

## Synthesis and characterization of proton conducting poly phosphate composites

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Ammonium polyphosphate composites were prepared by the sol-gel method and evaluated for use as proton conductive materials at intermediate temperatures. This study is an attempt to prepare protonic conductors based on ammonium polyphosphate. The chemical and mechanical stabilities in the presence of water depend on the composition and thermal history. 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 X-ray diffraction, Scanning electron microscopy, thermal analysis and impedance measurements. The conductivity of this system reached  $9.44 \times 10^{-5} \text{ S cm}^{-1}$  at  $50^\circ\text{C}$  and  $1.45 \times 10^{-2} \text{ S cm}^{-1}$  at  $300^\circ\text{C}$  in dry condition and  $3.27 \times 10^{-1} \text{ S cm}^{-1}$  at  $300^\circ\text{C}$  in humid hydrogen atmosphere. It represents therefore a potential proton conducting material for fuel cells working at high temperature.

Proton ( $\text{H}^+$ ) transport in solids has attracted much attention because of its potential use in clean energy fields such as fuel cells, batteries and chemical sensors. In terms of suitable candidate materials, polyphosphate seem to be promising candidates [1, 2]. In a recent communication [3] we have shown that a membrane formed from an inorganic polyphosphate composite has good ionic conduction at temperatures between 473 and 573 K especially in humidified atmosphere. The goal of our group is to develop a direct methanol fuel cell on the basis of this new material.

In the present contribution, we report on the preparation of polyphosphate composites by the sol-gel method, their structural and thermal properties and their Electrical conductivity at intermediate temperatures up to  $300^\circ\text{C}$ . We prepared ammonium silicon polyphosphate powder, compacted a pellet, and investigated the ionic conductivity. Based on the conductivity measurements for  $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$  composite materials with various gas environments in dry and humid atmosphere, we discuss the enhancement of conductivity in the composite system. The ammonium polyphosphate composite electrolytes were prepared by grinding for 1 hr and pressing at  $1.9 \times 10^4 \text{ Newton cm}^{-2}$  to form pellets (diameter 10 to 40 mm, thickness 0.5 to 3 mm). The pellets were sintered for two days at 673 K in a dry ammonia

atmosphere. Then gold was sputtered on both sides of the pellets to make the conductivity measurements.

X-ray diffraction (XRD) was carried out on  $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$  composites with a SEIFERT diffractometer using  $\text{Cu-K}_\alpha$  radiation 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 (TG) and differential thermal analysis (DTA) was performed with a PL STA-1500 from room temperature to  $300^\circ\text{C}$  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 (Solartron) in the frequency range 0.1– $10^6$  Hz.

Fig. 1 shows the XRD- patterns of ammonium phosphate and the final product thus obtained agreed with the ammonium phosphate phases [4]. The X-ray diffraction patterns given in the latter work are similar to that of an ammonium polyphosphate produced by a solid-state process method [5, 6].

Fig. 2 shows the surface morphology of the ammonium phosphate powder with different magnification. It seems a very sharp edge appearance in the crystal. The particle size of the  $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$  powder is 4  $\mu\text{m}$  to 7  $\mu\text{m}$ . It is useful as a flame retardant for many synthetic organic materials, which do not require a small particle size. SEM micrographs of ammonium silicon poly phosphate powder at different magnifications are shown in Fig. 3. It shows the surface morphology of the final stage powder. It seems the sharp appearance is absent in the crystal particle. However, well-defined homogeneous particles are observed in the SEM micrograph [5].

In the non-activated spectrum of  $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$  one can observe a signal at 7.4 ppm with weak rotational sidebands. This signal can be assigned to the protons of  $\text{NH}_4^+$  in  $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$ . Fig. 4a, the  $^1\text{H}$ -spectrum of the

