DEVELOPMENT OF NEW PROTON CONDUCTING MATERIALS FOR INTERMEDIATE TEMPERATURE FUEL CELLS

Xiaoxiang Xu

A Thesis Submitted for the Degree of PhD at the University of St. Andrews



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Development of New Proton Conducting Materials

for Intermediate Temperature Fuel Cells

A thesis submitted for the degree of Ph.D.

by

Xiaoxiang Xu

Supervised by Prof. John T.S. Irvine and Dr. Shanwen Tao



University of St Andrews

Submitted December 2009

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Abbreviations and Symbols Used in this Thesis

a	Distance between two defect positions
A	Area of the electrode
AFCs	Alkaline fuel cells
С	Capacitance
C _i	Concentration of ion i
CPE	Constant phase elements
D	Doping concentration
d	Diameter of the pellet
D_i	Diffusion coefficient of ion i
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
E_a	Equivalent energy barriers
E _{ai}	Energy barrier for interstitial ions
E_{av}	Energy barrier for ionic vacancies
EDS	Energy-dispersive X-ray spectroscopy
E_f	Formation energy of one Frenkel defect
EMF	Electromotive force
F	Faraday constant
FT-IR	Fourieer transformed infrared spectra
h	Planck constant
HT-PEMFCs	High temperature proton exchange membrane fuel cells
IS	Impedance spectroscopy
ITFCs	Intermediate temperature fuel cells
J	Current density
j	Imaginary unit
Κ	Equilibrium constant
k	Force constant
k_B	Boltzmann constant

l	Thickness of the pellet
LSGM	Lanthanum strontium gallium manganite
M	Number of ionic pairs in the crystal
m	Mass of a unit cell
MCFCs	Molten carbonate fuel cells
m_e	Mass of a electron
M_k	Characteristic constant of doping concentration for ion k
n	Defect concentration
Ν	Avogadro number
N_k	Characteristic constant of partial pressure for ion k
OCV	Open circuit voltage
Р	Pressure
PAFCs	Phosphoric acid fuel cells
PBI	Polybenzimidazole
PEMFCs	Proton exchange membrane fuel cells
PTFE	Polytetrafluoroethylene
PVA	Polyvinyl alcohol
PVP	Poly N-vinyl pyrrolidone
QAPPESK	Quaternized poly phthalzainone ether sulfone ketone
R	Gas constant
SAFCs	Solid acid fuel cells
SEM	Scanning Electron Microscope
SOFCs	Solid oxide fuel cells
SPBI	Sulfonated polybenzimidazole
SPEEK	Sulfonated poly ether ether ketone
SPSF	Sulfonated polysulfone
Т	Absolute temperature
ТЕМ	Transmission Electron Microscopy
TGA	Thermogravimetry analysis

ТМА	Thermomechanical analysis			
u_k	Mobility of ion k			
V	Velocity of defect transfer			
v_0	Hopping frequency			
XRD	X-ray diffraction analysis			
YSZ	Yttrium stabilized zirconium			
Z _i	Electrical charge on ion i			
a_k	Characteristic constant of ion k			
Yrk	Characteristic constant of equilibrium constant for ion k at reaction r			
3	External electrical field			
η	Viscosity			
θ	Incident angle			
λ	Wavelength of the light			
μ	Reduced mass			
$ ho_e$	Experimental density			
ρ_t	Theoretical density			
σ_i	Ionic conductivity of ion i			
φ	Phase angle shift			
ω	Angular frequency			

ABSTRACT

The work in this thesis mainly focuses on the preparation and characterization of several phosphates and solid oxide systems with the aim of developing new proton conducting materials for intermediate temperature fuel cells (ITFCs). Soft chemical methods such as sol-gel methods and conventional solid state methods were applied for the synthesis of these materials.

Aluminum phosphate obtained by a solution method is single phase and belongs to one of the $AI(H_2PO_4)_3$ allotropies with hexagonal symmetry. The material is stable up to 200 °C and decomposes into $AI(PO_3)_3$ at a higher temperatures. The electrical conductivity of pure $AI(H_2PO_4)_3$ is on the order of $10^{-6}-10^{-7}$ S/cm, very close to the value for the known proton conductors $AIH_3(PO_4)_2 \cdot 3H_2O$ and $AIH_2P_3O_{10} \cdot 2H_2O$. Much higher conductivity is observed for samples containing even a trace amount of excess H_3PO_4 . It is likely that the conduction path gradually changes from grain interior to the surface as the acid content increases. The conductivity of $AI(H_2PO_4)_3 - 0.5H_3PO_4$ exhibited a good stability over the measured 110 hours.

Although tin pyrophosphate (SnP_2O_7) has been reported to show a significantly high conductivity (~10⁻² S/cm) at 250 °C in various atmospheres, we observed large discrepancies in the electrical properties of SnP_2O_7 prepared by different methods. Using an excess amount of phosphorous in the synthetic procedure generally produces SnP_2O_7 with much higher conductivity (several orders of magnitude higher) than samples with stoichiometric Sn:P ratios in their synthetic procedure. Solid state ³¹P NMR confirmed the presence of residual phosphoric acid for samples with excess starting phosphorous. Transmission Electron Microscope (TEM) confirmed an amorphous layer covered the SnP_2O_7 granules which was probably phosphoric acid or condensed phases. Thereby, it is quite likely that the high conductivity of SnP_2O_7 results mainly from the contribution of the residual acid. The conductivity of these samples exhibited a good stability over the measured 80 hours.

Based on the observations for SnP_2O_7 , we developed a nano core-shell structure based on BPO_4 and P_2O_5 synthesised by solid state methods. The particle size of BPO_4 using this method varied between 10-20 nm depending on the content of P_2O_5 . TEM confirmed the existence of an amorphous layer that is homogeneously distributed. The composite exhibits the highest conductivity of 8.8×10^{-2} S/cm at 300 °C in air for 20% extra P_2O_5 and demonstrates a good stability during the whole measured 110 hours. Polytetrafluoroethylene (PTFE) was introduced into the composites in order to increase malleability for fabrication. The conductivity and mechanical strength were optimized by adjusting the PTFE and P_2O_5 content. These organicinorganic composites demonstrate much better stability at elevated temperature (250°C) over conventional SiC-H₃PO₄-PTFE composites which are common electrolytes for phosphoric acid fuel cells (PAFCs). Fuel cells based on BPO₄-H₃PO₄-PTFE composite as the electrolyte were investigated using pure H₂ and methanol as fuels. A maximum power density of 320 mW/cm² at a voltage of 0.31 V and a maximum current density of 1.9 A/cm² at 200 °C were observed for H₂/O₂ fuel cells. A maximum power density of 40 mW/cm² and maximum current of 300 mA/cm² 275 °C were observed when 3M methanol was used in the cell.

Phosphoric acid was also introduced into materials with internal open structures such as phosphotungstic acid ($H_3PW_{12}O_{40}$) and heteropolyacid salt ((NH_4)₃PW_{12}O_{40}), for the purpose of acquiring additional connections. The hybrids obtained have a cubic symmetry with enlarged unit cell volume, probably due to the incorporation of phosphoric acid into the internal structures. Solid state ³¹P NMR performed on $H_3PW_{12}O_{40}$ -x H_3PO_4 (x = 0-3) showed additional peaks at high acid content which could not assigned to phosphorus from the starting materials, suggesting a strong interaction between $H_3PW_{12}O_{40}$ and H_3PO_4 . The conductivity of hybrids was improved significantly compared with samples without phosphoric acid. Fourier transform infrared spectra (FT-IR) suggest the existence of large amount of hydrogen bonds (OH....O) that may responsible for the high conductivity. A H_2/O_2 fuel cell based on $H_3PW_{12}O_{40}$ -3 H_3PO_4 -PTFE exhibited a peak power density of 2.7 mW/cm² at 0.3 V in ambient temperature.

Solid oxide proton conductors based on yttrium doped BaZrO₃ were investigated by introducing potassium or lanthanum at the A-sites. The materials were prepared by different methods and were obtained as a single phase with space group Pm-3m (221). The unit cell of these samples is slightly smaller than the undoped one. The upper limit of solid solution formation on the A-sites for potassium is between 5 ~ 10% as introducing more K results in the occurrence of a second phase or impurities such as YSZ (yttrium stabilized zirconium). K doped Barium zirconates showed an improved water uptake capability even with 5% K doping, whereas for La doped ones, water uptake is strongly dependent on particle size and synthetic history. The conductivity of K doped BaZrO₃ was improved by a factor of two (2×10⁻³ S/cm) at 600 °C compared with undoped material. Fuel cells based on Pt/Ba_{0.95}K_{0.05}Zr_{0.85}Y_{0.11}Zn_{0.04}O₃₋₆/Pt under humidified 5% H₂/air conditions gave a maximum power density 7.7 mWcm⁻² at 718 °C and an interfacial resistance 4 Ω cm⁻². While for La doped samples, the conductivity was comparable with undoped ones; the benefits of introducing lanthanum at A-sites may not be so obvious as deficiency of barium is one factor that leads to the diminishing conductivity.

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CHAPTER 1 Introductions

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1.1. Fuel cells

Fuel cells are electrochemical devices that convert the chemical energy of a reaction directly into electrical energy. The fundamental physical structure of a fuel cell consists of an electrolyte layer in contact with a porous anode and cathode on either side. The mechanism of a H_2/O_2 fuel cell based on a proton (oxygen ion) conducting electrolyte is illustrated (Figure 1-1). Because of the absence of moving parts in these devices, they offer clean and noiseless electricity. Theoretically, they provide a much higher efficiency for the electricity generations than conventional methods [1].



Figure 1-1: Schematic illustration of fuel cell systems

1.1.1. Thermodynamics

The most common way to obtain electrical energy is using turbines driven by fuel burning, wind or falling water etc. where mechanical energy is transferred into electricity. In the chemistry domain, converting energy from fuels into electricity is of most interest. In the simplest case of generating

electricity, fuels (oil or gas) are fired in a container and drive turbines (such as diesels) to produce electricity. There are at least three types of energy transfer occurring in this process, namely: (a) from chemical energy into heat energy, (b) from heat energy into mechanical energy and (c) from mechanical energy into electricity. Suppose the first and third transfers are 100% ideally, the whole efficiency of transferring would be limited by the second one. The highest efficiency during this type of transfer between a hot reservoir at temperature T_1 and a cold reservoir at T_2 is given

by Carnot cycles (Figure 1-2) and efficiency can be expressed as $\eta = 1 - \frac{T_2}{T_1}$



Figure 1-2: A Carnot cycle acting as a heat engine, illustrated on a pressure-volume diagram to illustrate the work done. Q_1 is the thermal energy the engine obtains from the hot reservoir and Q_2 is the thermal energy it releases to the cold reservoir.

This equation clearly tells us that energy must always be lost as heat for the process to be spontaneous and, in practice, real efficiency is always much lower than the value given by Carnot cycles.

However, fuel cells are not confined by the Carnot limitation since they do not undergo so many energy conversions. Instead, they complete the energy conversion in one step. Take hydrogen and oxygen for example. At standard conditions (298.15K and 1atm), the following reaction (Equation 1.1) has enthalpy ΔH° =-285.83kJ/mol and Gibbs free energy ΔG° =-237.09kJ/mol [2].

$$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O \tag{1.1}$$

Therefore, it would be theoretically possible to extract 237kJ/mole of electrical work from 1mol of hydrogen, which is only slightly lower than the heat evolved from firing 1 mol of hydrogen. In this case, the efficiency would be

$$\frac{-237.09}{-285.83} \times 100\% = 82.9\%$$

which is much higher than Carnot cycle and the energy wasted is solely due to the loss of entropy of reactions (Equation 1.1)

1.1.2. Fuel cell technology

The discovery of fuel cells can be dated back to 1839 by Grove and in his prototype fuel cells, sulphuric acid was used as the electrolyte [3]. Although high efficiency and environmental benefits were promised by fuel cell concepts, developing the early scientific experiments into commercial products proved difficult. The main problems are associated with developing appropriate materials and manufacturing techniques that enable fuel cells to become competitive with existing power generation methods in terms of cost per kWh. In the past decades, fuel cells with different compositions and working principles were substantially investigated and could be classified in many ways such as working temperatures or electrolyte materials etc. Several types of fuel cells according to their electrolytes are listed in Table 1-1 and information about working temperatures, electrolyte materials and conducting mechanism are also displayed for comparison.

Fuel cells	Electrolyte	Charge carrier	Working temperatures
Proton exchange membrane fuel cells (PEMFCs)	Ion exchange membranes	H^{+}	<120°C
High temperature proton exchange membrane fuel cells (HT-PEMFC)	Polybenzimidazole (PBI)- H_3PO_4	H⁺	~180°C
Solid acid fuel cells (SAFCs)	Solid acids	H⁺	20~250°C
Alkaline fuel cells (AFCs)	KOH solution	OH	<120°C
Phosphoric acid fuel cells (PAFCs)	H ₃ PO ₄	H^{+}	180~200°C
Molten carbonate fuel cells (MCFCs)	Immobilized liquid molten carbonates	CO32-	~650°C
Solid oxide fuel cells (SOFCs)	ceramics	O²⁻ or H⁺	550~1000°C

Table 1-1: Summary of major types of fuel cells

1.1.2.1. Proton exchange membrane fuel cells (PEMFCs)

PEMFCs are composed of an ion exchange membrane sandwiched between two electrode sheets (Figure 1-3). Various proton conducting polymers could be fabricated as electrolytes in PEMFCs such as Nafion and Sulfonated poly ether ether ketone (SPEEK). The only liquid in this kind of fuel cell is water so that corrosion problems could be minimized. Water management in these systems is crucial since ion exchange membranes rely on water to be conductive but electrodes prefer a relatively "dry" condition for fuel transportations. A typical working temperature for PEMFCs is around 80°C and could be increased to 120°C at high pressure. This is mainly

limited by the water balance in the membrane and electrodes. Noble metals such as platinum were used as catalysts due to their high catalytic activity at low temperatures and highly pure hydrogen was chosen as fuel. Impurities such as H₂S and CO are detrimental to platinum catalysts and would lead to a remarkable degradation of fuel cell performance. This is due to the poisoning effect of CO on Pt as CO is more stably absorbed on Pt surface than H₂ at low temperatures (Figure 1-4). The main challenges for PEMFCs are high catalysts loading (Pt on anodes and cathodes), requisite for cooling systems and purifying systems. Recent work is mainly focusing on developing high temperature ion exchange membranes so that fuel cells could be operated at higher temperatures. This gives the benefits of decreasing or even replacing the loading of noble metals and enables the fuel cells to be self-sustainable, avoiding the requirements of cooling and purifying systems.



Figure 1-3: A PEM fuel cell consists of Nafion as electrolyte and Pt/C as electrodes



Figure 1-4: CO coverage on a platinum surface as a function of temperature and CO concentration.H₂ partial pressure is 0.5 bar [4]

1.1.2.2. Solid acid fuel cells (SAFCs)

Solid acid fuel cells use solid acids as electrolyte. The charge carriers within the fuel cells are protons in most cases so that fuels and products can be well separated by the electrolyte, a great advantage over oxygen ion conductors. However, some problems still need to be solved. One is the solubility of most solid acids (such as $H_3PW_{12}O_{40}$ •x H_2O) in the water product that may lead to the collapse of the fuel cell infrastructures. Another is the requirement for humidified environments during fuel cell operations in many cases. Other technical problems such as thin membrane fabrication and fuel cell sealing were also encountered during fuel cell manufacturing. Recent studies are mainly focused on synthesizing and developing stable solid acids that are independent of humidity at elevated temperatures. Figure 1-5 is a schematical display of a solid acid fuel cell constitution based on CsH_2PO_4 [5]. Thanks to the advanced fabricating techniques; the fuel cells could work on various fuels that give promising applications in the future.



Figure 1-5: Schematically display the constitution of solid acid fuel cells based on CsH_2PO_4 as electrolyte [5].

1.1.2.3. Phosphoric acid fuel cells (PAFCs)

Phosphoric acid fuel cells (PAFCs) are the first commercialized and widely used type of fuel cells. Hydrogen or a hydrogen rich gas mixture is used as fuel. The electrolyte, primarily composed of phosphoric acid (H_3PO_4) is a pure proton conductor with good thermal, chemical and electrochemical stability. The operating temperature of the PAFCs is typically between 150~200°C and is a compromise between the electrolyte conductivity (increased with temperature) and the cell life (decrease with the temperature) [6]. The electrolyte, however, is highly corrosive so that only a noble metal such as Pt could be used, but this would indicate a large capital cost for PAFCs. This was only improved when Pt /carbon or graphite electrodes were deployed around 1960s [7]. Evolution of the cell components for PAFCs are listed in Table 1-2. However, one of the major problems in such fuel cells is the accelerated carbon corrosion and Pt dissolution when cell voltages are above 0.8V, therefore, long time hot idles at open circuit have to be avoided. Another problem usually encountered is electrode flooding and drying and this has been recognized as one of the major causes of declining fuel cell performance. Migrations of phosphoric acid between the matrix and the electrodes during cell load cycling are responsible for these problems and an alternative matrix that is capable of maintaining the acid is still under development [7]. Recently, introducing phosphoric acid into polymers bearing basic groups such as ether, alcohol, imine, amide, or imide groups has attracted much interest. The resulting acid-base complex systems not only exhibit a high conductivity but also possess

reasonable mechanical stability at elevated temperatures (>100 $^{\circ}$ C) such as polybenzimidazole (PBI)/H₃PO₄ systems [8].



