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A simple and practical synthesis route for $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ by rheological phase method with composite chelating reagents.

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Carbon-coated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ composite material has been successfully synthesized by a simple and practical rheological phase method with composite chelating reagents of citric acid and glycine. The as-prepared $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite material have a stable cycle performance, capacity retention and thermostability.

Rechargeable lithium ion batteries have been considered as promising power sources for hybrid electric vehicles (HEVs) and electric vehicles (EVs) for their various advantages.¹ In consideration of the high safety, polyanion-type material have attract a significant interest in recent years. Among these materials, $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ is one of the most promising candidates for cathode materials of lithium ion batteries owing to its high ionic diffusion coefficient, discharge voltage and power density, high theoretical capacity (133 mAhg^{-1} at 3-4.3 V), long cycle life, and remarkable thermal stability.² However, the intrinsic low electronic conductivity ($2.4 \times 10^{-7} \text{ Scm}^{-1}$) limits the practical application of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$.³ Therefore, various approaches have been used to solve this problem, such as carbon coating,⁴⁻⁶ metal doping⁷⁻⁹ and particle size reduction.¹⁰⁻¹² In particular, carbon coating has been widely used for enhancing the specific capacity and rate capacity. The conductive carbon around the particles can not only effectively improve the electronic conductivity of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, but also suppress the particle growth in the sintering process.^{2,4} Furthermore, reducing the particle size can shorten the distance of lithium ion diffusion and electrons transportation distances, which is beneficial to the rate capability of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$.^{13, 14}

Various synthesis routes have been employed to prepare $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, such as solid-state reaction,^{3,15,16} sol-gel method,^{2,4,14} hydrothermal synthesis,^{8,10,17} rheological phase method^{16,18-20} etc.. However, The materials synthesized by conventional solid-state reaction are likely to have a larger or nonuniform particle size,²¹ while the procedure of sol-gel method and hydrothermal synthesis are complicated and costly.^{2,10} Rheological phase method, which is

between solid-state reaction and liquid phase method, has been successfully used to prepare $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ in recent years.^{6,18-20}

In this work, we firstly synthesize the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite material via a simple and practical rheological phase method with composite chelating reagents and carbon sources of citric acid and glycine. The electrochemical properties, especially the stability at high rates of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite have been studied. The simple synthetic method is suitable for industrial production.

The XRD pattern of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite material is presented in Fig. 1a. All the diffraction peaks of the as-synthesized powder can be indexed as monoclinic structure (PDF #47-0107) with space group P21/n, which are consistent with the previous work.^{2,16} Furthermore, no evidence of diffraction peaks from coating carbon is detected, which indicates that the residual carbon in the composite is amorphous or the coating carbon layer is very thin. According to element analysis, the carbon content in the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ is 7.2 wt.%. Fig. 1b shows the Raman spectrum of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite in the range of 500~2000 cm^{-1} . In the spectrum, two intense broad bands at 1594 cm^{-1} and 1350 cm^{-1} are attributed to the graphite band (G-band) and the disorder-induced phonon mode (D-band), respectively.^{17,20} The I_D/I_G value of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite is about 0.87. This suggests that the graphite-like carbon in the residual carbon is about 50%, which is helpful for improving the electronic conductivity and electrochemical performance of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$.^{17,20} However, the graphite crystallites in the residual carbon are very small and ranged in a disordered form. Hence, it is difficult to detect any graphite crystallites from XRD.^{20,22} In addition, there are two weak Raman bands at 1053.4 and 1145.6 cm^{-1} , which correspond to the vibrations of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$.²³

Morphological features of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ were examined by SEM, as shown in Fig. 2a. It can be observed that the particles have sphere-like morphology with size of 1~2 μm (for particle size distribution, see Fig. S1, ESI[†]), which may be attributed to

