Preparation of Nanostructured $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ Glass-Ceramics by a Citrate Process

Xiaoxiong Xu, Zhaoyin Wen,* Zhonghua Gu, Xiaohe Xu, and Zuxiang Lin
Shanghai Insitute of Ceramics, Chinese Academy of Sciences,
1295 Ding-Xi Road, Shanghai 200050, P. R. China

(Received December 27, 2004; CL-041602)

A $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ gel was successfully prepared by a citrate process and converted into nanostructured and highly Li^+-conductive $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ glass-ceramics through heat treatment at 700–900 °C. The experimental results indicated that the Li-ion conductivity of the glass-ceramics depended greatly on the grain size of the conducting phase in the specimens. An excellent room-temperature conductivity as high as $1.36 \times 10^{-3}\,S\,cm^{-1}$ was obtained, which is one of the highest lithium-ion conductivity for solid electrolytes.

Lithium-ion batteries have a safety issue caused by flammable organic solvents used in their electrolytes. The solvent-free all-solid-state rechargeable lithium battery has been therefore considered as one of the safest and most suitable candidates for use in large-scale battery system.[1,2] Glass-ceramics are a category of materials exhibiting great potential as solid electrolytes. Compared to sintered polycrystalline materials, they can be made into desired shape and size more easily, display good chemical stability and high conductivity.[3–5] The $LiTi_2(PO_4)_3$ glass-ceramics with NASICON-type structure were reported to exhibit ionic conductivity of $10^{-6}\,S\,cm^{-1}$ at room temperature and an enhancement of more than two orders of magnitude in conductivity was realized in the Al^{3+}-substituted $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ system for $x = 0.4$.[8] Because of their high ionic conductivity, the glass-ceramics of $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ are of great significance in practical applications and fundamental investigations.

So far, the $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$-based glasses were prepared by conventional melt-quenching methods which required very high temperature up to 1500 °C. Furthermore, such melting process generally leads to obvious lithium loss. Sol–gel process is a well-known technique to synthesize multicomponent oxides at lower temperature. It offers several advantages over the conventional melt-quenching method in preparing amorphous powders such as highly controlled stoichiometry and morphology.[7,8] In this work, a citrate process will be applied to synthesize $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ nanopowders. Furthermore, nanostructured glass-ceramics of this composition will be obtained by heat treatment at a temperature much lower than that for conventional solid-state reaction method.

Reagent-grade $Ti(OC_4H_9)_4$, $LiNO_3{\cdot}H_2O$, $Al(NO_3)_3{\cdot}9H_2O$ (AR) and $NH_4H_2PO_4$, were used as starting materials with citric acid as the polymer precursor and deionized water as the solvent. The molar ratio of Li:Al:Ti: citric acid was 7:2:8:17. Figure 1 showed the detailed procedure of the synthesis for the $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ dried gel.

Thermal analysis (DTA-TG) was performed at a heating rate of $10\,K\,min^{-1}$ in the range of 30–1000 °C under N_2 atmosphere. An abrupt weight loss of about 57% in the temperature range from 200 to 500 °C was found, which was due to the decomposition of the polymer to CO_2 and H_2O. No further weight loss up to 1000 °C was observed. An exothermic peak around 650 °C was ascribed to the crystallization of the $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ amorphous powders. On the basis of the DTA-TG data, thermal treatment was done in two steps. Firstly, the dried gel was heat-treated at 500 °C for 4 h to obtain an amorphous powder, and then further heat-treated at 700–900 °C for another 2 h in air to prepare the $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ crystalline powders.

