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ORIGINAL PAPER

Synthesis, characterization and electrochemical performance of $LiNiVO_4$ anode material for lithium-ion batteries

Xiaoyan Han · Wenchao Tang · Zonghui Yi · Jutang Sun

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Abstract A rheological phase reaction method was introduced to synthesize $LiNiVO_4$ powder material. The product was tested using XRD, SEM and electrochemical measurement methods. It was found that single crystal grain $LiNiVO_4$ is easily prepared with the rheological phase reaction; the intermediate product $NiV(IV)O_3$ is the electrochemical active center; the product prepared at 700 °C for 18 h possess the best morphology of single crystal body and exhibits excellent performance as anode material with a small capacity fade. This indicates that $LiNiVO_4$ is a good anode material for lithium-ion batteries and the rheological phase reaction is a simple, economical and effective method to synthesize a series of functional materials.

Keywords Anode material · Lithium-ion batteries · Lithium-nickel vanadium oxide ($LiNiVO_4$) · Rheological phase reaction

1 Introduction

With the development of portable electronics applications, a great deal of effort has been devoted to developing transition metal oxides as potential cathode materials for lithium-ion batteries [1, 2]. The compound $LiNiVO_4$ with spinel structure is of importance as active cathode material because of its high voltage performance that can be applied to high energy density batteries [3–6]. Moreover, $LiNiVO_4$ can react with 7 mol lithium ions per formula unit when discharged to voltages lower than 0.2 V, leading to 1,039 mAh g^{-1} specific capacities, about twice as large as graphite electrodes [7, 8]. Therefore $LiNiVO_4$ is of potential interest as anode material in lithium-ion batteries [9–12]. However, some problems remain, in particular, cycle performance. Work is needed to overcome the capacity fade in order to implement these materials in practical applications [13].

As is well-known, good battery materials should possess the following qualities: good phase purity, homogeneity, uniform particle morphology, etc. In order to achieve these properties, various preparation methods have been used such as sol–gel [14], solid-state thermal reaction [5], radio frequency sputtering [8, 10], co-precipitation [15], combustion [4, 5], soft-chemistry synthesis [16], electrostatic spray deposition [17], hydrothermal synthesis [18], etc. Different preparation routes lead to materials with different electrochemical properties. Conventional methods have many disadvantages, including high temperature processing, large crystallite size, impure phase, agglomerated particles, broad particle size distribution, long production times, sophisticated processing equipment, low product yield, etc., which have restricted improvement in electrochemical performance.

In order to avoid the above deficiencies, we have studied a rheological phase reaction method. This approach does not require troublesome processes such as washing, filtering, palletized and repeated sintering with grinding [19]. Rheological phase reaction is a process for preparing compounds or materials from a solid-liquid rheological mixture. First, the solid reactants were fully mixed in the required molar ratio. Then an appropriate amount of liquid (such as water or ethanol) was added to form a solid-liquid rheological mixture in which the solid particles and liquid substance were uniformly distributed. After further treatment the final product was obtained.

X. Han · W. Tang · Z. Yi · J. Sun (✉)
Department of Chemistry, Wuhan University, Wuhan 430072, People's Republic of China
e-mail: jtsun@whu.edu.cn

The rheological phase reaction method makes use of simple equipment, saves energy and time, and results in small particle size with good repeatability and low environmental impact. So it is a simple, economical and effective route to prepare functional materials such as electrode materials [20–26]. In this work, $LiNiVO_4$ was successfully synthesized by rapid rheological phase reaction, and the physical properties and electrochemical efficiency of $LiNiVO_4$ was investigated.

2 Experimental process

2.1 Material preparation and characterization

$LiNiVO_4$ anode materials were synthesized by the rheological phase reaction method. $LiNO_3$, $Ni(CH_3CO_2)_2 \cdot 2H_2O$, and NH_4VO_3 were used as starting materials and were fully mixed in the stoichiometric ratio by grinding. An appropriate amount of distilled water was added to obtain a rheological mixture. The mixture was transferred into a Teflon container that was then sealed in a stainless steel reactor at 80 °C for 8 h. After drying at 120 °C, the mixture was heated at 700 °C for 6, 12 and 18 h in air, resulting in yellow colour samples.

X-ray diffraction (XRD) patterns were obtained with a Shimadzu XRD-6000 diffractometer with a Ni filter and Cu-Kα_1 radiation ($\lambda = 1.54056$ Å), and the data were collected over 6–80° (2θ) with a scan speed of 4° min^{-1}. The refined crystal lattice parameters were calculated by the JADE5.EXE procedure. The particle sizes and morphological features were revealed by a scanning electron microscope (Hitachi SEM X-650).

