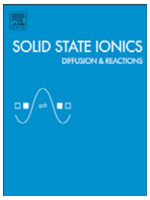
Solid State Ionics 183 (2011) 26–31

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi



Proton conduction in acceptor doped SnP_2O_7

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ARTICLE INFO

Article history:
Received 12 October 2009
Received in revised form 16 November 2010
Accepted 24 December 2010
Available online 15 January 2011

Keywords:
Proton conduction
Fuel cells
Tin pyrophosphate
Impedance spectroscopy
Nuclear magnetic resonance
Transference number

ABSTRACT

Undoped and acceptor doped tin pyrophosphate with composition $D_{0.1}Sn_{0.9}P_2O_{7-\delta}$ (D = In, Ga, Zn, Sc, and Mg) were synthesized by the conventional solid state reaction method and sintered to obtain well densified pellets (>90% relative density). The conductivity of all the synthesized materials was measured in unhumidified atmosphere in the temperature range 300 °C–600 °C using electrochemical impedance spectroscopy (EIS). The conductivity of acceptor doped SnP_2O_7 was found to be significantly higher than undoped SnP_2O_7 for all the dopants. Proton transference number measurements indicated that the charge transport in acceptor doped SnP_2O_7 was mostly protonic. Within the dopants analyzed, $Zn_{0.1}Sn_{0.9}P_2O_{7-\delta}$ showed the highest conductivity of 2.84×10^{-6} S/cm at 600 °C. This value is several orders of magnitude lower than previously reported for doped tin pyrophosphate compounds but it is consistent with a recent publication. The reason for the discrepancy was investigated and a possible explanation has been proposed based on results obtained from ^{31}P MAS–NMR spectroscopy as follows. It was observed that the as-calcined powder of doped SnP_2O_7 contained a significant fraction of leftover phosphoric acid from synthesis procedure. This phosphoric acid is likely to be responsible for the high conductivity values for acceptor doped SnP_2O_7 previously reported by other research groups.

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1. Introduction

Protonic conduction has been shown to occur in many different types of materials containing structural protons such as $CsHSO_4$, $CsHSeO_4$, and $Cs_5H_3(SO_4)_4$, as well as in materials which do not have structural protons such as $Ba_3Ce(PO_4)_3$, Sr doped $LaPO_4$, Eu doped $SrCeO_3$, and Yb doped $BaCeO_3$ [1–9]. In the latter type, acceptor doping leads to the formation of charge compensating oxygen ion vacancies. These vacancies can be filled up by protonated oxygen ion species ($OH_O^\bullet$) formed by the dissociative absorption of ambient water vapor. These so called protonic defects are responsible for protonic conduction in such materials [10]. Recently, Hibino et al. [11] reported $In_{0.1}Sn_{0.9}P_2O_{7-\delta}$ as a candidate material for proton conducting electrolyte and reported a high conductivity value of 1.95×10^{-1} S/cm at 250 °C. In another recently published article by Tao [12], which involves synthesis by an aqueous route, a much lower conductivity of 8×10^{-9} S/cm (400 °C) is reported for $In_{0.08}Sn_{0.92}P_2O_{7-\delta}$. In the former work, pressed pellets made from as-calcined powder were used for characterization; however in the latter study, samples sintered at 1000 °C were used for conductivity measurement. In the present work, the microstructural and electrochemical impedance spectroscopy (EIS) characterization of undoped and acceptor doped SnP_2O_7 is presented. An attempt has been made to explain the large differences in the reported conductivity values in literature using ^{31}P MAS–NMR (magic angle spinning–nuclear magnetic resonance) spectroscopy.