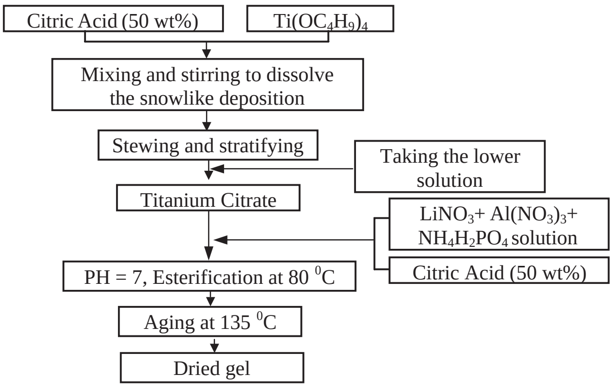

Figure 1. Flow chart for preparing dried gel of $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ by a citrate process.

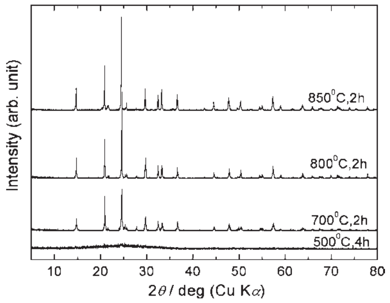

Figure 2. XRD patterns of the powders prepared by heat-treating the precursor at different temperatures.

Crystalline phases were identified by X-ray diffraction (XRD) analysis at room temperature with Cu Kα radiation as shown in Figure 2. It could be seen that the powder heat-treated at 500 °C for 4 h was amorphous, suggesting that homogeneous glassy powders were obtained using gels as starting materials as described in ref 9. The products by the crystallization of the glassy powders made from gels can also be expressed as glass-

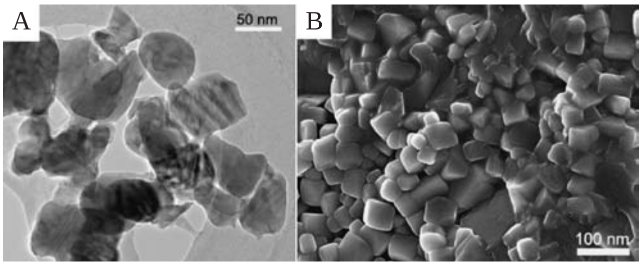

Figure 3. (A) TEM image showing the particle size of the powders heat-treated at 800 °C for 2 h. (B) FESEM micrograph of $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ glass ceramics heat-treated at 900 °C for 6 h.

ceramics, although they are different from the glass made by high-temperature melting process of oxides.[9] Diffraction peaks arising from the $LiTi_2(PO_4)_3$-type phase were observed in the specimens treated at temperatures higher than the crystallization point for 2 h in air, and no impure peaks were found as Al^{3+} ions replaced Ti^{4+} ions, indicating that only the crystalline NASICON-type phase was formed. It was also seen that there was no obvious difference of XRD patterns for the specimens treated at 700–900 °C and the peaks became gradually sharpen with increasing treating temperature, designating gradual growth of the $LiTi_2(PO_4)_3$-type phase.

A transmission electron microscopy (TEM) study was undertaken to highlight the size and the size distribution of the powders as shown in Figure 3A. As seen, the average particle size of the powder heat-treated at 800 °C for 2 h was about 50 nm. Dense glass-ceramic pellets (13 mm in diameter) were obtained by cold pressing (6 MPa) the amorphous powders, and then sintering at different temperatures for 6 h. Figure 3B showed typical microstructure of $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ glass-ceramics heat-treated at 900 °C for 6 h by means of field emission scanning electron microscopy (FESEM). It was clearly seen that the specimen was very dense, and the grains were uniform with average size under 100 nm. Density of the glass-ceramics was determined by the Archimedes method with water as the immersion medium. The relative density of the disc heat-treated at 900 °C for 6 h was about 96%.

