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Stability and conductivity study of NH_4PO_3–PTFE composites at intermediate temperatures

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ABSTRACT

NH_4PO_3–PTFE inorganic–organic composite electrolytes were prepared. Their phase compositions, thermal stability and morphologies were investigated. The composites obtained demonstrate improved thermal stability comparing with commercial NH_4PO_3. The morphology of pellets under the same conditions shows the smoother and denser surface with more PTFE content added. The conductivity was measured by ac impedance spectroscopy under different atmospheres. The composites were found to exhibit a higher conductivity in humid 5% H_2/Ar compared with open air atmosphere. A maximum conductivity of 2.3 mS/cm is obtained at 250 °C for NH_4PO_3–PTFE (volume ratio = 2:1) sample in humid 5% H_2/Ar.

1. Introduction

In the last decade, fuel cells have attracted widespread attention due to their advantages of high efficiency in energy conversion and low emission [1]. Various types of fuel cells, including high-temperature (above 550 °C) and low-temperature (below 150 °C) fuel cells, are under extensive development owing to their environmental compatibility, potential for use in stationary and distributed electric power stations, as well as in transportation applications [2–4]. However, high-temperature operation of fuel cells will cause some problems such as severe restriction on the choice of materials, electrode sintering programme, interfacial diffusion across the electrolyte and electrodes and mechanical stresses due to difference in their thermal expansion/shrinkage value [5]. On the other hand, low-temperature fuel cells generally require an extra humidifier, which will make the whole system complex and large [6]. Moreover, the CO poisoning of Pt catalyst is also serious when operating at low temperatures [7]. Intermediate temperature fuel cells (150–550 °C), which combine many advantages of both high- and low-temperature fuel cells, are promising to solve these problems.

Recently, ammonium polyphosphate (APP, NH_4PO_3) has been studied as a intermediate-temperature proton conducting electrolyte [8–13]. However, pure phase APP is not stable at the temperature of more than 250 °C. Considerable efforts have recently been devoted to the application of supporting matrix, which can enhance its stability, mechanic strength and ionic conductivity. Many inorganic supporting matrixes, such as SiO_2, $(NH_4)_2SiP_4O_{13}$, TiP_2O_7, $(NH_4)_2Mn(PO_3)_4$, etc. have intensively been studied in APP composite electrolyte [10–13]. However, it is difficult to obtain dense NH_4PO_3 electrolyte with inorganic supporting matrix. On the other hand, to mix NH_4PO_3 with thermally stable polymers such as poly(tetrafluoroethylene) (PTFE) is much easier to get dense film [14]. But till now, there is still lack of the study of APP-based inorganic–organic composite electrolyte, the latter of which has received a great deal of attention due to their advantages in improving mechanic and thermal properties as well as protonic conductivity.

In the present study, we developed APP–PTFE inorganic–organic composite electrolytes and investigated their electrochemical properties and stabilities under various conditions.

2. Experimental

The commercial ammonium polyphosphate powders with crystal phase of form II (NH_4PO_3, APP, FR CROS 489) were used as a starting material. The inorganic–organic composite electrolytes were prepared by mixing NH_4PO_3 with PTFE suspension (Aldrich, 60 wt% in water) in volume ratios of 2:1 and 1:1 for NH_4PO_3 and PTFE. The obtained mixtures were stirred for 2 h and then left to dry overnight in an oven at 80 °C for the evaporation of water. The resulting composite was pressed at 800 MPa into pellets, 13 mm in diameter and approximately 5 mm in thickness, which were used for the scanning electron microscope (SEM) examination and conductivity measurements. In order to simplify expressing the description of composite electrolytes, the composites of NH_4PO_3–PTFE (2:1) and NH_4PO_3–PTFE (1:1) are hereafter referred as NP21 and NP11, respectively.

