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Structural transformation of an imidazolium-templated two-dimensional aluminophosphate and its proton conduction under anhydrous conditions

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ABSTRACT

We focused on an imidazolium-templated two-dimensional aluminophosphate $(C_3N_2H_5)[Al(HPO_4)_2(H_2O)_2]$ (denoted as AlPO-PC-1) with complex hydrogen bonding network to show inherent proton conductivity under anhydrous conditions. Inherent proton conductivity was studied under a N_2 atmosphere (zero-humidity conditions). Notably, the AlPO-PC-1 suffers the ordered-to-disordered structural transformation induced by the increase of temperature, which influences the proton conduction process and conduction mechanism. The resulting material shows a proton conductivity of 1.1×10^{-4} S cm^{-1} at 150 °C. At 25–100 °C, the proton conduction is controlled by Grotthuss mechanism. While at 115–150 °C, the transformation of the structure affords highly mobile proton carriers and both vehicle and Grotthuss mechanism contribute to the proton conduction.

1. Introduction

Anhydrous proton conducting materials with proton conductivities under moderate temperature (100–400 °C) are critical for the development of proton exchange membrane fuel cells [1]. An approach to reach such goal is to replace the traditional proton carrier (H_2O) to *N*-heterocyclic molecules (e.g., imidazole). Based on this idea, many researchers have explored new kinds of materials [2]. Inorganic open-framework materials have shown their amazing advantages in many fields such as catalysis and separation [3,4]. As for the proton conduction under moderate temperature and anhydrous conditions, remarkable materials with proton conductivities ranging from 10^{-5} to 10^{-3} S cm^{-1} at 100–150 °C have been achieved by metal-organic frameworks (MOFs) or porous coordination polymers (PCPs) by introducing *N*-heterocyclic molecules as the proton carriers [5–8]. The crystal structure and complex hydrogen bonding network determine the proton conductivity. However, the development of anhydrous proton conduction is still in its infancy. More examples to elucidate the relationship between the structures and properties are needed [9]. Open-framework aluminophosphates are an important class of inorganic-organic hybrid materials with various structural compositions and rich structural architectures [10]. As for the anhydrous proton conduction of aluminophosphates, an aluminum phosphate was used to synthesize a solid-state hybrid with imidazole by using mechanical milling method. The definite structure of the material could not be given [11]. However, to our knowledge, the open-framework crystalline aluminophosphates with inherent proton conduction under anhydrous conditions have not been reported.

$(C_3N_2H_5)[Al(HPO_4)_2(H_2O)_2]$ (denoted as AlPO-PC-1) was reported as a two-dimensional (denoted as 2D) aluminophosphate [12]. Its anionic layers are composed of alternating $AlO_4(H_2O)_2$ octahedra and $PO_2(OH)(=O)$ tetrahedra, and protonated imidazole molecules are located in the interlayer region. Because of the existence of complex hydrogen bonding network and proton-carrier molecules, AlPO-PC-1 is desirable to provide the effective proton transport pathway. In this work, we investigate the anhydrous proton conductivity of AlPO-PC-1. Strikingly, activated proton carriers by the temperature and structural amorphization improve the carrier mobility and proton conductivity.

2. Experimental

The 2D aluminophosphate (AlPO-PC-1) was synthesized referring to the literature with an overall molar composition of 1.0 Al$(NO_3)_3$: 11 H_3PO_4: 11 imidazole: 350 H_2O [12]. The crystalline product was separated by filtration after stirring at room temperature for 7 days.

Powder X-ray diffraction (PXRD) was recorded on a Rigaku D/max-2550 diffractometer. Thermogravimetric analysis (TG) was

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performed on a TA Q500 analyzer. ^{31}P and ^{27}Al NMR experiments were performed on Bruker AVANCE III 400 WB spectrometer. Differential scanning calorimetric (DSC) analysis was carried out on a TA instrument DSC Q100. The IR absorption spectrum was recorded on a Bruker FTIR IFS-66V/S spectrometer. Scanning electron microscopy (SEM) image was taken with a JSM-6510 (JEOL) electron microscope. Impedance analysis was carried out with an impedance and gain-phase analyzer (Solartron SI 1260) under dry nitrogen flow atmosphere.

Detailed information on the synthesis and characterization can be found in the supplementary material.

3. Results and discussion

The as-synthesized AlPO-PC-1 is a pure phase according to the XRD pattern (Fig. 1a) and the SEM image (Fig. S1). The calcined samples remain unchanged at 100 °C as indicated by the XRD pattern. When the calcined temperature was increased to 150 °C, the structure collapses to amorphous. For TG analysis, there is no clear weight loss below 100 °C. At 100–150 °C, the material suffers from a gradual loss of 10.5%, which is matched with the weight of losing the crystalline water (theoretical value 11.1%). At 150–400 °C, the weight loss of 20.7% attributes to the decomposition of imidazole molecules (theoretical value 21.0%). DSC curve showed the endothermic peak appeared at 169 °C, corresponding to the decomposition and melt of imidazole (Fig. S2).

