

Proceeding paper

Synthesis and Ionic Conductivity of Lithium-Titanium Phosphate with NASICON-Type Structure Doping with Zirconium and Aluminum [†]

Anastasia Bocharova ¹, Irina Stenina ^{1,*}

¹ Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, Russia; ab.bocharova@mail.ru

* Correspondence: stenina@igic.ras.ru

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Abstract: In this work, new solid electrolytes $\text{Li}_{1+y}\text{Ti}_{2-x-y}\text{Zr}_x\text{Al}_y(\text{PO}_4)_3$ ($0 \leq x \leq 0.2$, $0 \leq y \leq 0.2$) were prepared by the sol-gel and solid-state methods (sintering temperatures 800–1000 °C). The prepared materials were characterized by X-ray powder diffraction and scanning electron microscopy. Their conductivity was investigated by impedance spectroscopy in the temperature range of 25–200 °C. The activation energies of Li^+ transfer were calculated. The $\text{Li}_{1.2}\text{Ti}_{1.7}\text{Zr}_{0.1}\text{Al}_{0.2}(\text{PO}_4)_3$ material prepared by solid state reaction exhibits the highest conductivity at 25 °C (6.2×10^{-4} S/cm).

Keywords: solid electrolyte; NASICON-type; lithium-ion conductor

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1. Introduction

Today, due to the growing demand for mobile power sources, lithium-ion batteries are becoming increasingly important because of their high-power density and quite low self-discharge. However, there is still a problem with their application caused by the flammability and insufficient electrochemical stability of the liquid electrolytes in most commercial batteries. In this regard, it is necessary to develop solid electrolytes with good stability and high ionic conductivity. Among all types of solid electrolytes with lithium conductivity, compounds with the NASICON-type structure are the most promising. However, a significant disadvantage of these materials is their insufficiently high ionic conductivity compared to liquid electrolytes. To increase the bulk conductivity, point defects can be created in their structure by isovalent (Zr^{4+}) and heterovalent (Al^{3+}) doping. This approach can significantly increase the bulk conductivity of lithium-titanium phosphate by simultaneously changing the channel size and introducing additional Li^+ ions. In this work, $\text{Li}_{1+y}\text{Ti}_{2-x-y}\text{Zr}_x\text{Al}_y(\text{PO}_4)_3$ materials ($0 \leq x \leq 0.2$, $0 \leq y \leq 0.2$) were synthesized by both sol-gel (SG) and solid-state (SS) methods by varying the final annealing temperature to determine the optimal synthesis method.

2. Methods

2.1. Materials and Reagents

The following raw materials were used for the synthesis of $\text{Li}_{1+y}\text{Ti}_{2-x-y}\text{Zr}_x\text{Al}_y(\text{PO}_4)_3$ ($0 \leq x \leq 0.2$, $0 \leq y \leq 0.2$): Li_2CO_3 (Sigma-Aldrich, 99%), $(\text{C}_4\text{H}_9\text{O})_4\text{Ti}$ (Alfa Aesar, 99%) (or TiO_2 (Chimmed, 98%) in case of SS), $\text{NH}_4\text{H}_2\text{PO}_4$ (Sigma-Aldrich, 99%), $(\text{C}_3\text{H}_7\text{O})_4\text{Zr}$ (Sigma-Aldrich, 70 wt.%) (or $\text{Zr}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ (Sigma-Aldrich, 99.99%) in case of SS), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sigma-Aldrich, 99.997%).

2.2. Methods

In both synthesis methods, the initial reagents were mixed in a stoichiometric ratio. In the case of sol-gel method, a water-ethanol mixture was used and citric acid was added as a chelating agent. Figures 1 and 2 show the $\text{Li}_{1+y}\text{Ti}_{2-x-y}\text{Zr}_x\text{Al}_y(\text{PO}_4)_3$ synthesis by sol-gel and solid-state method, respectively.



Figure 1. Scheme of synthesis the $\text{Li}_{1+y}\text{Ti}_{2-x-y}\text{Zr}_x\text{Al}_y(\text{PO}_4)_3$ materials by sol-gel method.



Figure 2. Scheme of synthesis the $\text{Li}_{1+y}\text{Ti}_{2-x-y}\text{Zr}_x\text{Al}_y(\text{PO}_4)_3$ materials by solid-state method.

