



Enhanced proton conductivity of niobium phosphates by interfacing crystal grains with an amorphous functional phase



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ABSTRACT

Niobium phosphate is an interesting proton conductor operational in the intermediate temperature range. In the present work two forms of phosphates were prepared: an amorphous one with high specific area and a crystalline one with low specific surface area. Both phosphates exhibited very low proton conductivities. An activation process was developed to convert the phosphates into crystal grains with a phosphorus rich amorphous phase along the grain boundaries. As a result, the obtained niobium phosphates showed considerably enhanced and stable proton conductivities. The activation effect was prominent when the high surface area amorphous phosphate was used as the precursor. At 250 °C thus obtained niobium phosphate showed a high and stable conductivity of 0.03 S cm⁻¹ under dry atmosphere and of 0.06 S cm⁻¹ at a water partial pressure of 0.12 atm.

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1. Introduction

Due to the surface Lewis and Brønsted acidity, both niobic acid and niobium phosphate have been used as solid acid catalysts in acid-catalyzed reactions such as esterification, polycondensation and dehydration reactions [1–5]. Interaction of niobic acid with phosphoric acid, resulting in formation of niobium phosphates, is well known to strength the acidity and therefore catalytic activity at elevated temperatures [5,6]. Recently niobium phosphates have also been explored as proton conductive electrolytes. Cantero et al. [7], studied the proton conductivity of niobium phosphates in a low temperature range from 27 to 140 °C. A conductivity of 10⁻⁶ S cm⁻¹ level was achieved at near 100 °C and attributed to the presence of water species in the inter-layer space of phosphates. Chai et al. [8] synthesized niobium phosphates from niobium chloride and phosphoric acid and determined the proton conductivity of about 0.017 S cm⁻¹ at room temperature in 100% relative humidity. Niobium phosphates were prepared from niobium oxide and phosphoric acid, exhibiting conductivities of the 0.01 S cm⁻¹ level under dry air condition at 250 °C [9]. In the work by Shen et al. [10] iron was introduced into niobium phosphate to form Fe_{0.5}Nb_{0.5}P₂O₇, showing a conductivity of as high as 0.14 S cm⁻¹ at 150 °C. Sørensen et al. [11] investigated composite materials of NbOPO₄ and H₃PO₄. They emphasized the importance of the excess acid in the composite and claimed that the NbOPO₄ phase by its own

is unlikely exhibiting significant conductivity. A composite containing 74% H₃PO₄ displayed a conductivity of 0.0025 S cm⁻¹ at temperature of 250 °C and water partial pressure of 0.31 atm.

These results are indicative of the interest of niobium phosphates as a potential intermediate temperature proton conductor as well as the importance of preparation procedures of the materials. It is a general practice to prepare phosphates by use of excess phosphoric acid, as the acid is volatile during the high temperature treatment. The present work is devoted to an exploration of preparation methods and their correlation to the phase composition and performance. Two types of phosphates, an amorphous form with high specific area and a crystalline form with low specific surface area were first prepared. Both possessed relatively low proton conductivities. A secondary process was then developed to convert the phosphates into crystal grains with a phosphorus rich amorphous phase along the boundaries. As a result, the obtained niobium phosphates exhibit considerably enhanced and stable proton conductivity under both anhydrous and hydrous conditions.

2. Experimental

2.1. Synthesis

The amorphous niobium phosphate was first prepared, as briefly described below and the details can be found in the reference by Mal et al. [12]. NbCl₅ was first hydrolyzed in water. Then H₃PO₄ was tipped into the hydrolysate for reaction. After about 30 min, the pH of the above solution was adjusted to 2.6 by addition of aqueous ammonia. In the next step, hexadecyl amine as the surfactant was added and gelation was carried out in a Teflon lined autoclave at 65 °C for 2 days. Thus obtained

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phosphate by this sol-gel process was finally heated at 450 °C for 6 h and referred to as NbP-G. The molar ratio of P/Nb in the product was about 1.1 [12].

For preparation of crystal niobium phosphate, Nb₂O₅ was first mixed with H₃PO₄ at 200–300 °C under mechanical stirring until a viscous paste was obtained. The initial molar ratio of P/Nb was 2. The paste was heat treated in an alumina crucible at 650 °C for 3 h. The obtained solid was then ground to powder and referred to as NbP-C.

These two Nb phosphate powders were further activated by submerging in 85% H₃PO₄. After being mixed with phosphoric acid, the powder was collected and transferred to an alumina crucible and further heat treated at 650 °C for 3 h. The metal/phosphorus molar ratios were controlled to be 1:3 for the activation treatment. The obtained activated products were referred to as NbP-G-A650 and NbP-C-A650, respectively. As the precursor of NbP-C, other two samples were also prepared by the same method except that the treatment temperatures were changed to 500 °C and 800 °C, and the final phosphates were referred to as NbP-C-A500 and NbP-C-A800, respectively.

For the comparison purpose, both the NbP-G-A650 and NbP-C-A650 were further washed with hot water for 12 h under continuous stirring. After filtrating, washing and drying, the product was obtained and referred to as NbP-G-A-W and NbP-C-A-W.