Crystal structure and phase purity were examined by X-ray diffraction (XRD, Cu Kα, λ = 0.15418 nm) analysis of powders on a Stoe STADI/P powder diffractometer. The chemical stability of NH_4PO_3–PTFE composites was carried out on a thermogravimetry (TG, Rheometric Scientific TG 1000M) with heating and cooling rate of

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5 °C/min under flowing air at a rate of 20 mL/min. The morphologies of pellets were examined by JEOL 5600 scanning electron microscope (SEM). The conductivity measurements were carried out by the A.C. method using a Schlumberger Solartron 1250 Frequency Response Analyzer coupled with a 1287 Electrochemical Interface controlled by *Z*-plot electrochemical impedance software over the frequency range 65 kHz to 100 mHz. PTFE bonded carbon (Carbot Vulcan 72R) was dabbed on both sides of the pellets which served as electrodes. Carbon paper (Torory TGPH-090) was subsequently pressed on as current collector. The impedance spectra were recorded after holding 1 h at each temperature to reach equilibrium by using a 4-electrode technique. The measurements were conducted in air and wet 5% H_2/Ar by passing the gas through room temperature water, respectively. The data were analyzed using a Z-View software (version 2.1).

3. Results and discussion

3.1. Phase composition, thermal stability and morphology

Fig. 1(a, c and e) shows the XRD patterns of the commercial NH_4PO_3 (FR CROS489) and NH_4PO_3–PTFE composite samples. The CROS 489 used (Fig. 1a) is a pure phase NH_4PO_3 with orthorhombic structure (NH_4PO_3 II), which is consistent with the standard spectra of JCPDS #22-0062 (Joint Committee on Powder Diffraction Standards) [15]. In the patterns of NH_4PO_3–PTFE composite samples, the peak with high intensity at around 18° can be found, which can be indexed to the typical peak of PTFE (JCPDS #47-2217) [15].

In order to investigate the stability of composite electrolytes, thermal analysis was carried out in a flowing air atmosphere. Commercial NH_4PO_3 was also shown for comparisons. Fig. 2(a and b) shows all the three TG curves as well as the temperature programme curve. For pure NH_4PO_3 sample, it starts to lose weight slowly within the range of 50–250 °C and then lose weight significantly above 250 °C due to the partial decomposition of sample. After held isothermally at 300 °C for 30 min, the total weight loss of sample is about 15.4%. A weight gain of 2.3% is found when the temperature returns to room temperature, which is due to the adsorption of water and subsequent reactions. For NH_4PO_3–PTFE composite samples, they start to lose weight at about 160 °C. After held isothermally at 300 °C for 30 min, the weight losses of NP21 and NP11 are 10.5% and 9.5%, respectively. The samples after TG test were also analysed by XRD, as shown in Fig. 1(b, d and f). It could be seen that peaks indexing to NH_4PO_3 phase II of all three samples disappear due to the thermal decomposition of NH_4PO_3 to HPO_3 [8]. These results indicate a relatively better stability of the composites comparing with pure commercial NH_4PO_3 sample.

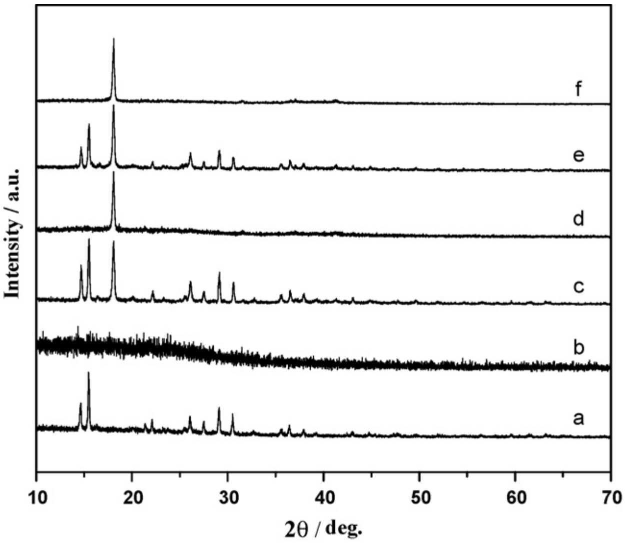

Fig. 1. X-ray diffraction patterns of (a) commercial NH_4PO_3; (b) commercial NH_4PO_3 after TG test; (c) NP21; (d) NP21 after TG test; (e) NP11; and (f) NP11 after TG test.

