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Preparation of $Li_x Ca_{1-x} TiO_3$ solid electrolytes by the sol-gel method

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Abstract

Solid electrolytes based on lithium doped CaTiO₃, Li_xCa_{1-x}TiO₃ (x = 0-0.5) were prepared by the sol-gel method in an ethanol and water mixture medium. Phase identification and morphology observation of the products were carried out by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The results show that the Li_xCa_{1-x}TiO₃ powders sintered above 700 °C are of cubic perovskite structure and the mean size of Li_xCa_{1-x}TiO₃ powders is about 80 nm. A study of ionic conductivity by AC impedance implies that the conductivity of Li_xCa_{1-x}TiO₃ increases with the increase of substituted Li⁺ ions and reaches a maximum value of 4.53×10^{-4} S cm⁻¹ at x = 0.1, and then decreases for x > 0.1.

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Solid electrolytes have been widely used in sensors, batteries, chemical processing and combustion control, because of their superior ionic conductivities, implying vast using prospect in energy, metallurgy, chemical and environmental fields [1-5]. Perovskite-type solid electrolyte is one of the important solid electrolytes. ABO₃-type perovskite is a cubic crystal system at high temperature; while the temperature decreases, structure distortions will take place and the symmetry of the cubic crystal system will be changed [6]. There exist three distortions in different perovskite-type structures: a cubic crystal system turning to a tetragonal crystal system, a cubic crystal system turning to an orthorhombic crystal system and a cubic crystal system turning to a trigonal crystal system [7]. Some perovskite crystals have a spontaneous dipole moment because of these distortions, which can be used to prepare ferroelectric or antiferroelectric materials [8]. CaTiO₃ is an ABO₃-type perovskite, which is an orthorhombic system below 600 °C, but it will turn into a cubic system at higher temperature. In the cubic system, the doping of metal

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0038-1098/\$ - see front matter © 2007 Elsevier Ltd. All rights reserved. doi:10.1016/j.ssc.2007.04.018 cations with different valances can induce the distortions of the oxygen stoichiometric ratio and crystal lattice to form nonstoichiometric compounds easily. Due to the flowability of high concentrated oxygen ions, the electric and magnetic properties can be controlled by changing the amount of order oxygen vacancies [9].

Based mainly on an inorganic polymerization reaction, the sol-gel method is a chemical synthesis method initially used for the preparation of inorganic materials such as glasses and ceramics [10]. In general, metal alkoxides or metal salts are used as raw materials in the sol-gel method, then a solution consisting of metal alkoxides is changed into a wet gel by hydrolysis and condensation; finally, the glasses or ceramics are obtained from the wet gel by heat treatment at low temperature. The sol-gel method with the advantages of a low calcination temperature, shorter heat treatment time and homogeneities of the resulting powder can sufficiently overcome the drawbacks of the solid-state method, which has been introduced to prepare some solid electrolytes [11,12]. In this work, we prepared series of $Li_x Ca_{1-x} TiO_3$ solid electrolytes by a sol-gel method and investigated the phase, morphology and ionic conductivity of $Li_rCa_{1-r}TiO_3$ solid electrolytes.



Fig. 1. XRD patterns of $\rm Li_{0.5}Ca_{0.5}TiO_3$ powders sintered at different temperatures.

1. Experimental

A stoichiometric amount of $Ca(NO_3)_2 \cdot 4H_2O$ and $LiNO_3$ was dissolved in deionized water, then $Ti(OC_4H_9)_4$, absolute alcohol and acetylacetone (volume ratio employed was $Ti(OC_4H_9)_4$:absolute alcohol:acetylacetone = 4:4:1) were consecutively dripped into the mixture under constant stirring. After reaction at 40 °C for 4 h, $Li_xCa_{1-x}TiO_3$ sol was obtained. Then the sol was kept in an oven at 80 °C for 7 days to get the $Li_xCa_{1-x}TiO_3$ dried gel. After the dried gel was sintered in air at 600 °C, 700 °C and 800 °C for 2 h respectively, the needed powders were obtained. Finally, the powders were pressed into pellets at a pressure of 30 MPa and sintered in air at 700 °C for 6 h. To measure the ionic conductivity of pellets, the silver paste conductive adhesive was coated on the surfaces.