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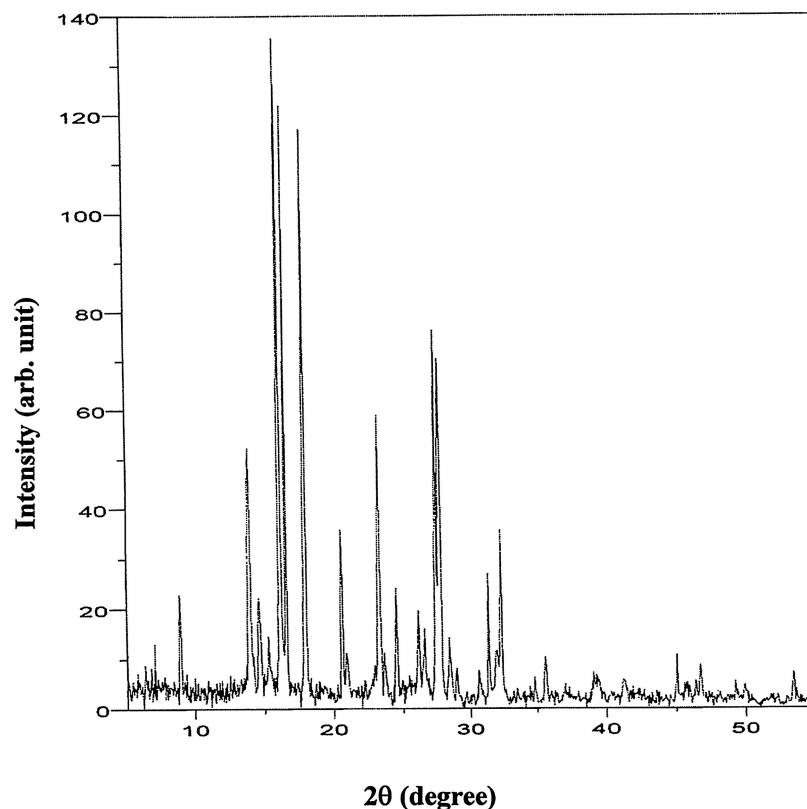


Figure 1 X-ray diffraction patterns of ammonium phosphate ( $\text{NH}_4\text{PO}_3$ ) powder prepared by sol-gel method.

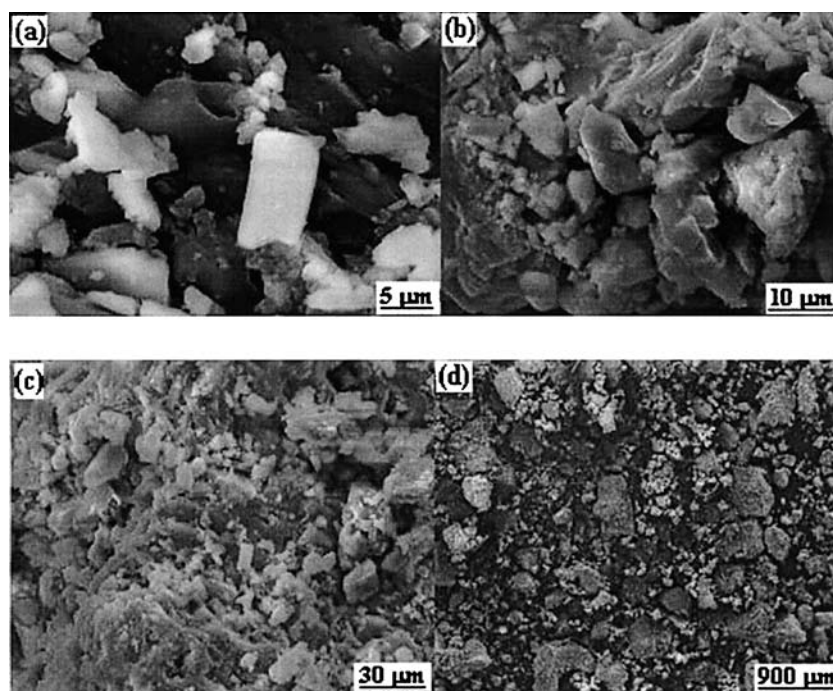


Figure 2 SEM images for ammonium phosphate ( $\text{NH}_4\text{PO}_3$ ) powder with different magnifications.

activated  $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$ , shows two signals at 7.1 ppm and at 12.8 ppm. The aberration of the signal at 12.8 ppm [6], that no chemical exchange could be observed in the activated  $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$  prepared by solid state process method. So it can be supposed that this signal belongs to the protons remaining in the material after ammonia gas was separated during the activating process. These protons are located at  $\text{PO}_4^-$  Tetrahedrons of the polyphosphate chains. From Fig. 4b, the proton response in spectra of  $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$  is assigned to the

$\text{NH}_4^+$  species ( $\delta = 7.4$  ppm) and additional resonance at  $\delta = 12.8$  ppm in the spectra of  $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$  is due to protons in hydrogen bridges. There is only one signal at  $\delta = 12.8$  ppm in the spectrum of the non-activated composite.

