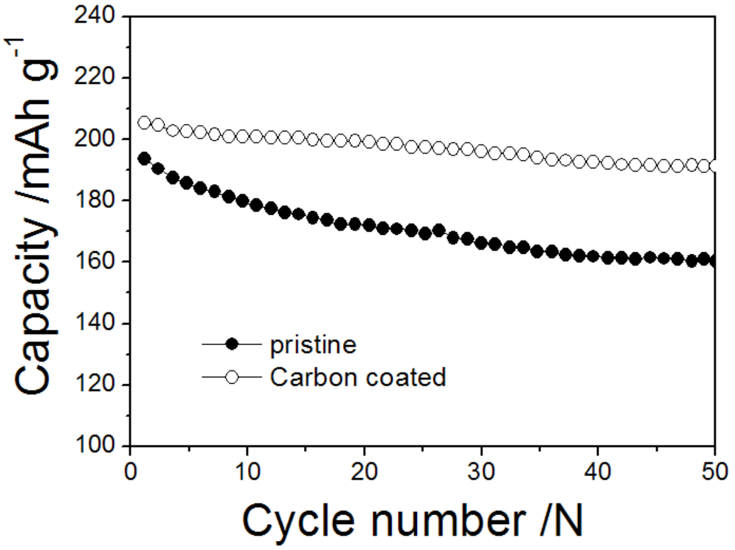

Figure 6. Cycling performance of the pristine and carbon coated $0.5Li_2MnO_3$-$0.5LiNi_{1/4}Mn_{1/4}Co_{1/2}O_2$

Figure 5 compares the rate capability of both the pristine and carbon-coated $0.5Li_2MnO_3$-$0.5LiNi_{1/4}Mn_{1/4}Co_{1/2}O_2$ samples. Both cells were charge/discharged at different current densities in the voltage range of 2.0 and 4.8 V. The discharge capacity of each sample declines with an increase in current density. When the same current density is applied, the carbon coated sample exhibits higher capacities than the pristine one. The result indicated that the carbon coating enhanced the rate capability of the $0.5Li_2MnO_3$-$0.5LiNi_{1/4}Mn_{1/4}Co_{1/2}O_2$ material.

The cycling performance of both the pristine and the carbon coated $0.5Li_2MnO_3$-$0.5LiNi_{1/4}Mn_{1/4}Co_{1/2}O_2$ were compared in Figure 7. Both cells were cycled at the current density of 30 $mA\cdot g^{-1}$ in the voltage range of 2.0 and 4.8 V. The carbon coated sample exhibits less capacity lose during cycles than the pristine one, which indicates its better cycling stability. Based on above results, the carbon coated sample exhibits better electrochemical properties such as less irreversible capacity, higher rate capability and better cycle property than the pristine one. The improvement can be attributed to the increased electrochemical kinetic and enhanced conductivity induced by conductive surface layer of residual carbon.

4. CONCLUSIONS

Carbon coated $0.5Li_2MnO_3$-$0.5LiNi_{1/4}Mn_{1/4}Co_{1/2}O_2$ was prepared by coprecipitation method and its physicochemical characteristics were compared with the pristine one in detail. No impurities were observed in the XRD patterns of carbon coated composite, which indicated that the residual carbon didn't affect the structure of $0.5Li_2MnO_3$-$0.5LiNi_{1/4}Mn_{1/4}Co_{1/2}O_2$. From the SEM observation, the particles of the carbon coated material were more aggregated and coarse than the pristine one. TEM images further confirmed that a thin layer existed on the surface of the $0.5Li_2MnO_3$-$0.5LiNi_{1/4}Mn_{1/4}Co_{1/2}O_2$/C composite. Electrochemical testing results reveal that the carbon coated material obtained improved charge/discharge capacities, high rate capability and cycle stability than the pristine one, which can be attributed to the increased electrochemical kinetic and enhanced conductivity induced by carbon coating.

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References

1. S. Sivaprakash, S. B. Majumder, *J. Electrochem. Soc.*, 157 (2007) A418.
2. T. A. Arumkumar, Y. Wu, A. Manthiram, *Chem. Mater.*, 19 (2007) 3067.
3. Z. Li, F. Du, X. Bie, D. Zhang, Y. Cai, X. Cui, C. Wang, G. Chen, Y. Wei, *J. Phys. Chem. C*, 114 (2010) 22751.
4. D. Shin, C. Wolverton, J. R. Croy, M. Balasubramanian, S. H. Kang, C. M. Lopez Rivera, M. M. Thackeray, *J. Electrochem. Soc.*, 159 (2012) A121.
5. J. Jiang, K. W. Eberman, L. J. Krause, J. R. Dahn, *J. Electrochem. Soc.*, 152 (2005) A1879.
6. N. Yabuuchi, K. Yoshii, S. T. Myung, I. Nakai, S. Komaba, *J. Am. Chem. Soc.*, 133 (2011) 4404.
7. E. S. Lee, A. Huq, H. Y. Chang, A. Manthiram, *Chem. Mater.*, 24 (2012) 600.
8. S. H. Kang, P. Kempgens, S. Greenbaum, A. J. Kropf, K. Amine, M. M. Thackeray, *J. Mater. Chem.*, 17 (2007) 2069.
9. C. S. Johnson, N. C. Li, C. L. J. T. Vaughey, M. M. Thackeray, *Chem. Mater.* 20(2008) 6095.
10. D. Y. W. Yu, K. Yanagida, H. Nakamura, *J. Electrochem. Soc.*, 157 (2010) A1177.
11. J. Liu, B. R. Jayan, A. Manthiram, *J. Phys. Chem. C*, 114 (2010) 9528.
12. L. Y. Yu, W. H. Qiu, F. Lian, W. Liu, X. L. Kang, J. Y. Huang, *Mater. Lett.*, 62 (2008) 3010.
13. G. N. Zhu, C. X. Wang, Y. Y. Xia, *J. Electrochem. Soc.*, 158 (2011) A102.
14. C. Deng, S. Zhang, Z. Dong, Y. Gao, Y. Shang, Y. H. Sun, *Int. J. Electrochem. Sci.,* 7 (2012) 6951.
15. C. Deng, Y. H. Sun, S. Zhang, H. M. Lin, Y. Gao, B. Wu, L. Ma, Y. Shang, G. Dong, *Int. J. Electrochem. Sci.,* 7 (2012) 4559.
16. J. Gao, J. J. Li, X. M. He, C. Y. Jiang, C. R. Wen, *Int. J. Electrochem. Sci.,* 6 (2012) 2818.
17. J. H. Kim, C. W. Park, Y. K. Sun, *Solid State Ion.*, 164 (2003) 43.
18. A. R. Armstrong, M. Holzapfel, P. Novak, C. S. Johnson, S. H. Kang, M. M. Thackeray, P. G. Bruce, *J. Am. Chem. Soc.*, 128 (2006) 8694.