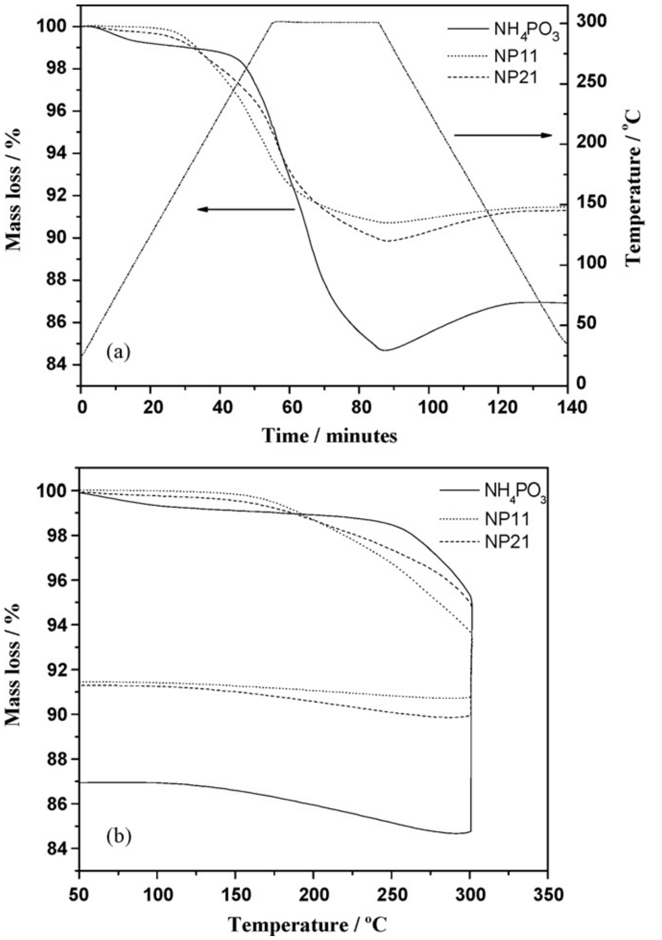

Fig. 2. TGA curves of commercial NH_4PO_3, NP21 and NP11 from 25 °C to 300 °C (5 °C/min up and down) in air and holding at 300 °C for 30 min.

The morphologies of pellets of the composites and commercial NH_4PO_3 were examined by SEM. Fig. 3 shows the pictures taken at a magnification of 500. Unlike the pellet of commercial NH_4PO_3 where the surface is very coarse, the pictures of composites present much smoother surfaces. Furthermore, with more PTFE content added, pellets with smoother and denser surface were obtained.

3.2. Conductivity

The conductivities of the composites were determined at various temperatures in air and wet 5% H_2/Ar (humidified at 20 °C) by impedance measurements. Fig. 4 shows the typical impedance spectra of NP21 composite in air. It is clear that the impedance spectra are characterized by straight lines with high frequency intercepts on the real axis. The resistance of the composite was estimated from the intercept on the real axis.

In order to achieve a steady state of measurements, each sample was annealed in air at 250 °C for 24 h. The dependence of conductivities of composites on annealing time is shown in Fig. 5. The initial conductivity of NP21 is about 0.23 mS/cm, which is about four times of that of NP11. Then both the conductivities of NP21 and NP11 are increasing along with the annealing process. For NP21 sample, it takes about 20 h to achieve a stable state. On the other hand, it takes about twice time to achieve a stable state for NP11 sample, which is due to the different decomposition process of NH_4PO_3.

Fig. 5 shows the Arrhenius plots of the composites in air and humid 5% H_2/Ar within the temperature range of 150–250 °C. The measurements were conducted after each sample was annealed at

