

Solid state protonic conductor $\text{NH}_4\text{PO}_3-(\text{NH}_4)_2\text{Mn}(\text{PO}_3)_4$ for intermediate temperature fuel cells

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Abstract

A new proton-conductive composite of $\text{NH}_4\text{PO}_3-(\text{NH}_4)_2\text{Mn}(\text{PO}_3)_4$ was synthesized and characterized as a potential electrolyte for intermediate temperature fuel cells that operated around 250 °C. Thermal gravimetric analysis and X-ray diffraction investigation showed that $(\text{NH}_4)_2\text{Mn}(\text{PO}_3)_4$ was stable as a supporting matrix for NH_4PO_3 . The composite conductivity, measured using impedance spectroscopy, improved with increasing the molar ratio of NH_4PO_3 in both dry and wet atmospheres. A conductivity of 7 mS cm⁻¹ was obtained at 250 °C in wet hydrogen. Electromotive forces measured by hydrogen concentration cells showed that the composite was nearly a pure protonic conductor with hydrogen partial pressure in the range of 10²–10⁵ Pa. The proton transference number was determined to be 0.95 at 250 °C for $2\text{NH}_4\text{PO}_3-(\text{NH}_4)_2\text{Mn}(\text{PO}_3)_4$ electrolyte. Fuel cells using $2\text{NH}_4\text{PO}_3-(\text{NH}_4)_2\text{Mn}(\text{PO}_3)_4$ as an electrolyte and the Pt–C catalyst as an electrode were fabricated. Maximum power density of 16.8 mW/cm² was achieved at 250 °C with dry hydrogen and dry oxygen as the fuel and oxidant, respectively. However, the $\text{NH}_4\text{PO}_3-(\text{NH}_4)_2\text{Mn}(\text{PO}_3)_4$ electrolyte is not compatible with the Pt–C catalyst, indicating that it is critical to develop new electrode materials for the intermediate temperature fuel cells.

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1. Introduction

While some oxide materials are protonic conductors at temperatures as high as 600 °C [1,2], most protonic conductors have an operating temperature below 150 °C. A solid protonic conductor that has a high conductivity at 150–500 °C would be most useful as electrolyte for applications in intermediate temperature fuel cells [3]. However, only a few studies have been conducted on electrolytes for use at 150–500 °C [4–6] and protonic conductors that operate at this temperature range have not been developed yet.

Recently, ammonium polyphosphate (APP, NH_4PO_3) has been studied as a proton conductive electrolyte [6–8]. Ammonium polyphosphate composites, APP– $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$ [7] and APP– TiP_2O_7 [8], were reported to exhibit very high conductiv-

ities at 250 °C under dry and wet atmospheres. In these composites, APP provides high ionic conductivity, and $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$ and TiP_2O_7 are used as supporting matrix [6]. The high ionic conductivity originates in the thermal decomposition of APP to HPO_3 at around 250 °C. While the decomposition is necessary to increase APP conductivity to an appreciable level, it also lowers APP's melting point and thus softens the electrolyte. Therefore, APP is usually made into composite to enhance its mechanical strength. $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$ [7] and TiP_2O_7 [8], which have much higher melting points than APP and chemically compatible with APP, have been recently used as supporting matrixes.

$(\text{NH}_4)_2\text{Mn}(\text{PO}_3)_4$ is an analogue of APP and stable below 400 °C [9]. It may be a good supporting matrix. In this paper, we report the preparation, proton-transport properties of APP– $(\text{NH}_4)_2\text{Mn}(\text{PO}_3)_4$ composites, and the contribution of supporting matrix to conduction at 130–250 °C. Further, fuel cells that incorporate a APP– $(\text{NH}_4)_2\text{Mn}(\text{PO}_3)_4$ composite as electrolytes are evaluated.

