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Continuous solid solutions $LiFe_{1-x}Co_xPO_4$ and its electrochemical performance

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Abstract

$LiFe_{1-x}Co_xPO_4$ ($0 \leq x \leq 1.0$) solid solutions were prepared by solid-state reactions. X-ray diffraction and X-ray photoelectron spectroscopy were employed to analyze the variation of their structures and the chemical environments around the P and O atoms of the solid solution with various Co contents. The electrochemical performance of $LiFe_{1-x}Co_xPO_4$ was also comparatively studied with cyclic voltammetry, and galvanostatic charge–discharge.

Keywords: Solid solution; $LiFe_{1-x}Co_xPO_4$

1. Introduction

In recent years, considerable attention has been paid to develop cathode materials for lithium ion batteries with high capacity, safety, and reliability. Since the pioneering work of Goodenough and coworkers [1] on $LiFePO_4$, much effort has been made to improve the performance of this material [2–12]. Other $LiMPO_4$ (M = Co, Mn, and Ni) olivine-structured materials have also been investigated as attractive cathode candidates due to their higher theoretical capacity and/or energy density than that of $LiFePO_4$ [13–16]. Among these materials, $LiCoPO_4$ is expected to have a high energy density due to its 4.8 V discharge plateau.

In addition to the olivines with single transition metal atoms, olivine solid solutions are become attractive recently. For example, the charge–discharge profiles of $LiFe_{1-x}Mn_xPO_4$ [17–21] show two pairs of voltage plateaus, one at 4.1 V and the other at 3.5 V, corresponding to the conversions of $Mn^{2+} \leftrightarrow Mn^{3+}$ and $Fe^{2+} \leftrightarrow Fe^{3+}$, respectively. However, some of these solid solutions have obvious amount of Li_3PO_4 impurity [22].

In this paper, we will report the preparation of a series of pure $LiFe_{1-x}Co_xPO_4$ solid solutions and evaluate their electrochemical performances as cathode materials for lithium ion batteries.

2. Experimental

$LiFe_{1-x}Co_xPO_4$ ($0 \leq x \leq 1.0$) was prepared by solid state reactions. Stoichiometric amounts of $FeC_2O_4{\cdot}2H_2O$ (99%, Aldrich), $Co(AC)_2{\cdot}4H_2O$ (99%, Beijing Chemicals), $NH_4H_2PO_4$ (99.5%, Beijing Chemicals) and LiF [23] (99.99%, Beijing Chemicals) were mixed and ball-milled for 3 h. The mixture was sintered in a tube furnace with flowing $Ar–H_2$ mixture (92:8, v/v) at 400 °C for 8 h. After cooled down to room temperature, the samples were re-ground and kept at 600 °C for 24 h in the same atmosphere.

$LiFe_{1-x}Co_xPO_4$ electrode was prepared with $LiFe_{1-x}Co_xPO_4$, carbon black and polyvinylidene fluoride (PVDF) at a weight ratio of 75:15:10 with Al foil as the current collector. Lithium foil was used as the counter electrode, 1 mol L^{-1} $LiPF_6$ dissolved in ethylene carbonate/dimethyl carbonate (1:1, v/v) as electrolyte, and Celgard® 2300 as the separator. Test cells were assembled in an MBraun glove box filled with pure argon. The cell was cycled between 2.0 and 4.95 V on a Land battery tester (Wuhan, China) at room temperature. The cell was first charged to 4.95 V at a constant current density and then kept at that voltage until the current density faded to less

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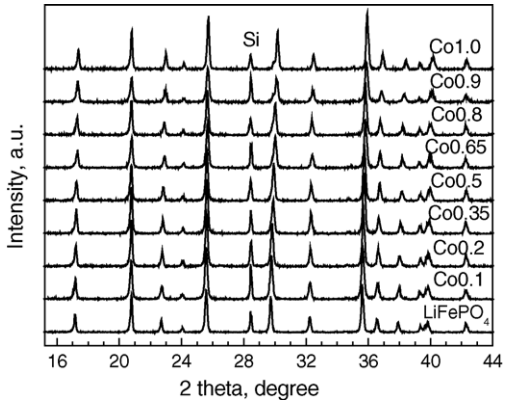

Fig. 1. The XRD pattern of $LiFe_{1-x}Co_xPO_4$.

than 0.1 mA g^{-1}. Cyclic voltammetry (CV) was carried out between 2.7 and 5.2 V at a scan rate of 0.05 mV s^{-1} on CHI660A electrochemical workstation at room temperature.