Figure 1-6: The 1kW PAFC stack assembly with the gas diffusion porous carbon electrodes, graphite bipolar plates, cooling plates and thermocouples [9].

Component	ca.1965	ca. 1975	Current status
Anode	PTFE-bonded Pt black	PTFE-bonded Pt/C	PTFE-boned Pt/C
		Vulcan XC-72 ^ª	Vulcan XC-72 ^ª
	9mg/cm ²	0.25mg Pt/cm ²	0.1 mg Pt/cm ²
Cathode	PTFE-bonded Pt black	PTFE-bonded Pt/C	PTFE-bonded Pt/C
		Vulcan XC-72	Vulcan XC-72
	9mg/cm ²	0.5mg Pt/cm ²	0.5mg Pt/cm ²
Electrode Support	Ta mesh screen	Carbon paper	Carbon paper
Electrolyte Support	Glass fiber paper	PTFE-bonded SiC	PTFE-bonded SiC
Electrolyte	85% H ₃ PO ₄	95% H ₃ PO ₄	100% H ₃ PO ₄

Table 1-2: Evolution of cell component technology for phosphoric acid fuel cells [7]

a-Conductive oil furnace black, product of Cabot Corp. Typical properties: 002 d-spacing 3.6 Å by X-ray diffusion, surface area of 220 m²/g by nitrogen adsorption, and average particle size of 30 μ m by electron microscopy.

1.1.2.4. Solid Oxide Fuel Cells (SOFCs)

Solid oxide fuel cells have grown in recognition as a feasible high temperature fuel cell technology in the world. SOFC techniques are fast developing in the recent decades and several types of SOFCs have already been commercialized [10]. The compositions of the cells are almost entirely solid oxides so that corrosion problems in liquid electrolyte could be avoided [11]. The high operation temperatures (usually > 550°C) allow internal reforming of the fuels and promote rapid kinetics with non-noble catalysts [10]. Meanwhile, byproduct heat generated during operation could be utilized in other ways and give a high total efficiency.

1.2. Electrolytes for fuel cells

The electrolyte is one of the most important components in fuel cells. It is not only responsible for charge transport that generates electricity but also separating the fuels and oxidants so that electromotive force (EMF) is maintained. In the mean time, it almost determines the fuel cell operation conditions (temperatures and fuels) as different electrolytes only work in specific environment. Therefore, a good electrolyte must be absolute ionic conducting (transference number ~ 1) and dense (gas tight). Additional qualities for practical applications are robust (as a support for electrodes), easy fabrication (thickness controlled) and cheap (reduce cost). Table 1-1 lists some prevalent electrolytes that have been developed during the past.

The most commonly used electrolytes for fuel cells are proton and oxygen ion conductors such as Nafion proton-exchanged membrane and Yttrium Stabilized Zirconium (YSZ). They generally exhibit reasonable conductivity (> 10^{-2} S/cm) at certain conditions so that charge transportation is fast and easy. However, proton conductors are more favorable for fuel cells as fuels and products can be well separated by the electrolyte so that fuels at the anode will not be diluted by the products (Figure 1-7). This gives a high efficiency of fuel utilization and besides, proton conductors generally exhibit a higher conductivity at low temperatures than oxygen ion conductors which is favorable for low temperature applications [12].



Figure 1-7: Schematic illustration of fuel cells using a proton conductor and an oxygen ion conductor as electrolyte. Hydrogen and oxygen are used as fuel and oxidant respectively.

1.2.1. Proton conducting mechanism

The absence of electron shells for proton H^+ makes it quite different from other ions (Na⁺, K⁺, Ag⁺) primarily due to some covalent nature of bonds between protons and other elements. Unlike metal ions in ionic solids that experience Coulomb forces more or less from all sides, bonds between proton and other nonmetal elements have directional character. Regardless of the situation in metals where proton has high coordination number up to four or six, the interaction of proton with the environment is usually limited to the nearest one or two neighbors in the nonmetallic compounds. Figure 1-8 shows the three possible kinds of states that the protons may stand with oxygen atoms.



Figure 1-8: Schematic representation of different states of hydrogen and oxygen atoms, the curves below the image illustrate the energy level of proton as a function of positions correspondingly [13].

If the proton only has interactions with single oxygen i.e. the proton is well separated from other possible negative species, then a short O-H bond which is less than 100pm is formed. Taking 140pm as the ionic radius for the oxide ion, the proton is almost embedded in the electron shell of the oxygen atom (Figure 1-8 a) and It will take fairly high energy for the proton to escape and migrate away from the oxygen atom. However, if there is another oxygen at a medium distance $(\sim 250-280 \text{ pm})$, the proton may be involved in two asymmetrical bonds: a short, strong bond with the so-called proton donor and a longer, weak bond with the so-called proton acceptor (Figure 1-8 b). In this case, the energy barrier for the transfer of proton (from old oxygen atom to the new one) is lowered to some extent. Moreover, if these two oxygen is close enough (\sim 240pm), two symmetrical bonds may be formed i.e. the proton is equally embedded in the shells of two oxygen atoms (Figure 1-8 c) and the transfer of proton between these two atoms is guite easy and fast [13]. After that, the proton acceptor has to reorient for the next transfer so that continuous proton transferring can be realized. The detailed proton transfer mechanism is quite complicated and has not yet been clearly understood. In general, two types of proton conducting mechanisms were proposed, one is Grotthuss type where protons hop from one position to the other individually [14] and the other is vehicle type where protons move together with other molecules. The vehicle type is first suggested by Kreuer et al. [15] in 1982 on understanding the large temperature factors observed in X-ray and neutron diffraction studies. The activation energy for translational modes (vehicle type) was generally much higher than the rotational modes (Grotthuss type), which means that the latter might be more favored. Furthermore, these two types of mechanisms should not be strictly separated since they usually coexist in a specific system.

1.2.1.1. Proton conduction mechanism in liquid state

Vehicle type transfer seems to be preferable in liquid state due to the relatively loose structures compared with solid. However, the mechanism of proton conduction in a liquid can be varied from case to case.

For the simplest case, water, Kreuer *et al* [16] cited a new type of conducting mechanism; they called it "structure diffusion" (i.e. Grotthuss type) which could be dated back to the work of Eigen and De Maeyer [17,18]. In contrary to many physical chemistry textbooks, they demonstrated that proton transfer took place in a low-dimensional structure such as Eigen ion $(H_9O_4^+)$ and Zundel ion $(H_5O_2^+)$ instead of transfer within extended hydrogen-bonded water chains as usually described in the textbooks. One of the main reasons is that the extended chains described in textbooks need more energy which is unfavorable for fast proton transfer process. Another important point Kreuer *et al* [16] mentioned is that the diffusion of protonated water molecules

makes some contribution to the total proton conductivity (i.e. Vehicle type). This is almost as high as 22% when assuming that the diffusion coefficients of H_2O and H_3O^+ (or $H_5O_2^+$) are identical. However, water is not a good proton conductor although the mobility of protons in the system is extremely high; the proton defect concentration remains too low $\approx 10^{-7}$ mol/L. Externally introducing some proton defects is a good method to enhance proton conductivity of water such as dissolving HCl into pure water. This leads to a mechanism turnaround from structure diffusion to vehicle type since the diffusion coefficient of protons calculated from the Nernst-Einstein equation (equation 1.2) is almost equal to the water diffusion coefficient at high HCl concentration. This is probably due to suppression of the intermolecular proton transfer at high proton defect concentration.

$$\sigma_i = \frac{c_i D_i z_i^2 F^2}{RT}$$
(1.2)

Where σ_i is the conductivity of ion **i**, c_i is the concentration of the ion **i**, D_i is its diffusion coefficient, z_i is the charge on ion, *F* is the Faraday constant and *R* is the gas constant [19].

Another example is H₃PO₄. Although the detailed conducting mechanism of H₃PO₄ has not been completely understood, the conductivity of H₃PO₄ is high enough for practical application (phosphoric acid fuel cells). Unlike HCI in water, the mechanism for conduction remains the same-typical Grotthuss type since the diffusion coefficient of protons calculated by conductivity is almost two orders of magnitude higher than the values for the diffusion coefficient of diverse phosphate species obtained by ³¹P PFG NMR [20] and estimated from viscosity measurements via the Stokes-Einstein relation (equation 1.3). The high proton conductivity is most likely ascribed to the extremely high proton mobility which must involve proton transfer between phosphate species and some structural rearrangements [21].

$$D = \frac{k_B T}{6\pi\eta R} \tag{1.3}$$

Where *D* is the diffusion constant, k_B is the Boltzmann constant, *T* is the temperature and η is the viscosity [19].

1.2.1.2. Proton conduction mechanism in solid state

In a solid, vehicle mechanisms could also exist and are usually observed in materials with open structures (channels, layers). For instance, SiO_2 and many other silicates allow diffusion of H_2O

molecules and β -Al₂O₃ allows migration of H₃O⁺ and NH₄⁺ ions [16]. In these proton conductors, solids actually perform as a stationary support or matrix for proton conductions. However, for those solids without open channels such as CsHSO₄, the Grotthuss mechanism dominates. Proton transfer in these materials shares some similarities with transfer behavior of other ions (Na⁺, K⁺, Ag⁺). However, the difference is obvious, as mentioned above; the bond between proton and other non-metal elements is covalent and directional in character. Therefore proton transfer is "selective" in directions [22] and in consequence, highly dependent on the microstructures.

Ionic conductivity arises from the net ion defects transferring in one specific direction and is a function of concentration and mobility [23]:

$$\sigma_k(T,P) = \left| z_k \right| F u_k(T) c_k(T,P) \tag{1.4}$$

Where z_k is the charge number, F is the Faraday constant, u_k is the mobility and c_k is the equilibrium molar concentration.

For proton defects, Frenkel type defects are preferred (Figure 1-9) and can be expressed in Krőger-Vink notation:

$$H_{H}^{\times} + V_{i} \longleftrightarrow V_{H}^{i} + H_{i}^{\bullet}$$
(1.5)

Figure 1-9: The formation of Frenkel type defects in HM compound.

If no external proton defects are introduced, the proton defect concentration could be calculated from the mass action law under Brouwer approximations (only interstitial protons and proton vacancies are considered):

$$\left[H_{i}^{\bullet}\right] = \left[V_{H}^{\bullet}\right] = \sqrt{K(T)}$$

$$(1.6)$$

Where K(T) is the equilibrium constant.

More general expression of concentration has to consider various parameters such as pressure and external doping:

$$c_k(P,T,D) = \alpha_k P^{N_k} D^{M_k} \prod_r K_r^{\gamma_{rk}}$$
(1.7)

Where α_k , N_k , M_k and γ_{rk} are the characteristic constants; *P*, *D*, *T* and $K_r^{\gamma_{rk}}$ is partial pressure of X₂, doping concentration, temperature and equilibrium constant.

The transfer of proton defects within a solid crystal will encounter series of equivalent energy barriers (E_a) due to the orderly repeating of constituent atoms in all three spatial dimensions. Figure 1-10 shows the proton defects transfer in only one dimensions.



Figure 1-10: Proton transfer in one dimension of the crystal lattice. *E_a* represents the energy barrier.

The energy barriers E_a also know as activation energy could be used as an approximate evaluation for the mobility of proton defects.

If we consider the proton transfer in one dimension, the number of hops *N* that can overcome the energy barrier E_a per unit time can be expressed by an Arrhenius equation:

$$N = \frac{v_0}{2} \exp(-\frac{E_a}{kT}) \tag{1.8}$$

Where v_0 is the hopping frequency (this is a frequency of vibration of the lattice in the order of 10^{12} - 10^{13} Hz); E_a , k and T are the energy barrier, Boltzmann constant and temperature, respectively)

Since the hopping of proton defects to the right and left side is statistically equal, there is no macroscopic migration of protons (Figure 1-10). However, after introducing an external electrical field ε in one direction, the energy surface for the hopping is tilted accordingly and quantitatively the energy barrier for the left and right side would change by a factor of $q\varepsilon a/2$ (see Figure 1-11).



Figure 1-11: The energy barriers tilt after introducing external electrical field, ε is the strength of the electrical field, *a* is the distance between two defect positions

This would result in a difference in the times of defects hopping to the left and right (equation 1.9 and 1.10):

$$N_{left} = \frac{V_0}{2} \exp(-\frac{E_a + \frac{q \mathcal{E} a}{2}}{kT})$$
(1.9)

$$N_{right} = \frac{V_0}{2} \exp(-\frac{E_a - \frac{q\varepsilon a}{2}}{kT})$$
(1.10)

So net hopping times to the right would be expected in the situation above (equation 1.11)

$$N_{right} - N_{left} = \frac{V_0}{2} \exp(-\frac{E_a}{kT}) \left[\exp(\frac{q\varepsilon a}{2kT}) - \exp(-\frac{q\varepsilon a}{2kT})\right] \approx \frac{V_0 q\varepsilon a}{2kT} \exp(-\frac{E_a}{kT})$$
(1.11)

The velocity of defect transfer and electrical density are (equation 1.12 and 1.13)

$$V = (N_{right} - N_{left}) \times a = \frac{\nu_0 q \varepsilon a^2}{2kT} \exp(-\frac{E_a}{kT})$$
(1.12)

$$J = nqV = \frac{V_0 q^2 \varepsilon a^2 n}{2kT} \exp(-\frac{E_a}{kT})$$
(1.13)

(*n* is the defect concentration)

According to $J = \sigma \varepsilon$, the conductivity is finally expressed as (equation 1.14):

$$\sigma = \frac{v_0 q^2 a^2 n}{2kT} \exp(-\frac{E_a}{kT}) \tag{1.14}$$

For Frenkel defects, the interstitial ions and vacancies concentration can be expressed as $n_F = M \exp(-\frac{E_f}{2kT})$ (where **M** is the number of ionic pairs in the crystal and **E**_f is the formation energy of one Frenkel defect).

Herein, for Frenkel defects, the intrinsic ionic conductivity should be attributed to both interstitial ions and vacancies (equation (13)):

$$\sigma_{F} = \frac{v_{0}q^{2}a^{2}M}{2kT}\exp(-\frac{E_{ai}+E_{f}}{kT}) + \frac{v_{0}q^{2}a^{2}M}{2kT}\exp(-\frac{E_{av}+E_{f}}{kT})$$
(1.15)

(Where E_{ai} and E_{av} are the energy barrier for interstitial ions and vacancies respectively)

However, for a solid with amorphous structure, the energy barriers for conduction are not equal due to the disordered states in the microstructure of amorphism (Figure 4). In this case, an average energy barrier could be introduced to simplify this situation and the final conductivity still

can be written in the form of $\sigma = \frac{A}{T} \exp(-\frac{E_{average}}{kT})$ (Where **A** is the characteristic value and **E**_{average} is the average energy barrier).



Figure 1-12: The energy barrier of amorphism.

At a given temperature, the defects from intrinsic thermodynamic equilibrium remain too low, this is one of the reasons why pure crystals like SrHPO₄ or Ba(H₂PO₄)₂ have quite a low conductivity (<10⁻⁷S/cm) even at 320°C [21] and this could be changed by external doping. For example, by substituting some zirconium ions with niobium in acid zirconium phosphate with the NASICON structure (HZr₂(PO₄)₃·H₂O), additional proton vacancies are formed in the structure of obtained material (H_{1-x}Zr_{2-x}Nb_x(PO₄)₃·H₂O) [24](equation 1.16):

$$NbZr(PO_4)_3 / HZr_2(PO_4)_3 = V_H + Zr_{Zr}^* + Nb_{Zr}^{\bullet} + 3(PO_4)_{(PO_4)_3}^*$$
(1.16)

Or substituting yttrium or scandium, additional interstitial protons were introduced into materials [25] (equation 1.17):

$$H_{3}Y_{2}(PO_{4})_{3} / HZr_{2}(PO_{4})_{3} = H_{H}^{*} + 2H_{i}^{\bullet} + 2Y_{Zr}^{'} + 3(PO_{4})_{(PO_{4})_{3}}^{*}$$
(1.17)

And this is quite similar to produce n-type and p-type semiconductors (Figure 1-13) and could significant enhance the proton conductivity.



Figure 1-13: Schematic energy diagram for proton location in $HZr_2(PO_4)_3$, $H_{1-x}Zr_{2-x}Nb_x(PO_4)_3$ and $H_{1+x}Zr_{2-x}Y_x(PO_4)_3$ [25].

1.2.2. Proton conducting materials

1.2.2.1. Water containing systems

As mentioned above, the mobility of protons in water is extremely high although pure water is not a good proton conductor. This is due to the fast reorientation between water molecules so that water becomes an ideal media for proton conduction. Most of the proton conductors currently under investigations are dependent on or related to water and water indeed plays a vital role in proton conduction processes. These types of proton conductors usually possess internal open structures (layers, channels) so that water molecules are maintained and "free" to move. The most famous and well-investigated proton conductor is Nafion and was already commercialized by the company DuPont de Nemour. Figure 1-14 shows the structure of Nafion, it has a fully fluorinated backbones and side chains terminated by strongly acidic sulfonic groups.



Figure 1-14: Chemical structure of Nafion [16].