2.2 Electrochemical measurements

The characterized $LiNiVO_4$ powders of preferable crystal structure and surface morphology were subjected to electrochemical characterization. The electrochemical experiments were examined on a Neware cell test system at room temperature. A composite electrode was constructed by mixing the $LiNiVO_4$ materials, polytetrafluoroethylene (PTFE) binder and acetylene black, in the weight ratio of 80:15:5, and the mixture was then compressed onto a stainless steel current collector. $LiPF_6$ solution (1 M) dissolved in EC/DMC (1:1 volume ratio) was used as the electrolyte. Then the electrode was incorporated into a coin cell (size 2016) with a lithium foil counter electrode separated by a Celgard 2300 microporous membrane. The cells were assembled in an argon-filled glove box (Mikrouna, Super 1220/750, China). The cells were discharged and charged between 0.01 and 3.0 V versus Li at a constant current density of 100 mA g^{-1}.

3 Results and discussion

3.1 Powder XRD analysis

Figure 1 shows the X-ray diffraction (XRD) patterns of $LiNiVO_4$ powders prepared by heating the precursors at 700 °C for 6, 12 and 18 h. All diffraction peaks are very sharp, which indicates that the crystallinities of products are high. The XRD data agree well with JCPDS Card No. 73-1636. The strongest diffraction peaks are assigned to the (311) plane. The (220) peaks are more intense than the (111) peaks, whereas for normal spinel-like $LiMn_2O_4$, the (111) peak is the strongest peak and the (220) peak is very weak [27]. The presence of V atoms on the tetrahedrally coordinated 8a sites leads to the increase in the (220) intensity at the expense of the (111) peak [10, 28]. This shows that $LiNiVO_4$ has an inverse spinel structure with V^{5+} ions in the tetrahedrally coordinated oxygen interstices. Moreover, the 16d sites are occupied by Li and Ni, and the 32e sites are occupied by O [10, 12, 27].

All diffraction lines of the samples could be indexed as the inverse spinel type $[V]_{8a}[LiNi]_{16d}O_4$ structure with the space group $Fd\text{-}3m$ (No. 227). The refined crystal lattice parameters calculated by the JADE5.EXE procedure are presented in Table 1. The lattice parameter of the compound (a = 8.2184 Å) agrees well with Reddy et al. [29].

The results indicate that the well-ordered inverse spinel structure of $LiNiVO_4$ is formed within 6–18 h, but prolonging the heated time leads to a decrease of the lattice parameters. The decrease of crystal cell volume results in Li volatilization, which leads to the formation of the vacancy V_{Li} and $Ni_{Ni}^{\bullet}$ defects.

In this rheological phase reaction system, $LiOH \cdot H_2O$ and other reactants are homogeneously mixed at ionic

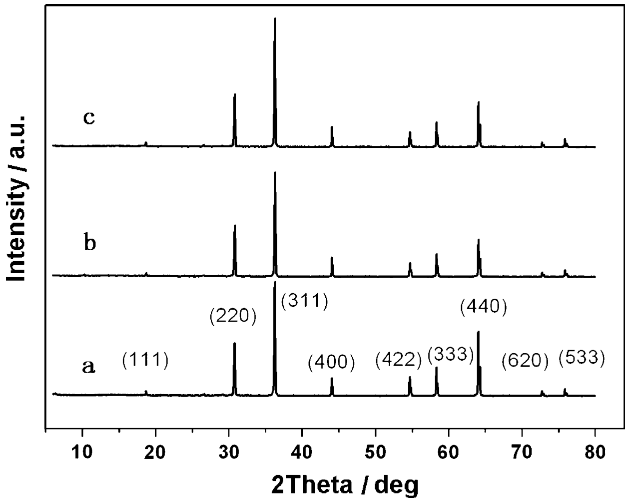

Fig. 1 XRD patterns of $LiNiVO_4$ heated at 700 °C for 6 h (**a**), 12 h (**b**) and 18 h (**c**)

Table 1 Lattice parameters of $LiNiVO_4$ heated at 700 °C for 6, 12 and 18 h

Parameter	6 h	12 h	18 h
a (Å)	8.2199(6)	8.2162(5)	8.2134(3)
V (Å^3)	555.39(7)	554.65(6)	554.08(4)
Z	8.0	8.0	8.0
D_{calc} (g cm^{-3})	4.3193	4.3250	4.3295

scale, which is beneficial to the diffusion process and reaction process. The possible contamination of NiO and Li_3VO_4 impurities is completely absent for all samples. The observed crystal lattice parameters for the three samples coincide well with the standard values. It is clear that the single crystal phase $LiNiVO_4$ is easily prepared by means of this rheological phase reaction.