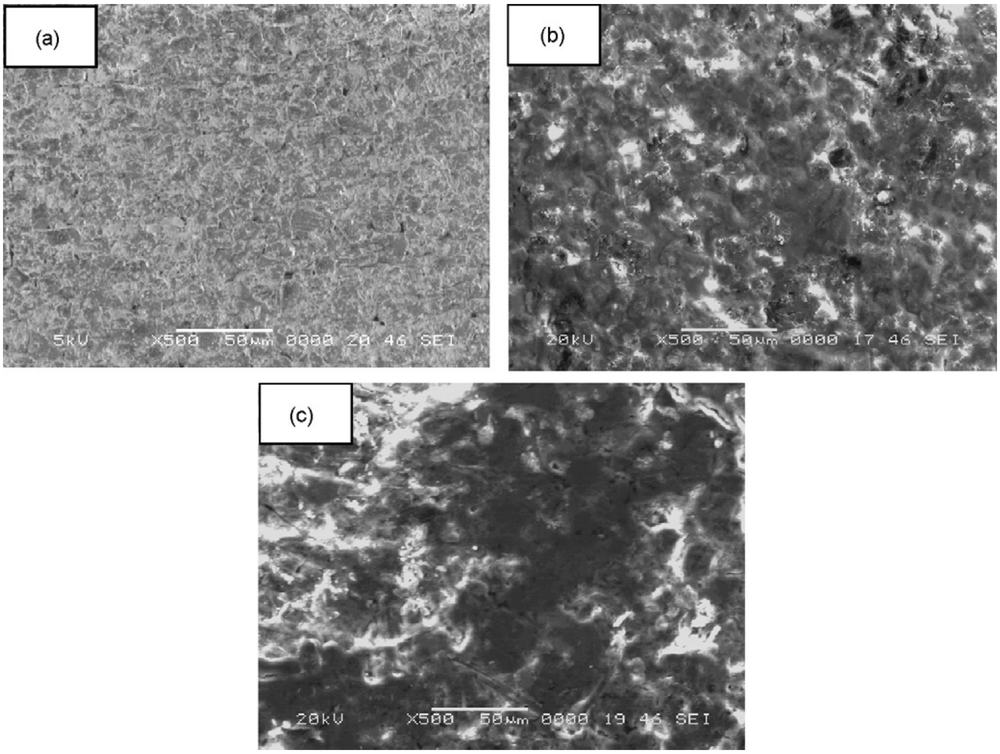

Fig. 3. SEM pictures of pellet surface morphologies of (a) commercial NH_4PO_3; (b) NP21; and (c) NP11 at a magnification of 500, respectively.

250 °C for certain hours to achieve a steady state. The conductivity is improved by increasing the volume ratio of NH_4PO_3 in the composite at each given temperature whenever in air or humid 5% H_2/Ar. In air, a maximum conductivity of 1.1mS/cm is obtained at 250 °C for NP21. After measuring the conductivity in air, the gas environment was changed to humid 5% H_2/Ar. In humidified 5% H_2/Ar, the conductivities are about one magnitude higher than those in air for both NP21 and NP11. In comparison, the Arrhenius plot of NP11 in humid 5% H_2/Ar is not linear in the whole temperature range. The conductivity increases gradually from 150 to 225 °C and then decreased at 250 °C, which was also reported by Sun and Stimmng [16]. This phenomenon may be interpreted by the hydrophobic property of PTFE. The maximum conductivity are 1.3 mS/cm at 225 °C for NP11 and 2.3 mS/cm at 250 °C under humid 5%H_2/Ar, respectively (Fig. 6).

In order to investigate the proton migration mechanism and inorganic–organic composite effect, the values of the activation energy (E_a) were calculated by linear regression of the Arrhenius equation $\sigma = \sigma_0 \exp(-E_a/kT)$, where σ_0 is a pre-exponential parameter and k is the Bolzmann's constant. In air, the activation energy values for NP21 and NP11 are about 0.15 and 0.16 eV, respectively. According to these values, proton migration is dominated by the Grotthuss mechanism. In this mechanism, the proton forms a H_3O^+

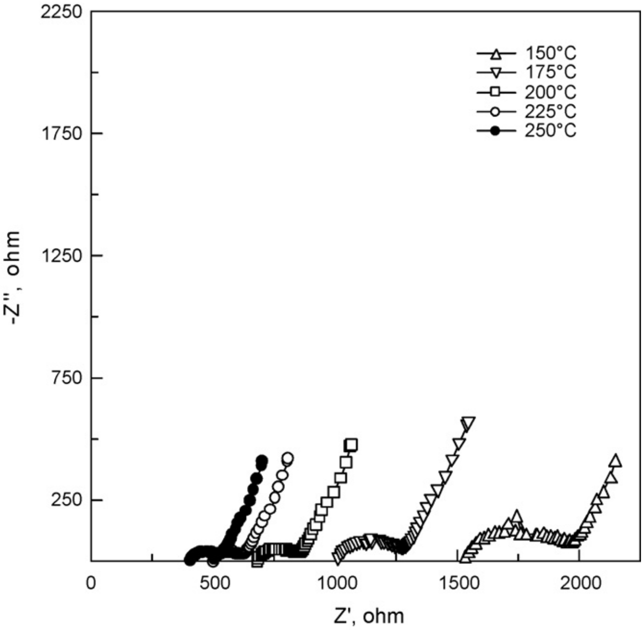

Fig. 4. Impedance spectra of the NP21 in air at different temperatures.