The fluorinated backbones are hydrophobic and lead to the formation of the continuous network of channels where hydrophilic sulfonic groups form aqueous domain even under low humidified atmospheres. The aqueous domain contained only protons as mobile species in addition to water molecules and protons are charge-balanced by immobilized anionic sulfonic groups. This specific structure allows fast exchange and migration of protons therefore high proton conductivity can be obtained. For inorganic materials, open structures are either maintained by their internal crystal structures or by rebuilding of external morphologies. A typical example of internal open crystal structures is β -alumina. Its chemical formal can be expressed as M₂O·nX₂O₃ (M = alkali⁺, Cu⁺, Ag⁺, Ga⁺, NH₄⁺ and H₃O⁺; X = Al³⁺, Ga³⁺ and Fe³⁺; n = 5~11). Take sodium β -alumina (NaAl₁₁O₁₇) for example, its structure can be visualized as an alternative stacking of "spinel blocks" and "conduction planes" as shown in figure 1-15. A "spinel block" consists of four oxide layers and is stacked in cubic sequence ABCA. Adjacent "spinel blocks" form the oxygen deficient "conduction planes" where Na⁺ ions reside. Since there is only one quarter of oxygen sites occupied, the "conduction planes" are actually two dimensional channels for Na⁺ ions which have a smaller size than O²⁻ [19, 26]. Proton conducting β -alumina can be produced by ion exchanging Na⁺ with NH₄⁺ or H₃O⁺ which all have a similar structure [27, 28].



Figure 1-15: Schematic illustration of NaAl₁₁O₁₇ structures.

For those materials that do not possess open internal structures, external open structures can be intentionally designed and rebuilt such as mesoporous materials. A simple case is mesoporous silica which usually synthesized by template method. Figure 1-16 shows the microstructure of silica gel prepared using alkyltrimethylammonium chlorides [29]. High surface area is one character of these materials and is favorable for proton conductions at humidified conditions.

Table 1-3 shows some other external open structure materials with measured proton conductivity under different conditions.



Figure 1-16: TEM pictures of mesoporous silica gel [29].

Proton conductor	σ (S/cm)	Conditions	E _a (ev)	Reference
$H_2Sb_4O_{11}$ ·3 H_2O	2×10 ⁻³	Room temperature	0.42	30
HSbO ₃ ·2H ₂ O	10 ⁻²	80°C		31
Tin-mordenite	1×10 ⁻²	temperature 100%RH		32
Nanoporous TiO ₂	3.78×10 ⁻²	80°C 81%RH		33
Mesoporous TiO ₂ +P ₂ O ₅	2×10 ⁻²	160°C 100%RH		34
β "-NH ₄ (H ₃ O) _{0.66} AI _{10.34} Mg _{0.66} O ₁₇	3×10⁻⁵-1×10⁻³	air	0.27-0.31	35
$H_2Ti_4O_9$ ·1.2 H_2O	10 ⁻³	20°C 75% RH		36
α -Zr(HPO ₄) ₂ · <i>n</i> H ₂ O	10 ⁻⁴	20°C 90%RH	0.3	37
$\begin{array}{l} Mesoporous\\ Zr(P_2O_7)_{0.81}(O_3POH)_{0.38}\end{array}$	2.6×10 ⁻³	100°C 90%RH Boom		38
$H_3PMo_{12}O_{40} \cdot 29H_2O$	0.17	temperature 100%RH		39
$Ca(H_2PO_4)_2 \cdot H_2O$	3.8×10 ⁻²	50°C 70%RH	0.25	40

The advantages of water containing systems are relatively high proton conductivity, and chemical and thermal stability. While the disadvantages are low conductivity at high temperatures (>150 °C) due to evaporation of water molecules, therefore, these materials generally find their applications below 100 °C and stringent conditions (high pressures) have to be satisfied at elevated

temperatures (>120 °C). Another disadvantage is the requirement of precious metal catalysts (platinum) to promote the electrochemical reactions, which also places some demand on purity of incoming fuels.

1.2.2.2. Solid acid salts

Solid acid salts, mainly based on tetrahedral oxyanion groups have received attention recently due to their unusual proton conductivity at anhydrous conditions. Unlike the water containing systems discussed above, proton conduction in oxyanion solid acid salts does not rely on the migration of hydronium ions. Consequently, the requirement for humidification and temperature control, in principle, can be eliminated. The enhanced operation temperatures furthermore imply a fast catalysis rate, opening up possibilities for reduction or even replacing precious metal catalysts. This advantage additionally implies a high tolerance of catalysts to poisons, particularly CO so that it may avoid using fuel purifying systems. The oxyanion solid acid salts can be written in formula MHXO₄, $M_3H(XO_4)_2$, $M_2H(X'O_4)$ or some variation thereof, where M= alkali metal including NH₄; X = S, Se and X' = P, As. These salts generally undergo phase transitions in response to temperature change or application of pressure where a dramatic increase in conductivity of several orders of magnitude can be achieved in the so-called superprotonic phase. The most famous and widely investigated oxyanion solid acid salts are CsHSO₄ and CsH₂PO₄. Although there has been a long term argument over the existence of such a superprotonic transition, Haile et al. made it clear that a transition from low to high symmetry do exists ($P2_1/c$ to I_4_1/amd at 414K for CsHSO₄ and P_{2_1}/m to Pm-3m for CsH₂PO₄ at 515K) and conductivity evolution comes from the dynamic disordering of hydrogen bond network with increased proton mobility being the main contribution to the high conductivity [41]. In the case of CsHSO₄, although single fuel cell demonstrates a current density of 44mA/cm² at short circuit [42], CsHSO₄ has been confirmed to be unstable under reduced conditions. The decomposition can be expressed in Equation 1.18

$$2C_sHSO_4 + 4H_2 \rightarrow Cs_2SO_4 + 4H_2O + H_2S \tag{1.18}$$

Similar reduction reactions also observed in the case of $M_3H(XO_4)_2$ compounds where M=Cs, NH₄ or Rb and X= S or Se (Equation 1.19) [43].

$$2M_{3}H(XO_{4})_{2} + 4H_{2} \rightarrow 3M_{2}XO_{4} + 4H_{2}O + H_{2}X$$
(1.19)

However, for CsH_2PO_4 , a single fuel cell experiment exhibited a peak power density of 415mW/cm² with no decomposition of CsH_2PO_4 due to the relative inertness of phosphate at

reduced conditions [41]. The high conductivity at moderate temperatures in anhydrous conditions implies promising applications in the domain of fuel cells and other electrochemical areas.

The main disadvantages for these materials are relatively low conductivity at low temperatures (before superprotonic phase transition temperature) which in fuel cell conditions would not allow faster startups and immediate response to changes in the demand for power. Heterogeneous doping could be an efficient way to improve the low temperature performance; SiP_2O_7 has been introduced to form CsH_2PO_4/SiP_2O_7 composites and efficiently improve the conductivity before phase transitions [44]. Another problem is the high solubility of these salts in water, so elegant engineering designs are necessary in order to prevent condensed water from contacting the electrolyte, particularly during fuel cell shutdown [41].

1.2.2.3. Impregnated membranes

Polymer electrolytes are receiving extensive attention in fuel cells recently. Their desirable properties such as chemical resistance and malleability guarantee promising applications. The conventional way to prepare ionic conducting polymers is by attaching charged units within their structures thereafter ionic conductivity is acquired. In the case of proton conducting polymers, the charge units are anions, typically sulfonic groups $(-SO_4^{2-})$ in the sulfonated hydrocarbon polymers (Nafion, sulfonated polysulfone (SPSF), sulfonated polyetheretherketone (SPEEK), sulfonated polybenzimidazole (SPBI)). These polymers exhibit reasonable proton conductivity under humidified atmospheres and relatively low temperatures, which already find their applications in PEMFCs [45,46,47]. However, as already discussed above, their conductivity is highly water dependent therefore operating temperatures are strongly limited. An effective way to modify the polymers is by impregnating or filling with inorganic compounds. The addition of inorganic materials into polymer membranes can alter and improve physical and chemical properties of interest (such as elastic modulus, proton conductivity, solvent permeation rate, tensile strength, hydrophilicity, and glass transition temperature). These combinations namely, impregnated membranes, have demonstrated encouraging results. Typical examples are Nafion/Zr(HPO₄)₂ and polybenzimidazole (PBI)/ H_3PO_4 systems. In the case of Nafion/Zr(HPO₄)₂, Zr(HPO₄)₂ can be homogeneously distributed in the Nafion architecture and act as scaffold to prevent the Nafion membrane from shrinking and swelling during dehydration and rehydration. The water uptake of the composite membranes were improved significantly and presented much better fuel performance compared with unimpregnated ones [48]. For the PBI/ H₃PO₄ systems, the introduction of inorganic H_3PO_4 not only improves mechanical properties but also enhances the proton conductivity [49,50]. The chemical structure of PBI is shown in Figure 1-17.


Figure 1-17: Chemical structure of PBI

It has two N-heterocycles per repeat unit which provides four nitrogen sites for the formation of hydrogen bonds. Up to two H_3PO_4 molecules per repeat unit in PBI are capable of being chemically bound to the PBI matrix and the maximum protonation of PBI are supposed to be achieved at this point [49]. Introducing more H_3PO_4 will soften the PBI membrane and the conduction behavior of the membrane becomes more similar to pure acids [51]. Other systems such as SPEEK/BPO₄ [52] and PVP/H₃PO₄ [53] systems are of much similarity. These combinations of organic and inorganic part offer a new route to improve membranes and achieve the desired properties. Table 1-4 lists some other impregnated systems investigated recently and their conductivity at relevant conditions were also listed.

Compositions	Proton conductivity	Measured conditions	Referance
NH_4NO_3 +chitosan+ethylene carbonate	9.93±1.9×10 ⁻³ S/cm	Room temperature	54
NH ₄ NO ₃ +hydroponics gels (HPG)	6×10⁻¹S/cm	25°C	55
H3PO4+epoxycyclohexylethyltrimethoxysi lane (EHTMS)+3- glycidoxypropyltrimethoxysilane (GPTMS)	1×10 ⁻² S/cm	130°C under 25% RH	56
Nafion+α-Zr(HPO ₄) ₂ ·H ₂ O	1×10 ⁻² S/cm	100°C under 90% RH	57
Nafion+ α -Ti(HPO ₄) ₂ ·H ₂ O	1×10 ⁻² S/cm	100°C under 90% RH	71
Nafion+imidazole+H ₃ PO ₄	2×10⁻³S/cm	150°C under anhydrous condition	58
Nafion+TiO ₂	8.93×10 ⁻³ S/cm	110°C under 70% RH	59
Nafion+SiO ₂	1.07×10 ⁻² S/cm	110°C under 70% RH	59
Nafion+WO ₃	1.01×10 ⁻² S/cm	110°C under 70% RH	59
Nafion+SiO ₂ +PWA	2.67×10 ⁻² S/cm	110°C under 70% RH	59
Nafion+ZrO ₂ -SO ₄ ²⁻ Nafion+ZrSPP	1.05×10 ⁻¹ S/cm 3 5×10 ⁻¹ S/cm	90°C under 90% RH 110°C under 98% RH	60 61
Zr(PBTC)+PBI	3.82×10 ⁻³ S/cm	200°C under 100%	62
α-Zr(HPO ₄) ₂ +PEI (polyethyleneimine) H ₂ SO ₄ +SiO ₂ +PTFE	2.6×10 ⁻⁵ S/cm 1.1×10 ⁻¹ S/cm	100°C under 82% RH Room temperature	63 64
Phosphosilicate colloidal particles+PVA (Polyvinyl alcohol)	2×10 ⁻² S/cm	Room temperature, under 100% RH	65
NH₄SCN+PVP (Poly N-vinyl pyrrolidone)	1.7×10 ⁻⁴ S/cm	Room temperature	66
(phthalazinone ether sulfone	7.2×10 ⁻² S/cm	150°C	67
Heteropolyacid-loaded Y-Zeolite+SPEEK	1×10 ⁻² S/cm	120°C	68

Table 1-4: Some impregnated systems reported recently

1.2.2.4. Perovskites

Perovskite oxides based on SrCeO₃ have been recognized to exhibit predominate proton conduction under hydrogen containing atmosphere at elevated temperatures many years ago [69]. Thereafter numerous perovskite oxides with similar compositions have been synthesized and investigated such as CaZrO₃ [70,71,72], BaCeO₃ [73,74,75,76]. Their chemical compositions could be written as $AB_{1-x}M_xO_{3-\delta}$, where M is some trivalent elements like rare earth elements and δ is the oxygen deficiency per perovskite unit cell. These perovskite-type ceramics exhibit p-type electronic (hole) conduction under oxidizing atmospheres by the following equation:

$$O_2 + 2V_0^{\bullet\bullet} \longleftrightarrow 4h^{\bullet} + 2O_0^{\times} \tag{1.20}$$

while they become a proton conductor in the presence of water vapor and hydrogen by equation:

$$H_2O(g) + O_0^{\times} + V_0^{\bullet\bullet} \longleftrightarrow 2(OH)_0^{\bullet} \tag{1.21}$$

Their intrinsic proton conducting species offer them great advantages for their application as electrolyte in SOFCs since the water product was generated in cathode so that the fuels in anode would not be diluted, which is one of the major problems for oxygen ion conductors (YSZ, lanthanum strontium gallium manganite (LSGM)) as mentioned above.

Among these perovskite oxides investigated, cerate-based oxides generally present the highest conductivity but suffer from decomposition under atmospheres containing CO_2 or H_2O below $500^{\circ}C$ [77,78]. Great efforts have been devoted to partially substitute cerium with zirconium in the hope to improve the stability [79,80]. It has been found that the stability of these partially replaced cerates depends strongly on the zirconium content [79], in other words, complete replacement of cerium for zirconium is expected to exhibit the highest stability under atmospheres containing CO_2 and H_2O therefore allowing hydrocarbon fuels to be utilized. Although zirconates such as doped BaZrO₃ demonstrates similar conducting behavior to cerates in terms of formation and mobility of protonic charge carriers [81], their conductivity is usually one order of magnitude lower than cerates [82]. This is attributed to the highly refractory properties of zirconates with low rates of grain growth under typical sintering conditions which limit the overall proton transport [81]. Recently, complex perovskites (such as Ba₃Ca_{1.18}Nb_{1.82}O_{8.73}) have attract extensive attention in

which charge deficit and compensating protons are achieved by cation nonstoichiometry rather than normal doping, in this case, the proton trapping at dopants was alleviated [21].

1.3. Aim of project

Proton conductors that maintain a reasonable conductivity at intermediate temperatures $(100~600 \ ^{\circ}C)$ are highly desirable. Most of the proton conductors currently under investigations are not ideal for applications as electrolytes in intermediate temperature fuel cells (ITFCs). Nafion based electrolyte could not exceed operating temperatures beyond 120 $\ ^{\circ}C$ under ambient conditions; oxyanion solid acid salts are fragile, soluble and difficult to fabricate into thin membrane; PBI/H₃PO₄ membranes are not stable; perovskite oxides exhibit low conductivity.

The aims of this study are to develop appropriate materials as electrolyte for ITFCs at intermediate temperatures. The aims are essentially threefold:

- In the search for new proton conducting materials, characterizing and measuring their proton conductivity, evaluating the possibility of applying these new materials into fuel cells.
- To improve the properties of some existing proton conductors via chemical methods so that they could be more suitable for ITFCs.
- 3. To increase the knowledge and understanding of the proton conducting mechanism.

CHAPTER 2 Experimental

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2.1. Sample Preparation

The properties of electrochemical materials such as conductivity are highly dependent on synthetic methods. Particle sizes, impurity content as well as density can vary a lot during different synthetic histories and might become the critical factors that affect the properties. Therefore, proper synthetic methods should be chosen in order to obtain the desired materials.

2.1.1. Powder preparation

2.1.1.1. Solid state synthesis

Conventional solid state reactions were used to synthesize powders such as $Ba_{1-x}M_xZr_{1-y}Y_yO_{3-\delta}$ (M=K, La). The oxide or carbonate powders for synthesis such as ZrO_2 and $BaCO_3$ were dried in muffle furnace at 500°C to eliminate absorbed water before weighing. Stoichiometric amounts of the pre-dried powders were mixed and ball milled using acetone for 30 minutes to ensure thorough mixing. The mixtures were then calcined or sintered at target temperature for certain hours.

2.1.1.2. Solution synthesis

Conventional liquid synthesis was used to synthesize powder such as $AI(H_2PO_4)_3$ - $xH_3PO_4(x=0-3)$. Calculated amounts of nitrates or acids were dissolved in deionised water. The solvents were heated at target temperatures such as 200°C with continuous stirring until water was removed. The resultant powders were then treated at certain temperatures at a muffle furnace to complete reactions or eliminate the remaining water. The powders obtained were ground using agate mortars and pestles before collected for characterization.

2.1.1.3. Ball milling

Ball milling was conducted using a Fritsch planetary micro mill "pulverisette 7". Powders were placed into Zirconia grinding bowls (100ml in volume) with 6 Zirconia balls (12mm in diameter). An appropriate amount of acetone was used as suspension liquid. Individual processing procedures will be described in more detail within the relevant chapters.

2.1.2. Powder compaction

Powders for experiments were uniaxially pressed using cylindrical steel dies of typically 13mm diameter. The dies were cleaned regularly using paraffin to prevent rusting. Typical pressure for

pressing is 500MPa. Pellets obtained were generally sintered at certain temperatures for further densifications.