3.2 SEM analysis

Figure 2 presents the SEM images of $LiNiVO_4$ samples. The images of three samples heated for 6, 12 and 18 h are similar, and with increasing calcination time the particle size gradually increases. The samples exhibit particles possessing the unusual morphology of single crystal

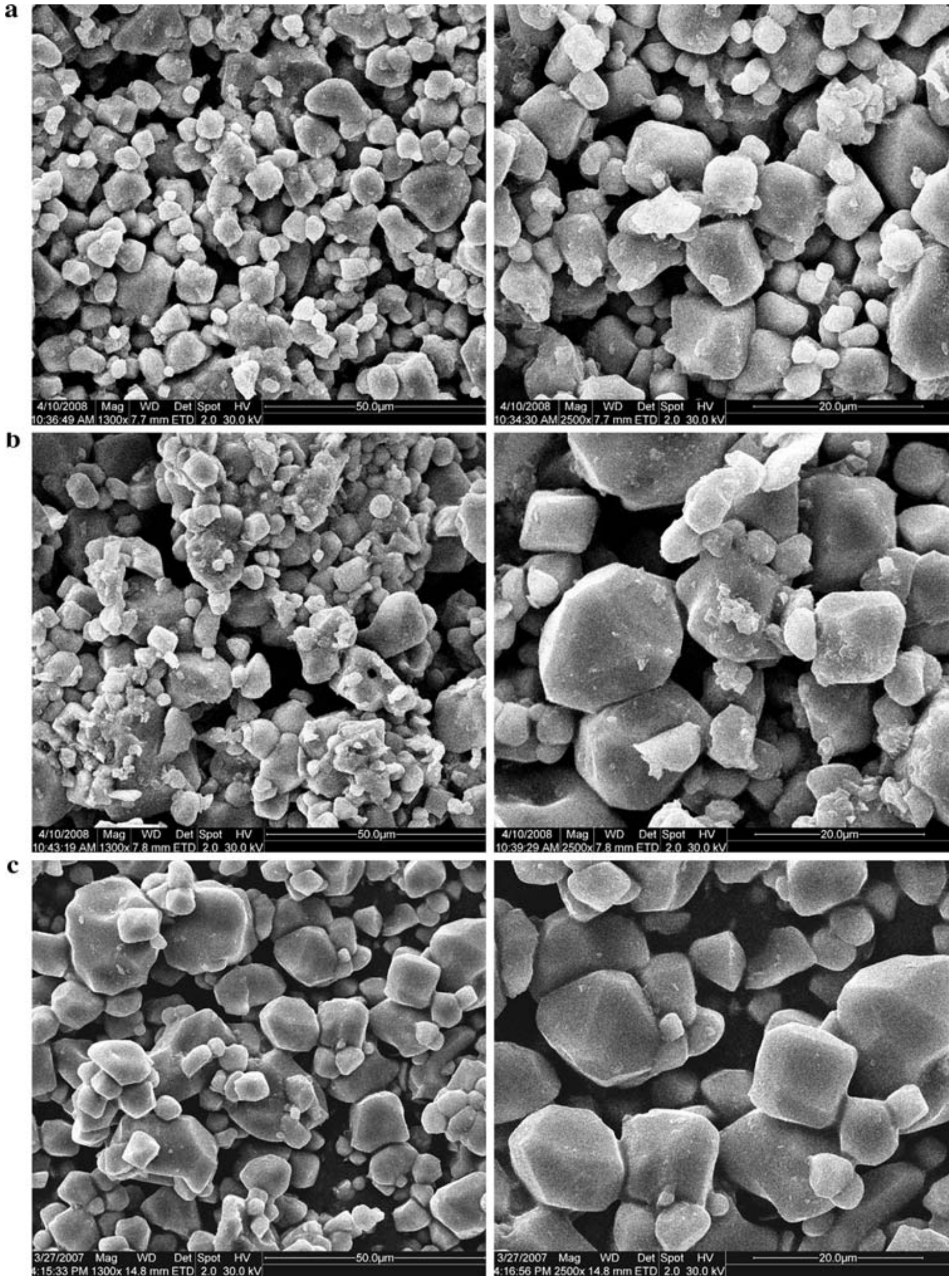

Fig. 2 SEM images of $LiNiVO_4$ heated at 700 °C for 6 h (**a**), 12 h (**b**) and 18 h (**c**)

bodies, with very clear crystal face and arris, which is different from that reported in the literatures [5, 29, 30]. It is singly dispersive with almost no agglomerated particles, with particle sizes of 5–10 μm.