D/MAX-RC X-ray diffractometer (XRD) with Cu Kα radiation was used to characterize the structure and phase purity of these materials. X-ray photoelectron spectroscopy (XPS) analysis was carried out on Sigma Probe (Thermo VG Scientific Co. Ltd.) to probe the chemical environments around the O and P atoms in the material.

3. Results and discussion

Fig. 1 shows the XRD patterns of $LiFe_{1-x}Co_xPO_4$ solid solutions. All samples show well-defined olivine structures. No diffraction peaks belonging to Li_3PO_4 are recognized in the XRD patterns of the $LiFePO_4$, $LiCoPO_4$ and their solid solutions. Both $LiFePO_4$ and $LiCoPO_4$ show ordered olivine structures belonging to orthorhombic pnmb. Calculation indicates that the difference of lattice constants between $LiFePO_4$ and $LiCoPO_4$ is very small, $a = 10.32$ Å, $b = 6.01$ Å, $c = 4.69$ Å and $V = 290.9$ Å^3 for $LiFePO_4$ versus $a = 10.20$ Å, $b = 5.92$ Å, $c = 4.70$ Å and $V = 283.8$ Å^3 for $LiCoPO_4$.

Fig. 2 shows the dependence of the orthorhombic lattice parameters on the Co content. The a and b values of the

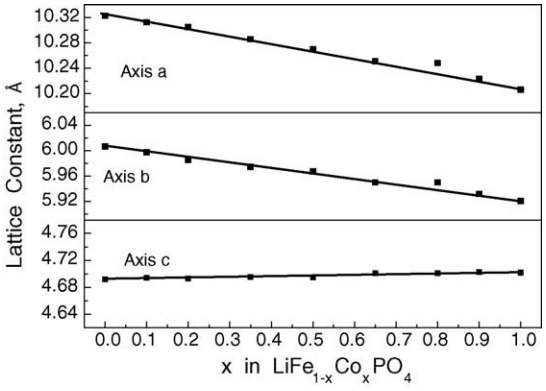

Fig. 2. Variation of the lattice constants as a function of x in $LiFe_{1-x}Co_xPO_4$.

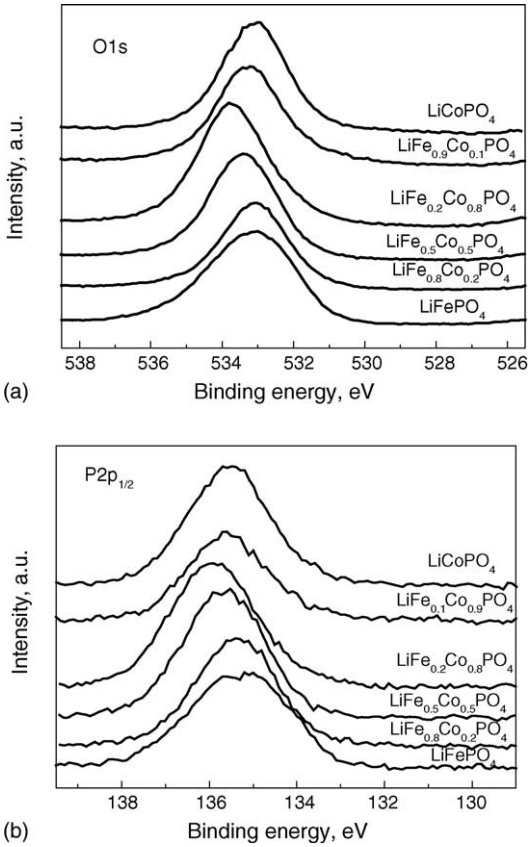

Fig. 3. The XPS spectra of O 1s (a) and P $2p_{1/2}$ (b).

prepared samples vary linearly with the increasing Co content except for that of the $LiFe_{0.2}Co_{0.8}PO_4$ which deviates from the linear relationship.

