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Solid state ^{31}P MAS NMR spectroscopy and conductivity measurements on $NbOPO_4$ and H_3PO_4 composite materials

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ABSTRACT

A systematic study of composite powders of niobium oxide phosphate ($NbOPO_4$) and phosphoric acid (H_3PO_4) has been performed in order to characterize the material's ability to perform as an electrolyte material in medium temperature fuel cells and electrolyzers. Powders of H_3PO_4 contents between 13.1 and 74.2 M% were produced and characterized with powder X-ray diffraction, ^{31}P MAS NMR and impedance spectroscopy. NMR revealed that a significant degree of dehydration and vaporization of H_3PO_4 takes place above 200 °C, and increases with temperature. At 500 °C the $NbOPO_4$ and H_3PO_4 has reacted to form niobium pyrophosphate ($Nb_2P_4O_{15}$). Impedance spectroscopy showed an increase in conductivity with increasing acid concentration, whereas the conductivity decreased slightly with increasing temperature. The highest conductivity measured was $2.5 \cdot 10^{-3}$ S/cm for a sample containing 74.2 M% of H_3PO_4. Lastly, it was shown that $NbOPO_4$ has no significant conductivity of its own.

1. Introduction

Solid phosphates have recently drawn attention for use as electrolytes in medium temperature fuel cells and electrolyzers working in the temperature range of 100–500 °C. It is hoped that working in this temperature range will yield higher CO tolerance compared with Nafion©-based low-temperature fuel cells, and may even allow for non-platinum catalysts due to the better kinetics at higher temperatures [1]. At the same time the start-up time should be shorter compared with the high-temperature solid oxide fuel cells, and the long-term stability improved [2].

Fuel cells working above 100 °C need water management systems unless they are based on electrolytes with anhydrous protonic conduction, and phosphoric acid based systems have been commercially available for many years since phosphoric acid has a very low vapor pressure below 200 °C [3,4]. In phosphoric acid fuel cells, pure phosphoric acid is immobilized in a polytetrafluoroethylene (PTFE) coated silicon carbide matrix which yields mechanical strength [5]. Since the phosphoric acid is only immobilized by capillary forces in the porous matrix, phosphoric acid tends to leave the matrix and flood the electrodes [5]. It would therefore be advantageous to find alternative support and/or proton-conducting materials entirely. Much research has been performed on the polybenzimidazole (PBI) membrane system [6,7]. This membrane is capable of taking up huge amounts of phosphoric acid by hydrogen bonding to nitrogen in the polymer backbone giving high protonic conductivities, though the membranes contain more acid than can pair with the PBI repeat unit. However, these materials suffer from long-time stability problems [6,8].

Recently, phosphate-based systems have emerged with oxoanion solid acid systems with cesium hydrogen sulfate ($CsHSO_4$) and cesium dihydrogen phosphate (CsH_2PO_4) being among the most successful. CsH_2PO_4 exhibits a change in crystal structure around 230 °C from a monoclinic phase to a cubic phase accompanied by a large increase in protonic conductivity to around 10^{-2} S/cm [9,10]. Good fuel cell performance has been demonstrated using this material as the electrolyte [11]. Unfortunately, the material exhibits an irreversible dehydration to cesium metaphosphate, which has no significant conductivity [9], close to the transition temperature. Strict water partial pressure management is needed to suppress the dehydration [12].

Recently, reports of other phosphates such as $NbOPO_4$ [13–15] and SnP_2O_7, having high anhydrous protonic conductivities at 250 °C have been published. 1.95×10^{-1} S/cm has been reported for SnP_2O_7 doped with 10% In [16,17]. Some of these metal phosphates have no intrinsic protons in their crystal structure, and the observed conductivity is thought to arise from induced

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protons defect, e.g. from insertion of water on oxygen vacancies. The detailed conduction mechanism in these materials is as yet unknown but it has been shown that the synthetic history of the materials has a high impact on the conductivity [18,19]. Both $NbOPO_4$ and SnP_2O_7 can be prepared from their respective oxides and phosphoric acid. Some authors have ascribed the observed conductivity to residual phosphoric acid even though the prepared powders have been calcinated at temperatures as high as 650 °C [18,19] where the phosphoric acid would be expected to have been lost by evaporation or dehydration [20,21]. If this is true, the metal phosphates have no intrinsic protonic conductivity, but are merely substrates for the residual phosphoric acid. This is in contrast to CsH_2PO_4 which has true intrinsic protonic conductivity. The conduction mechanism will then be expected to be similar to that in free phosphoric acid [22], i.e. transport of protons via extensive auto-protolysis of phosphoric acid itself. If phosphoric acid is responsible for the conductivity, it seems that these materials are somehow able to stabilize the acid at high temperatures (active substrates).

This work is a continuation of the work by Huang et al. [13–15], aimed at finding the origin of the conductivity in $NbOPO_4$. In the present paper, an investigation of the conductivity of $NbOPO_4$/H_3PO_4 composites with 13.1–74.2 M% phosphoric acid is performed. Here, $NbOPO_4$ is not made from Nb_2O_5 and phosphoric acid but instead from $NbCl_5$ and phosphoric acid in order to perform a precipitation reaction after which any remaining phosphoric acid is washed out. Since dehydration and evaporation is an issue in all phosphoric acid based systems, we have also investigated the dehydration behavior of the samples at different temperatures. Solid state NMR has proven to be extremely useful in the investigation of samples containing amorphous phases [18], and in the present work solid state ^{31}P Magic Angle Spinning (MAS) NMR was used to probe the contents of the samples. Niobium pyrophosphate ($Nb_2P_4O_{15}$) was also prepared in order to be able to check for its formation in the composite pellets.