This material can be expected to exhibit excellent electrochemical behavior for lithium-ion batteries. Our results show that the $LiNiVO_4$ powder with a single dispersivity and homogeneous microcrystalline morphology can be obtained very easily by the rheological phase reaction method. The particle features of the samples are desirable for the intercalation-deintercalation reaction of Li^+ ions on the anode surface during the discharge-charge process, resulting in a larger capacity.

3.3 Electrochemical properties

Typical 1st, 2nd and 10th discharge–charge profiles of the three $LiNiVO_4$ samples are presented in Fig. 3a–c. The $LiNiVO_4$/Li cells were cycled over 0.01–3.0 V vs. Li with a constant current density of 100 mA g^{-1}. The initial discharge and charge profiles of the three $LiNiVO_4$ electrodes are almost the same (presented in Fig. 3d) and show clear plateaus, indicating the same electrochemical behavior of the three samples. The distinct plateaus in the discharge–charge curves correspond to structural changes in the discharge–charge process, which is a unique characteristic of $LiNiVO_4$ compounds [5]. The samples heated for 6, 12 and 18 h deliver initial discharge and charge capacities of 1,006, 1,017, 1,267 mAh g^{-1} and 736, 772, 1,026 mAh g^{-1}, respectively. The coulombic efficiencies are 73.2%, 75.9%, and 81.0%, respectively. The second discharge and charge capacity of three samples (6, 12 and 18 h) are 795, 810, 1,066 mAh g^{-1} and 734, 748, 1,002 mAh g^{-1}, respectively. The coulombic efficiencies are 92.3%, 92.3%, and 94.0%, respectively. As calcination time increase, the capacities increase. The reason for the higher first capacity for $LiNiVO_4$ heated for 18 h is attributable to the presence of Li vacancy defects. This is in agreement with the XRD analysis results (the number of Li vacancy defects is 6 < 12 < 18 h).

There is a large plateau around 0.54 V in the initial discharge curve for the three samples, but there are two plateaus near 1.75 and 0.75 V in the following 2nd and 10th cycles, which is in accord with other results [12]. But the three charge curves (1st, 2nd, and 10th) are very similar. As further cycles suggest the original material becomes modified during the first discharge so that successive discharge-charge cycles have two new plateaus. This also suggests that after the first discharge the compound has formed a new structure arrangement which is very stable and favorable to the electrochemical behavior [12].

For the $LiNiVO_4$ sample heated for 18 h, for example, the first discharge capacity is 1,267 mAh g^{-1}, but about 80 mAh g^{-1} in the range 2.8–0.54 V is consumed in the formation of the solid-electrolyte-interface (SEI). The actual capacity of inserted Li is 1,187 mAh g^{-1}, which equals that of 8 mol Li. The first charge capacity is 1,026 mAh g^{-1}, which is equivalent to 7 mol Li. This means that only 1 mol Li is irreversible in the first cycle. The reaction mechanism