The variation of the chemical environments of O and P in the solid solutions with different Co contents is studied by XPS (Fig. 3). The O 1s peak of $LiFePO_4$ is at 533.2 and is enhanced with increasing Co content in the solid solution (Fig. 3a). It reaches 533.7 eV in $LiFe_{0.2}Co_{0.8}PO_4$ but then decreases when the Co content is further increased. The O 1s peak is at 533.1 eV for $LiCoPO_4$. The changing rule of P $2p_{1/2}$ binding energy (Fig. 3b) is the same as that of O 1s.

Clearly, $LiFe_{0.2}Co_{0.8}PO_4$ shows the highest O 1s binding energy in all the samples. Considering that the dependence of its cell parameters deviates obviously from the linear relationship of a or b versus the Co content, it seems that $x = 0.2$ is a critical point for the properties of the material. The obvious deviation of $LiFe_{0.2}Co_{0.8}PO_4$ is tentatively attributed to the change of M–O (M = Fe, Co) interaction at different Co contents.

The CV curves of $LiFePO_4$, $LiFe_{0.5}Co_{0.5}PO_4$ and $LiCoPO_4$ are compared in Fig. 4. As the electrolyte will be severely decomposed above 5.0 V, the charge cut-off voltage is set at 4.95 V for the CV and 4.90 V for the charge–discharge cycling. As shown in Fig. 4, the oxidation-reduction peaks of $LiFePO_4$ and $LiCoPO_4$ are centered at around 3.5 and 4.8 V, respectively. Two pairs of peaks are found in the CV of

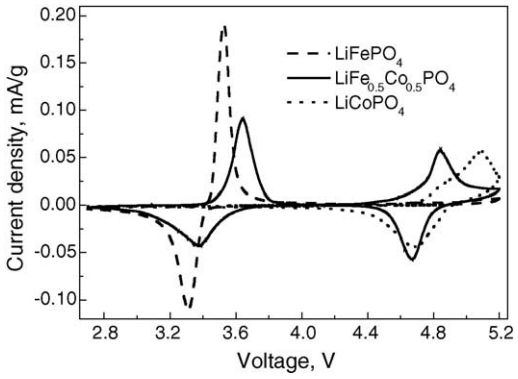

Fig. 4. The CV curves of $LiFe_{1-x}Co_xPO_4$, $x = 0$, 0.2, 0.5, 0.8, 1.0. The cells were cycled between 2.7 and 5.2 V at a scan rate of 0.05 mV s^{-1}.

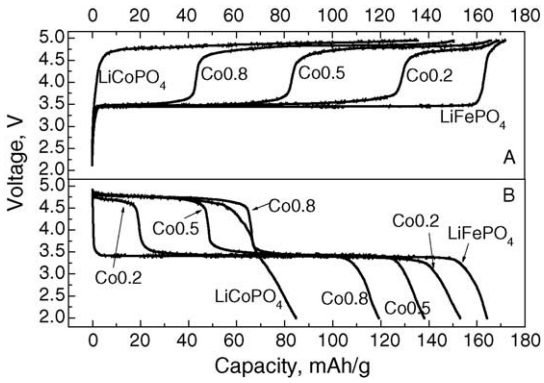

Fig. 5. The charge (A) and discharge (B) plateaus of $LiFe_{1-x}Co_xPO_4$ with $x = 0$, 0.2, 0.5, 0.8, 1.0.

