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Bismuth phosphates as intermediate temperature proton conductors: From polycrystalline powders to amorphous glasses

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ABSTRACT

Proton conducting electrolyte materials operational in the intermediate temperature range of 200–400 °C are of special interest for applications in fuel cells and water electrolyzers. Bismuth phosphates in forms of polycrystalline powders and amorphous glasses are synthesized and investigated by scanning electron microscopy, X-ray diffraction, FT-IR, thermogravimetric analysis and AC impedance. Under dry atmosphere the pure crystalline and amorphous phosphates exhibit an intrinsic conductivity of up to 10^{-5} S cm⁻¹ at 250 °C. In the presence of atmospheric humidity the conductivity of both types of phosphates is significantly enhanced, reaching about 10^{-2} S cm⁻¹ at a water vapor partial pressure above 0.5 atm. During a period of more than 100 h with four humidity cycles from zero to 0.58 atm of the water vapor partial pressure, the phosphates show good stability, suggesting the potential as an intermediate temperature electrolyte.

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Introduction

The development of fuel cells and electrolyzers operational at intermediate temperatures from 200 to 400 °C is strategically significant for applications of energy conversion in association with renewable energy technologies. Compared with low temperatures typically around 80 °C, this temperature range will bring faster electrode kinetics and consequently the possible usage of non-noble metal catalysts [1–3]. Compared with solid oxide based technologies, on the other hand, this

temperature range is low enough to allow for use of a wide selection of construction materials, which may lead to a simplified cell and stack construction as well as low costs and long-term durability [4–6]. Great effort has been devoted to development of highly proton conductive solid electrolytes [7–13]. Of special interest are metal pyrophosphates which were reported to show a proton conductivity of 10^{-2} – 10^{-1} S cm⁻¹ level in the intermediate temperature range under non-humidified conditions. For instance, Hibino et al. [7,8] synthesized SnP₂O₇ from tin oxide and phosphoric acid

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and reported conductivities of about 0.05 S cm^{-1} and even as high as of 0.2 S cm^{-1} after the indium doping. They suggested that the proton-containing species from interactions between water molecules, lattice oxides and electron holes or oxygen vacancies bring out these high conductivities. However, Tao [9] prepared a single phase of SnP_2O_7 from an aqueous solution and found that the SnP_2O_7 itself is not a good proton conductor. An amorphous phosphate layer surrounding the crystals, as residues of the excess phosphoric acid, might have facilitated the proton conductivity, as recently reported by Anfimova et al. [10].

CsH_2PO_4 is an interesting example of proton conducting solid acids, undergoing a superprotonic phase transition at about $230 \text{ }^\circ\text{C}$, where the dynamically disordered hydrogen bond network is formed, exhibiting a proton conductivity of 0.01 S cm^{-1} level [2,11]. One challenge for the pure CsH_2PO_4 is the very narrow temperature range of the superprotonic phase, below which the conductivity is insufficient, while the chemical stability, mechanical strength and integrity, and therefore long-term durability are of critical concern in the high temperature regime. As a result, a certain atmospheric humidity is necessary to maintain the stability of the acidic salt. In views of the conductivities, stability and operational temperature range, it is significant to synthesize and screen novel phosphates as intermediate temperature proton conductors.

In this work, both polycrystalline powders and amorphous glasses of bismuth phosphates were prepared from bismuth oxide and phosphoric acid and characterized as intermediate temperature proton conductors.

Experimental sections

Chemicals and preparation

Bi_2O_3 and H_3PO_4 (85 wt.%) were used as received from Aldrich Co. Deionized water was used for humidification during the conductivity measurement.

For preparation of crystal bismuth phosphates, Bi_2O_3 was first mixed with H_3PO_4 at $200 \text{ }^\circ\text{C}$ under mechanical stirring until a viscous paste was obtained. The initial molar ratio of P/Bi was 1.8. The paste was further divided into four portions and put into four alumina crucibles and heated to $300 \text{ }^\circ\text{C}$, $500 \text{ }^\circ\text{C}$, $650 \text{ }^\circ\text{C}$ and $800 \text{ }^\circ\text{C}$, respectively. The heating rate was $10 \text{ }^\circ\text{C min}^{-1}$. After being kept at the temperature for 3 h, the phosphates were cooled in the furnace to room temperature with no temperature control. Thus obtained bismuth phosphates were finally ground into powder and referred to as BiP300, BiP500, BiP650 and BiP800, respectively.

Part of the BiP650 was further washed for comparison. 5 g of BiP650 were added into 250 mL of hot water. The suspension was ultrasonically dispersed for 30 min and then filtered and washed with the distilled water. The obtained precipitate was then dried at $80 \text{ }^\circ\text{C}$ overnight and referred to as BiP650W.

For preparation of amorphous bismuth phosphate glasses, the equal weight of BiP650 and phosphoric acid was first mixed in a mortar. After being ground, the mixture was transferred to an alumina crucible and heat-treated at $1000 \text{ }^\circ\text{C}$ for 3 h. The obtained amorphous phosphates in form of

transparent glasses were obtained and for further characterization ground to powders (sample BiPGP) or polished to a tablet (sample BiPGT) using sand papers.

Characterization

The crystalline structure of the prepared bismuth phosphates were characterized by X-ray diffraction (XRD) using a Huber G670 X-ray diffractometer with copper rotating anode (CuK radiation, $\lambda = 1.54056 \text{ \AA}$). Scanning electron microscopy (SEM) measurements were performed on a Carl Zeiss EVO MA10 microscope. FT-IR spectra of the phosphate powders were recorded on a PerkinElmer 1710 spectrometer under ambient atmosphere. Thermogravimetric analysis (TGA) was performed using a Netzsch STA 409 PC system. Air was used as the purge gas and the samples were heated in alumina crucibles with a rate of $10 \text{ }^\circ\text{C min}^{-1}$. The molar ratio of phosphorus to bismuth was analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Optima 5300DV, PerkinElmer SCIEX).

For conductivity measurements, the phosphate powders were first pressed into pellets with a diameter of 13 mm and a thickness of about 2 mm under a pressure of $5 \times 10^3 \text{ kg cm}^{-2}$. A gold mesh with the same area as the pellet was placed on each side of the pellet. The assembly was held together by two pieces of porous SiC disks in order to allow for access of the humidified air and contained in a stainless steel chamber (the conductivity cell) with inlet and outlet of an air flow of controlled humidities. Two silver wires were connected to the gold meshes for the electrical measurement. The humidity of the air flow was controlled by means of a water pump (Prominence LC-20AD, Shimadzu Co.) and air flowmeter through an evaporator. Both the conductivity cell and the evaporator were placed in the same furnace for temperature control. Electrochemical impedance spectroscopy (Princeton versaSTAT 3) was used for the conductivity measurement with frequency in a range of $1\text{--}10^6 \text{ Hz}$ and ac amplitude of 10 mV.

Results and discussion

Elemental analysis

The molar ratios of phosphorus to bismuth were checked by ICP-AES. As shown in Table 1, the obtained molar ratios for BiP300, BiP500, BiP650 and BiP800 were very close to those in their corresponding precursors, indicating the formation of a stable phase during the preparation process. However, the

Table 1 – The phosphorus to bismuth molar ratios in the initial precursors and final phosphate samples as measured by ICP-AES.

Samples	Initial P/Bi ratio in precursors	Final P/Bi ratio in the samples
BiP300	1.80	1.72
BiP500	1.80	1.72
BiP650	1.80	1.73
BiP800	1.80	1.73
BiP650W	1.80	1.25

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