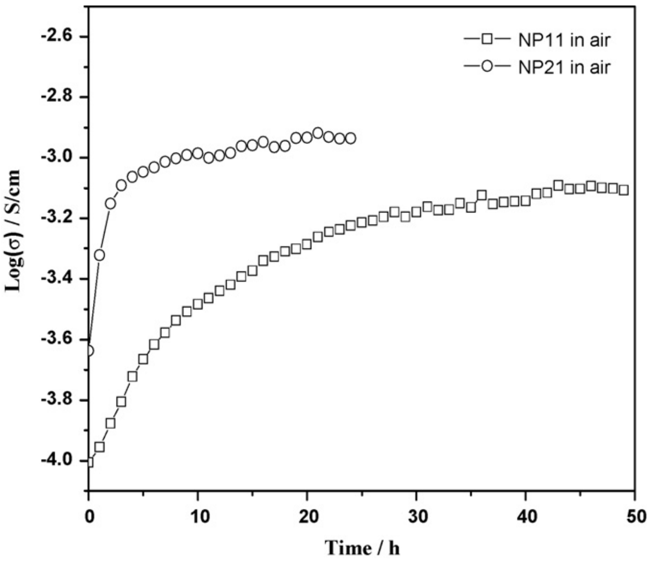

Fig. 5. The dependence of conductivity in air of NP11 and NP21 on annealing time at 250 °C.

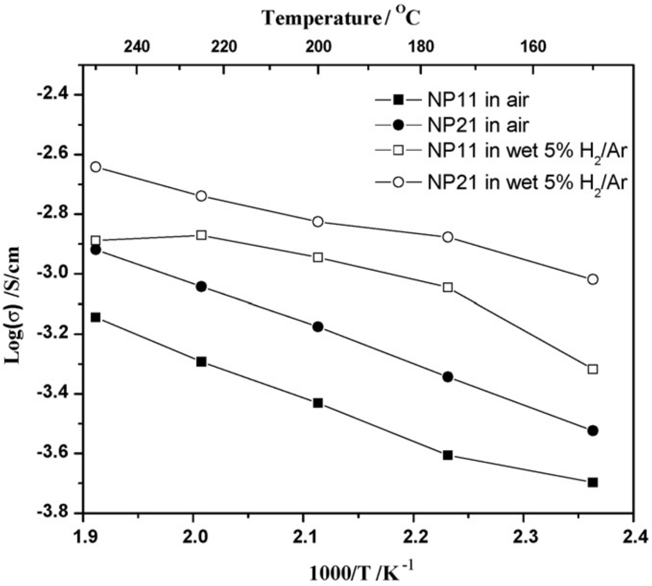

Fig. 6. Conductivity of NP11 and NP21 in air and in wet 5% H_2/Ar (humidified at 20 °C).

ion and jumps to the neighboring lone pair of electrons of a water molecule. For such a mechanism, the activation energy for proton conduction should be about 0.14–0.40 eV [17]. The values of activation energy are reduced slightly in humid 5% H_2/Ar, which is due to the more water molecules participating in the proton conduction.

4. Conclusions

In this work, we prepared NH_4PO_3–PTFE inorganic–organic composite electrolytes for the first time. Their phase compositions, thermal stability and morphologies were investigated in detail. The composites obtained demonstrate improved thermal stability comparing with commercial NH_4PO_3. The morphology of pellets under the same conditions shows the smoother and denser surface with more PTFE content added. The conductivity was measured by ac impedance spectroscopy under different atmospheres. The composites were found to exhibit a higher conductivity in humid 5% H_2/Ar compared with air atmosphere. A maximum conductivity of 2.3 mS/cm is obtained at 250 °C for NP21 in humid 5% H_2/Ar. Unfortunately, the conductivity of the composites is not high enough to be used as electrolyte for fuel cells, but they may be used for other applications such as gas sensors.

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