$LiFe_{0.5}Co_{0.5}PO_4$. Similar to $LiFe_{1-x}Mn_xPO_4$, the peaks near 4.8 V are the reaction of Co^{2+}/Co^{3+}, and the peaks around 3.4 V correspond the reaction of Fe^{2+}/Fe^{3+}. This indicates that Co and Fe are oxidized or reduced subsequently during charge and discharge. This also verifies that $LiFe_{0.5}Co_{0.5}PO_4$ (and analogously other $LiFe_{1-x}Co_xPO_4$ materials here) is a solid solution. Meanwhile, the redox potential of the Fe^{2+}/Fe^{3+} couple is 100 mV higher than in $LiFePO_4$ while that for the Co^{2+}/Co^{3+} couple is about 100 mV lower than in $LiCoPO_4$. In this sense, the solid solution is different from a simple mixture of $LiFePO_4$ and $LiCoPO_4$. The interference between Co and Fe changes the Fermi level or the structure of the energy band of each obviously. This explains the variation of the biding energy of O 1s and P $2p_{1/2}$ in the above XPS study.

Table 1 lists the reduction and oxidation potentials of the series of materials in CV curves.

The charge profiles of the solid solutions are compared in Fig. 5A. All the cells were charged to 4.90 V at the same current density, 2 mA g^{-1}. $LiCoPO_4$ shows the lowest charge capacity (135 mAh g^{-1}) with a voltage plateau at 4.90 V for the $Co^{2+} \rightarrow Co^{3+}$ conversion. In the solid solutions with $x = 0.2$, 0.5 and 0.8, this plateau shifts to 4.82, 4.78, and 4.75 V respectively, consistent with the above CV results.

The discharge profiles of the solid solutions are shown in Fig. 5B. $LiFePO_4$ has a capacity of 164 mA g^{-1}, close to its theoretical capacity (170 mA g^{-1}). However, $LiCoPO_4$ exhibits only a capacity of 85 mA g^{-1} with a discharge plateau around 4.74 V, much lower than its theoretical capacity (165 mA g^{-1}). The capacity of $LiFe_{1-x}Co_xPO_4$ at $x = 0.2$, 0.5, 0.8 is 153, 138, and 119 mA g^{-1}, respectively. The contribution of the reaction $Co^{2+} \leftrightarrow Co^{3+}$ to the capacity should be around 110 mA g^{-1} for $LiCoPO_4$, assuming that the contribution of the $Fe^{2+} \leftrightarrow Fe^{3+}$ conversion in solid solution is the same as in $LiFePO_4$. This indicates that more capacity from $Co^{2+} \leftrightarrow Co^{3+}$ conversion can be utilized or this conversion can be more complete in the solid solutions than in $LiCoPO_4$. The reason might be that the potential for the $Co^{2+} \rightarrow Co^{3+}$ reaction is lower in the solid solution than in $LiCoO_2$ and this reaction finishes below the charge cut-off voltage.

Table 1
Comparison of the redox potentials of solid solutions with different Co contents

	$Fe^{2+} \leftrightarrow Fe^{3+}$		$Co^{2+} \leftrightarrow Co^{3+}$	
	Charge	Discharge	Charge	Discharge
$Co_{0.0}$	3.526	3.310	–	–
$Co_{0.2}$	3.612	3.344	4.755	4.642
$Co_{0.5}$	3.631	3.374	4.840	4.667
$Co_{0.8}$	3.673	3.378	4.999	4.682
$Co_{1.0}$	–	–	5.087	4.687

The cyclic performance of $LiFe_{1-x}Co_xPO_4$ is shown in Fig. 6. The cells were cycled at a current density of 10 mA g^{-1}. $LiFePO_4$ and $LiCoPO_4$ exhibit poor cyclic performance, only 76.2% and 58.2% the capacity of the first cycle can be remained after 20 cycles for $LiFePO_4$ and $LiCoPO_4$, respectively. On the contrary, the solid solution samples keep a rather high capacity in 20 cycles, remaining 88.4% of the original capacity for $LiFe_{0.8}Co_{0.2}PO_4$, 86.3% for $LiFe_{0.5}Co_{0.5}PO_4$, and 88.1% for $LiFe_{0.2}Co_{0.8}PO_4$. Particle cracking is one of the reasons for the capacity loss of $LiFePO_4$ [24]. Electrolyte decomposition should be another reason for the capacity fade of the solid solutions as well as for $LiCoPO_4$.

