

## Characterisation of intermediate temperature polyphosphate composites

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High temperature proton conducting solids are useful materials for many electrochemical applications such as high temperature fuel cells, hydrogen sensors, and hydrogen gas separators. However, many protonic conductors decompose at temperatures above 300 °C. For high-temperature proton conductors, progress is a matter of combining high mobility with a high concentration of protons, but also of avoiding accompanying contributions from oxygen ions and electrons. The intermediate-temperature (200–600 °C) fuel cells are very attractive since they combine the advantages of high- and low-temperature fuel cells. A membrane formed from an inorganic polyphosphate composite has good ionic conduction properties at temperatures between 473 and 573 K especially in a humidified atmosphere [1, 2].

The number of fast protonic conductors, organic or inorganic, crystalline and amorphous, have been prepared during the past two decades [3], which are categorized into two types based on their operating temperatures. One is hydrated crystalline compounds [4], and the other is perfluorinated ionomers [5] showing high conductivities of  $\sim 10^{-2} \text{ S cm}^{-1}$  below 100 °C, but their chemical degradation limits their use in practical applications. On the other hand, fast proton conducting glasses, if developed, extend beyond the limitation of the above compounds because of their high chemical and mechanical durability and easy formation into films and plates.

Solid state proton conductors which show high conductivities in the medium temperature range (100–200 °C) with low humidity have been required as the electrolyte for polymer electrolyte fuel cells and direct methanol fuel cells operating in the temperature range [6]. The operation of fuel cells in the medium temperature range improves the efficiency of energy conversion in the cells and reduces the poisoning of Pt catalysts with CO in the fuel gases. In addition, working of the fuel cells under the condition of low humidity permits the reduction of the weight and volume of humidifiers, so that the fuel cells should have advantages for application in electric vehicles. The situations described

above are the background for the high proton conductive solid-state materials in the medium temperature range with low humidity.

In the present work, ammonium polyphosphate electrolytes were prepared by the sol-gel method [7] and evaluated for use as proton conductive materials at intermediate temperatures. Polyphosphate composites consisting of  $\text{NH}_4\text{PO}_3$  and  $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$  were prepared and characterized by structural, thermal, and electrical conductivity measurements.

The specific amount of  $(\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_7$  (ammonium dihydrogen phosphate) and  $(\text{NH}_2)_2\text{CO}$  (urea) for each composition was weighed using an electronic balance (Sartorius,  $d = 0.01$ ) having an accuracy of 0.01 mg. After the compositions were dissolved completely in water, they were mixed with an equal volume of  $\text{CH}_3\text{OH}$  (methanol) in a conical flask. The mixture was stirred at room temperature for 1 hr and then TEOS (tetra ethoxy silane) was added. The solution so prepared was stirred for 2 hrs at 50 °C and then maintained at 70–75 °C in a closed glass vessel. A gel forms after 1–2 days. A white powder formed when the gel was dried at 120 °C under vacuum for 12 hrs. A schematic diagram of the procedure used to synthesise amorphous ammonium silicon polyphosphate gel is shown in Fig. 1. The ammonium polyphosphate composite electrolyte was prepared then ground for 1 hr and pressed at  $1.9 \times 10^4 \text{ N cm}^{-2}$  to form pellets (diameter 10 to 40 mm, thickness 0.5 to 3 mm). The formed pellets were sintered for two days at 673 K in a dry ammonia atmosphere. Fig. 2 shows a picture of an ammonium polyphosphate composite material after sintering.

X-ray diffraction (XRD) was carried out on  $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$  with a SEIFERT diffractometer using  $\text{Cu-K}\alpha$  with a step size of 0.02 degrees and a count time of 1.2 s per point. The peak profiles were obtained from  $\text{Cu K}\alpha$  line-corrected data. The morphology of the samples was examined with a HITACH, S-4000 scanning electron microscope. Nuclear magnetic measurement (NMR) was performed by Bruker GmbH (Type MSL 500 and MSL 300) spectrometer. Thermo gravimetric analysis measurements (TGA) were performed