2.2. Characterization

The crystalline structures of the prepared phosphates were characterized in an X-ray diffraction (XRD) by using a Huber G670 X-ray diffractometer with copper rotating anode (CuK radiation, $\lambda = 1.54056\text{\AA}$). The morphologies of the samples were studied by field-emission scanning electron microscopy (SEM, FEI Nova 450 Nano). X-ray photoelectron spectroscopy (XPS) measurements were carried out by using a Kratos XSAM-800 spectrometer with an Mg K α radiator. FT-IR spectra of the phosphate powders were recorded on a PerkinElmer 1710 spectrometer under ambient atmosphere. Specific surface area measurements were carried out by N₂ adsorption-desorption analysis using a Micromeritics ASAP 2020 HD88 system. In 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 a pellet was placed on each side of every pellet. Then the assembly was held together by two pieces of porous SiC plates and contained in a stainless steel tube with an inlet and an outlet of an air flow. Finally two silver wires were connected to the gold meshes and extended outside of the cell for measurements. Electrochemical impedance spectroscopy (Princeton versaSTAT 4) was used for the conductivity measurement in a frequency range of 1–10⁶ Hz and ac amplitude of 10 mV. The conductivity was determined by the intercept on the real axis at high frequency regions in the complex plane. The sample was kept at 250 °C overnight before the conductivity measurements. The anhydrous conductivity was obtained under decompressed dry air atmosphere while the humidified conductivity was measured under a mixture of water vapour and air at ambient pressure.

3. Results-discussion

3.1. XRD analysis

Fig. 1 shows the XRD patterns of the prepared amorphous (a, NbP-G) and crystalline (d, NbP-C) phosphates, their analogues after phosphoric acid activation (b, NbP-G-A650 and e, NbP-C-A650) and wash treatment (c, NbP-G-A-W). The histogram pattern of monoclinic Nb₅P₇O₃₀ phase (JCPDS 48-840) is also presented for comparison. It can be clearly seen that the prepared NbP-G and NbP-C shows an amorphous and a main monoclinic Nb₅P₇O₃₀ phase, respectively. By comparing the molar ratio of P/Nb in the crystal phase with that in the precursors of preparation, one can deduce that there are some phosphorus rich amorphous

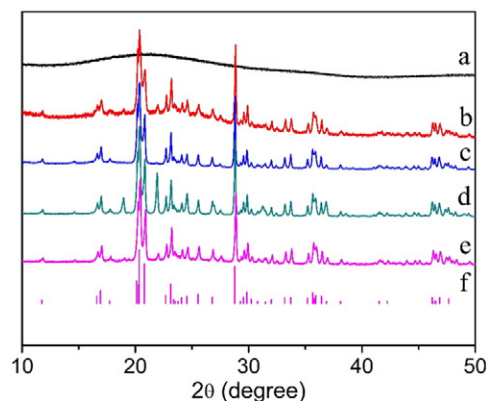


Fig. 1. XRD patterns of niobium phosphates (a) NbP-G, (b) NbP-G-A650, (c) NbP-G-A-W, (d) NbP-C, (e) NbP-C-A650 and (f) monoclinic Nb₅P₇O₃₀ phases.

phases in the NbP-C. The amorphous NbP-G is converted to a monoclinic Nb₅P₇O₃₀ phase while the monoclinic Nb₅P₇O₃₀ phase of crystal NbP-C preserves well after activation treatment. This preservation is also observed for NbP-G-A650 after wash treatment. Then, it seems that the monoclinic Nb₅P₇O₃₀ phase is easily formed and very stable under these experimental conditions including washing with hot water. The sharp lines presented in the diffractogram for NbP-C and two activated phosphate samples seem indicative of the high degree of crystallinity. In addition, the small wide peaks between 15 and 30 degrees in the NbP-G-A650 and NbP-C-A650 sample suggest the formation of amorphous phosphorus-containing phases in the samples. The disappearance of these peaks after the hot water washing imply a fact that the phosphorus rich amorphous phase is water soluble and might have existed at the boundaries of the crystalline grains.

3.2. XPS analysis

XPS was employed to analyze the composition of the prepared phosphates. The well-defined peaks of Nb, P and O elements could be observed for all the samples as shown in Fig. 2. The molar ratio of P/Nb in NbP-G was calculated to be 1.11 and agreed well with that from literature [12]. After the activation treatment, a high P/Nb molar ratio of 3.51 was obtained for NbP-G-A650. It is reasonable because phosphoric acid has been introduced into the sample during the activation treatment. The P/Nb molar ratio decreased to 1.51 after the wash treatment. This result indicated that some phosphorus rich compounds was removed by washing, in agreement with the above XRD results.

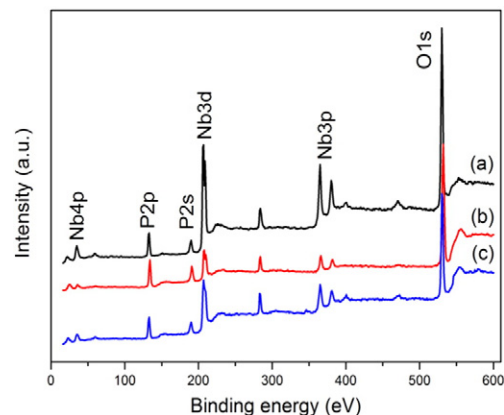


Fig. 2. XPS patterns of niobium phosphates (a) NbP-G, (b) NbP-G-A650 and (c) NbP-G-A-W.

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