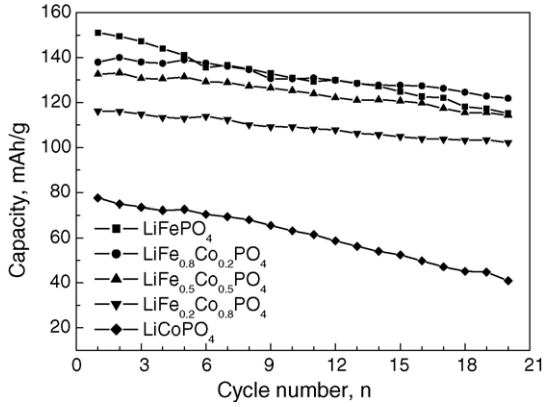

Fig. 6. The cyclic performance of $LiFe_{1-x}Co_xPO_4$.

4. Conclusion

The structure, electrochemical performances and the chemical environments around the O and P atoms of $LiFePO_4$, $LiCoPO_4$ and their solid solutions are compared as cathode materials for lithium ion batteries. The Formation of a solid solution lowers the oxidation potential of the Co^{2+} ions and make the $Co^{2+} \rightarrow Co^{3+}$ reaction complete at a lower voltage. As a result, this reaction makes more contribution of capacity in the solid solution than in $LiCoPO_4$.

Acknowledgement

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References

[1] A. Padhi, K. Nanjundaswamy, J. Goodenough, J. Electrochem. Soc. 144 (1997) 1188.
[2] A. Yamada, S. Chung, K. Hinokuma, J. Electrochem. Soc. 148 (2001) A224.
[3] N. Ravet, J. Goodenough, et al., Proceedings of the 196th Meeting of the Electrochemical Society, vol. 127, Hawaii, USA, 1999.
[4] H. Huang, S. Yin, L. Nazar, Electrochem. Solid-State Lett. 4 (2001) A170.
[5] S. Franger, F. Le Cras, et al., Electrochem. Solid-State Lett. 5 (2002) A231.
[6] G. Li, H. Azuma, M. Tohda, J. Electrochem. Soc. 149 (2002) A743.
[7] Z. Chen, J.R. Dahn, J. Electrochem. Soc. 149 (2002) A1184.
[8] N. Ravet, Y. Chouinard, et al., J. Power Sources 97/98 (2001) 503.
[9] S. Yang, Y. Song, et al., Electrochem. Commun. 4 (2002) 239.
[10] F. Croce, A. Epifanio, et al., Electrochem. Solid-State Lett. 5 (2002) A47.
[11] S. Chung, J. Bloking, Y. Chiang, Nat. Mater. 2 (2002) 123.
[12] S.Q. Shi, L.J. Liu, C.Y. Ouyang, D.S. Wang, Z.X. Wang, L.Q. Chen, X.J. Huang, Phys. Rev. B 68 (2003) 195108.
[13] K. Amine, H. Yasuda, M. Yamach, Electrochem. Solid-State Lett. 3 (2000) 178.
[14] S. Okada, S. Sawa, et al., J. Power Sources 97/98 (2001) 430.
[15] J. Lloris, C. Vicente, J. Tirado, Electrochem. Solid-State Lett. 5 (2002) A234.
[16] G. Li, H. Azuma, M. Tohda, Electrochem. Solid-State Lett. 5 (2002) A135.
[17] G. Li, Y. Kudo, et al., J. Electrochem. Soc. 149 (2002) A1414.
[18] G. Li, H. Azuma, M. Tohda, J. Elctrochem. Soc. 149 (2002) A743.
[19] A. Yamada, Y. Kudo, K. Liu, J. Electrochem. Soc. 148 (2001) A747.
[20] A. Yamada, S. Chung, J. Electrochem. Soc. 148 (2001) A960.
[21] A. Yamada, Y. Kudo, K. Liu, J. Electrochem. Soc. 148 (2001) A1153.
[22] N. Penazzi, M. Arrabito, et al., J. Eur. Ceram. Soc. 24 (2004) 1381.
[23] D.Y. Wang, L.Q. Chen, et al., J. Solid State Chem. 177 (2004) 4582.
[24] D. Wang, X. Wu, Z. Wang, L. Chen, J. Power Sources 140 (2005) 125.