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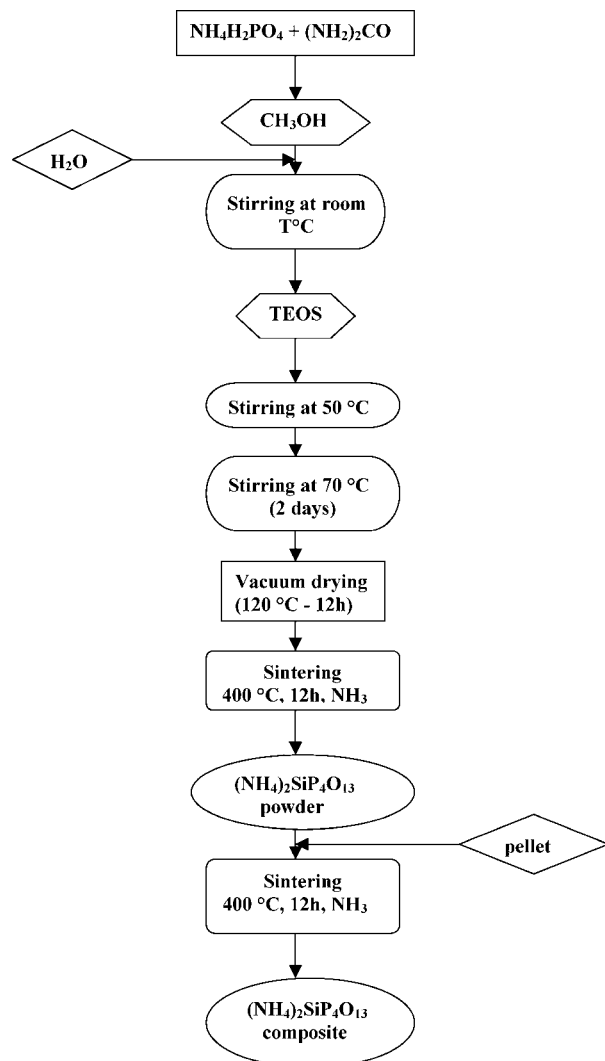
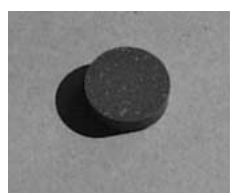


Figure 1 Flow chart of the sol-gel synthesis of ammonium silicon polyphosphate  $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$ .



[diameter = 10 mm, thickness = 2.8 mm]

Figure 2 Picture of an ammonium silicon polyphosphate  $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$  composite material.

with PL STA-1500 from room temperature to  $300\text{ }^\circ\text{C}$  in dry Argon. Conductivity measurements were carried out by means of AC impedance spectroscopy with an oscillating voltage of 100 mV, using a PC controlled SI 1260 impedance/gain-phase analyser (Solarton) in the frequency range  $0.1\text{--}10^6$  Hz. The pellet samples, which were connected to the impedance analyser with Au wire, were placed in a glass tube, and then gases were passed through the glass tube at atmospheric pressure. Then Pt electrodes were attached to both sides of the pellets by golden sputters. The temperature was measured by a chromel-alumel thermocouple placed close to the pellets and controlled by a tube furnace in which the glass tube was placed. During the conductivity measurement, the temperature was kept constant or

changed stepwise from  $50$  to  $300\text{ }^\circ\text{C}$ . The conductivity of each sample was determined from the frequency dependence of the real and imaginary impedance plotted in the complex plane.

Fig. 3 shows the X-ray diffraction pattern of the product thus obtained. The phase analysis confirmed the formation of  $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$ . The X-ray diffraction patterns given in this work are similar to that of an ammonium polyphosphate produced by a solid-state process method [8–10].

SEM micrographs of ammonium silicon polyphosphate powder for different magnifications are shown in Fig. 4. It shows that the surface morphology of the ammonium silicon polyphosphate composite is devoid of a crystal appearance [10].

The  $^{31}\text{P}$ -MAS-NMR spectra show five resonance's in  $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$  prepared by the sol-gel method in Fig. 5. These resonances represent different molecular groups. The first signal at 0.7 ppm in the non-activated and at 0.4 ppm in the activated spectrum represent monophosphates. The second signal ( $-11.6$  ppm/ $-9.4$  ppm) represents the end-groups of the polyphosphate chains and the third signal ( $-25.6$  ppm/ $-24.6$  ppm) the inner chain-groups in the phosphate chains. So if one compares the signal intensities one can estimate the chain length. The chain length in the non-activated  $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$  is about 300 phosphate units (Fig. 5a). The two signals at  $-29.4$  and  $-35$  ppm belong to 3-dimensional links in the polyphosphate chains. The labelled signals (\*, +, ~) are due to non-crystallographic sites in ammonium silicon polyphosphate. The central sharp signal is due to impurity in the material.

In Fig. 5b the spectrum of (non-activated) composite shows the same  $^{31}\text{P}$  resonance positions with the same chemical shift anisotropies as observed in the single components. The chain length dramatically decreased around 300 phosphate-units and increased again after activation up to 55 units.

The thermal stability of the composite electrolytes has been determined by means of TGA measurement. In Fig. 6, the TGA curve shows that the weight decreases gradually around  $300\text{ }^\circ\text{C}$ . After an initial mass loss (mostly  $\text{NH}_3$ ) of 3.5% the material is thermally stable upon cycling between  $50$  and  $300\text{ }^\circ\text{C}$ .