The proton conductivity of AlPO-PC-1 was measured from room temperature to 150 °C under dry N_2 atmosphere. According to the A.C. impedance plots, AlPO-PC-1 shows the conductivity of 3.7×10^{-8} S cm^{-1} at room temperature. While, the conductivity increases with the temperature, which turns to 1.2×10^{-7} S cm^{-1} at 100 °C (Fig. 2a) and 1.1×10^{-4} S cm^{-1} at 150 °C (Fig. 2b). The proton conductivity of AlPO-PC-1 is comparable with some reported metal phosphates [13,14] and PCPs/MOFs [15] at 150 °C under anhydrous conditions.

The proton conduction mechanism is generally identified by the activation energy (*E*a) [8]. According to the Arrhenius plots [ln

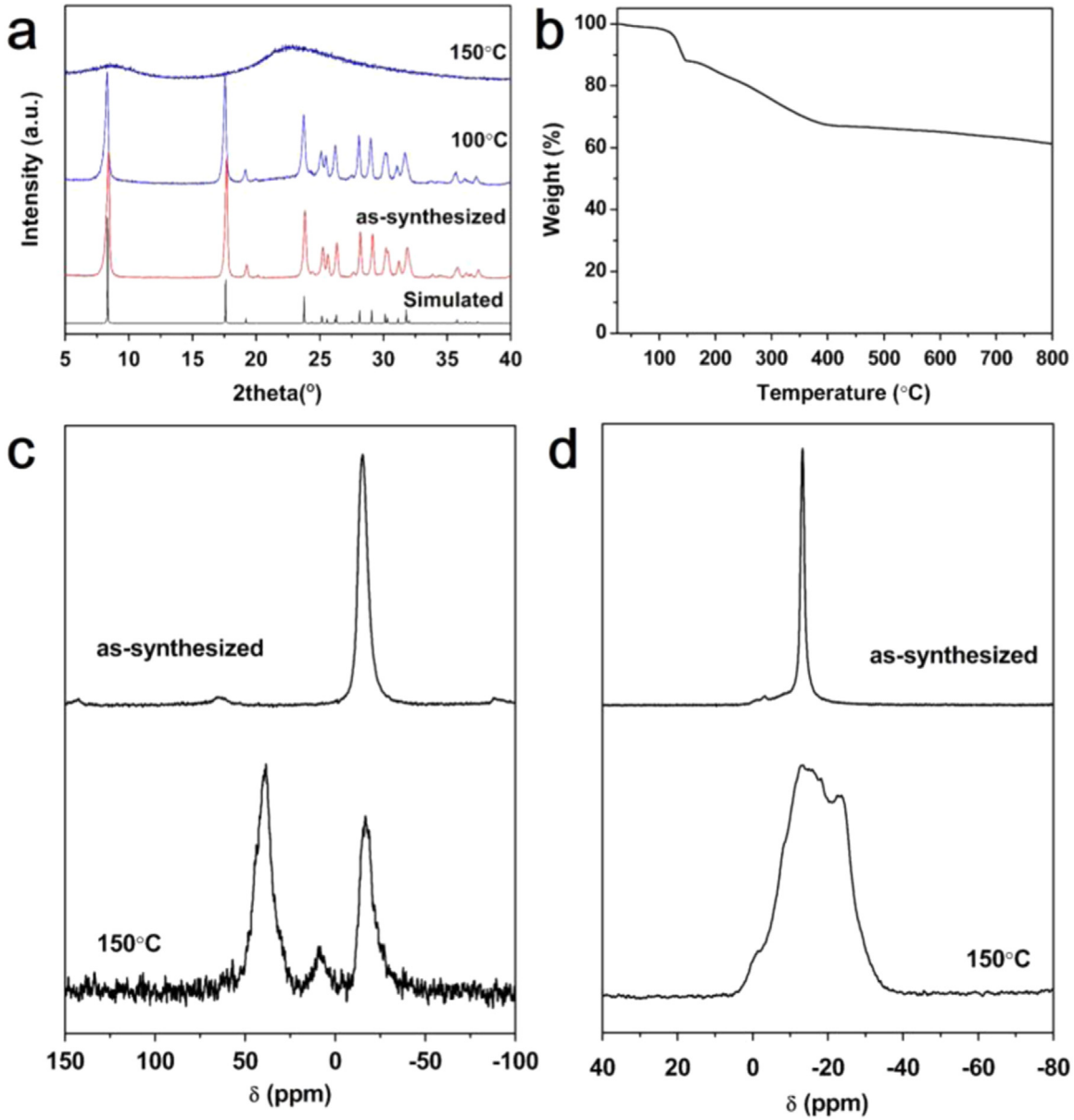

Fig. 1. (a) XRD patterns of AlPO-PC-1 and the calcined samples at different temperatures compared with the simulated XRD pattern. (b) TG curve of AlPO-PC-1. (c) ^{27}Al MAS NMR spectra of AlPO-PC-1 and the calcined samples at 150 °C. (d) ^{31}P MAS NMR spectra of AlPO-PC-1 and the calcined samples at 150 °C.