2. Experimental

2.1. Sample preparation and characterization

Powders of doped SnP_2O_7 were prepared by heating a mixture of SnO_2 (tin (IV) oxide, 99.9%, Alfa Aesar), the oxide of the dopant (D = In, Al, Ga, Zn, and Sc) and H_3PO_4 (phosphoric acid, 85%, ACS) in the proper molar ratio. A 1:3 ratio of (Sn + D):P was used instead of 1:2, to compensate for the loss of phosphoric acid during the heating procedure. To the foregoing mixture 100 mL of deionised water was added and the contents were heated and maintained at a temperature of 300 °C with stirring until a viscous slurry was obtained. The slurry was then calcined in a covered alumina crucible for 2.5 h at 650 °C. The calcined powder obtained was ground and then sieved through 212 μm mesh.

A small part of the powder was removed for X-ray diffraction (XRD) analysis and mixed with tungsten (internal standard), while the rest was uniaxially pressed (200 MPa) into flat cylindrical pellets with diameter of 7 mm and 12 mm with a thickness of about 1–3 mm. The green pellets were placed in a covered alumina crucible with sacrificial powder of the same material and then the crucible was sealed using ceramic cement (EA139-B50, Saint Gobain™). The pellets were then sintered at 1400 °C for 10 h. The relative density of the sintered pellets was above 90%. Undoped SnP_2O_7 pellets had a higher

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0167-2738/$ – see front matter. Published by Elsevier B.V.
doi:10.1016/j.ssi.2010.12.011

relative density of about 95%. Some pellets were crushed and ground for powder XRD analysis.

2.2. Electrochemical impedance spectroscopy

For EIS measurements, the pellets were painted on both sides with platinum paste (CL11-5349, Heraeus) to serve as the electrode. The pellets were then fired at 900 °C for 1 h. Platinum wires (99.9%, 0.127 mm dia.) were attached to the electroded surfaces of the pellet using silver paste (part # 5063, SPI Supplies). For impedance measurements at different temperatures, the sample was placed inside a quartz reactor, itself placed inside a tube furnace. To minimize the errors in temperature measurement an independent thermocouple was placed right next to the sample. EIS measurements were done in unhumidified air in the temperature range of 300 °C–600 °C using the two point probe technique (Solartron SI 1260). Frequency sweeps were taken in the range 32 MHz–0.1 Hz and applied voltage was kept constant at 1000 mV. Fitting of the spectra was carried out using ZView™ software.

2.3. MAS–NMR spectroscopy

The ^{31}P MAS–NMR spectra were acquired at a magnetic field of 9.4 T using a Bruker Avance NMR spectrometer operating at 161.974 MHz. Each sample was ground into a fine powder, loaded into a 4 mm MAS rotor, and spun at approximately 10 kHz. The fully relaxed ^{31}P spectra were acquired at ambient temperature by signal averaging 128 transients using a recycle delay of 4 s and a $\pi/2$ pulse width of 5 μs. A Gaussian line broadening of 50 Hz was applied prior to Fourier transformation. Chemical shifts are referenced to 85 vol.% orthophosphoric acid.

2.4. Transference number measurement

The experimental setup used for transference number measurement is shown in Fig. 1. Platinum paste was applied to both sides of the sample and platinum wires were attached by using silver paste. The sample was attached to the tube using ceramic sealing cement (Cermabond, Aremco). The whole setup was heated to 450 °C and held at that temperature overnight for the seal to form. Gas flow into the reactor was controlled by using mass flow controllers (model # C100L, Sierra instruments). Open circuit voltage was measured by using a multimeter (model # 34410A, Agilent Technologies).

The transference number measurement was carried out by using the following dry hydrogen concentration cell,

$$\left(P^{I}_{H_2}\right), 80\ \mathrm{vol.\%}\ H_2 + \mathrm{balance}\ N_2, \mathrm{Pt}/D_{0.1}Sn_{0.9}P_2O_{7-\delta}/\mathrm{Pt}, 4\ \mathrm{vol.\%}\ H_2$$
$$+\mathrm{balance}N_2, \left(P^{II}_{H_2}\right).$$

The total flow rate was controlled at 100 sccm in both the chambers of the reactor. The theoretical electromotive force can be expressed as,

$$E_{\mathrm{theoretical}} = -\frac{RT}{2F}\ln\left(\frac{P^{I}_{H_2}}{P^{II}_{H_2}}\right). \qquad (1)$$