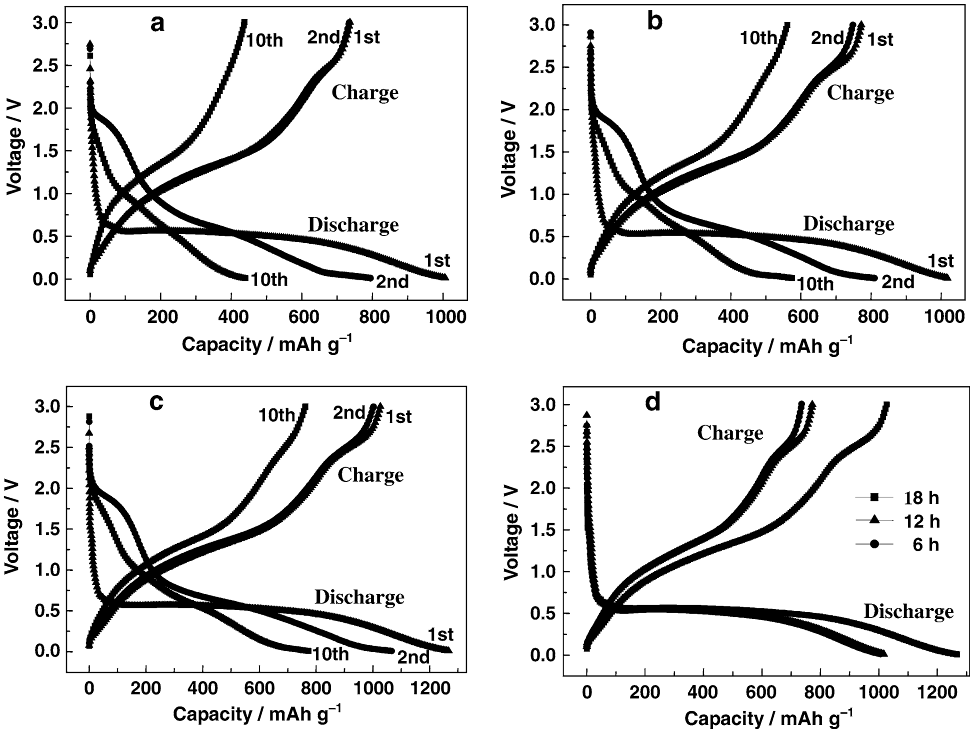

Fig. 3 Discharge-charge performance of $LiNiVO_4$ heated at 700 °C for 6 h (**a**), 12 h (**b**) and 18 h (**c**) over 0.01–3.0 V (**d** is comparison of the first discharge-charge curves)

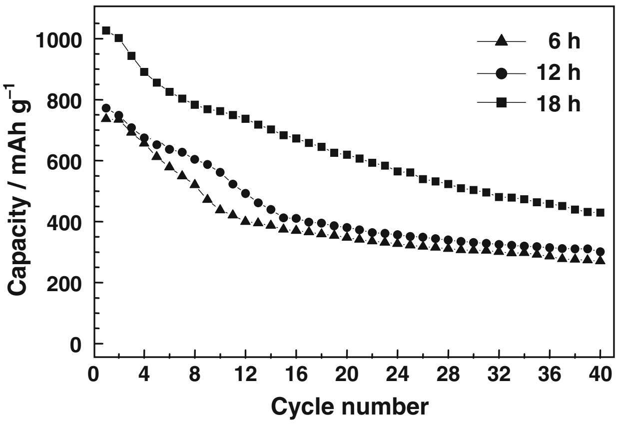

Fig. 4 Cycle behavior of charge capacity of the $LiNiVO_4$ heated at 700 °C for 6, 12 and 18 h over 0.01–3.0 V

of intercalation-deintercalation of Li ions can be expressed as follows:

$$LiNiVO_4 + 8Li \rightarrow Li_2O + (Li_7NiV)O_3 \quad (1)$$

$$(Li_7NiV)O_3 \rightarrow NiV(IV)O_3 + 7Li \quad (2)$$

In Eq. 1 the $(Li_7NiV)O_3$ composite is formed. The second Eq. 2 shows that $NiV(IV)O_3$ composite is the electrochemical active center, indicating an intercalate-deintercalate of 7 mol Li in the discharge and charge reaction process.

Figure 4 shows the cycle performances of charge capacity of the three $LiNiVO_4$ tested. The initial charge capacities of $LiNiVO_4$ heated for 6, 12 and 18 h are 736, 772 and 1,026 mAh g^{-1}, respectively. After 14 cycles, the charge capacities of $LiNiVO_4$ (6, 12 and 18 h) are 387, 440, and 702 mAh g^{-1}, respectively. The capacity retentive efficiencies are 52.6%, 57.0% and 68.4%, respectively. After 40 cycles, the charge capacities still remain at 271, 301, 429 mAh g^{-1} and the capacity retentive efficiencies are 36.8%, 40.0% and 41.8%, respectively, which is much better than that of $LiNiVO_4$ prepared by the traditional solid-state method. The results demonstrate that from the 14th cycle the charge capacity curves of the three samples fade a small amount and that $LiNiVO_4$ heated for 18 h yielded the best results. The improvement in the cycle performances of the anode shows the effect of the synthesis process. The rates of capacity fade of the materials heated for 6 h and 12 h are faster than that of 18 h, which may be related to the particle sizes. The bigger particles tend to improve the structural stability of electrode materials during insertion-desertion processes of Li^+ ion.