2.1.3. Firing

Raw powders were usually fired at certain temperatures with controlled procedures in order to produce desired microstructures. The changes occurring during firing could be fairly complex, depending on the various parameters such as temperatures and atmospheres. Two terms are used to refer to this heating process: calcining and sintering. Generally, the term calcining is a thermal treatment process applied to raw materials in order to bring about a thermal decomposition, phase transition, or removal of a volatile fraction. The calcination process normally takes place at temperatures below the melting point of the product materials. For sintering, a compact porous powder is heated to a temperature that is usually 0.5~0.9 times of the melting temperature in K. The powder does not melt; instead, atomic diffusion in the solid state takes place and leads to the joining of the particles and reduction in porosity. A common difficulty in sintering is that diffusion may be so slow that high densities are difficult to achieve even at high temperatures. One solution is the use of an additive referred as sintering aid. The additive forms a small amount of liquid phase between the grains at the sintering temperatures and helps densification [83]. Appropriate firing procedures for experiments were programmed individually and will be discussed within different chapters.

2.2. Sample Characterization

2.2.1. Density measurements

Pinholes and cracks in a ceramic body are detrimental to conductivity since they separate the conduction path. Therefore, the conductivity of ceramic bodies can be maximized when the density of the body reaches 100% of the theoretical density where all those holes and cracks are eliminated. The theoretical density of ceramics was calculated from the unit cell parameter using the following equation:

$$\rho_t = \frac{m}{V} = \frac{\frac{M}{N} \times Z}{V} = \frac{MZ}{NV} = \frac{M \times Z \times 1.66}{V}$$
(2.1)

Where *m* is the mass of a unit cell, *V* is the volume of a unit cell, *M* is the formula weight in g/mol, *Z* is the numbers of formula in each unit cell and *N* is the Avogadro number (6.022×10^{23} /mol) [26].For perovskite type materials such as BaZrO₃, *Z* usually equals 1.

Experimental density (Sintering density) was obtained from the mass and geometric dimensions of the pellets. The density was calculated from the equation

$$\rho_e = \frac{Mass}{Volume} = \frac{4Mass}{\pi d^2 l}$$
(2.2)

Where *d* is the diameter of the pellet and *l* is the thickness of the pellet.

The relative densities were expressed as a ratio in percentage of the experimental density to theoretical density (equation 2.3).

$$\eta = \frac{\rho_e}{\rho_t} \times 100\% \tag{2.3}$$

2.2.2. X-Ray Diffraction

2.2.2.1. Laue equations

Crystals are solid substances in which the atoms, molecules or ions are arranged in an orderly repeating pattern extending in all three spatial dimensions. An optical grating can be used to simulate the crystal in 1-dimension.



Figure 2-1: An optical grating to simulate the crystal in 1-dimension

The directions where constructive interference occurs at the emergent light is governed by the wavelength of the light λ and the separation of the grating unit *a*. If the beam 2 and 3 are in phase with each other, the distance *AB* must equal a whole number of wavelengths; i.e.

$AB = \lambda, 2\lambda, \dots, n\lambda$	
While $AB = a \sin \theta$	
Therefore $a\sin\theta = n\lambda$	(2.4)

However, the separation of the grating unit must be of the same order of magnitude as, but somewhat larger than, the wavelength of the light. Since $\sin\theta \leq 1$, in order to observe the first order diffracted beam $a \sin \theta = \lambda$, *a* must larger than λ . If, on the other hand, $a \gg \lambda$, individual diffraction orders (n=1, 2, 3, ..., etc) are so close together as to be unresolved and a diffraction continuum will occur. In a real crystal where atom separations are in the magnitude of Å, the appropriate incident lights are X-ray, electrons and neutrons.

The equation deals only with 1-dimensional diffraction; however, in a real crystal, 3-dimensional diffractions occur. So the equation should be written for all dimensions:

$a_1 \sin \theta_1 = n\lambda$	(2.5)
$a_2 \sin \theta_2 = n\lambda$	(2.6)
$a_3 \sin \theta_3 = n\lambda$	(2.7)

These are the Laue equations and for a diffracted beam to occur, these three equations must all be satisfied simultaneously.

2.2.2.2. Bragg's Law

However, the Laue equations are cumbersome to use although they provide a rigorous and mathematically correct way to describe diffraction of crystal. A more simple and straightforward way to describe crystal diffraction is Bragg's Law:



Figure 2-2: Illustration of Bragg's law.

It treats one layer of atoms (*A* and *B*) in crystal as a plane and the smallest unit to diffract incident light. If the emergent light 1" and 2" are in phase, the following equation must be satisfied:

$$2d\sin\theta = n\lambda\tag{2.8}$$

Where *d* is the distance between adjacent atom planes, θ is the incident angle and λ is the wavelength of the light.

For a given set of planes, several solutions of Bragg's Law are usually possible, for n=1, 2, 3, etc. It is customary to set *n*=1 since for *n*=2, the *d*-spacing is instead halved by doubling up the number of planes in the set $(2d \sin \theta = 2\lambda \text{ equals } 2(d/2) \sin \theta = \lambda)$, so *n* is kept equal to 1 [26].

2.2.2.3. d-spacing formula

The distance between adjacent atomic planes *d* can be obtained from Bragg's Law and can be used to calculate the unit parameters of a crystal. For an orthorhombic crystal (i.e. $\alpha = \beta = \gamma = 90^\circ$), the d-spacing for any set of planes is given by the formula:

$$\frac{1}{d_{hkl}} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$
(2.9)

Where h, k, and I are Miller indices for each set of planes and *a*, *b*, and *c* are unit cell parameters. For cubic crystals (a = b = c and $\alpha = \beta = \gamma = 90^{\circ}$),

$$\frac{1}{d_{hkl}} = \frac{h^2 + k^2 + l^2}{a^2}$$
(2.10)

So by using different d-spacings obtained from Bragg's Law, the unit parameters could be calculated [26].

X-ray powder diffraction was a convenient and powerful tool for materials investigation and was used in all the following experiments for evaluating crystal structure and examining purities. A Stoe STADI/P powder diffractometer was used in transmission mode. Incident radiation was generated using a $Cu_{K\alpha1}$ source ($\lambda = 1.540598$ Å) with curved Germanium as a monochromator.

X-POW software was used to perform least square refinement of the lattice parameters of the samples.

2.2.2.4. Debye-Scherrer equation

Useful information that X-ray powder diffraction can also give is the particle size calculation by Debye-Scherrer equation:

$$t = \frac{0.9\lambda}{[(Bm^2 - Bs^2)^{1/2}\cos\theta]}$$
(2.11)

Where *t* is the crystallite size; λ is the wavelength (0.1540598 nm); *Bm* and *Bs* are the FWHM (full width at half maximum) in radians of the sample peaks and the standard peaks at X-ray powder diffraction patterns [84]. High crystalline materials such as silica give standard values. The calculations are performed using peaks with significant intensities [26].

2.2.3. Impedance Spectroscopy

2.2.3.1. Theory

Impedance spectroscopy is a powerful technique for characterizing electrochemical properties of materials and their interfaces. The response of a process occurring within a material or an interface toward applied voltages is characteristic; in particular, the relaxation time of each electric process is distinct. Impedance spectroscopy is able to convert the response of several processes from a time dependency to frequency-related phenomena. In principle, this technique is based on applying an AC perturbation voltage to the studied material through different

frequencies and records the AC current responses. Impedance is a complex vector; therefore it possesses information both in scale and in direction. In general, the scale (amplitude of the AC current) and the direction (phase angle shift of the AC current towards AC voltage) will vary corresponding to the frequency changes of the applied voltage; through analyzing the variations as a function of frequency, information about the resistance and capacitance of the electrochemical system could be obtained [85].

If a small ac-perturbation, $V_0 e^{jwt}$, is applied to an electrochemical system, the impedance is defined as:

$$Z(w) = \frac{V(w)}{I(w)} = \frac{V_0 e^{jwt}}{I_0 e^{j(wt + \varphi(w))}} = \frac{V_0}{I_0} (\cos \varphi(w) - j \sin \varphi(w))$$
(2.12)

Where *w* is the angular frequency (2 π f), *j* is the imaginary unit ($j = \sqrt{-1}$) and φ the phase angle shift.

Since impedance Z(w) is a complex vector, it is customary to plot the impedance in a complex plane (Nyquist diagrams) where imaginary and real components are displayed at the same time. Equations 2.13 and 2.14 represent the real and imaginary components of the impedance and Figure 2-3 demonstrates this graphically. Sometimes impedance is also presented in Bode mode (Figure 2-3b) where imaginary and real component are plotted as a function of frequency. In certain cases, a bode plot can give a better insight about the relaxation times of overlapping processes.

$$Z_{real} = Z' = |Z| \cos \varphi \tag{2.13}$$

$$Z_{imaginary} = Z'' = -j|Z|\sin\varphi$$
(2.14)



Figure 2-3: Impedance represented in (a) complex plane and in (b) Bode plot

There are several other measured or derived quantities related to impedance which also play an important role in impedance spectroscopy (IS). For example, the admittance, $Y = Z^{-1} = Y' + jY''$ is also widely used in IS and similar to impedance, it emphasizes those processes with largest resistance. Other related quantities and their inherent relations are listed in table 2-1 [85]. All these quantities have their own dependence on and weighting with frequency and have found their applications in various systems.

	М	Ζ	Y	3
M (modulus)	М	μZ	$\mu \Upsilon^1$	ε ⁻¹
Z (impedance)	$\mu^{-1}M$	Ζ	Υ^1	$\mu^{-1} \varepsilon^{-1}$
Y (admittance)	μM^{-1}	Z^{1}	Y	με
ε (permittivity)	M^{-1}	$\mu^{-1}Z^{-1}$	$\mu^{-1}Y$	3

Table 2-1: Impedance related quantities and their relations [85]

^a $\mu = jwC_0$, where C_0 is the capacitance of the empty cell.

Analysis of an impedance spectrum is carried out by simulating the impedance data with a model. The model should contain considerations of possible processes occurred within studied systems and is represented as electrical circuits using ideal physical elements (resistance, capacitance, inductance, constant phase elements (CPE) etc.), in other words, using physical elements to understand the electrochemical processes that occur within the systems.

In the simplest case, an ionic conducting crystal is sandwiched between two blocking electrodes (Figure 2-4). The impedance plot, Bode plot and suggested mode are presented. Here, the resistance of the electrolyte is represented by R and the geometrical and interfacial capacitance

are represented using C_{geom} and C_{int} , respectively. The values of each component are chosen arbitrarily.



Figure 2-4: (a) Schematic illustration of ionic conducting electrolyte sandwiched between two blocking electrodes and the equivalent circuit proposed; (b) Impedance of such system in complex plane (c) and (d) Impedance of such system in Bode plot.

2.2.3.2. Equivalent circuits

Simulating impedance involves fitting the impedance data with an equivalent circuit. The equivalent circuit is proposed according to the model that should offer a reasonable explanation of the studied systems. For instance, processes that are expected to occur simultaneously or after each other will be represented by parallel or series circuit elements. A good simulation depends on the similarity between the experimental spectra and the simulated ones. Various

electrical elements have been established to symbolize different processes and complicated systems could be analyzed separately and conveniently. Elements that are commonly used in equivalent circuits are listed in Table 2-2, along with their impedances and admittances. R is a resistor, C is a capacitor, L is a inductor, W is a Warburg element which is used to describe semiinfinite diffusion processes, Q is a constant phase element (CPE) and its value is adjusted by its exponent α (-1≤ α ≤1). For α = -1, Q becomes an inductor, α =0 a resistor, α =0.5 a Warburg and α =1 a capacitor. The deviation of α from these values implies distributed characteristic of the systems (range of hopping sites, non-homogeneity, rough and porous surface, etc.).

Element	Description	Impedance	Admittance
L	Inductor	jωL	$\frac{1}{j\omega L}$
R	Resistor	R	$\frac{1}{R}$
С	Capacitor	$\frac{1}{j\omega C}$	jωC
W	Warburg	$rac{Z_0}{\sqrt{j arnothing on}}$	$Y_0\sqrt{j\omega}$
Q	CPE	$rac{Z_0}{\left(j\omega ight)^{\!lpha}}$	$Y_0(j\omega)^{lpha}$

Table 2-2: Impedance and admittance of different electrical elements [85]

Some typical equivalent circuits and their impedance spectra are shown in Figure 2-5. The simulations are performed using Z-View software.



Figure 2-5: Some typical equivalent circuits and their impedance in complex plane. Here CPE-T corresponds to Z_0 of Q and CPE-P corresponds to α .

2.2.3.3. Measuring conductivity by using impedance spectroscopy

When conductivity of a material is studied, information obtained from DC (direct current) measurement is often limited, especially when bulk and grain boundary responses are the main features of interest. Impedance spectroscopy, which uses AC techniques, can properly extract that information through equivalent circuit. For solid state inorganic materials, bulk and grain boundary transport processes can generally be described by placing a resistor and capacitor in parallel. Such combination will give a relaxation time τ :

$$\tau = \frac{1}{w_{summit}} = RC \tag{2.15}$$

Where, w_{summit} is the summit frequency of the semi circle that is described by the RC parallel element. So the bulk or grain boundary resistance and capacity equals to *R* and *C* if geometrical factors are subtracted. Additional information such as permittivity ε is also obtained. Consider a flat plane capacitor, the capacitance is related to permittivity by equation 2.16

$$C = \frac{\varepsilon_0 \varepsilon A}{d}$$
(2.16)

Where ε_0 is the permittivity of vacuum, 8.854×10⁻¹² F/m, *A* is the area of the plate and *d* the distance between two plates.

In a typical sintered pellet, A/d~ 1-10 cm and with permittivity of ~10, the bulk usually gives capacitances in the order of 10^{-11} ~ 10^{-12} F/cm [86].

If we use "brickwork" model (Figure 2-6) to simulate the bulk and grain boundary regions in a ceramic placed between blocking electrodes, the following equation can be derived:

$$\frac{C_b}{C_{gb}} = \frac{d_{gb}}{d_b}$$
(2.17)

Where C_b and C_{gb} is the capacitance of bulk and grain boundary, d_b and d_{gb} is the length scale of bulk (grain size) and grain boundary. It also tells us that well sintered, narrow intergranular regions samples will give a high grain boundary capacitance [86]. A typical capacitance of grain boundary is in the order of $10^{-11} \sim 10^{-8}$ F/cm.



Figure 2-6: Brickwork model of bulk and grain boundary regions for sintered ceramics [86].

The electrode processes such as charge transfer/electrochemical double layer, oxidation/reduction process, adsorption and desorption of electrochemical species etc. are of large relaxation time, so the capacitance for these processes is generally larger than 10^{-7} F/cm [86,87].

2.2.4. Electron Microscopy

Electron Microscopes (EM) are microscopes that use electron beams to create highly magnified images of a specimen. They are powerful instruments that can give a direct and detailed description concerning the morphologies or compositions of a specimen. Clean investigations of samples become feasible and EM have found their utilizations in various domains such as materials chemistry, biology etc.

EM has distinct advantages over traditional light microscopes in terms of resolution and depth of field. The resolution of a light microscope can hardly go down to ca. 400nm which is due to the wavelength limitation of visible light (400-800nm). Electrons have much smaller wavelength according to the De Broglie relationship (equation) and are capable to give a clear discrimination in the range of nano meters.

$$\lambda = \frac{h}{m_e V}$$
(2.18)

Where *h* is the Planck constant 6.63×10^{-34} J·s and m_e is the mass of a electron and *V* is the velocity of the electrons.

There are mainly two types of electron microscopes that are generally used, Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM); both are used for different purposes: SEM is generally for the detection of the surface of a solid object and TEM is essentially capable of looking through a thin slice of specimen.

2.2.4.1. Scanning Electron Microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDS)

SEM is performed by applying a beam of accelerated electrons which interact with the atoms that make up the sample. The signals produced contain information about the sample's surface topography, composition and other properties such as electrical conductivity. Figure 2-7 schematically demonstrates the components of the instrument and how it works. Electron beams

are thermionically emitted from the Electron Gun which has a tungsten filament cathode. The electron beams are then focused by passing through several condenser lenses to a spot around 0.4-5 nm in diameter and are adjusted and controlled by the scanning coils before finally cast onto the sample. X-rays, electrons etc. are generated and collected using different collectors such as Backscattered Electron Detector and Secondary Electron Detector. A number of species are generated after the incident electron beams contact the specimen; Figure 2-7 gives a illustrations about several species generated: X-rays (Continuum X-rays, characteristic X-rays), cathodoluminescence, backscattered electrons and secondary electrons etc. These species are collected selectively and transformed into signals that finally make up a whole image.





Gold sputtering techniques are necessary when a poorly conductive sample is to be investigated. The small gold particles will cover the surface of samples and will give a better resolution.



Figure 2-8: Schematic illustration of the principles for EDS [90].

Energy dispersive X-ray spectroscopy (EDS) is a powerful technique that is capable of elemental analysis or chemical characterization for a sample. It relies on interactions between incident charged particles such as electrons and the sample. In principle, a high energy incident beam will knock out an electron in an inner shell of atoms in the sample, creating an electron hole where the electron was. Then an electron from an outer, higher-energy shell will fill that hole and release the energy differences between these two shells in the form of an X-ray (Figure 2-8). Since the energy differences between electron shells are closely related to the atomic structure, the emitting X-ray shall be a characteristic of an atom, which allows the elemental composition of the specimen to be measured.