2. Materials and methods

2.1. Synthesis of niobium oxide phosphate, $NbOPO_4$

The synthesis route for $NbOPO_4$ in this work is inspired by other authors [23–26]. 50 g of $NbCl_5$ (99.995% Sigma-Aldrich) was dissolved in 400 mL 37% w/w hydrochloric acid (ACS reagent grade, Sigma-Aldrich). An 85% w/w aqueous solution of phosphoric acid (Sigma-Aldrich) was added dropwise in slightly over-stoichiometric amounts. A precipitate was formed after few minutes of stirring and the solution was heated at 80 °C for 12 h. The solution was then neutralized with an ammonia solution until the pH reached a value of approximately 7 which was checked with a piece of pH-paper. The precipitate was washed with distilled water and centrifuged several times and then dried overnight at 80 °C. The powder was then calcined at 900 °C for 12 h.

An important point in the preparation of $NbOPO_4$ was the pH of the solution before filtering off the powder. If the pH was below 7, the powder was hard and very hard to grind, making the material difficult to handle. If the pH was raised above 7, the powder was very loose and soft and no grinding was needed. Both powder types had identical X-ray diffraction patterns. Optical microscopy revealed the hard powder consists of a mixture of different grain sizes, whereas the soft powder had a narrower size distribution with smaller grains than the hard powder. In all experiments the loose powder was used. It should also be noted that $NbOPO_4$ exists as a layered structure after precipitation with water in between the layers. Heating the powders above 250 °C will remove the water and create a 3-dimensional structure [27].

2.2. Synthesis of niobium pyrophosphate, $Nb_2P_4O_{15}$

5 g Nb_2O_5 (99.99% Sigma Aldrich) and 2.3 g $(NH_4)H_2PO_4$ (99.99% Sigma Aldrich) were mixed in a mortar with the phosphate in slight stoichiometric excess. The mixture was heated from room temperature to 300 °C in air in an alumina crucible with a matching lid, at a heating rate of 1 °C/min, and then kept at 300 °C for 6 h. The mixture was then heated to 650 °C with a heating rate of 3 °C/min and kept at 650 °C for 12 h. The oven was then turned off and the sample allowed to cool to room temperature. After cooling, the mixture was ground with an additional 2.3 g $(NH_4)H_2PO_4$. This new mixture was then given the same heat treatment as before.

2.3. Powder X-ray diffraction (XRD) characterization

The niobium phosphate powders were analyzed using a Siemens D5000 Powder X-ray diffractometer using Cu$K\alpha_1$ radiation with a wavelength of 1.540 Å. Data were collected from $2\theta = 5$ to 60° in steps of 0.01°, each step lasting 4 sec.

2.4. $NbOPO_4$ and H_3PO_4 mixtures

To obtain a uniform mixture of $NbOPO_4$ and H_3PO_4, $NbOPO_4$ was mixed with appropriate amounts of P_2O_5 in a glove box. The mixtures were prepared in glass vials and simply stirred with a spatula for around 10 min as both the powders were very fine grained. The mixtures were then allowed to equilibrate with atmospheric moisture for at least five days. During that period the following reaction happens:

$$P_2O_5 + nH_2O \rightarrow 2H_3PO_4 \cdot (n-3)H_2O \quad (1)$$

Mixtures were prepared with P_2O_5 contents between 5 and 50% w/w.

2.5. Solid state MAS NMR

^{31}P and ^{1}H MAS NMR was performed at 11.7 T (202.3 MHz for ^{31}P and ^{1}H at 499.9 MHz) on a Varian INOVA spectrometer using a 3.2 HX MAS NMR probe tuned to ^{1}H and ^{31}P. ^{31}P and ^{1}H NMR spectra are referenced relative to 85% H_3PO_4 ($\delta(^{31}P) = 0$ ppm) and TMS using a secondary reference of H_2O ($\delta(^{1}H) = 4.6$ ppm). ^{31}P MAS NMR spectra were recorded using 10 kHz spinning with ^{1}H decoupling and relaxation delay of 400 s in order to ensure full relaxation of all species in the spectra. In addition, single pulse liquid state ^{1}H and ^{31}P NMR was recorded using relaxation delays of 1.5 and 2 s, respectively. The ^{1}H and ^{31}P NMR spectra were analyzed by deconvolution using SpinWorks [28].

2.6. Dehydration experiments

Hydrated composite samples were made by mixing NbOPO4 with P_2O_5 such that the P_2O_5 content constituted 20% w/w. The samples were heated in glass vials to 200, 300, 400 and 500 °C, respectively, for 18 h, in order to investigate the dehydration of phosphoric acid. After the heat treatment, the vials where immediately sealed with Parafilm© to suppress rehydration and an NMR spectrum was recorded. The glass vials were then left open in atmospheric air at room temperature to allow the samples to rehydrate. After 10 and 24 h, respectively, NMR spectra were again recorded. Furthermore, 85% w/w phosphoric acid was heated at 180 °C for 24 h and investigated with ^{31}P liquid state NMR in order to obtain the chemical shifts of any polymerization products produced from the acid alone.