The ac conductivity of the sample obtained by this heating procedure is shown in Fig. 7. The conductivity increases with rising temperature up to  $300\text{ }^\circ\text{C}$ , but it passes through a maximum above this temperature and then decreases with rising temperature. The conductivity decrease is due to the loss of protons by the thermal dehydration of  $\text{HPO}_3$ . The change of conductivity with time was measured at this temperature. The conductivity passed through a maximum after 10–13 hrs and then decreased with time. This is due to the proton production by thermal decomposition of  $\text{NH}_4^+$  and the subsequent proton loss by dehydration [9]. Heating for too short a time results in less proton production and for too long a time in a proton loss, and therefore the heating at  $300\text{ }^\circ\text{C}$  for 10 hrs is an optimum to obtain the most conductive material. The measured conductivity values for  $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$  lie in the range  $10^{-5}\text{--}10^{-2}\text{ S cm}^{-1}$

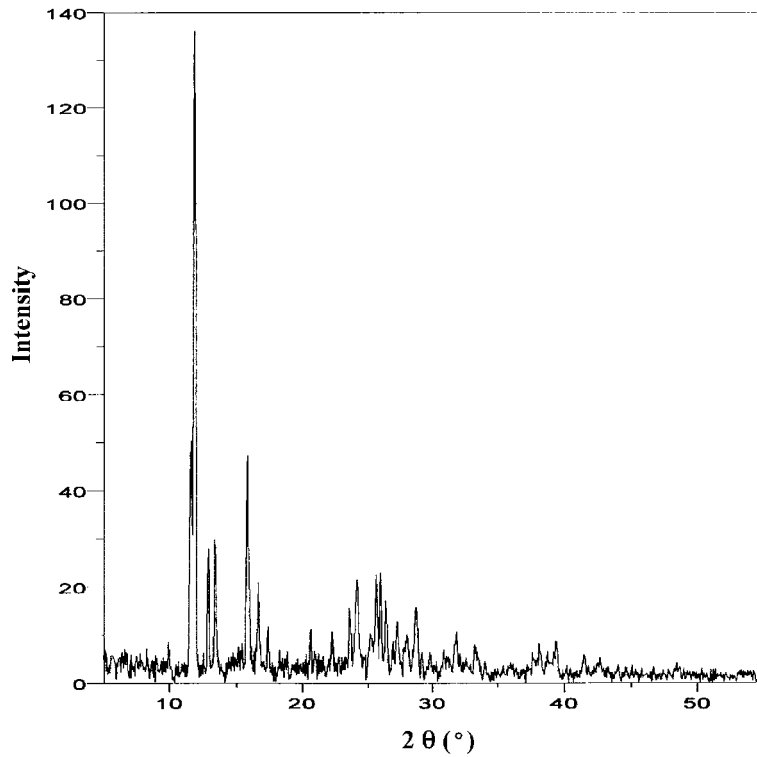


Figure 3 X-ray diffraction patterns of ammonium silicon polyphosphate  $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$  composite material by sintering temperature  $400^\circ\text{C}$  for 24 hrs.

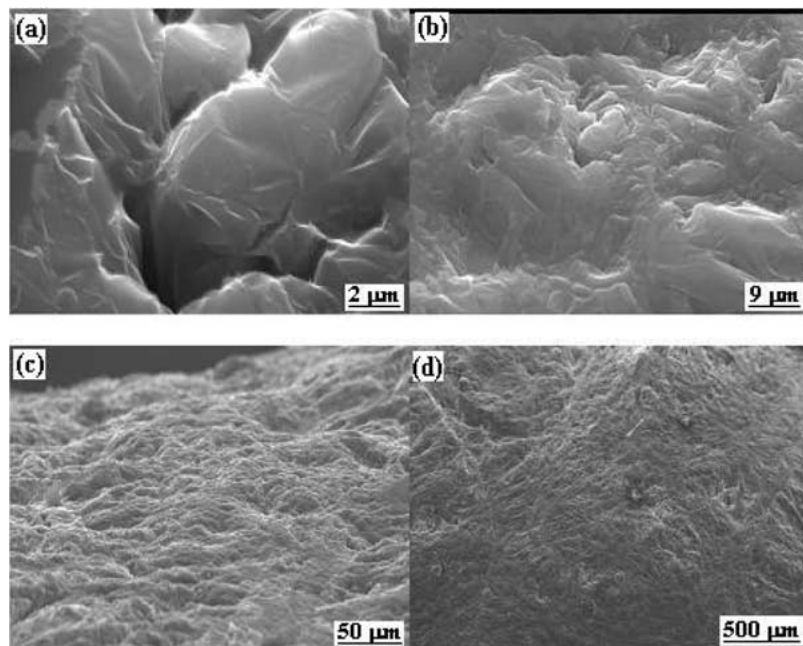


Figure 4 SEM micrographs for ammonium silicon polyphosphate  $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$  composite with different magnifications.