JEOL 5600 scanning electron microscope were used when a morphological investigation was required and a Mica energy dispersive X-ray spectroscopy (EDS) analysis system was used for elemental analysis of samples. The systems provide limited detection of elements below Na in the periodic table and no detection of elements below C in the periodic table. The detection limit is around 0.1% depending on the element.

2.2.4.2. Transmission Electron Microscope (TEM)

TEM is performed by applying a beam of electrons transmitted through an ultra thin specimen. The electron beams that pass through will interact with the specimen and contain interior information such as crystal orientation, electronic structure etc. Figure 2-9 is a simple illustration of how TEM works. Similar to SEM, an electron beam is generated in an electron gun by heating a tungsten or LaB₆ filament in a vacuum. After accelerating the electrons from the gun (cathode) toward the anode by applying a high voltage (200kV), the high speed electron beams are focused by a series of condenser lens and projected onto the specimens that are mounted on a specimen

grid. The electron beams that pass through the specimen can form a primary magnified image of the specimen at the objective lens and further enlargement is conducted by passing through a number of projective lenses. Final images are cast and displayed on the phosphor screen for evaluating.



Figure 2-9: Schematic illustration of TEM infrastructures [91].

A JEOL JEM 2011 transmission electron microscope was used in our experiments, both in low resolution and high resolution mode. The TEM is fitted with LaB₆ filament and operated at 200kV. Images were recorded using a Gatan CCD camera and analyzed using Gatan Digital Micrograph software.

2.2.5. Fourier Transformed Infrared Spectroscopy (FT-IR)

2.2.5.1 Introduction

Infrared Spectroscopy is one of the most common and powerful techniques used by organic and inorganic chemists. Basically, it is the absorption measurement of the IR electromagnetic waves within different frequencies. Electromagnetic waves used in infrared spectroscopy have frequencies ranging from 1.9×10^{13} to 1.2×10^{14} Hz, corresponding to photon energies ranging from 0.078 to 0.5eV from the Plank relation (equation 2.19).

$$E = hv \tag{2.19}$$

Where *h* is the Planck constant and *v* the frequency.

This level of energy is inadequate to excite electrons but may induce vibrational excitation of covalently bonded atoms or groups. The frequencies that an absorption happens are closely related to the structure of the molecules, i.e. atom species, bonding types and ways of possible vibration (stretching, scissoring, rocking and twisting). For a typical IR spectrum, studied samples are exposed to a beam of infrared light and transmitted light is collected which reveals the absorption of the samples. From their characteristic absorption frequencies, different functional groups can be quickly identified. Table 2-3 lists the absorption frequencies of some typical function groups [92].

Functional groups	Characteristic Absorptions (cm ⁻¹)
O-H, N-H stretching	>3200
P=O (free)	1175-1350
P=O (H boned)	1150-1250
P-OR esters	900-1050
P-H stretching	2350-2440
P-OH	2560-2700
PO ₄ ³⁻ , HPO ₄ ²⁻ , H ₂ PO ₄ ⁻	950-1100
NO ₃ ⁻	1340-1410, 800-860
B-O	1310-1350
B-N	1330-1380

Table 2-3: some absorption frequencies of typical functional groups [92].

The vibrations of two covalently bonded atoms could be simplified and treated as a harmonic oscillator with 2 masses (atoms) linked by a spring (Figure 2-10).



Figure 2-10: a harmonic oscillator with two masses

In this simple model, Hooke's Law could be used to approximate and understand stretching frequencies (equation 2.20).

$$v = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$
(2.20)

Where k is the force constant for the bond, μ is the reduced mass of A-B systems (equation 2.21):

$$\mu = \frac{m_A m_B}{m_A + m_B} \tag{2.21}$$

 m_A and m_B are mass of A and B atoms.

Hydrogen is the lightest species among all atoms, which gives a small reduced mass for X-H systems. Therefore, the stretching frequencies of the X-H bond are relatively high (>2500cm⁻¹).

2.2.5.2. Hydrogen bonds

Hydrogen bonds play a vital role in proton migration as they can significantly shorten the distance between two electronegative species (proton donor and proton acceptor) [93]. Infrared spectroscopy is a useful tool in examining hydrogen bonding as it will strongly affect the vibrations of the original X-H bonds [94]. Hydrogen-bonded protons are characterized by shifts to lower frequencies of the X-H stretching vibration mode, coupled with a marked increase in intensity of this absorption [95]. Table 2-4 listed the four possible ways that hydrogen bonding will affect the vibration of original X-H bond [97]. Generally, the first way is directly related to proton transfer between two atom sites and is of most importance. Take the O-H bond for instance, the strongly hydrogen bonding O-H groups generally give significantly lower absorption frequencies (<3000cm⁻¹) when compared with hydrogen bonding-free O-H groups (>3500cm⁻¹), implying a decreased connection between O and H atoms; the proton transfer in the hydrogen bonding O-H groups is faster and easier [96].

Type of vibration	Description	Notation
$\leftarrow X - H \rightarrow \cdots \qquad Y \rightarrow$	(X-H) stretch (3600-2500 cm ⁻¹)	v (X-H)
$ \begin{array}{c} \uparrow \\ \times \\ \downarrow \end{array} \begin{array}{c} \uparrow \\ \downarrow \end{array} \end{array} $	(X-H) in-plane bend (1650-1000 cm ⁻¹)	δ(X-H)
- + - X — H Y	(X-H) out-of-plane bend (900-250 cm ⁻¹)	γ(X-H)
$\leftarrow X \leftarrow H \cdots Y \rightarrow$	H-bond stretch (200-30 cm ⁻¹)	v(XHY)

Table 2-4: possible ways a hydrogen bonding will affect original X-H vibrations [97]

2.2.6. Thermogravimetry Analysis (TGA)

Thermal analysis is the measurement of physical and chemical properties of a certain material as a function of temperature. It is a crucial technique that allows various useful parameters to be readily obtained such as enthalpy, heat capacity, mass and coefficient of thermal expansion. In the domain of solid state science, thermal analysis is a fundamental technique to evaluate solid state reactions, thermal decompositions and phase transitions and ultimately the determination of phase diagrams.

The most common thermal analysis techniques are thermogravimetry analysis (TGA) and differential thermal analysis (DTA). The former is a record of mass change as a function of either temperature or time and the latter is a measurement of the difference in temperature ΔT between a sample and an inert reference material as a function of temperature. Another technique that is closely related to DTA is differential scanning calorimetry (DSC) which allows a quantitative measure of the enthalpy changes that occur in a sample as a function of temperature and time. A fourth thermal analysis techniques is dilatometry, in which the change in linear dimension of a sample as a function of temperature is recorded so that the coefficients of thermal expansion of a sample can be determined and this technique now has a new name called thermomechanical analysis (TMA).

A typical TGA plot is schematically shown in Figure 2-11. The sample (usually a few milligrams) has a starting weight W1 and is stable until it begins to lose weight at temperature T1. The weight change could cover a range of temperatures from T1 to T2 and a second plateau could be observed indicating the end of the process. The total weight change could then be calculated W1-W2 and possible reactions can be proposed.



Figure 2-11: Typical TGA plot illustrate a weight loss of ΔW .

2.2.7. Solid State NMR

Many nuclei possess a quantized property called nuclear spin which can be described only by quantum mechanics. Nuclei with even mass number and even charge number have zero spin and can not be used in NMR spectroscopy. The angular momentum of a spinning nucleus is a function of its spin quantum number which can have either integer or half-integer values. If such a nucleus is placed in a strong magnetic field, the energy levels between various spin states are split (the Zeeman interaction). Different structural environments can affect the splitting since the surrounding electrons have a shielding effect of the magnetic field placed on the nucleus. Therefore transitions between adjacent energy levels of the nucleus with the absorption or emissions a photon in the radiofrequency (rf) range will be slightly different with respect to different structural environments. Since the absolute NMR frequencies are difficult to measure with sufficient accuracy, the resonance frequencies are normally recorded as chemical shifts (δ) relative to an external standard compound. In ³¹P NMR, the external standard compound is normally 85% H₃PO₄.

The NMR spectra of solids are usually broad compared with liquid NMR spectra. This is due to various interactions between the dipole moments of the nuclei, between the quadrupole moments of quadrupolar nuclei and the electric field gradient (EFG) at the nucleus, and by anisotropy of the electronic shielding at different sites in the structure. These broadening effects do not arise in the liquids because their atomic motion is faster than the interaction frequency, allowing all the nuclei in the particular atomic environment to experience the same average magnetic field, thus producing extremely narrow NMR spectra. Magic angle spinning (MAS) can significantly remove the dipole-dipole and chemical shift anisotropy (CSA) interactions, as well as the first-order quadrupolar interactions, narrowing the resonance lines to reveal spectral details.

In some cases where two different nuclei exist in the same molecules, the spectra of NMR also experience broadening effects (heteronuclear broadening) and are too large to be removing completely by MAS. Typically the existence of ¹H as second nuclei is observed in many cases. By continuously irradiating the proton at their Larmor frequency, the effect of their dipole moment can be cancelled and the spectrum of other nucleus is collected during this decoupling period and is thus free of heteronuclear broadening [98].

³¹P has a spin of ½ and is 100% natural abundance with a high resonance frequency. All factors make it readily observable. 400 MHz Bruker Avance III spectrometer was used for characterization of solid state ³¹P NMR (MAS and decoupling were applied for the elimination of broadening effects) and Bruker AVANCE II 400 was used for liquid state ³¹P NMR.

CHAPTER 3 Phosphate and Phosphoric Acid Systems

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3.1. Introduction

Phosphoric acid is one of the most well-known liquid proton conductors. It has extremely high proton conductivity (~10⁻¹S/cm) over a wide range of temperatures (40~200°C) and has already been commercially used as an electrolyte for phosphoric acid fuel cells (PAFCs). One of the major disadvantages of such liquid conductors during applications are migration problems due to its liquid nature that will cause electrode "flooding" and "drying" and evaporation problems at enhanced temperatures (~250°C) [7]. Stablizing acid in the solid state might be an efficient approach to solve these problems. In this chapter, several phosphates were synthsised and their conductivity before and after combination with phosphoric acid were characterized systematically.

3.2. Composite of AI(H₂PO₄)₃-H₃PO₄ systems

3.2.1. Background

As was discussed in Chapter 1, oxyanion solid acid salts such as CsHSO₄ exhibit unusual high conductivity under anhydrous conditions and at elevated temperatures. They are promising candidates as electrolytes for intermediate temperature fuel cells [41]. However, sulfates undergo irreversible decomposition in reducing atmospheres [99], while phosphates demonstrate their good stability at both reducing and oxidizing atmospheres due to the chemical inert PO₄³⁻ group such as CsH₂PO₄. However, relatively stringent conditions such as pressure or humidified conditions are required in order to maintain the "superprotonic" phase of CsH₂PO₄. Otherwise it will decompose under ambient atmosphere just a few degrees above the phase transition temperature [100]. Al(H₂PO₄)₃ is a hydrophilic material which has been widely used as a fire-retardant compound and agglutinants in many applications such as in cookers and ovens. Its excellent absorption properties towards infrared radiation endow a potential application in heat preserving areas. Two polymorphs of Al(H₂PO₄)₃ have been reported [101]. The α -form is isostructural with Fe(H₂PO₄)₃ [102] and consists of a 3D framework of corner, sharing MO₆ and PO₂(OH)₂ tetrahedra. The MO₆ octahedra are isolated and form columns along the c axis [101,102]. The β -form of Al(H₂PO₄)₃ has not had its structure fully resolved but it seems to be closed related to the a-form with the a axes of the rhombohedral structures being related to each other by a factor of $\sqrt{3}$. The phase AlH₂P₃O₁₀·2H₂O has the same stoichiometry but its monoclinic structure consists of layers of $(H_2P_3O_{10}^{3-})$ units octahedrally coordinates to Al^{3+} with water molecules between the layers [103]. AIH₂P₃O₁₀·2H₂O dehydrates at 150°C to form AIH₂P₃O₁₀ which decomposes to form Al₄(P₄O₁₂)₃ at 500°C[104]. The β -form of Al(H₂PO₄)₃ dehydrates at above 250°C to form glassy aluminium phosphates [101]. To the best of our knowledge, the conductivity of Al(H₂PO₄)₃ has not been reported yet. Two aluminium phosphates AlH₂P₃O₁₀·2H₂O and AIH₃(PO₄)₂·3H₂O have been reported as proton conductors although the conductivity is only of 10^{-8} - 10^{-7} S cm⁻¹ at 130 °C [105]. It should be of great interest to have a careful investigation on the conducting properties of the related compound Al(H₂PO₄)₃.

3.2.2. Experimental

Samples were synthesised by dissolving Al(NO₃)₃·9H₂O in 85% phosphoric acid according to different Al/P molar ratio with addition of deionised water in PTFE beakers. The solutions were heated at 200°C with continuous stirring until water was totally evaporated. The resultant powders were then treated at 200°C for 2 hours to complete reaction. For comparison, powders with an Al/P ratio of 1:3 were washed with acetone for three times using an ultrasonic bath in order to remove the residual acid during weighing and preparation and were labelled as AP1. The unwashed powders with Al/P=1/3, Al/P=1/3.007, Al/P=1/3.1, Al/P=1/3.5 were labelled as AP2, AP3, AP4, AP5, respectively. Fourier transform infrared spectrum (FTIR) was applied to have a careful investigation of internal bonding conditions and to check if the reactions had reached completion.

Crystal structure and phase purity were examined by X-ray diffraction (XRD) analysis of powders on a Stoe Stadi-P diffractometer. Microstructure was inspected on a JEOL 5600 scanning electron microscope. Thermal analysis of $AI(H_2PO_4)_3$ was carried out on a Rheometric Scientific TG 1000M 1000M+ TA instruments SDT 2960 from room temperature to 300°C (5°C/min), and then cooling down to 30°C (5°C/min) under flowing air at a rate of 20ml/min.



Figure 3-1: Schematic diagram of cell structure for impedance measurement.

The conductivity of $Al(H_2PO_4)_3$ - H_3PO_4 composites was measured by a.c. impedance spectroscopy. The pellets for measurement were 13mm in diameter and 3-4 mm in thickness and were obtained by pressing powders under 5×10³ kg cm⁻². For samples AP1 and AP2, silver ink was coated on both sides of the pellets to serve as electrodes. For other compositions with additional acid, carbon black (CABOT VULCAN XC72R) bonded by PTFE (Aldrich 60 wt% dispersion in water) was used as electrodes. The whole assembly was then pressed between two pieces of carbon paper for current collection. The detailed construction is schematically shown in Figure 3-1. Heat treatment of all pellets was carried out at 200°C for 30 minutes before impedance measurements. The impedance data were collected from highest (200°C) to lowest temperature (100°C) after holding for one hour at each temperature to reach equilibrium. A Schlumberger Solartron 1255 frequency response analyzer coupled with a 1287 electrochemical interface controlled by Z-plot electrochemical impedance software was used. The frequency range was from 1MHz to 100mHz at 100 mV r.m.s..

3.2.3. Phase composition, thermal stability, FT-IR and morphology

The XRD patterns of two typical samples AP1 and AP5 are presented in Figure 3-2.



Figure 3-2: X-ray diffraction patterns of acetone washed Al(H_2PO_4)₃ (a); Al:P=1:3.5 (b); α -form Al(H_2PO_4)₃ (c); labelled peaks for α -form Al(H_2PO_4)₃ (d); Al $H_2P_3O_{10}$ ·2 H_2O (e); labelled peaks for Al $H_2P_3O_{10}$ ·2 H_2O (f) respectively.

Aluminium phosphate patterns reported in earlier literature are also exhibited for comparison. According to Yoire, two polymorphs of Al(H₂PO₄)₃ have been reported: the α -form Al(H₂PO₄)₃ is hexagonal with parameter *a* = 7.849Å, *c* = 24.87Å and β -form of Al(H₂PO₄)₃ is hexagonal with parameter *a* = 13.69Å, *c* = 9.135Å [101]. It was found that Al(H₂PO₄)₃ synthesised in our experiments (sample AP1) is a single phase of β -Al(H₂PO₄)₃. The lattice parameters of Al(H₂PO₄)₃ are essentially invariant apart from the acetone washed sample which has a slightly smaller unit cell (Table 3-1).

Symbol	Sample	a/Å	c/Å	V∕Å ³	Measured pellet density (g/cm ³)
	Acetone washed	13 687(3)	0 1328(14)	1481 6(6)	1 84(2)
	$AI(H_2PO_4)_3$	13.007(3)	9.1020(14)	1401.0(0)	1.04(2)
۸ ロ2	unwashed	12 600/2)	0 1200/10)	1402 2(4)	1 01(2)
AFZ	AI(H ₂ PO ₄) ₃ 13.690(2	13.090(2)	2) 9.1366(10)	1403.2(4)	1.91(2)
AP3	AI:P=1:3.007	13.689(4)	9.1400(20)	1483.3(7)	1.80(2)
AP4	AI:P=1:3.1	13.692(3)	9.1403(18)	1483.9(6)	2.15(2)
AP5	AI:P=1:3.5	13.693(5)	9.1406(20)	1484.3(9)	1.82(2)

Table 3-1: Lattice parameters of $AI(H_2PO_4)_3$ and the $AI(H_2PO_4)_3$ -xH₃PO₄ composites.