The X-ray diffraction (XRD) patterns were collected using Rigaku D/MAX 2200 (Cu $K\alpha$ -radiation). The ion conductivity of the sintered pellets with silver electrodes was measured by impedance spectroscopy using an Elins Z1500 PRO impedancemeter with AC amplitude of 80 mV from 10 Hz to 2×10^6 MHz in the temperature range of 25–200 °C. Scanning electron microscopy (SEM) (Tescan Amber GMH (Czech Republic)) was used to analyze the morphology of samples.

3. Results and Discussion

3.1. XRD

Figures 3 and 4 present X-ray diffraction patterns of $\text{Li}_{1+y}\text{Ti}_{2-x-y}\text{Zr}_x\text{Al}_y(\text{PO}_4)_3$ ($0 \leq x \leq 0.2$, $0 \leq y \leq 0.2$) prepared by sol-gel and solid-state method.

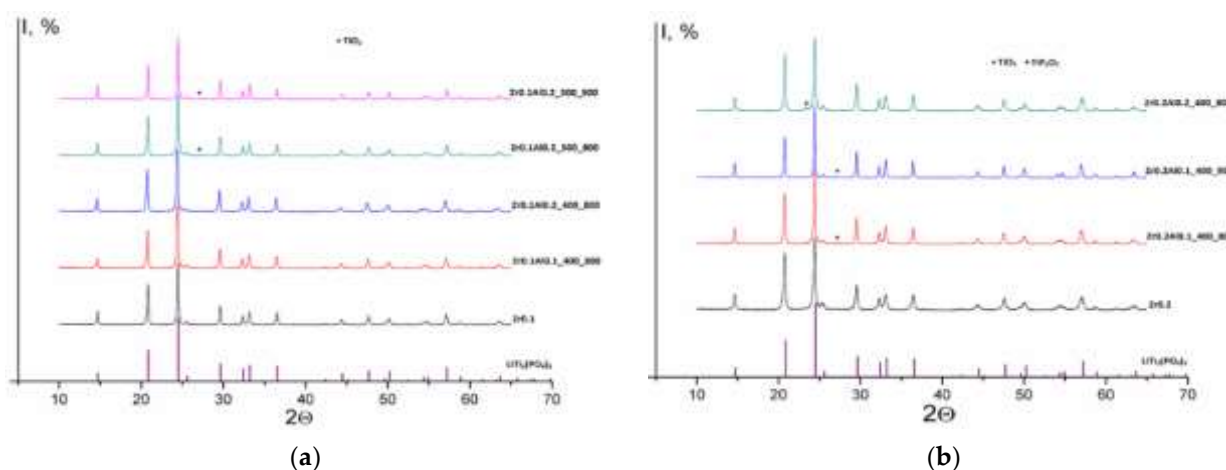


Figure 3. X-ray diffraction patterns of $\text{Li}_{1+y}\text{Ti}_{1.9-y}\text{Zr}_{0.1}\text{Al}_y(\text{PO}_4)_3$ (a) and $\text{Li}_{1+y}\text{Ti}_{1.8-y}\text{Zr}_{0.2}\text{Al}_y(\text{PO}_4)_3$ ($y = 0-0.2$) (b) prepared by sol-gel method.

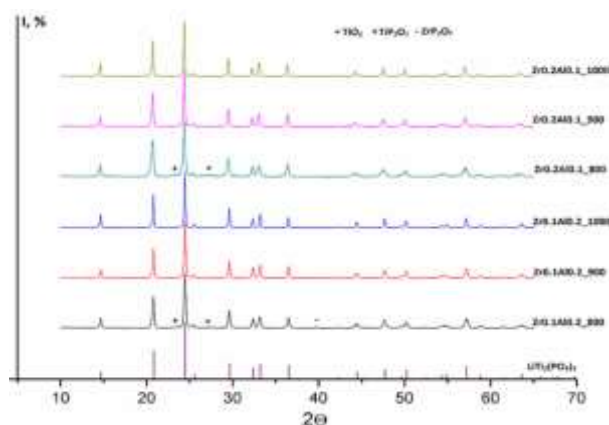


Figure 4. X-ray diffraction patterns of $\text{Li}_{1+y}\text{Ti}_{2-x-y}\text{Zr}_x\text{Al}_z(\text{PO}_4)_3$ ($x = 0-0.2$, $y = 0-0.2$) prepared by solid-state reaction.