X-ray diffraction (XRD) analysis was measured with a Japanese $D/\max -\gamma B$ rotating diffractometer. with the CuK_{α} line ($\lambda = 0.15406$ nm), and the diffractograms were scanned in 2θ from 10° to 70° at a rate of 6°/min. Transmission electron microscopy (TEM) photographs were taken on a JEM-100SX transmission electron microscope. The measurement of AC impedance was performed with an electrochemical workstation CHI660B at a frequency range of 1–10⁵ Hz at room temperature.

2. Results and discussion

2.1. Phase of $Li_x Ca_{1-x} TiO_3$

The XRD patterns of $Li_{0.5}Ca_{0.5}TiO_3$ powders sintered at different temperatures are shown in Fig. 1. The patterns were indexed on the basis of a distorted perovskite structure with cubic symmetry (space group Fd3m). Fig. 1 is the XRD patterns of $Li_{0.5}Ca_{0.5}TiO_3$ powders sintered at different temperatures. No typical diffraction peaks of perovskite structure occur at 600 °C, but when the sintering temperature increases to 700 °C, the appearance and evolution of the 111, 311, 400 and 222 typical short-range supercell peaks indicate that the $Li_{0.5}Ca_{0.5}TiO_3$ powders have crystallized well and formed a cubic perovskite structure. Moreover, no significant difference is found between the XRD patterns at 700 °C and 800 °C, implying that the $Li_{0.5}Ca_{0.5}TiO_3$ powders conduct the transition from amorphous to crystalline at 600 °C–700 °C.

The mean size of the prepared powders was calculated to be about 80 nm based on the Scherrer formula.



Fig. 2. XRD patterns of $\text{Li}_x \text{Ca}_{1-x} \text{TiO}_3$ (x = 0-0.5) sintered at 700 °C.

Table 1 Phase symmetry, lattice parameters of the system $Li_xCa_{1-x}TiO_3$

X (mol)	Phase symmetry	<i>a</i> (Å)
0	Cubic	8.372
0.05	Cubic	8.362
0.1	Cubic	8.361
0.2	Cubic	8.358
0.3	Cubic	8.353
0.4	Cubic	8.345
0.5	Cubic	8.342

$$D = 0.89\lambda/B\cos\theta \tag{1}$$

where λ is the wavelength of X-ray, θ is the diffraction angle, $B = \sqrt{Bm^2 - Bs^2}$ is the corrected halfwidth of the observed halfwidth: *Bm* is that of the (111) reflection in samples and *Bs* is that of the (111) reflection in a standard sample.

Fig. 2 is the XRD patterns of $\text{Li}_x \text{Ca}_{1-x}\text{TiO}_3$ (x = 0-0.5). It can be found that all these XRD patterns are similar to that of CaTiO₃. As illustrated in Table 1, the calculated lattice parameter (cubic 'a') is slightly shorted with the amount of the substituted Li⁺ ions, but not obvious. When Ca²⁺ ions of CaTiO₃ were substituted by Li⁺ ions partially, Li_xCa_{1-x}TiO₃ was formed. Because the amount of Li⁺ ions is not more and the ionic radius of Li⁺ (0.078 nm) is much smaller than that of Ca²⁺ (0.1 nm), this change is not strong enough to distort the CaTiO₃ structure, and Li_xCa_{1-x}TiO₃ remains a cubic perovskite structure similar to CaTiO₃ [13].