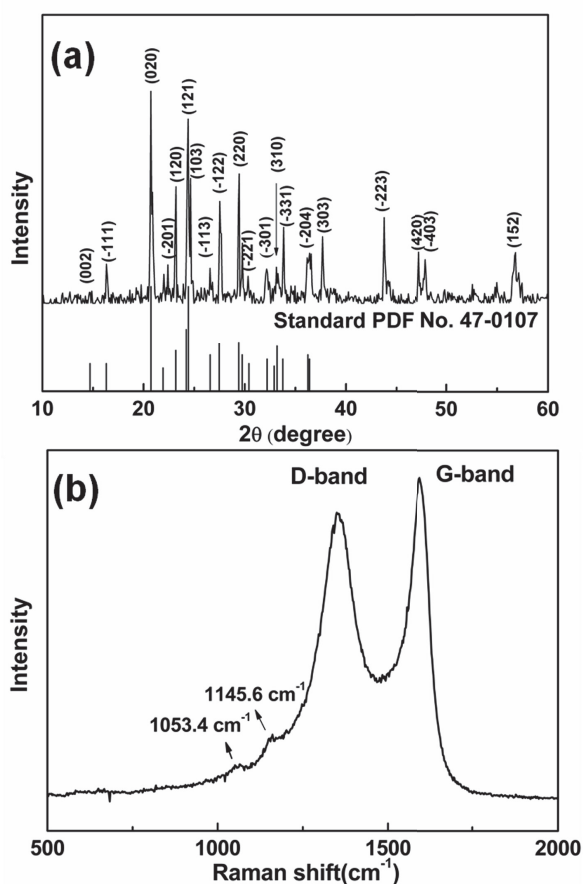


Fig. 1. X-ray diffraction pattern (a) and Raman scattering spectrum (b) of the as-prepared $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite material.

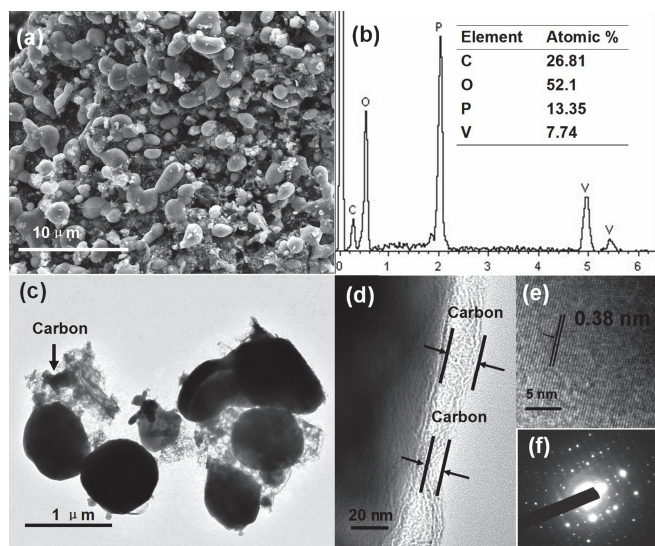


Fig. 2. SEM image (a), EDS spectrum (b), TEM image (c), HR-TEM image (d), (e) and corresponding SAED pattern (f) of the as-prepared $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite material.

the composite chelating reagents of citric acid and glycine. Meanwhile, the amount of C, O, P and V is determined by EDS

(Fig. 2b). It can be found that the as-prepared $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite have a strict stoichiometric ratio of V:P:O= 2:3:12. TEM is used to further investigate the microstructure of the as-synthesized particles (Fig. 2c, d and e). The network formed by amorphous carbon can be seen between the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ particles (Fig. 2c), which is believed that can inhibit the growth of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ particles and improve the electronic conductivity of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ material.^{2,4} In HR-TEM image (Fig. 2d and e), it is clear that the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ particles are coated with a carbon layer about 7~16 nm in thickness. The observed lattice fringes with a spacing of 0.38 nm corresponding to the (120) planes of monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, and the SAED pattern in Fig. 2f further confirm the single-crystal feature of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ particles.

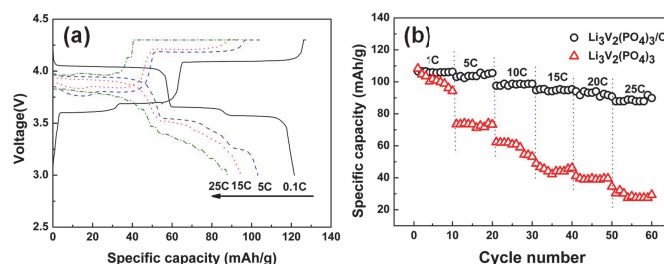


Fig. 3. Charge-discharge curves of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite material in the range of 3.0-4.3 V (a), rate performance of both uncoated and coated sample in the range of 3.0-4.3 V (b).