The diffraction peaks are similar for all samples and correspond to lithium-titanium phosphate (PDF-2, card #35-0754). Some samples have TiO_2 , TiP_2O_7 and ZrP_2O_7 impurities, the presence of which can negatively affect the ionic conductivity.

3.2. SEM

Scanning electron microscopy images are shown in Figures 5 and 6.

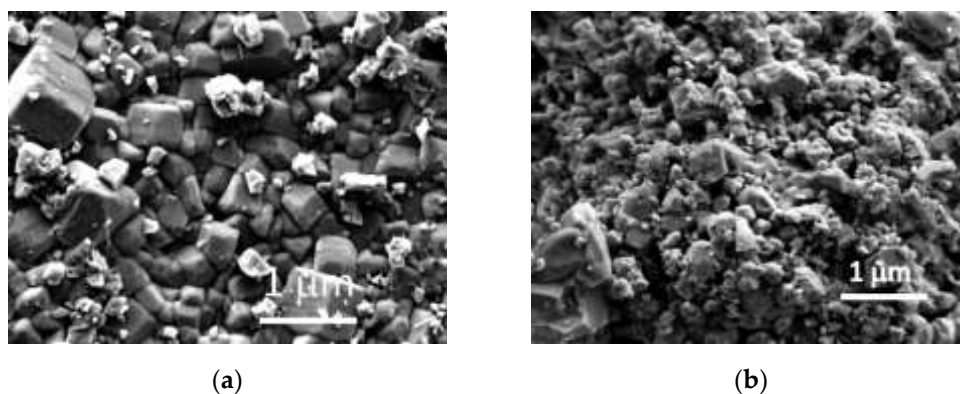


Figure 5. SEM images of $\text{Li}_{1.2}\text{Ti}_{1.7}\text{Zr}_{0.1}\text{Al}_{0.2}(\text{PO}_4)_3$ (a) and $\text{Li}_{1.2}\text{Ti}_{1.6}\text{Zr}_{0.2}\text{Al}_{0.2}(\text{PO}_4)_3$ (b) prepared by sol-gel method at 800 °C.

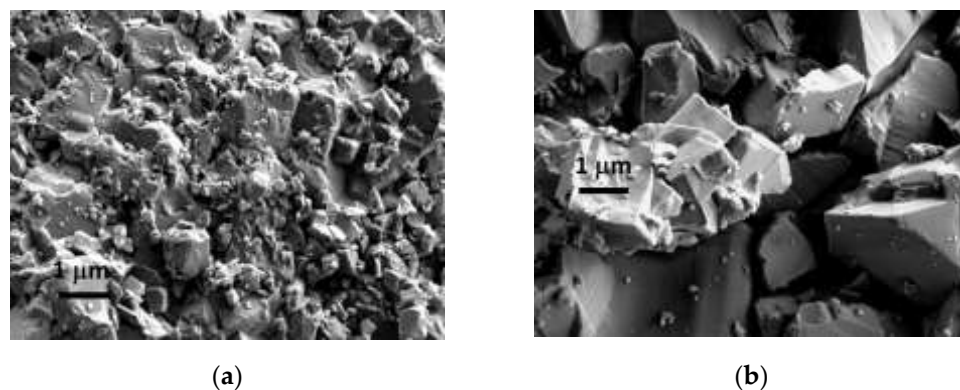


Figure 6. SEM images of $\text{Li}_{1.2}\text{Ti}_{1.7}\text{Zr}_{0.1}\text{Al}_{0.2}(\text{PO}_4)_3$ (a) and $\text{Li}_{1.2}\text{Ti}_{1.7}\text{Zr}_{0.1}\text{Al}_{0.2}(\text{PO}_4)_3$ (b) prepared by solid-state method at 900 °C and 1000 °C, respectively.

The SEM images demonstrate that the solid-state method results in a more sintered ceramics with a larger particle size, which in turn agrees with the density of the produced

ceramics. Thus, for samples prepared by the sol-gel method, its values are in the range of 1.87–2.28 g/cm³, while for materials prepared by the solid-state method ceramics density is in the range of 2.13–2.75 g/cm³.