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2. Experimental

$(\text{NH}_4)_2\text{Mn}(\text{PO}_3)_4$ was synthesized using commercial ammonium polyphosphate (APP, NH_4PO_3) and manganese dioxide (MnO_2) as raw materials. The APP had form I structure as identified with X-ray diffraction (XRD) pattern [10]. MnO_2 was prepared by oxidizing MnCl_2 with KMnO_4 in solutions, resulting in a black precipitate. Fine MnO_2 powders were obtained by filtering the precipitate and drying in vacuum. The MnO_2 was then mixed with APP in the molar ratio required to form $(\text{NH}_4)_2\text{Mn}(\text{PO}_3)_4$. The mixed powders were subsequently heated at 400°C for 10 h in NH_3 . The resulting products were ground into powders.

Composite electrolytes were prepared by mixing $(\text{NH}_4)_2\text{Mn}(\text{PO}_3)_4$ and APP in various molar ratios as $x\text{APP}-(\text{NH}_4)_2\text{Mn}(\text{PO}_3)_4$, where $x=2, 4, \text{ and } 6$. The mixtures were milled, pressed at 250 MPa into pellets and fired at 400°C for 10 h in NH_3 . The pellets were 15 mm in diameter and 0.9–2 mm in thickness.

Both the anode and cathode contained two overlapped conductive porous layers: a diffusion layer formed from Toray TGP 090 carbon paper having a thickness of 0.3 mm, a porosity of 76% and wet-proofed with polytetrafluoro-ethylene (PTFE), and a catalyst layer formed from APP, Pt–C catalyst (Dalian sunrise power Co. Ltd) and PTFE. The catalyst ink was prepared by mixing APP, distilled water, 50% Pt–C, glycerol and a 60 wt% PTFE dispersion (Teflon-30 dispersion–DuPont). The ink was spread onto the carbon paper, dried at 200°C and sintered at 370°C for 30 min. Both the PTFE and the APP contents in the catalyst layer were 23 wt.% and the platinum loading was 0.8 mg/cm^2 . The composite pellet was sandwiched by the two electrodes to form a single cell.

The crystalline structures of composite electrolytes were examined by XRD patterns (Philips X'pert PROS diffractometer). Thermo gravimetric analysis measurements (TGA) were performed with TA-50 (SHIMADZU) thermal analyzer at a heating rate $10^\circ\text{C}/\text{min}$ under nitrogen flow of 100 ml/min. Conductivity measurements were carried out by means of ac impedance spectroscopy with Zahner IM6e electrochemical workstation in the frequency range of $1-10^6$ Hz. Single cells of gas (H_2), Pt–C|APP– $(\text{NH}_4)_2\text{Mn}(\text{PO}_3)_4$ |Pt–C, gas (H_2/Ar or O_2) were fabricated in order to measure proton transference number and fuel cell performance. The thickness of the electrolyte was 0.9 mm and the fuel/oxidant flow was about 50 ml/min.

3. Results and discussions

The thermal stability of the $(\text{NH}_4)_2\text{Mn}(\text{PO}_3)_4$ has been determined by means of TGA measurement. As shown in Fig. 1, the weight decreases gradually around 300°C . After an initial mass loss of 0.9%, the material is thermally stable below 300°C . This result is consistent with the previous report that $(\text{NH}_4)_2\text{Mn}(\text{PO}_3)_4$ is thermally stable up to 400°C [9]. The mass loss corresponds most probably to a loss of H_2O which was absorbed from air into $(\text{NH}_4)_2\text{Mn}(\text{PO}_3)_4$ or/and NH_3 which was absorbed into $(\text{NH}_4)_2\text{Mn}(\text{PO}_3)_4$ when it was treated in NH_3 . When increasing the temperature from 150 to 250°C again, the