The charge-discharge curves of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite at 0.1C, 5C, 15C and 25C rates in the range of 3.0-4.3 V are shown in Fig. 3a. For the 0.1C charge curve, three plateaus at 3.60, 3.69 and 4.09 V are observed, which correspond to the extraction of two lithium ions and the phase transitions of $\text{Li}_x\text{V}_2(\text{PO}_4)_3$ from $x=3.0$ to 2.5, 2.0 and 1.0, respectively. The first lithium ion is extracted in two steps (3.60 V and 3.69 V) because of the existence of an ordered mesophase of $\text{Li}_{2.5}\text{V}_2(\text{PO}_4)_3$. Then the second lithium ion is extracted by a single step, accompanied with the complete oxidation of $\text{Li}_2\text{V}_2(\text{PO}_4)_3$ to $\text{LiV}_2(\text{PO}_4)_3$. Three discharge plateaus at 3.57, 3.66 and 4.05 V are attributed to the reinsertion of the two lithium ions, correspond to the phase transitions of $\text{Li}_x\text{V}_2(\text{PO}_4)_3$ from $x=1.0$ to 2.0, 2.5 and 3.0, respectively. The initial discharge capacity is 121.6 mAhg^{-1} at 0.1C rate, and the coulombic efficiency reached 95.6%. As shown in the Fig. 3b, 106.6 mAhg^{-1} is obtained at 1C rate, while that the uncoated one is 108.3 mAhg^{-1} , which is a little higher than $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ and decreasing to 94.3 mAhg^{-1} after 10 cycles. When operated to 5C rate, the discharge specific capacity of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ is 103.1 mAhg^{-1} and the uncoated one decreasing rapidly after 1C rate. As the rate is raised to 10C, 15C and 20C, the cell delivers a capacity of 97.6, 94.8, and 94.1 mAhg^{-1} , respectively. It is obvious that the rate performance of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ is better than uncoated one.

Since the good electrochemical performance at low discharge rates and high charge rates is suitable for practical application, the discharge curves of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite material at different charge rates are tested. Fig. 4 shows the discharge curves without obviously change and the discharge capacities maintain in about 110 mAhg^{-1} at 1C discharge rates with charge

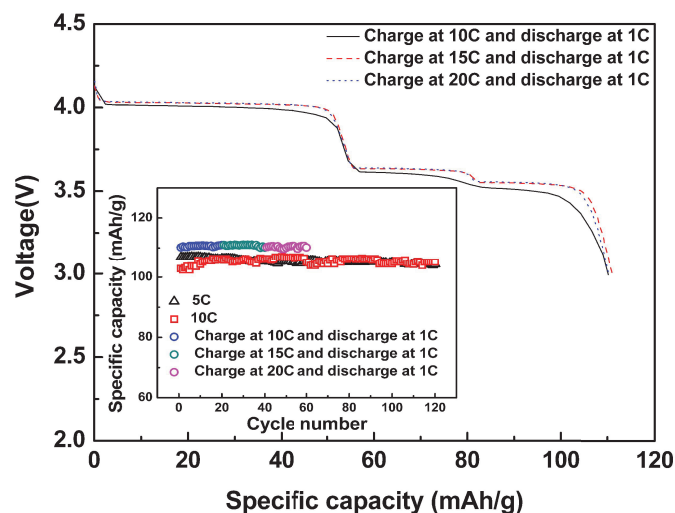


Fig. 4. Discharge curves and cycle performance (insert) of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite material at various charge-discharge rates in the range of 3.0-4.3 V.

(shown in the insert), the largest capacities reach 107.1 and 104.7 mAhg^{-1} , 98.1% and 94.4% of the largest values are still retained for the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ electrodes after 120 cycles, respectively. The stable electrochemical performance of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite may be related to the existence of the composite chelating reagents and carbon sources in the synthetic process, the uniform particle size and the carbon coating.

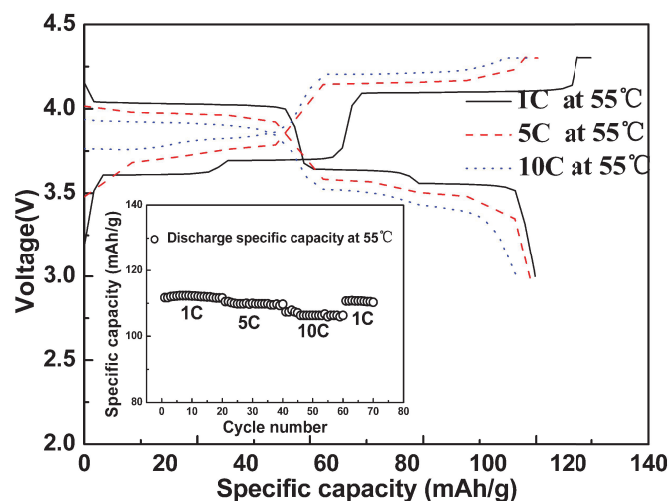


Fig. 5. High-temperature ($55 \text{ }^\circ\text{C}$) performance of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite material at various charge-discharge rates in the range of 3.0-4.3 V.