The thermal stability of the composite electrolytes has been determined by means of TG/DTA measurement. After an initial mass loss (mostly  $\text{NH}_3$ ) of 3.5% the material is thermally stable upon cycling between  $50^\circ\text{C}$  and  $300^\circ\text{C}$  (Figs 5 and 6). In addition, an

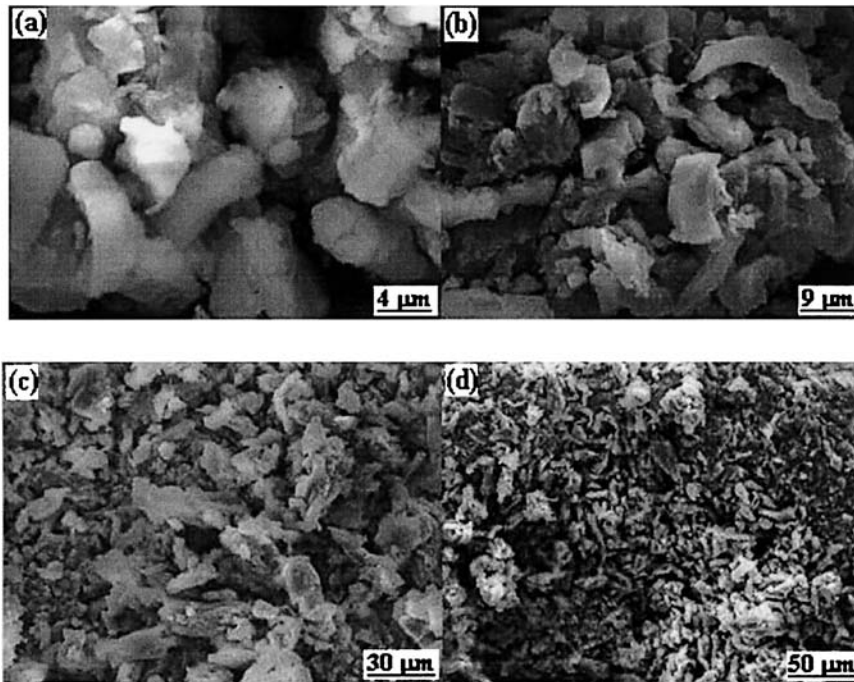


Figure 3 SEM images for ammonium silicon polyphosphate  $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$  powder with different magnifications.

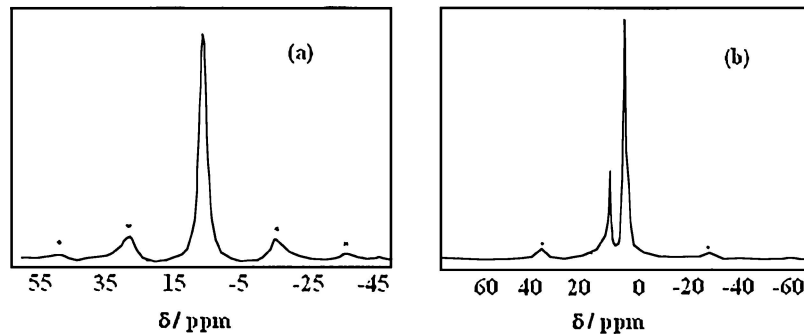


Figure 4  $^1\text{H}$  MAS NMR spectrum of non-activated ammonium silicon polyphosphate  $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$  composite (a) compared to the spectral addition of  $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$  single components (b).

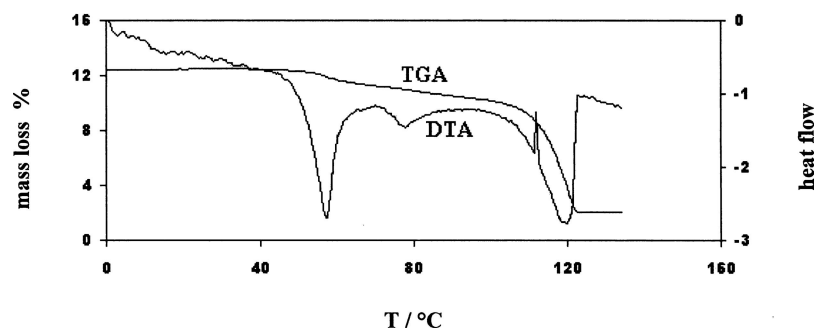


Figure 5 TG/DTA curve for the ammonium silicon polyphosphate  $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$  powder with the heating rate of  $5^\circ\text{C}/\text{min}$ .