The extra H_3PO_4 in the composites can not be detected by XRD because it should be amorphous. However, two very small peaks were observed in samples with extra acid in Xray patterns with large *d* values: *d* = 5.23 Å, 4.68 Å indicating the presence of second phases. The densities of the pellets are fairly close except sample AP4 which could be related to the deviation in pressure during pressing (Table 3-1).

Thermal stability of $AI(H_2PO_4)_3$ was evaluated using thermogravimetric analysis (TGA) curves. Figure 3-3 shows the TGA curves of samples AP1-AP5 from room temperature to 300°C at 5°C per minute on both heating and cooling without dwelling.



Figure 3-3: TGA analysis of samples AP1-AP5 from room temperature to 300°C in air (water content~0.6%) (5°C/min up and down) without dwelling.

The observed weight loss in different temperature regions is listed in Table 3-2.

		Woight loss	Weight loss	Weight loss		Corresponding
Sampla	Formula unit		(%) between	(%) between	Total weight	water molecules
Sample			100°C and	200°C and	loss (%)	loss per formula
		100 C	200°C	300°C		unit
AP1	$AI(H_2PO_4)_3$	1.35(1)	0.42(1)	2.55(1)	4.32(1)	0.76(1)
AP2	$AI(H_2PO_4)_3$	1.18(1)	0.67(1)	8.59(1)	10.41(1)	1.84(1)
AP3	AI(H ₂ PO ₄) ₃ •0.007 H ₃ PO ₄	0.10(1)	0.67(1)	8.81(1)	9.59(1)	1.70(1)
AP4	AI(H ₂ PO ₄) ₃ •0.1 H ₃ PO ₄	0.10(1)	0.77(1)	7.97(1)	8.83(1)	1.60(1)
AP5	$AI(H_2PO_4)_3 \bullet 0.5 H_3PO_4$	0.21(1)	2.24(1)	6.59(1)	9.02(1)	1.84(1)

Table 3-2: Weight loss of all samples in different temperature regions.

Different thermogravimetric behaviours were revealed according to composition. For samples AP1 and AP2, a relatively large weight loss (>1%) below 100°C was observed, which was generally deemed as the desorption of physically absorbed water. While for samples AP3-AP5 in which certain amounts of extra phosphoric acid were introduced, only a small weight loss (<0.25%) was observed in the same region. Therefore, it can be postulated that phosphoric acid seems to preserve $AI(H_2PO_4)_3$ from either absorption or desorption of water. However, Sample AP1 exhibited the smallest weight loss at higher temperature especially above 200°C where great weight loss took place for other samples. This could be attributed to the loss of water from H₃PO₄ to form pyrophosphoric acid or possibly even volatilisation of H_3PO_4 together with the possible loss of water from Al(H_2PO_4)₃ to form Al(PO_3)₃. Nevertheless, weight loss between 100°C to 200°C for all samples was generally small (Table 3-2) indicating that decomposition of $Al(H_2PO_4)_3$ is not significant below 200°C. Herein, all impedance measurements were carried out below 200°C. It has been confirmed that after heating at 300°C for 12 hours, Al(H_2PO_4)₃ finally transformed into Al(PO_3)₃ [106] (Figure 3-4) with some AIH₂P₃O₁₀ impurities indicating AI(H₂PO₄)₃ is not thermally stable at 300°C and the decomposition is a multistep process.



Figure 3-4: X-ray diffraction pattern of Al(H₂PO₄)₃ after treated at 300°C for 12 h. $\circ \alpha$ -Al(PO₃)₃, $\nabla \beta$ -Al(PO₃)₃, $\diamond AlH_2P_3O_{10}$.

The final product $AI(PO_3)_3$ exists as two phases (Figure 3-4) with one dominates the other implying the phase transition also takes place simultaneously. However, the XRD pattern of $AI(H_2PO_4)_3$ after TG analysis to 300°C without dwelling is almost identical to that before heat treatment in air indicating the decomposition of $AI(H_2PO_4)_3$ is rather slow below 300°C. This can be recognised by the total weight loss during TG analysis which corresponds to less than 2 water molecules per formula unit for all samples (Table 3-2). According to XRD analysis, this process is thermodynamically reversible if the sample is not held at a temperature above 300°C for a long time.

Fourier transform infrared (FT-IR) spectrum was applied to investigate internal bonding and to check the completion of the reactions. Figure 3-5 shows the IR spectra of samples AP1 and AP5 together with spectra of commercial $AI(NO_3)_3 \cdot 9H_2O$ (Figure 3-5a) and 85wt% phosphoric acid (Figure 3-5d).



Figure 3-5: FTIR spectra of (a) Al(NO₃)₃•9H₂O; (b) AP1; (c) AP5 and (d) 85wt% H₃PO₄, respectively.

According to Pathak *et al.* [107], nitrate generally exhibits a characteristic absorption peak around 1400 cm⁻¹ due to the asymmetric stretching vibrations of N=O bond. For commercial Al(NO₃)₃·9H₂O (Figure 5a), a broad adsorption was observed at this region while for samples AP1 and AP5, there is no detectable adsorption at the same region, which is a clear sign of completed reactions between Al(NO₃)₃·9H₂O and H₃PO₄. Additionally, a strong peak around 1600 cm⁻¹ and a broad peak from 2700 cm⁻¹ to 3700 cm⁻¹ were observed for all samples and are generally attributed to the different vibration modes of the O-H bond. The absorption peaks around 1000 cm⁻¹ and 1250 cm⁻¹ were thought to belong to symmetric and asymmetric stretching of P=O and P-O-P bonds [108]. SEM was used to examine the morphology of four samples. Figure 3-6 shows the SEM images at a magnification factor of 2000.



Figure 3-6: SEM pictures of acetone washed $AI(H_2PO_4)_3$ sample (a); unwashed $AI(H_2PO_4)_3$ sample (b); AI:P=1:3.007 sample (c) and AI:P=1:3.5 sample (d).

Small rod-like particles were observed in the samples with high acid level and coarse particles in the samples with low acid level. This is reasonable since crystal growth could be much easier under conditions of high precursor concentrations. Particles of $AI(H_2PO_4)_3$ after washing with acetone in an ultrasonic bath (AP1) are slightly smaller than the unwashed one (AP2). One possibility is that this is due to the break down of large particles under ultrasonic conditions. Smaller particles have been observed when a small amount of H_3PO_4 (0.7%) was added in the composite (Figure 3-6c) compared with those in the one without excess H_3PO_4 (Figure 3-6b). However, rod shape particles were observed when further increase the content of H_3PO_4 (Figure 3-6d). Obviously the crystallisation process of $AI(H_2PO_4)_3$ is affected by the H_3PO_4 concentration presented which needs further investigation.

3.2.4. Impedance spectroscopy and conductivity

A.c. impedance measurements were carried out in both air (water content~0.6%) and humidified 5% hydrogen in Ar (water content~3%) between 100°C and 200°C. Figure 3-7 shows typical impedance curves obtained in air (water content~0.6%) at 175°C.



Figure 3-7: complex impedance plots of acetone washed $AI(H_2PO_4)_3$ (a); unwashed $AI(H_2PO_4)_3$ (b); AI:P=1:3.007 (c); AI:P=1:3.1(d) and AI:P=1:3.5(e).

For the pure Al(H₂PO₄)₃ (sample AP1) (Figure 3-7a), the impedance plot is composed of two depressed semicircles. The value of normalised capacitance for the first semicircle (4.8×10⁻¹²F/cm) suggests a bulk response while the response of grain boundary can not be observed clearly. It is believed that the second semicircle is the response of the Ag electrode. The conductivity of pure Al(H₂PO₄)₃ (AP1) is slightly lower than the Al(H₂PO₄)₃ sample which was not washed by acetone (AP2) which might be related to the remnant H₃PO₄ in sample AP2. Proton conduction has been reported in similar compounds AlH₂P₃O₁₀·2H₂O and AlH₃(PO₄)₂·3H₂O although the conductivities are at 10⁻⁸~10⁻⁷S/cm at 130°C [105] and it is likely that protons are also the dominant charge carriers in Al(H₂PO₄)₃ as well. The conductivity of pure Al(H₂PO₄)₃ is comparable to its polymorphs AlH₂P₃O₁₀·2H₂O and AlH₃(PO₄)₂·3H₂O.

The impedance spectrum of the composite sample AP2 (Figure 3-7b) is composed of three depressed semicircles. The first poorly resolved semicircle with approximate capacitance $\sim 2 \times 10^{-12}$ F/cm could be interpreted in terms of the bulk response [86]. The resistance is significantly smaller than that for sample AP1. A small amount of excess acid may cause the

decrease of bulk resistance: the "dissolved" acid in the $AI(H_2PO_4)_3$ crystal could decrease the bulk resistance by increasing the proton concentrations. One possible reason is due to the increase of interstitial protons as shown in Equation 3.1

$$3H_{3}PO_{4} \xrightarrow{Al(H_{2}PO_{4})_{3}} 3H_{i}^{\bullet} + V_{Al}^{"} + 3(H_{2}PO_{4})_{(H_{2}PO_{4})}^{\times}$$
(3.1)

whereas the second depressed small semicircle ($C \sim 3 \times 10^{-9}$ F/cm) is most likely attributed to the grain boundary. The low frequency 'spike' relates to the response of electrode reaction. However, the sample with 0.7% excess H₃PO₄ (AP3 Figure 3-7c) shows only one semicircle at high frequency. Unlike a bulk response ($C \sim 10^{-12}$ F/cm) or grain boundary response ($C \sim$ 10^{-9} F/cm), the capacitance value becomes much larger ($C \sim 2.9 \times 10^{-8}$ F/cm) which probably corresponds to a surface layer formed by the interaction between Al(H₂PO₄)₃ grains and the extra H₃PO₄ on the surface. This is reasonable since only a limited amount of H₃PO₄ could enter the crystal structure in the form of defects and the surface layer formed by this interaction should be much more conductive than the bulk. The low frequency 'spike' represents charge build-up at the electrodes which could be explained by the ionic conducting behaviour rather than electronic. With increased amounts of H₃PO₄ in the composites, the semicircle for surface layer response disappeared, leaving only the electrode response in samples AP4 (Figure 3-7d) and AP5 (Figure 3-7e). This is typically a charge blocking effect due to the utilization of irreversible carbon black electrodes [109]. Capacitance values for the bulk and grain boundary (GB)/surface components of AP1 to AP5 are listed in table 3-3.

Table 3-3: capacitance values for the bulk and grain boundary (GB)/surface components of the impedance curves reported in Figure 3-6.

Sample	C _{Bulk} F/cm	$C_{\text{GB}} \text{ or } C_{\text{surface}} \text{ F/cm}$	C _{Electrode} F/cm
AP1	4.8(1)×10 ⁻¹²	-	1.2(1)×10⁻⁵
AP2	2.0(1)×10 ⁻¹²	3.0(1)×10⁻ ⁹	-
AP3	-	2.9(1)×10 ⁻⁸	-
AP4	-	-	2.8(1)×10 ⁻⁵
AP5	-	-	1.1(1)×10 ⁻³

The conductivity of pure Al(H₂PO₄)₃ (AP1) is 3.33×10^{-7} S/cm in air (water content~0.6%) at 200 °C; however, under the same conditions, the conductivity is 5.54×10^{-3} S/cm for the composite sample AP5 with excess H₃PO₄ which is four orders of magnitude higher. We postulated the possible internal structure as follows: the excess H₃PO₄ might coat on the Al(H₂PO₄)₃ surface to form a core-shell structure. A path for proton diffusion will be formed resulting in high ionic conductivity. Similarly, it has been reported that AlH₂P₃O₁₀·nH₂O has only one semicircle (C ~ 4.58×10^{-11} F/cm) corresponding to bulk response at 75°C in 60% RH and only a 'spike' like response in 94% RH. This was explained by the increased surface conduction at high relative humidity since the total resistance decreases more than one order

of magnitude after an increase in relative humidity from 60% to 94%RH [110]. It is almost certain that the conduction of $AI(H_2PO_4)_3$ - H_3PO_4 composites is dominated by protons as protons are the only ionic species that are likely to be mobile and there is no evidence to suggest electronic conduction from impedance measurements.

Possible conducting paths within the composite series are shown in Figure 3-8.



Figure 3-8: Possible proton transfer paths of $Al(H_2PO_4)_3$ - H_3PO_4 systems. The small circles represent the particles of $Al(H_2PO_4)_3$, while the shells represent the conductive layers formed by additional acid. Different defect concentration is expressed by the density of black dots in the circles. Possible paths are shown by arrows.

According to the impedance plots, the dominant conduction behaviour is thought to change from grain interior conduction to a surface/interfacial conduction. By considering the particles in a core shell structure, a conductive surface layer may connect together and bypass the particles of $AI(H_2PO_4)_3$ and hence only one compressed semicircle was observed. This core shell structure could also be used to explain the different thermogravimetric behaviours below 100°C: Since phosphoric acid formed a shell around the particles of $AI(H_2PO_4)_3$, the adsorption of water by the hydrophilic $AI(H_2PO_4)_3$ grains would be inhibited and the weight loss of AP3-AP5 below 100°C is consequently smaller than those in samples AP1 and AP2. $AI(H_2PO_4)_3$ acts as a matrix to hold the acid. Table 3 shows the capacitance of different parts of the equivalent circuit from AP1 to AP5.

Conductivities of all samples at different temperatures and atmospheres were measured and are plotted in Figure 3-9.


Figure 3-9: Arrhenius plots of conductivity for the five samples (acetone washed $AI(H_2PO_4)_3$, circle; unwashed $AI(H_2PO_4)_3$, square; AI:P=1:3.007, up triangle; AI:P=1:3.1, down triangle; and AI:P=1:3.5, diamond). The open and solid symbols correspond to the measuring atmosphere in air and wet 5% H_2 in Ar, respectively.

The conductivity increases by three orders of magnitude with the increase of acid amount from AP1 to AP5. The acid effect on enhancing conductivity is not significant in composite samples at high acid level like AP4 and AP5 compared with those in samples AP2 and AP3. The slight increase in slope in Figure 3-9 between AP3 and AP5 suggests increased conduction activation energy. Water has a strong effect on conductivity especially in pure $Al(H_2PO_4)_3$ since the conductivity increases quite a lot from air (~0.6% H₂O) to wet 5% H₂ (~3% H₂O). The apparent slope of the conductivity behaviour for AP1 and AP2 undergoes a steady increase from low temperature to high temperature suggesting an increase in the activation energy. The overall conduction activation energy of sample AP1 and AP2 is slightly higher than the H₃PO₄-rich composite (AP3 to AP5) indicating that the H₃PO₄ could be the major conducting path. A slight decreasing trend for the AP4 curve was also observed, possibly due to the formation of pyrophosphoric acid (Equation 3.2). According to Chuang *et al.* [111] a decrease of conductivity of orthophosphoric acid was observed on the formation of pyrophosphoric acid at higher temperatures [112]. The activation energy calculated from the regression lines of samples AP4 and AP5 are listed in Table 3-4.

Sample	Activation energy in air (water content~0.6%)	Activation energy in wet 5% H_2	
AP4 (A:P=1:3.1)	0.13(2)eV	0.09(1)eV	
AP5 (A:P=1:3.5)	0.12(1)eV	0.09(1)eV	

Table 3-4: Activation energy of AP4 and AP5 calculated from the regression line in Figure 3-9.

By comparing these values with previously reported values, the activation energies of AP4 (0.13(2)eV) and AP5 (0.12(1)eV) in air (water content~0.6%) agree well with the value of 85% phosphoric acid (0.12eV) further confirming the acid conducting behaviour [113,49]

$$2H_3PO_4 \xrightarrow{175^\circ C} H_4P_2O_7 + H_2O\uparrow$$
(3.2)

3.2.5. Effect of water on conductivity

As mentioned above, water plays an important role in most proton conduction mechanisms. Figure 3-10 shows the conductivity of sample AP2 in different atmospheres corresponding to different water contents: Ar (<0.01% H₂O by volume), air (~0.6% H₂O by volume), wet 5% H₂ (~3% H₂O by volume) and wet Ar (~3% H₂O by volume).



Figure 3-10: Arrhenius plots of conductivity for unwashed Al(H₂PO₄)₃ in different atmospheres (in air, circle; in wet 5% H₂, square; in Ar, up triangle; and wet Ar, down triangle).

Low conductivity in Ar was observed which might be due to lower pH_2O in Ar (<0.01% H_2O) than in air (~0.6% H_2O). Indeed, the conductivity of sample AP2 in wet Ar and wet air are comparable indicating that it is pH_2O rather than pO_2 that causes the observed difference in conductivity in the two atmospheres. The conductivity was sensitive to pH_2O under dry conditions, whereas when once the humidity has reached certain levels, the conductivity dependence on humidity is insignificant. The conductivity data were reproducible.

3.2.6. Stability of proton conductivity

The stability of conductivity is another important factor for evaluating the potential application of an ionic conductor as an electrolyte for an electrochemical device. The stability of samples after introducing additional acid is evaluated by measuring the conductivity (AP5) against time and under several thermal cycling. Figure 3-11 shows the conductivity change of sample AP5 at 175°C in air (water content~0.6%) for more than 100 hours.



Figure 3-11: conductivity of AP5 (AI: P= 1:3.5) as a function of time at 175°C in air (water content~0.6%).