Complex impedance measurements were carried out on a Solartron 1260 impedance analyzer over the frequency range of 10^{-1}–10^6 Hz. Figure 4 showed the room-temperature complex impedance plots of the $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ glass-ceramics discs heat-treated at different temperatures for 6 h. From the plots, the total resistance (R_t) and the bulk resistance (R_b) of the sample were obtained from the right and left intercepts of the semicircle with the real axis in the plots, respectively. The R_b and R_t were used to calculate the corresponding conductivity values of σ_b (bulk conductivity) and σ_t (total conductivity), respectively. As seen, both R_b and R_t decreased with increasing treating temperature when the treating temperature was less than 900 °C, but further increase in treating temperature to 950 °C led to increase of R_t, while R_b was nearly kept constant. The increase in R_t was probably due to the appearance of pores and cracks in intergranular region, which caused the decrease in the total lithium-ion conductivity of the specimens. The maximum lithium-ion conductivity of 1.36×10^{-3} S cm^{-1} was obtained at room temperature for the specimen treated at 900 °C for 6 h. The plots of log (σT) against $1000/T$ were found to be linear and fit the Arrhenius equation. In the testing range of 18–300 °C, no break was observed on the Arrhenius plot. From the lines, the activation energy (E_a) could be obtained. As calculated, the E_a increased with the increased treating temperature from 700 °C to 900 °C, further increase of treating temperature to 950 °C increased the E_a value unexpectedly. A minimal E_a value of 0.28 eV was obtained for the specimen treated at 900 °C, which might be the reason why the glass-ceramics treated at 900 °C demonstrated the highest room-temperature conductivity.

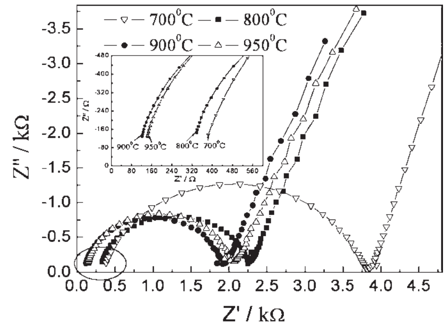

Figure 4. Room-temperature complex impedance plots for the $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ glass-ceramics treated at different temperatures for 6 h.

In conclusion, nanostructured $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ glass-ceramics were obtained for the first time by heat-treating its precursor powders which were successfully synthesized by a citrate process. The specimen exhibited a high lithium-ion conductivity of 1.36×10^{-3} S cm^{-1} at room temperature, which was about twice of the sintered ceramics in the $LiTi_2(PO_4)_3$ system obtained by normal solid-state reactions.[10] The enhancement of the conductivity could be ascribed to the nanostructure of the conducting phase in the glass-ceramics, which has been expected previously.[6]

We are thankful for financial support from National Natural Science Foundation of China (No. 20071033).

References

1 T. Iwahori, Y. Ozaki, A. Funahashi, H. Momose, I. Mitsuishi, S. Shiraga, S. Yoshitake, and H. Awata, *J. Power Sources*, **81–82**, 872 (1999).
2 J. B. Bates, N. J. Dudney, B. Neudecker, A. Ueda, and C. D. Evans, *Solid State Ionics*, **135**, 33 (2000).
3 H. Hosono and Y. Abe, *Solid State Ionics*, **44**, 293 (1991).
4 X. X. Xu, Z. Y. Wen, Z. H. Gu, Z. X. Lin, and X. H. Xu, *Solid State Ionics*, **171**, 207 (2004).
5 X. Xu, Z. Wen, Z. Gu, X. Xu, and Z. Lin, *Electrochem. Commun.*, **6**, 1233 (2004).
6 J. Fu, *Solid State Ionics*, **96**, 195 (1997).
7 M. Vijayakumar, Y. Inaguma, W. Mashiko, M. P. Crosnier-Lopez, and C. Bohnke, *Chem. Mater.*, **16**, 2719 (2004).
8 M. Kakihana, M. Tada, M. Shiro, V. Petrykin, M. Osada, and Y. Nakamura, *Inorg. Chem.*, **40**, 891 (2001).
9 S. P. Mukherjee, *J. Non-Cryst. Solids*, **42**, 477 (1980).
10 H. Aono, E. Sugimoto, Y. Sadaoka, N. Imanaka, and G. Adachi, *Acc. Chem. Res.*, **27**, 265 (1994).

Published on the web (Advance View) March 5, 2005; DOI 10.1246/cl.2005.512