2.2. Morphology of $Li_xCa_{1-x}TiO_3$

Fig. 3(a) and (b) are the TEM photographs of $Li_{0.5}Ca_{0.5}TiO_3$ powders sintered at 600 °C and 700 °C respectively. Fig. 3(a) shows that the powders sintered at 600 °C are agglomerated in lump, moreover, the shape of each grain is irregular and the grain boundary is obscure. But when sintered at 700 °C, the powders are mono-dispersed and the mean size of each hexagon grain is about 80 nm shown as Fig. 3(b). These results indicate that the $Li_{0.5}Ca_{0.5}TiO_3$ powders are amorphous at 600 °C, but have crystallized well at 700 °C. This fact supports the conclusion drawn from XRD analysis.



Fig. 3. TEM photographs of $Li_{0.5}Ca_{0.5}TiO_3$ powders sintered at 600 $^\circ C$ (a) and 700 $^\circ C$ (b).

2.3. Ionic conductivity of $Li_xCa_{1-x}TiO_3$

In principle, a semicircle between the origin and the intercept would be observed if a much higher frequency was used in the experiment, but the high-frequency limit used in this study (100 kHz is the upper limit for the electrochemical workstation CHI660B) is not sufficient and caused the incomplete semicircle [14]. Fig. 4 is the AC impedance spectra of $\text{Li}_x \text{Ca}_{1-x}\text{TiO}_3$ pellets sintered at 700 °C. Each spectrum consists of an incomplete semicircle and an inclined line shown as Fig. 4. Based on the intercept of each inclined line in Fig. 4 and Eq. (2), the ionic conductivities of CaTiO₃, Li_{0.05}Ca_{0.95}TiO₃, Li_{0.1}Ca_{0.9}TiO₃, Li_{0.2}Ca_{0.8}TiO₃ and Li_{0.3}Ca_{0.7}TiO₃ pellets can be estimated to be 2.3 × 10⁻⁵ S cm⁻¹, 4.66 × 10⁻⁵ S cm⁻¹, 4.53 × 10⁻⁴ S cm⁻¹, 4.42 × 10⁻⁴ S cm⁻¹ and 2.89 × 10⁻⁴ S cm⁻¹ respectively.

$$\sigma = L/R \cdot S \tag{2}$$

where *L* is the thickness of the pellet, *S* is the area of the pellet, and *R* is the resistance of the sample. These datum indicate that the $\text{Li}_x \text{Ca}_{1-x} \text{TiO}_3$ ionic conductivity increases with the increase of substituted Li^+ ions, reaches a maximum value at x = 0.1, and then decreases for x > 0.1. When the oxygen vacancies were substituted by Li^+ ions, the ionic conductivities of $\text{Li}_x \text{Ca}_{1-x} \text{TiO}_3$ solid electrolytes were significantly improved, but when the amount of the substituted Li^+ ions exceeded a certain value, the interactions among dopant cations (Li^+) and higher concentrations of oxygen vacancies caused the aggregating of oxygen vacancies, so the effective oxygen vacancies concentration did not increase and the ionic conductivity was lower for x > 0.1.



Fig. 4. AC impedance curves of pellets, (a) x = 0, (b) x = 0.05, (c) x = 0.1, (d) x = 0.2, (e) x = 0.3.

3. Conclusions

Solid electrolytes $\text{Li}_x \text{Ca}_{1-x} \text{TiO}_3$ were prepared by the sol-gel method in an ethanol and water mixture medium. When sintered over 700 °C, the $\text{Li}_x \text{Ca}_{1-x} \text{TiO}_3$ (x = 0-0.5) powders are of cubic perovskite structure and the mean size of $\text{Li}_x \text{Ca}_{1-x} \text{TiO}_3$ powders is about 80 nm. The ionic conductivity of $\text{Li}_x \text{Ca}_{1-x} \text{TiO}_3$ increases with the increase of substituted Li^+ ions and reaches a maximum value of $4.53 \times 10^{-4} \text{ S cm}^{-1}$ at x = 0.1, and then decreases for x > 0.1.

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