The small increase in conductivity at the beginning might be due to the conversion of pyrophosphoric acid to orthophosphoric acid on uptake of water at 175°C (Equation 3.3) since the composite has been heated at 200 °C for more than one hour during fabrication and under the circumstance formation of some pyrophosphoric acid is possible:

$$H_4 P_2 O_7 + H_2 O \xrightarrow{175^\circ C} 2H_3 PO_4 \tag{3.3}$$

No significant change in conductivity was observed during the measured 80 hours (Figure 3-11). It is assumed that the conductivity was stable but longer time investigation is needed. A 9% increase in conductivity (from 9.44 to 9.53mS/cm) was observed and finally conductivity reached a plateau after 20 hours. The conductivity under different thermal cycles was shown in Figure 3-12.



Figure 3-12: Conductivity of sample AP5 (AI: P= 1:3.5) in air under several heating and cooling cycles.

It was found that the conductivity increased slightly during the first cooling cycle and became reproducible in the next two thermal cycles indicating good stability of $AI(H_2PO_4)_3$ · H_3PO_4 composite which is a potential electrolyte for electrochemical devices. The possible H_3PO_4 leaching in $AI(H_2PO_4)_3$ · H_3PO_4 composites does not appear to be a major problem although longer term testing is required.

3.2.7. Comparison and application

Solid inorganic proton conductors have wide applications in many areas such as fuel cells and gas sensors, and show good thermal stability compared with organic ones. Different types of inorganic proton conductors CsH_2PO_4 [100,114], α -Zr(HPO_4)₂ [115,116], AlH₃P₃O₁₀·2H₂O [105] and AlH₃(PO₄)₂·3H₂O [105] have been widely investigated. Their proton conductivities against temperature are replotted and shown together with AP1 to AP5 under different atmospheres in Figure 3-13.



Figure 3-13: Temperature dependence of electrical conductivity of selected solid acid for comparison. O sample AP1; □ sample AP2; △ sample AP3; ▽ sample AP4; ◊ sample AP5. ● CsH₂PO₄ in air [100]; ■ CsH₂PO₄ in 30mol% H₂O [113]; ▲ Zr(HPO₄)₂ in dry N₂ [114]; ▼
Zr(HPO₄)₂ in dry N₂ [115]; ● AlH₂P₃O₁₀·2H₂O in air at 0.7% RH [105]; ● AlH₃(PO₄)₂·3H₂O [105] in air at 0.7% RH; ■ AlH₂P₃O₁₀·2H₂O after milling for 12 hours and kept at 130°C 0.7% RH for several hours [105]; ● AlH₃(PO₄)₂·3H₂O after milling for 12 hours and kept at 130°C 0.7% RH for

There may be some small deviations in the conductivity due to different measuring conditions by various authors. The conductivity of pure $Al(H_2PO_4)_3$ (AP1) is comparable with $AlH_2P_3O_{10}$ and $AlH_3(PO_4)_2 \cdot 3H_2O$ indicating that these pure aluminium hydrogen phosphate solid acids themselves are not very conductive. Although mechanical treatment of these aluminium hydrogen

phosphates is able to increase the total conductivity by 2 or 4 orders of magnitude due to the formation of H_3PO_4 , the enhanced conductivity is not stable against time probably due to the consumption of H_3PO_4 during the reformation of aluminium hydrogen phosphates [105]. Similarly the high ionic conduction in samples AP3-AP5 is likely due to the presence of excess H_3PO_4 but with more stability as H_3PO_4 would not be consumed. All samples AP1-AP5 show higher conductivity than α -Zr(HPO₄)₂. Unlike CsH₂PO₄, Al(H₂PO₄)₃-H₃PO₄ does not require extra steam to retain its conductivity. Furthermore, the better interface contact as well as relatively low phosphoric acid load suggests that this compound may be considered as an alternative or complimentary inorganic component to SiC in phosphoric acid fuel cells (PAFCs) [117,118,119].

3.3. Composite of SnP₂O₇-H₃PO₄ composites

3.3.1. Background

Quite lately, Nagao *et al.* reported that SnP_2O_7 and $Sn_{0.9}In_{0.1}P_2O_7$ have high proton conductivity over 0.1S/cm under anhydrous condition at 250°C [120] and fuel cells using $Sn_{0.9}In_{0.1}P_2O_7$ as electrolyte showed a good performance [121]. In our experiments, it was found that the conductivity of SnP_2O_7 , In or Sc doped SnP_2O_7 were generally of ~ $10^{-5}S$ /cm under the same conditions when prepared by an aqueous solution method [122, 123]. It seems that the performance of SnP_2O_7 is highly dependent on the synthetic route used. The conduction mechanism of SnP_2O_7 has not yet been fully understood. Nevertheless, SnP_2O_7 is quite stable above 200 °C in the presence of H_3PO_4 or polyphosphoric acid. We have already investigated the $Al(H_2PO_4)_3-H_3PO_4$ composites which showed a high and stable conductivity at 175 °C [124]. In this report, the microstructure and ionic conductivity of the $SnO_2-P_2O_5$ composites are explored.

3.3.2. Experimental

3.3.2.1. Preparation of SnO₂·nH₂O particles

According to Nagao, pure SnP₂O₇ was obtained by calcining the pretreated paste containing SnO₂ and H₃PO₄ at 650°C for 2.5 hours [115]. However, in our experiment, it was quite difficult to obtain the pure SnP₂O₇ under the same conditions without containing SnO₂ impurities. This is probably due to the large particles of the commercial SnO₂ (Aldrich 99%) forming a core-shell structure terminating the reaction [117]. Therefore, nano-sized SnO₂·nH₂O particles were used and were prepared by a precipitation method. The method for preparation of nano-sized SnO₂·nH₂O particles is as follows: 10g of SnCl₄·5H₂O (Aldrich 99%) was dissolved in de-ionised water. 1M of ammonium solution was then slowly added until the pH value reached 7. A white precipitate formed and was washed with de-ionised water several times in order to remove extra ions such as Cl⁻. The remaining precipitates were heated at 200 °C for 2 hours. The resulting solid was ground into powders and XRD (X-ray diffraction) confirmed it to be SnO₂·nH₂O [125]. The amount of crystallized water was determined by TGA (Thermogravimetric analysis) to be n=2.50±0.02.

3.3.2.2. Preparation of SnP₂O₇-H₃PO₄ composites

Calculated amounts of $SnO_2 \cdot nH_2O$ and $85\% H_3PO_4$ (Alfa) according to molar ratio 1:2, 1:2.6, 1:2.8 and 1:4 were dispersed in deionised water. The mixtures were then heated at 200 °C for 2

hours with continuous agitations in PTFE beakers. The resulting white paste was then calcined at 300°C for 2.5 hours for the reaction (3.4) to proceed. For samples with high acid content (P:Sn=4:1), the mixtures were still in a pasty form after being treated at 300°C for 2.5 hours so a following calcination at 650°C for 2.5 hours was performed until a white solid was obtained. Samples with P:Sn=4:1 was also calcined at 650°C for 2.5 hours for comparison. The synthetic history as well as sample nomenclatures is listed in Table 3-4.

$$SnO_2 \cdot nH_2O + 2H_3PO_4 \xrightarrow{\Delta} SnP_2O_7 + (3+n)H_2O \uparrow$$
(3.4)

P:Sn molar ratio	Raw materials	Synthetic history	Nomenclature	
2:1	SnO₂·nH₂O, H₃PO₄	300°C, 2.5 hours	SP01	
2.1	SpOund O. H. PO	300°C, 2.5 hours	5002	
2.1	3110 ₂ 111 ₂ 0, 11 ₃ 1 0 ₄	650°C, 2.5 hours	51.02	
2.6:1	SnO ₂ ·nH ₂ O, H ₃ PO ₄	300°C, 2.5 hours	SP1	
2.8:1	SnO ₂ ·nH ₂ O, H ₃ PO ₄	300°C, 2.5 hours	SP2	
4.1		300°C, 2.5 hours	602	
4.1	$5110_2 \cdot 110_2 \circ 0, \ 10_3 \circ \circ 0_4$	650°C, 2.5 hours	543	
0.4		300°C, 2.5 hours	004	
2.1	S11∪14·3⊓2∪, (NH4)2HPU4	650° C, 2.5 hours	324	

Table 3-4: Synthetic history and nomenclatures of all samples

Pure SnP_2O_7 was also synthesized by an aqueous solution method. Calculated amounts of $(NH_4)_2HPO_4$ and $SnCl_4$ were dissolved in de-ionised water separately. The $(NH_4)_2HPO_4$ solution was slowly added into the $SnCl_4$ solution under continuous stirring. The mixed solution was then heated at 80 °C for 1 hour until white precipitates were produced. After heated at 200 °C for 2 hours to remove the excess water a gel-like mixture formed. The mixture was then heated again at 650°C for 2.5 hours. The white powders were then finely ground and stored for further measurements.

3.3.2.3 Analytical procedures

Crystal structure and phase purity were examined by X-ray powders diffraction (XRD) analysis on a Stoe Stadi-P diffractometer. Incident radiation was generated using a CuK α 1 source (λ = 1.54056 Å). The step size for data collection was 0.02° with a collection time 10s at each step. Vaseline was used to mount the sample in the sample holder. X-POW software was used to perform least square refinement of the unit parameters. The microstructure was examined by JEOL 5600 scanning electron microscope and transmission electron microscope (JEOL JEM-2011). Solid state ³¹P NMR analysis was performed on 400MHz Bruker Avance III spectrometer with Larmor frequency of 202.466MHz, both magic angle spinning (MAS) and proton decoupling were applied for the elimination of broadening effects. One-dimensional (1-D) direct polarization magic angle spinning DP-MAS-NMR spectra were recorded at a spinning speed of 11 kHz at a 90° pulse duration and recycle delay of 6µs and 80s. Solution ³¹P NMR analysis for the filtrate of samples SP3 and SP4 was carried out on a Bruker AVANCE II 400 at the frequency of 161.97 MHz. All chemical shifts are expressed in ppm and referenced relative to H₃PO₄ (85% w/w, Alrich). Fourier transform infrared (FTIR) spectra of the samples were recorded at transmission mode using KBr disks on a PERKIN-ELMER Spectrum GX FT-IR system from 400 to 4000 cm⁻¹ with a resolution of 4 cm⁻¹.

The electrical properties of SnP₂O₇-H₃PO₄ composites were evaluated by a.c. impedance spectroscopy. The pellets used for electrical measurement were 13 mm in diameter and 3-4 mm in thickness and were obtained by pressing powders at 380 MPa. Carbon black (CABOT VULCAN XC72R) bonded with PTFE (Aldrich 60 wt% dispersion in water) were used as electrodes and were dabbed on each side of the pellets. Carbon paper (Torory TGPH-090) was then pressed on both sides for better contact. The samples with the electrodes were then mounted on a homemade jig placed in a temperature controllable furnace. All pellets were treated at 300 °C for 30 minutes before measurements and all measurements were carried out on cooling cycles after holding at each temperature for at least one hour to reach equilibrium. The measurements were repeated under different atmospheres for comparisons. A Schlumberger Solartron 1255 frequency response analyzer coupled with a 1287 electrochemical interface was used for the generation of ac perturbations. The whole systems were controlled by Z-plot software and the measurement was carried out at a frequency range from 1 MHz to 10 mHz with 100 mV r.m.s.

3.3.3. Phase composition, SEM, TEM, ³¹P NMR and FT-IR

The XRD patterns of as-prepared samples varies slightly according to the synthetic history (Figure 3-14).



Figure 3-14: X-ray diffraction patterns SP01 (a); SP02 (b); SP1 (c); SP2 (d); SP3 (e) and SP4 (f) respectively. (○) Sn(HPO₄)₂·xH₂O peaks, (▽) Vaseline peaks.

For SP01 which has P:Sn ratio 2:1, XRD indicates a poorly crystallized mixtures with $Sn(HPO_4)_2 \cdot xH_2O$ as the main impurities (Figure 3-14a). The reaction (3.4) was probably not yet completed at 300°C for 2.5 hours and complete reaction can be achieved after 650°C calcination (SP02, Figure 3-14b). XRD patterns for the rest of other samples exhibited clear peaks and can

be indexed basically as simple cubic symmetry with space group $Pa\overline{3}(205)$ [126] (Figure 3-15).



Figure 3-15: Overview of SnP₂O₇ structure.

Although a pseudo-cubic $3\times3\times3$ superlattice was reported by electron diffraction [127], XRD did not detect the superlattice peaks. The unit cell parameters, however, change slightly from sample to sample. Samples with higher acid loading and lower thermal treatment exhibited relatively larger unit cells (Table 3-5). The unit cells refined here, however, were all slightly bigger than the value (a = 7.94Å) reported from different synthetic routes [128]. One possible explanation is the dissolution of a small amount of H₃PO₄ into the SnP₂O₇ structure that leads to a nonstoichiometric composition and expands the lattice accordingly. Behan et al. reported a layer SnP₂O₇ decomposed from heating Sn(HPO₄)₂ at 650°C for 12 hours [129]. Although Sn(HPO₄)₂ impurities were observed during thermal treatment (Figure 3-14a), the layer polymorph was not detected, suggesting the final products are highly relevant to the synthetic conditions.

Sample	a (Å)	$V(Å^3)$
SP02	7.9638(12)	505.09(13)
SP1	7.970(3)	506.3(3)
SP2	7.979(3)	508.0(3)
SP3	7.9783(12)	507.85(14)
SP4	7 9629(16)	504 91(17)

Table 3-5: Lattice parameters of SnP_2O_7 in different samples when indexing as cubic.

The SEM pictures of as-prepared samples are shown in Figure 3-16.



Figure 3-16: The SEM pictures of SP01 (a); SP02 (b); SP1 (c); SP2 (d); SP3 (e) and SP4 (f) at a magnification of 2000.

Large particles with dimensions more than 100µm can be identified in sample SP01, and the particle size distribution is quite broad with no significant particle aggregations. Similar situation was also observed in SP02 and SP4 but with significantly smaller particles. On the contrary, samples with initial excess phosphorous exhibited different morphologies, irrespective of the thermal history. Samples of SP1 to SP3 all showed different extent of particle aggregation and particle sizes can be smaller and less dispersive. It is realized that the morphologies of samples are highly dependent on synthetic conditions with starting materials (i.e. P:Sn ratio) as the main crucial factors.

Samples with well crystallized SnP_2O_7 were also inspected by high-resolution TEM (HRTEM) (Figure: 3-17).



Figure 3-17: TEM images of SP02 (a) and (b); SP1 (c); SP2 (d); SP3 (e) and SP4 (f). The face distances marked of 3.22 Å, 3.51 Å, 3.98 Å, 4.59 Å, 3.55 Å and 2.81 Å corresponding to (211), (210), (200), (111), (210) and (220) plane respectively for cubic SnP₂O₇.

The most significant distinctions between different samples are the presence of an amorphous layer when the starting P:Sn ratio exceeds 2:1 which is the stoichiometric ratio for SnP_2O_7 . Although the amorphous layer is too thin to carry out an Energy dispersive X-ray spectroscopy (EDX) analysis, it should be rich in phosphorous as the thickness of layer increased from samples SP1 to SP3 (i.e. increased with acid loadings). Particles with relatively clean edges and grain boundaries were observed for samples with stoichiometric ratios, irrespective of the starting materials (Figure 3-17a, 3-17b and 3-17f). The grid distances marked on Figure 3-17 corresponds to (211), (210), (200), (111), (210) and (220) planes for cubic SnP_2O_7 with acceptable deviations.

Solid state ³¹P NMR techniques were applied for the examination of internal environment of phosphorous.



Figure 3-18: ³¹P MAS NMR spectrums of as-prepared samples. (•) spinning sidebands.

Sample	δ ₁ (ppm)	δ ₂ (ppm)	δ ₃ (ppm)	δ ₄ (ppm)	δ ₅ (ppm)	δ ₆ (ppm)	δ ₇ (ppm)	δ ₈ (ppm)
SP01	-1.3	-9.4	-14.3	-20.1	-	-38.6	-	-
SP02	-1.3	-	-	-	-25.3	-38.6	-	-
SP1	-1.3	-	-	-	-	-38.6	-	-
SP3	-1.7	-	-	-	-	-38.6	-47.3	-54.4
SP4	-	-	-	-	-	-38.6	-	-

Table 3-6: ³¹P MAS NMR line for as-prepared samples

DP-MAS-NMR spectra for sample SP4 shows only a broad and complex peak centered at -38.6 ppm. The peak is attributed to ³¹P nuclei resonance of SnP₂O₇ [127], suggesting that SP4 is essentially pure cubic SnP₂O₇. Similar resonance was also observed in sample SP02 with two small addition peaks at -1.3 ppm and -25.3 ppm. According to Brow *et al.* the phosphate units presented in phosphate glasses can be classified by Qⁿ where n is the number of bridging oxygen per phosphate tetrahedron [130]. Therefore, the unknown phosphate units can be identified by comparing their isotropic ³¹P shifts with known phosphate structures. Here, the first small shift of

sample SP02 is comparable with orthophosphoric acid (Q⁰) which is the reference material. This is probably due to the residue of excess phosphoric acid during initial weighing. The second shift, however, has not reported for tin phosphate compounds, but is comparable to relevant zirconium phosphate which has a very similar shift (-21.9 ppm) and was assigned to HPO_4^{2-} bonded to three Zr(IV) atoms of α-type layer [131]. Therefore, the second shift was likely due to the resonance of HPO₄²⁻ bonded to three Sn(IV) atoms with the same layer structures. It can be noticed that samples with stoichiometric ratios of Sn and P after high temperature treatment (650°C) almost have single resonance shift, implying most of the phosphorous is bearing the same internal environment (i.e. pure phase). This is guite different from samples treated at lower temperature or having non-stoichiometric ratios of Sn to P. In the case of samples (SP01) treated at lower temperatures (300°C), NMR indicates the presence of Q⁰ (-1.3 ppm) and Q¹ (-9.4 ppm and -14.3 ppm) in addition to the broad peaks at -20.1 ppm and -38.6 ppm. Chen, et al. have investigated the ³¹P NMR spectrum of Sn(HPO₄)₂ at different temperatures, only one resonance at -20.5 ppm was observed for Sn(HPO₄)₂ at room temperature [132]. Therefore, following the observation of $Sn(HPO_4)_2$ in XRD (Figure 3-14a), we can simply assign the -20.1 ppm shift to $Sn(HPO_4)_2$ resonance. On the contrary, samples with slightly different P:Sn ratios (SP1) exhibits only a sharp peak at -1.3 ppm (H_3PO_4) and a broad peak at -38.6 ppm (SnP_2O_7), suggesting the reaction (3.4) has been completed. However, for samples undergoing high temperature treatment (650°C) and with large stoichiometric ratios (SP3), the NMR spectrum shows four peaks at -1.7 ppm, -38.6 ppm, -47.3 ppm and -54.6 ppm (Table 3-6). The first two peaks can be assigned to Q⁰ (such as solid H_3PO_4 with melting point ~ $42^{\circ}C$ due to the broadened peak) and SnP₂O₇, while the last two peaks may belong to phosphates with much more bridging oxygens per phosphate tetrahedron (such as Q³). The composition of SP3 was further studied using solution ³¹P NMR: the samples was washed with deionised water and filtered; the filtrate was analyzed by solution ³¹P NMR (Figure 3-19).