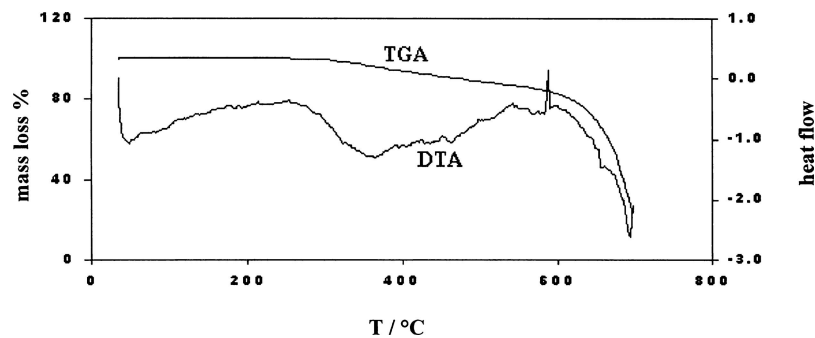


Figure 6 TG/DTA curve for the ammonium silicon polyphosphate  $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$  composite material with the heating rate of  $5^\circ\text{C}/\text{min}$ .

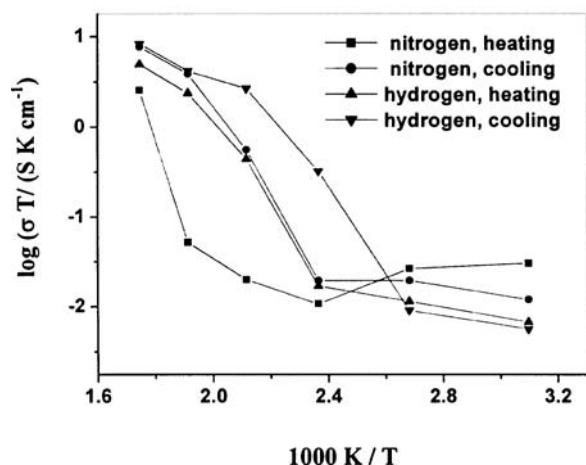


Figure 7 Arrhenius plots of conductivity of composite material measured by ac impedance spectroscopy in dry nitrogen and dry hydrogen.

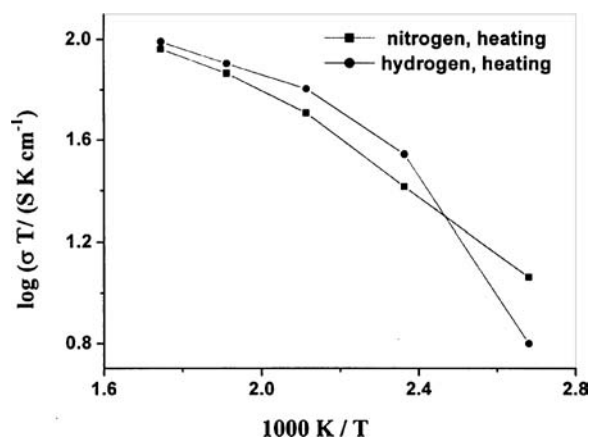


Figure 8 Arrhenius plots of conductivity of composite material measured by ac impedance spectroscopy in humid nitrogen and humid hydrogen.

endothermic peak is also noted, which may be attributed to the moisture. In the TGA curve, the weight decreases gradually around 300 °C (Figs 5 and 6). This agrees with the DTA results. These results indicate that the sample is stable up to about 300 °C before pyrolysis starts. The decomposition temperatures of the composite materials were obtained from the point of intersection of the extrapolated baseline and the linear heat-flow incline.

Figs 7 and 8 show the Arrhenius plot of the conductivity measured in dry and humid conditions with different gas atmospheres by ac impedance spectroscopy. The conductivity values for  $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$  are found in the range  $10^{-5}$ – $10^{-2}$  S  $\text{cm}^{-1}$  at various gas atmospheres (Table I). The high proton conductivity of

$(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$  is  $3.27 \times 10^{-1}$  S  $\text{cm}^{-1}$  at 300 °C in humid hydrogen atmosphere (Table II). This is in close agreement with the results of [6], which reported the conductivity values of ammonium silicon polyphosphate composite electrolytes in the  $10^{-7}$ – $10^{-2}$  S  $\text{cm}^{-1}$  range from 50–300 °C. We speculate that the mechanism of proton conductivity involves the hopping of hydrogen on the adsorbed water at low temperatures and the thermal vibration of OH bonds at high temperatures [7].