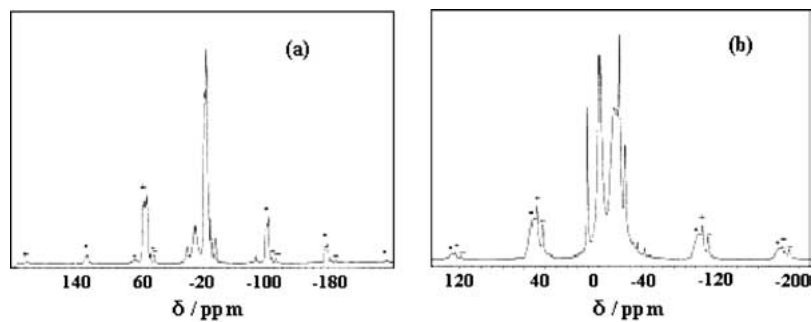


Figure 5  $^{31}\text{P}$  MAS NMR spectrum of non-activated ammonium silicon polyphosphate  $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$  composite (a) compared to the spectral addition of  $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$  single components (b).

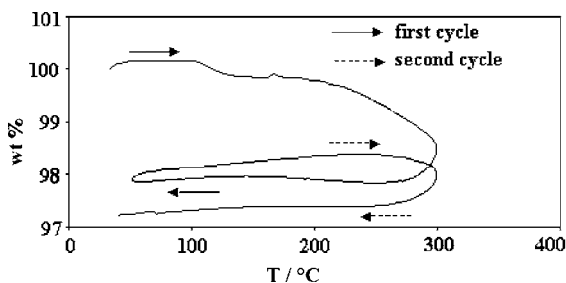


Figure 6 Mass loss of the ammonium silicon polyphosphate  $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$  composite due to the thermic cycling measurement with the heating rate of  $10^\circ\text{C}/\text{min}$ .

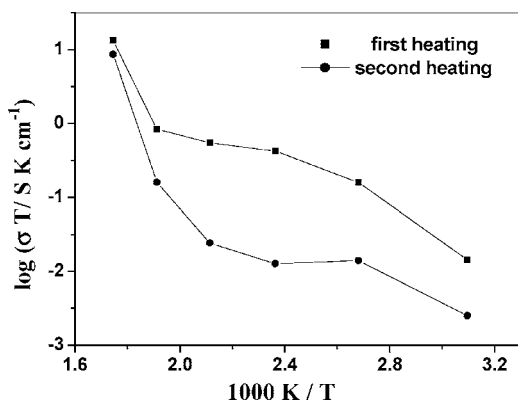


Figure 7 Arrhenius plots of conductivity of ammonium silicon polyphosphate  $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$  composite measured by ac impedance spectroscopy in dry  $\text{N}_2$  gas.

with first heating cycle and  $10^{-6}$ – $10^{-2}$   $\text{S cm}^{-1}$  with the second heating cycle in dry nitrogen gas atmosphere at 50 to  $300^\circ\text{C}$  (Fig. 7). This plot falls on a straight line up to  $300^\circ\text{C}$ , but deviates downwards at temperatures beyond that, which is due to the loss of proton by dehydration. This is in close agreement with the results of Haufe [10], who reported the conductivity values of ammonium silicon polyphosphate composite electrolytes in the  $10^{-7}$  to  $10^{-2}$   $\text{S cm}^{-1}$  range from 50 to  $300^\circ\text{C}$ .

In the present work the formation of  $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$  was confirmed by powder X-ray diffraction. The particle size of  $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$  was in the range  $4\text{--}7\ \mu\text{m}$ .  $^{31}\text{P}$  MAS NMR measurements showed that the phosphorous chain length of about 300 phosphate-units in  $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$  decreases upon processing to a value of 5 for  $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$  and increased again after activation up to 50. After an initial mass loss (mostly  $\text{NH}_3$ ) of 3.5% the material is thermally stable upon cycling between 50 and  $300^\circ\text{C}$ . The conductivity values varied from  $7.75 \times 10^{-6}$  at  $50^\circ\text{C}$  to  $1.45 \times 10^{-2}$   $\text{S cm}^{-1}$  at  $300^\circ\text{C}$  in dry nitrogen gas atmosphere.

## Acknowledgment

This work was financially supported by the Alexander Von Humboldt foundation in Bonn, Germany.

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Received 23 January

and accepted 23 January 2004