3.3. Ionic Conductivity

Temperature dependences of ionic conductivity of the $\text{Li}_{1+y}\text{Ti}_{2-x-y}\text{Zr}_x\text{Al}_y(\text{PO}_4)_3$ ($0 \leq x \leq 0.2$, $0 \leq y \leq 0.2$) materials prepared by sol-gel and solid-state methods are shown in Figure 7 and Figure 8, respectively.

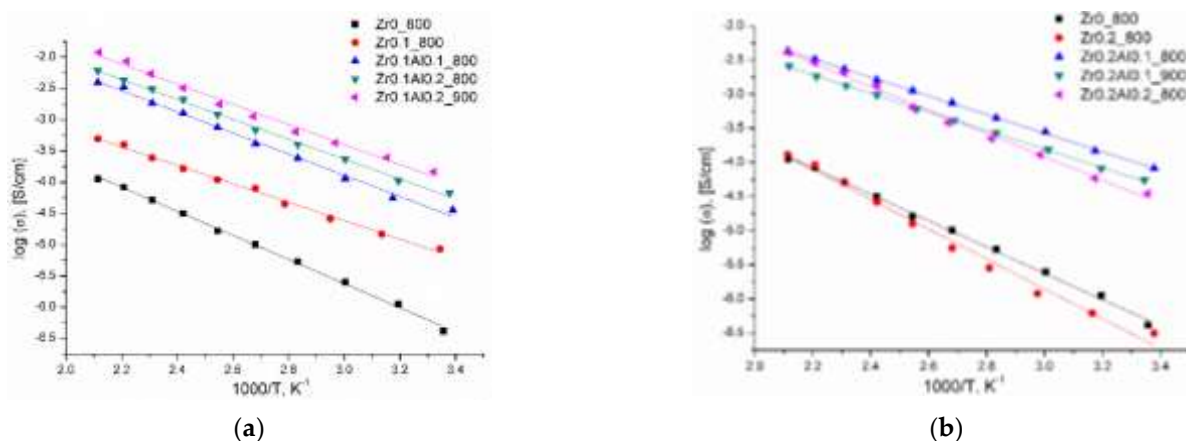


Figure 7. Plots of ionic conductivity vs. temperature of $\text{Li}_{1.2}\text{Ti}_{1.7}\text{Zr}_{0.1}\text{Al}_{0.2}(\text{PO}_4)_3$ (a) and $\text{Li}_{1.2}\text{Ti}_{1.6}\text{Zr}_{0.2}\text{Al}_{0.2}(\text{PO}_4)_3$ (b) prepared by sol-gel method.

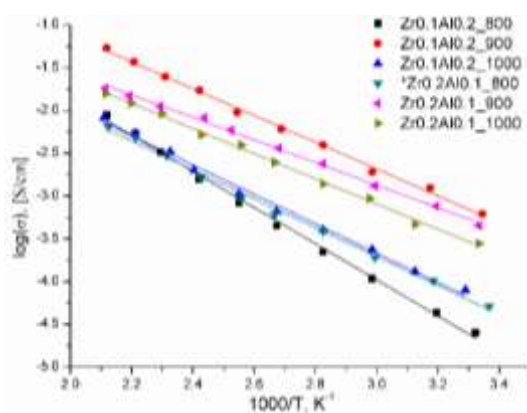


Figure 8. Plots of ionic conductivity vs temperature of $\text{Li}_{1+y}\text{Ti}_{2-x-y}\text{Zr}_x\text{Al}_y(\text{PO}_4)_3$, $x = 0-0.2$, $y = 0-0.2$ prepared by solid-state method.

Ion conductivity increases significantly with the substitution of 5% titanium by zirconium in $\text{LiTi}_2(\text{PO}_4)_3$. Increasing the zirconium content has the opposite effect, and the conductivity of the resulting material becomes like that of the pristine lithium titanium phosphate. A similar effect was reported elsewhere [1,2]. In all cases, the additional introduction of aluminum leads to an increase in conductivity. The optimal composition with the highest lithium conductivity was determined ($\text{Li}_{1.2}\text{Ti}_{1.7}\text{Zr}_{0.1}\text{Al}_{0.2}(\text{PO}_4)_3$ — 6.2×10^{-4} at 25 °C). The activation energies of conductivity of the obtained materials are in the range of 30–49 kJ/mol.

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