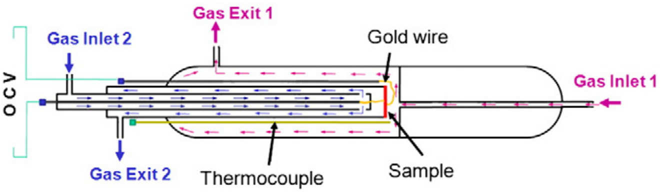

Fig. 1. Diagram of the quartz reactor used for transference number measurement.

If the material is a mixed ionic conductor then the measured value of the electromotive force is less than the theoretical value calculated above. The protonic transference number can be expressed as,

$$t_{\mathrm{ion}} = \frac{E_{\mathrm{measured}}}{E_{\mathrm{theoretical}}}. \qquad (2)$$

3. Results and discussion

3.1. Phase analysis

All the peaks observed for all of the undoped and doped samples (except Ga doped) were indexed according to the compound SnP_2O_7 (JCPDS 29-1352). The crystal structure was originally proposed to be cubic (Pa3), however recent studies by Gover et al. [13] suggest that the room temperature symmetry may be lower than cubic. The peaks in the XRD were labeled assuming cubic symmetry and the unit cell parameter for SnP_2O_7 was determined as 7.9331 ± 0.001 Å (the peak positions were obtained by fitting the data with the Pseudo–Voigt function using Xfit™ software). The effect of sample displacement during XRD data collection was accounted for as described elsewhere [14]. From Fig. 2, no shifting can be observed directly. The calculated lattice parameters are summarized in Table 2 and are in accordance with the expected trend since the Ga^{3+} ion has a smaller ionic radius as compared to Sn^{4+} while the others have higher ionic radii. Impurity peaks corresponding to unreacted SnO_2 were observed in samples that were initially prepared which was due to the loss of phosphoric acid during calcination. This was overcome and phase pure samples were obtained by increasing the (Sn + D):P ratio from 1:2 to 1:3 in the starting mixture.

Sintering in an open crucible resulted in insufficient densification of the pellet which was also accompanied by weight loss. Such weight loss has been previously reported during sintering of other phosphate materials such as GeP_2O_7 and high temperature heat treatment of higher condensed phosphates of lanthanum such as LaP_5O_{14} and La $(PO_3)_3$ [15,16]. In these cases, the weight loss was attributed to the loss of P_2O_5 (due to decomposition) and the issue was overcome by using a sealed vessel. The problems of weight loss and insufficient densification in the current work were avoided when sealed alumina crucibles were used for sintering heat treatments (as described earlier). The typical microstructure of a fractured surface of pellets obtained after sintering is shown in Fig. 3(a). It can be seen from the absence of any visible porosity that good densification was achieved in the pellets. The microstructure is shown at a higher magnification in Fig. 3(b) which shows a number of smooth surfaces as well as step

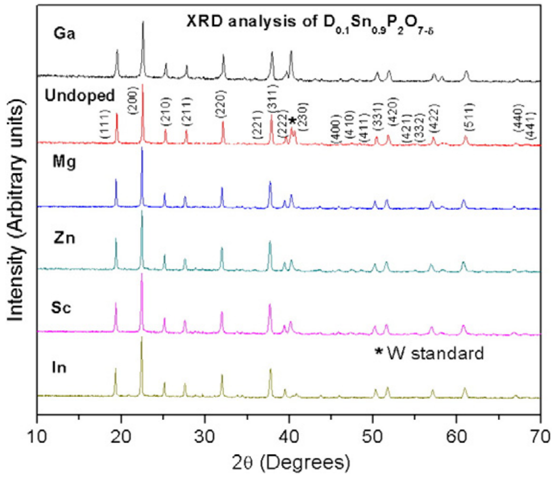

Fig. 2. XRD profiles of crushed as-sintered pellets of doped and undoped SnP_2O_7.