The electrochemical behaviors of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite at $55 \text{ }^\circ\text{C}$ have also been investigated at different rates in the range of 3.0-4.3 V (Fig. 5). The discharge capacities reach 111.7 , 110.5 and 107.4 mAhg^{-1} at 1C, 5C and 10C rates, respectively. After 60 cycles (shown in the insert), 110.7 mAhg^{-1} still can be obtained when reset to 1C rate, which is almost equal to the initial discharge capacity of the electrode at 1C. Furthermore, compared with Fig.2 (the insert figure), it can

be seen that the electrochemical performance at $55 \text{ }^\circ\text{C}$ are better than room temperature. This maybe attribute to the activity of electrodes are enhanced and the lithium ion diffusion rate is improved at high temperature.

Recently, the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composites synthesized by Wang et al.² exhibited good electrochemical performance at low charge rates and high discharge rates. In this work, the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composites prepared by rheological phase method were tested at high charge rates and low discharge rates. The stable electrochemical performance of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite may be related to the existence of the composite chelating reagents and carbon sources in the synthetic process, the uniform particle size and the carbon coating.

To conclude, the carbon-coated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cathode material has been successfully synthesized by a simple and practical rheological phase method with composite chelating reagents. The as-synthesized cathode material exhibits stable rate performance and capacity retention, which can be attributed to the uniform particle size and the carbon coating. The simple synthetic method is suitable for industrial production. These results demonstrate that the carbon-coated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cathode material prepared via rheological phase method is a potential cathode candidate for high-power lithium ion batteries.

Experimental

Sample preparation

The $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite material was prepared by a rheological phase method using $\text{LiOH}\cdot\text{H}_2\text{O}$ (A.R.), NH_4VO_3 (A.R.), $\text{NH}_4\text{H}_2\text{PO}_4$ (A.R.), $\text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O}$ (citric acid, A.R.), and $\text{C}_2\text{H}_5\text{NO}_2$ (glycine, A.R.) as starting materials. Both citric acid and glycine were employed as chelating reagents and carbon sources. First of all, stoichiometric amounts of $\text{LiOH}\cdot\text{H}_2\text{O}$, NH_4VO_3 , $\text{NH}_4\text{H}_2\text{PO}_4$ and citric acid in the 3.1:2:3:2 molar ratios and 3.7520g glycine were fully mixed by grinding. Then, an amount of deionized water was dropwise added to get a rheological body, followed by grinding for 0.5 h. The mixture was dried in the oven at $100 \text{ }^\circ\text{C}$ for 12 h to give a blue precursor. The precursor was ground and pre-heated at $300 \text{ }^\circ\text{C}$ for 3 h. The resulting powder was reground and sintered at $800 \text{ }^\circ\text{C}$ for 8 h under argon flow. As a comparison, the uncoated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ sample was prepared through the same method with out addition of glycine.

Characterization

XRD measurements were carried out with a Bruker D8-Advance powder X-ray diffractometer with $\text{Cu-K}\alpha$ radiation. The morphology and nanostructure of the products were characterized using a scanning electron microscope (QUANTA-FEG-250) and a transmission electron microscope (TEM, JSM-2010). The carbon content was measured by elemental analyser (Vario EI III, Elementar Analysen System GmbH, Germany).

Electrochemical measurement

The electrochemical properties of the products were characterized using CR2032 coin cells. The composite electrodes were prepared by mixing 80 wt.% active material powder with 10 wt.% acetylene black and 10 wt.% polyvinylidene flouride (PVDF) in an appropriate amount of N-methyl-2-pyrrolidone (NMP) to form slurry. Then the slurry was coated onto the aluminum foil and dried in a vacuum oven

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at 80 °C for 12 h. The cells were assembled in a glove box filled with high purity argon using a polypropylene micro-porous film (Celgard 2400) as the separator, lithium foil as the anode, and 1 M LiPF₆ in a mixture of ethylene carbonate (EC), diethyl carbonate (DEC) and ethyl methyl carbonate (EMC) (1:1:1 in volume ratio) as electrolyte. The electrochemical performance of the Li₃V₂(PO₄)₃/C composite was evaluated on a LAND CT2000A cell test instrument in the range of 3.0-4.3 V under different current densities and temperature.