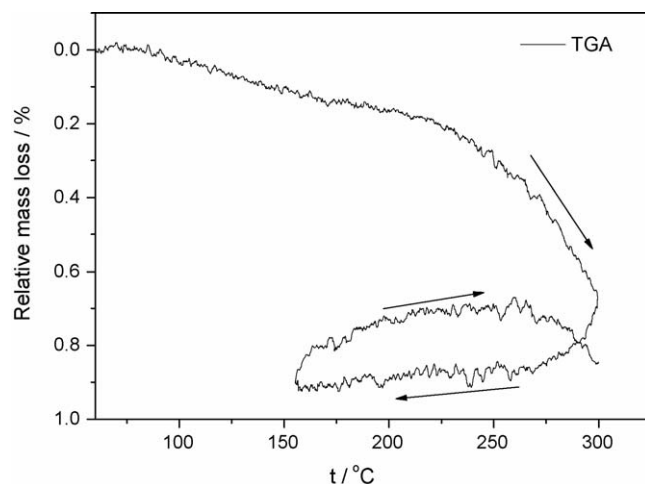


Fig. 1. The mass loss of $(\text{NH}_4)_2\text{Mn}(\text{PO}_3)_4$ as a function of temperature in nitrogen.

subsequent weigh gain is about 0.2%. The weigh gain maybe corresponds to the intrinsic errors of the apparatus.

Shown in Fig. 2 are XRD patterns for APP– $(\text{NH}_4)_2\text{Mn}(\text{PO}_3)_4$ composites. Fig. 2a shows that $(\text{NH}_4)_2\text{Mn}(\text{PO}_3)_4$ is well-crystallized when the pattern is compared with that reported in JCPDS 73-1060. Fig. 2e shows that a form V type of APP is formed when APP I is heated at 400°C in NH_3 [10]. Fig. 2b–d show that both patterns of APP V and $(\text{NH}_4)_2\text{Mn}(\text{PO}_3)_4$ are present in the composite. The intensity of the peak assigned to APP V increases with the increase of APP in the composite. Furthermore, no obvious interaction reactions are observed between the two components when these patterns are carefully examined. This implies that $(\text{NH}_4)_2\text{Mn}(\text{PO}_3)_4$ is chemically compatible with APP when the composites were fired at 400°C in NH_3 . The firing is necessary to increase the electrolyte density.

Shown in Fig. 3 are XRD patterns for $(\text{NH}_4)_2\text{Mn}(\text{PO}_3)_4$ and APP– $(\text{NH}_4)_2\text{Mn}(\text{PO}_3)_4$ composites fired at 250°C for 24 h in air. Comparing Fig. 3a with Fig. 2a it can be found that

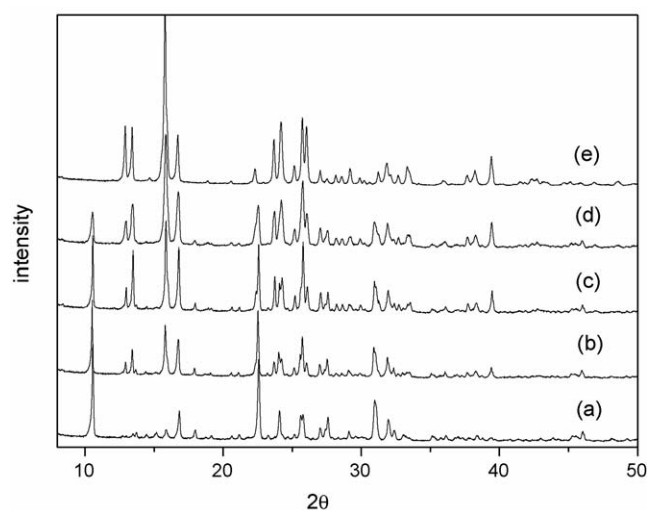


Fig. 2. XRD diffraction patterns for composites consisting of APP and $(\text{NH}_4)_2\text{Mn}(\text{PO}_3)_4$. The molar ratio of APP: $(\text{NH}_4)_2\text{Mn}(\text{PO}_3)_4$ is (a) 0:1, pure $(\text{NH}_4)_2\text{Mn}(\text{PO}_3)_4$, (b) 2:1, (c) 4:1, (d) 6:1, and (e) 1:0, pure APP.

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