4 Conclusions

$LiNiVO_4$ powder was successfully prepared by rheological phase reaction. Rheological phase reaction lowers the temperature required to synthesize highly crystalline $LiNiVO_4$ compared to traditional solid state reaction. The method is promising for other kinds of anode or cathode materials. The $LiNiVO_4$ with inverse spinel structure is prepared very easily by this method when heated at 700 °C for 6 h or longer. The products are pure crystal phase with crystal particle sizes of 5–10 μm. This material thus has application as anode material in lithium-ion batteries. However, some problems remain with respect to cycle efficiency. With sufficient effort and improved experimental technique our process may produce useful anode materials. The results encourage further study of this inverse spinel powder for lithium-ion batteries.

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References

1. Tan KS, Reddy MV, Subba Rao GV, Chowdari BVR (2005) J Power Sources 147:241
2. Nakayama M, Watanabe K, Ikuta H, Uchimoto Y, Wakihara M (2003) Solid State Ionics 164:35
3. Kovacheva D, Gadjov H, Petrov K, Mandal S, Lazarraga MG, Pascual L, Amarilla JM, Rojas RM, Herrero P, Rojo JM (2002) J Mater Chem 12:1184
4. Liu JR, Wang M, Lin X, Yin DC, Huang WD (2002) J Power Sources 108:113
5. Kalyani P, Kalaiselvi N, Muniyandi N (2002) Mater Chem Phys 77:662
6. Bhuvaneswari MS, Selvasekarapandian S, Kamishima O, Kawamura J, Hattori T (2005) J Power Sources 139:279
7. Lee SJ, Lee HY, Ha TS, Baik HK, Lee SM (2002) Electrochem Solid-State Lett 5:A138
8. Reddy MV, Wannek C, Pecquenard B, Vinatier P, Levasseur A (2003) J Power Sources 119–121:101
9. Tang SB, Xia H, Lai MO, Lu L (2006) J Power Sources 159:685
10. Reddy MV, Pecquenard B, Vinatier P, Levasseur A (2006) J Phy Chem B 110:4301
11. Tang SB, Xia H, Lai MO, Lu L (2006) J Electrochem Soc 153:A875
12. Reddy MV, Pecquenard B, Vinatier P, Levasseur A (2007) J Power Sources 163:1040
13. Denis S, Baudrin E, Orsini F, Ourvard G, Touboul M, Tarascon JM (1999) J Power Sources 81–82:79
14. Park SH, Park KS, Sun YK, Nahm KS, Lee YS, Yoshio M (2001) Electrochim Acta 46:1215
15. Chan HW, Duh JG, Sheen SR (2003) J Power Sources 115:110
16. Prabaharan SRS, Michael MS, Ikuta H, Uchimoto Y, Wakihara M (2004) Solid State Ionics 172:39
17. Chen CH, Kelder EM, Jak MJG, Schoonman J (1996) Solid State Ionics 86–88:1301
18. Kolenko YuV, Maximov VD, Burukhin AA, Muhanov VA, Churagulov BR (2003) Mater Sci Eng C 23:1033
19. Sun JT, Xie W, Yuan LJ, Zhang KL, Wang QY (1999) Mater Sci Eng B 64:157
20. Liu HW, Zhang KL (2004) Mater Lett 58:3049
21. Cao XY, Zhan H, Xie JG, Zhou YH (2006) Mater Lett 60:435
22. Wang CW, Ma XL, Li ZC, Liang YG, Sun JT, Zhou YH (2006) Electrochem Commun 8:289

23. Liu QY, Liu HW, Zhou XW, Cong CJ, Zhang KL (2005) Solid State Ionics 176:1549
24. Yuan ZY, Huang F, Sun JT, Zhou YH (2002) Chem Lett 3:408
25. Li ZC, Wang CW, Ma XL, Yuan LJ, Sun JT (2005) Mater Chem Phys 91:36
26. Liang YG, Yang SJ, Yi ZH, Sun JT, Zhou YH (2005) J Mater Sci 40:5553
27. Chitra S, Kalyani P, Yebka B, Mohan T, Haro-Poniatowski E, Gangadharan R, Julien C (2000) Mater Chem Phys 65:32
28. Subramania A, Angayarkanni N, Karthick SN, Vasudevan T (2006) Mater Lett 60:3023
29. Reddy MV, Wannek C, Pecquenard B, Vinatier P, Levasseur A (2008) Mater Res Bull 43:1519
30. Thongtem T, Kaowphong S, Thongtem S (2007) Ceram Int 33:1449