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Notes and references

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- 1 Q. Kuang, Y. M. Zhao, J. T. Xu, *The Journal of Physical Chemistry C*, 2011, **115**, 8422.
- 2 L. J. Wang, H. B. Liu, Z. Y. Tang, L. Ma, X. H. Zhang, *Journal of Power Sources*, 2012, **204**, 197.
- 3 Y. Q. Qiao, X. L. Wang, J. Y. Xiang, D. Zhang, W. L. Liu, J. P. Tu, *Electrochimica Acta*, 2011, **56**, 2269.
- 4 Q. J. Liu, F. Yang, S. P. Wang, L. J. Feng, W. J. Zhang, H. Y. Wei, *Electrochimica Acta*, 2013, **111**, 903.
- 5 L. L. Zhang, G. Liang, G. Peng, F. Zou, Y. H. Huang, M. C. Croft, A. Ignatov, *The Journal of Physical Chemistry C*, 2012, **116**, 12401.
- 6 Y. J. Li, L. Hong, J. Q. Sun, F. Wu, S. Chen, *Electrochimica Acta*, 2012, **85**, 110.
- 7 Q. Q. Chen, X. C. Qiao, Y. B. Wang, T. T. Zhang, C. Peng, W. M. Yin, L. Liu, *Journal of Power Sources*, 2012, **201**, 267.
- 8 C. W. Sun, S. Rajasekhara, Y. Z. Dong, J. B. Goodenough, *ACS Applied Materials & Interfaces*, 2011, **3**, 3772.
- 9 W. H. Wang, Z. Y. Chen, J. L. Zhang, C. S. Dai, J. J. Li, D. L. Ji, *Electrochimica Acta*, 2013, **103**, 259.
- 10 F. Teng, Z. H. Hu, X. H. Ma, L. C. Zhang, C. X. Ding, Y. Yu, C. H. Chen, *Electrochimica Acta*, 2013, **91**, 43.
- 11 A. Q. Pan, J. Liu, J. G. Zhang, W. Xu, G. Z. Cao, Z. M. Nie, B. W. Arey, S. Q. Liang, *Electrochemistry Communications*, 2010, **12**, 1674.
- 12 Y. Z. Li, X. Liu, J. Yan, *Electrochimica Acta*, 2007, **53**, 474.
- 13 S. P. Wang, H. X. Yang, L. J. Feng, S. M. Sun, J. X. Guo, Y. Z. Yang, H. Y. Wei, *Journal of Power Sources*, 2013, **233**, 43.
- 14 L. J. Wang, Z. Y. Tang, L. Ma, X. H. Zhang, *Electrochemistry Communications*, 2011, **13**, 1233.
- 15 Y. Q. Qiao, X. L. Wang, Y. Zhou, J. Y. Xiang, D. Zhang, S. J. Shi, J. P. Tu, *Electrochimica Acta*, 2010, **56**, 510.
- 16 Y. Q. Qiao, X. L. Wang, Y. J. Mai, J. Y. Xiang, D. Zhang, C. D. Gu, J. P. Tu, *Journal of Power Sources*, 2011, **196**, 8706.
- 17 Y. Q. Qiao, J. P. Tu, X. L. Wang, D. Zhang, J. Y. Xiang, Y. J. Mai, C. D. Gu, *Journal of Power Sources*, 2011, **196**, 7715.
- 18 F. Wu, F. Wang, C. Wu, Y. Bai, *Journal of Alloys and Compounds*, 2012, **513**, 236.
- 19 C. X. Chang, J. F. Xiang, X. X. Shi, X. Y. Han, L. J. Yuan, J. T. Sun, *Electrochimica Acta*, 2008, **53**, 2232.
- 20 J. S. Huang, L. Yang, K. Y. Liu, *Materials Letters*, 2012, **66**, 196.
- 21 L. J. Wang, X. C. Zhou, Y. L. Guo, *Journal of Power Sources*, 2010, **195**, 2844.
- 22 Y. S. Chen, D. Zhang, X. F. Bian, X. F. Bie, C. Z. Wang, F. Du, M. Jang, G. Chen, Y. J. Wei, *Electrochimica Acta*, 2012, **79**, 97.
- 23 C.M. Burba, R. Frech, *Solid State Ionics*, 2007, **177**, 3445.