The measurements were performed on the same sample varying the gas environment from dry to humid nitrogen and hydrogen in Fig. 8. Only slight differences can be observed in the two dry environments, yet the effect of water is dramatic and the conductivity is almost an order of magnitude higher in the humid environments. The increase of the conductivity is clearly due to water uptake by the sample. For a given humidity of the environment, i.e., given water content of the sample, the Arrhenius plots of the conductivity are quite reproducible.

As can be seen in Figs 7 and 8, the Arrhenius plots are not linear in the whole temperature range investigated. The general tendency is that the slope is steeper at lower temperatures and the slope becomes moderate with water content increase. It is possible to identify two linear regimes. In the case of conductivity measurements in water-rich environment, the activation energies have a very low value of about 0.25 eV and do not show such a clear change in slope, although the conductivity values also increase with decreasing temperature. Such low activation energies for the proton conduction are known for proton exchange membranes in a fully hydrated state [8]. The proton conduction in those materials is assumed to occur through a Grotthus-like mechanism.

In the present work, Ammonium silicon polyphosphate composite electrolytes were prepared by the sol–gel method. X-ray diffraction indicates the presence of formation of  $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$ . Scanning electron micrographs reveal the surface morphology.  $^1\text{H}$  MAS NMR measurements demonstrate that (non-ammonium) bridging protons are created by the activation procedure of the composite. After an initial mass loss (mostly  $\text{NH}_3$ ) of 3.5% the material is thermally stable upon cycling between 50 °C and 300 °C. It exhibits a very high ionic conductivity in humid atmosphere—very likely proton conductivity—and shows thermal and chemical stability after the first heating cycle. This makes it potentially suitable for fuel cells, sensor and battery applications. The conductivity values varied from  $2.11 \times 10^{-5}$  S  $\text{cm}^{-1}$  at 50 °C to  $8.65 \times$

TABLE I Conductivity values of  $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$  composite material in dry nitrogen and dry hydrogen

Gas	Cycle (dry)	$\sigma$ (S $\text{cm}^{-1}$ )					
		323 K	373 K	423 K	473 K	523 K	573 K
$\text{N}_2$	Heating	$9.44 \times 10^{-5}$	$7.13 \times 10^{-5}$	$2.54 \times 10^{-5}$	$4.22 \times 10^{-5}$	$9.97 \times 10^{-5}$	$4.45 \times 10^{-3}$
$\text{N}_2$	Cooling	$3.74 \times 10^{-5}$	$5.24 \times 10^{-5}$	$4.61 \times 10^{-5}$	$1.19 \times 10^{-3}$	$7.34 \times 10^{-3}$	$1.34 \times 10^{-2}$
$\text{H}_2$	Heating	$2.11 \times 10^{-5}$	$3.08 \times 10^{-5}$	$4.13 \times 10^{-5}$	$9.37 \times 10^{-4}$	$4.53 \times 10^{-3}$	$8.65 \times 10^{-3}$
$\text{H}_2$	Cooling	$1.75 \times 10^{-5}$	$2.45 \times 10^{-5}$	$7.63 \times 10^{-4}$	$5.64 \times 10^{-3}$	$7.96 \times 10^{-3}$	$1.45 \times 10^{-2}$

TABLE II Conductivity values of (NH<sub>4</sub>)<sub>2</sub>SiP<sub>4</sub>O<sub>13</sub> composite material in humid nitrogen and humid hydrogen

Gas	Cycle (humid)	$\sigma$ (S cm <sup>-1</sup> )				
		373 K	423 K	473 K	523 K	573 K
N <sub>2</sub>	Heating	$1.16 \times 10^{-1}$	$1.73 \times 10^{-1}$	$2.55 \times 10^{-1}$	$2.94 \times 10^{-1}$	$3.05 \times 10^{-1}$
H <sub>2</sub>	Heating	$6.29 \times 10^{-2}$	$2.33 \times 10^{-1}$	$3.18 \times 10^{-1}$	$3.21 \times 10^{-1}$	$3.27 \times 10^{-1}$

$10^{-3}$  S cm<sup>-1</sup> at 300 °C in dry hydrogen during the heating cycle, and the conductivity values varied from  $6.29 \times 10^{-2}$  S cm<sup>-1</sup> at 100 °C to  $3.27 \times 10^{-1}$  S cm<sup>-1</sup> at 300 °C in humid hydrogen atmosphere.

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