Figure 3-19 Solution ³¹P NMR spectrums of (a) filtrate of SP3 and (b) filtrate of SP4.

A sharp peak at -0.05 ppm was observed for sample SP3, in contrast to SP4 performed at the same conditions. The peak belongs to orthophosphate species which originated from dissolution of phosphate (such as H_3PO_4 or polyphosphoric acid after decomposition (3.5)) other than SnP_2O_7 since SP4 was essentially pure SnP_2O_7 with no detectable signals.

$$H_{3n-2x}P_nO_{4n-x} + xH_2O \longrightarrow nH_3PO_4 \tag{3.5}$$

The infrared (IR) spectra for as-prepared samples are shown in Figure 3-20.



Figure 3-20: Infrared spectrum of SP01 (a); SP02 (b); SP1 (c); SP2 (d); SP3 (e) and SP4 (f), repectively.

It can be realized that samples which undergo low temperature treatment (SP01, SP1 and SP2) have a distinct absorbance around 1350 cm⁻¹ which is assigned to H₂O deformation bending [133,134]. This is due to the residual water and can be eliminated at high temperatures (Sample SP02, SP3, SP4). The typical absorbance around 1650 cm⁻¹ is an indication of the P-O-H deformation mode [133] which is only exhibited for samples with non-stoichiometric ratios or low temperature treatment. It can also realized that these samples also show a broad absorption peak from 2500 to 3500 cm⁻¹ which, according to Tarafdar *et al.* [132] and Zouari *et al.*[135], originates from the vibration of O-H bond (PO-H or HO-H). This is quite consistent with Solid state ³¹P NMR spectrum where the presence of H₃PO₄ was confirmed in these samples (Figure 3-18). More specifically, the absorbance around 2600~ 3000 cm⁻¹ generally belongs to the stretching of

hydrogen bonded O-H groups (O-H···O) where protons are expected to be more mobile and easier to migrate [136,137]. The samples with non-stoichiometric ratios clearly show stronger absorbance at this range. The absorbance around 740 cm⁻¹, 1000 cm⁻¹ and 1200 cm⁻¹ can be assigned to the asymmetric vibration mode of bridge P-O-P, symmetric vibration mode $v_{s}(PO_{4})$ and asymmetric vibration mode $v_{as}(PO_{4})$ [127].

3.3.4. Conductivity

Figure 3-21 shows the conductivity of all samples measured in different atmospheres.



Figure 3-21: Conductivity versus temperature of SP01; SP1; SP2; SP3 and SP4 in different atmospheres

The conductivities differ from sample to sample by several orders of magnitude. The samples with non-stoichiometric ratios are highly conductive such as sample SP1, SP2 and SP3 in both air and wet reduced conditions. A slightly enhanced conductivity in wet conditions implies that these samples are essentially proton conductors. Samples with stoichiometric ratios show a much lower conductivity and the conductivity is highly dependent on thermal treatment. A different treatment at 300 and 650°C can yield a deviation of conductivity with almost three orders of magnitude (SP01 and SP02). In association with solid state NMR (Figure 3-18), the samples with poor

conductivity are actually pure cubic SnP_2O_7 (SP02 and SP4). The slightly higher conductivity in SP02 is attributed to the residual acid and the presence of HPO_4^{2-} groups (Figure 3-18). Therefore, the significantly higher conductivity in sample SP01, SP1, SP2 and SP3 is probably due to the presence of considerable amounts of phosphoric acid and the SnP_2O_7 per se is not directly contributing to the high conductivity. This is consistent with the results reported by Tao [138] but demonstrates large discrepancies with other groups [139,140,141]. This is probably because of the excellent thermal stability and versatility of phosphoric acid that is generally difficult to remove at normal conditions. However, the observed high proton conductivity suggests us a new routine to develop novel proton conductors since all samples are basically in solid state. The highest conductivity achieved was 3.5×10^{-2} S/cm at 300 °C in air for sample SP3.

3.3.5. Conductivity stability

The high conductivity of samples was recorded as a function of time in order to evaluate the stability at high temperature (250 °C).



Figure 3-22: Conductivity of SP1, SP2 and SP3 at 250 °C in different atmospheres as a function of time.

Figure 3-22 shows the conductivity of SP1 as a function of time in air and in wet 5% H₂. The conductivity of sample SP1 remains unchanged in both air and wet 5% H₂ for more than 50 hours, confirming a good stability. However, the conductivity of sample SP2 keeps on decreasing during the first 50 hours and tends to be stable thereafter which could be due to the slow evaporation of H₃PO₄ as the initial acid loading in SP2 is relatively higher. Another possible explanation is the condensation effect: the slow generation of pyrophosphoric acid could take place at high temperatures and decrease the conductivity to some extent [111]. However, the conductivity of SP3 was stable which was probably due to a better thermal stability after the treatment at a higher temperature (650° C). Since the sample SP3 not only exhibits a high conductivity but also demonstrates long time stability, it is considered as a promising material for fuel cells and other electrochemical devices [142].

3.4. Composite of BPO₄-H₃PO₄ systems

3.4.1. Background

It has been suggested in SnP_2O_7 -H₃PO₄ systems that an amorphous layer (thickness < 10nm) is responsible for the high conductivity. A plausible strategy to enhance the conductivity based on this observation is to increase the amorphous layer so that more conducting paths are available. This could be achieved by reducing the particle size of phosphate. Here we choose boron phosphate due to its stability toward phosphoric acid. BPO₄ itself has been reported as a proton conductor, it exhibits a water assisted conductivity (>10⁻² S cm⁻¹) at ambient temperature [143] and has been introduced into perfluorinated membranes such as sulfonated poly ether ether ketone (SPEEK) to improve water retention [144]. It is also well known that boron phosphate is a potential material for humidity sensors and a promising nonlinear optical (NLO) material [145, 146]. It has a corrugated structure by periodically connecting PO₄ and BO₄ tetrahedrons (Figure 3-23) and has been used as a hydrolysis catalyst for wide range organic compounds such as formic acid [147], 1-propanol [148] and ethanol [149].



Figure 3-23: Overvew of BPO₄ structure.

Various methods have been used to synthesize BPO₄ with different morphologies. Mulla *et al.* used boric acid and diammonium metaphosphate as starting materials; they pretreated the mixtures in vacuum and obtained pure BPO₄ with particle sizes less than 50 nm after calcining at various temperatures [145]. Moffat *et al.* used tri-n-propyl borate and orthophosphoric acid as starting materials and obtained a high surface area boron phosphate (200 m²g⁻¹) [150]. Different boron (B₂O₃, B(OEt)₃) or phosphorous (PO(OCH₃)₃, PCl₅) sources or various synthetic routes (CVD, hydrothermal) have been used to obtain BPO₄ with diverse morphologies [144,151,152,153]. Here we use a simple solid state reaction to synthesise nano-sized BPO₄ and the BPO₄-H₃PO₄ systems were also systematically investigated.

3.4.2. Experimental

BPO₄ was synthesised from boric acid and phosphorus pentoxide by solid state reaction. All materials were used as received. Phosphorus pentoxide was chosen due to its hydrophilic properties which can facilitate the reaction (equation 3.7) and reduce heat input required.

$$2B(OH)_3 + P_2O_5 \xrightarrow{\Delta} 2BPO_4 + 3H_2O^{\uparrow}$$
(3.7)

Calculated amounts of boron acid were mixed with phosphorus pentoxide according to different molar ratios at B:P=1:1, 1:1.1, 1:1.2, 1:1.3 and 1:1.4 without addition of any solvents and are labeled as BP1, BP2, BP3, BP4 and BP5 respectively. The mixtures were ball milled and transferred into alumina crucibles for heat treatment. After firing at 300 °C for 2 hours, the powders were ground again and collected for investigation. For comparison, boron phosphate was also synthesized by a solution method as reported elsewhere by using boric acid and H_3PO_4 [154]. The molar ratio was kept as B:P=1:1.3 and was labeled as BP6.

Crystal structure and phase purity were examined by X-ray diffraction (XRD) analysis of powders on a Stoe STADI/P powder diffractometer. Incident radiation was generated using a Cu_{Ka1} source (λ = 1.54056 Å). The microstructures were examined by transmission electron microscopy (TEM) JEOL JEM-2011. Fourier transform infrared spectrum (FT-IR) was chosen to inspect the interior bonding conditions for all samples. KBr pellets were made for each sample and the IR spectrum was collected on the PERKIN-ELMER Spectrum GX FTIR systems from 400 to 4000 cm⁻¹ with a resolution of 4 cm⁻¹.

The conductivity measurements were carried out by the a.c. impedance method over the frequency range from 1 MHz to 10 mHz at 100 mV r.m.s. Pellets were used for measurements and were obtained by pressing powders under a pressure of 5×10^3 kg·cm⁻². Both sides of the

pellets are dabbed with PTFE bonded carbon (Carbot Vulcan 72R) which serves as electrodes. Carbon paper (Torory TGPH-090) was subsequently pressed on as current collector. The pellets were mounted into the tube furnace for impedance measurements. Data were collected from the highest temperature (300°C) to the lowest (50°C) on cooling after holding for one hour at each temperature to reach equilibrium. Different atmospheres were applied to simulate fuel cell conditions. The stability of conductivity was measured after aging the samples at 250°C overnight.

3.4.3. Phase composition, particle sizes and morphology

X-ray powder diffraction patterns confirmed the existence of BPO₄ in all samples. The prepared BPO₄ samples exhibit the same structure as previously reported (S.G. $I\bar{4}(82)$ *a* = 4.332 Å, *c* = 6.64 Å, *V* = 124.61 Å³) [145] although there are some deviations in lattice parameters (Figure 3-25).



Figure 3-24: X-ray diffraction patterns of B:P=1:1 (a); B:P=1:1.1 (b); B:P=1:1.2 (c); B:P=1:1.3 (d); B:P=1:1.4 (e) and B:P=1:1.3 prepared by solution method (f) respectively. (•) BPO_4 peaks, (\mathbf{V}) Vaseline peaks

The vaseline peak is from sample preparation for XRD data collection.

It is believed that some extra P_2O_5 may dissolve into the BPO₄ lattice to form a solid solution when the B:P ratio is higher than 1. The cell parameters obtained from powder diffraction patterns are listed in Table 3-7 and plotted in Figure 3-25.



Figure 3-25: Cell parameters of all samples: (a) cell parameter *a*; (b) cell parameter *c* and (c) cell volume *V*. (•) samples prepared by solid state reactions and (\Box) samples prepared by a solution method.

Samples	B:P ratios	a (Å)	c (Å)	V (Å ³)
BP1	1:1	4.3424(17)	6.656(20)	125.51(10)
BP2	1:1.1	4.3393(9)	6.6481(18)	125.18(6)
BP3	1:1.2	4.3396(11)	6.6479(21)	125.19(7)
BP4	1:1.3	4.3406(10)	6.6486(24)	125.27(8)
BP5	1:1.4	4.3434(8)	6.6552(18)	125.55(6)
BP6	1:1.3 solution	4.3451(4)	6.6595(11)	125.73(3)

Table 3-7: Cell parameters calculated from X-ray powder diffraction patterns

It was found that the cell parameters had a sudden decrease first and then increase d slightly with the variations of B:P ratios. Most of the extra P_2O_5 are in amorphous form almost likely in the form of H_3PO_4 when observed by TEM (Figure 3-27). The existence of an amorphous phase makes it difficult to determine the exact composition of crystallized BPO₄ in the samples. The cell parameters are generally expected to increase in the presence of additional phosphorous since the size of P⁵⁺ (0.31 Å) ions is larger than B³⁺ ions (0.26 Å) at six coordination [155]. Increase of phosphorus in BPO₄ may cause lattice expansion which is observed from samples BP2 to BP5. The decrease of lattice parameters from samples BP1 to BP2 is probably due to the composition difference of crystallized BPO₄ phase but remains difficult to explain. It is worth noting that BPO₄

prepared by a solution method shows larger cell parameters compared with others (Figure 3-25) which could come from the different crystal-growth conditions and will be discussed later.

Samples	B:P ratio	Particle size calculated (nm)
BP1	B:P=1:1	10
BP2	B:P=1:1.1	12
BP3	B:P=1:1.2	14
BP4	B:P=1:1.3	15
BP5	B:P=1:1.4	21
BP6	B:P=1:1.3 (solution)	148

Table 3-8: Particle sizes of samples calculated by the Scherrer equation.

The particle sizes were estimated using the Debye-Scherrer equation (equation 2.11), It was found that particle sizes of BPO₄ increased from 10 to 20 nm with increasing B:P ratios (Table 3-8). The particle size of BPO₄ in sample BP1 is only 10 nm which is the smallest so far reported. A systematic increase in particle size was found with increasing phosphorous content. Samples synthesized by the solution method showed considerably larger particle sizes (150 nm). Nucleation of BPO₄ could easily take place as long as the initial components "bump" into each other in the correct orientations during the ball milling process. However, unlike solution conditions where mass transport for further crystal growth is continuously supported by laminar or turbulent flow, in a solid state reaction, all ions in solid B(OH)₃ and P_2O_5 are less mobile around the initial BPO₄ crystal therefore further growth of BPO₄ is consequently inhibited. TEM pictures (Figure 3-26) indicate that the crystallized BPO₄ in sample BP1 is about 10nm which is at the same level as that calculated by the Scherrer equation. Under low resolution TEM conditions (Figure 3-26a), tiny particles with a narrow distribution around 10 nm were observed in BP1, consistent with Scherrer estimations.



Figure 3-26: LRTEM (a) and HRTEM (b) images of BPO₄ nanoparticles (BP1). The lattice spacings marked corresponds to [101] and [002] *d* spacings.

Crystal structures of these particles were further confirmed under High-resolution TEM (HRTEM) conditions (Figure 3-26b) where only single crystalites were observed and the lattice spacing marked on the Fig. 3b corresponds well with the [101] and [002] *d* spacings, 0.363 nm and 0.332 nm respectively according to the PDF card 74-1169. However, larger particles (30 nm) were observed for sample BP5 (Figure 3-27a), slightly higher than estimations from XRD peak broadenings.



Figure 3-27: a) Typical TEM image of samples with extra phosphorus (BP5); b) HRTEM image of area selected on image (a); c) HRTEM image of area selected on image (b).

HRTEM pictures revealed an amorphous layer in addition to BPO₄ crystals (Figure 3-27b and 3-27c). This is reasonable since more phosphorous pentoxide was added at the beginning and the amorphous layer was believed to be dominated by phosphorous-containing phases. Most likely it is poly phosphoric acid $H_{3n-2x}P_nO_{4n-x}$ due to the strong hydrophilic properties of P_2O_5 .

3.4.4. IR spectroscopic characterization

Figure 3-28 shows the IR spectra of samples BP1, BP3, BP4, and BP5. No significant difference was observed at low wavenumbers. Peaks in this region correspond well with values previously reported for BPO₄ [156].



Figure 3-28: FT-IR spectrum of B:P=1:1 (a); B:P=1:1.2 (b); B:P=1:1.3 (c) and B:P=1:1.4 (d), respectively.

The absorbances at 620 cm⁻¹ and 550 cm⁻¹ could be assigned to the deformation absorption bands of O-B-O and O-P-O individually and strong peaks at 930 cm⁻¹, 1085 cm⁻¹ and 1190 cm⁻¹ could be attributed to ν (PO₄) and ν (BO₄) stretching modes respectively [153]. However, at high wavenumbers, a stronger peak at 1640 cm⁻¹ and wide peaks from 2600 cm⁻¹ to 3700 cm⁻¹ were observed from samples BP2 to BP5 compared to BP1. The intensity of these peaks was found to increase monotonically from samples BP2 to BP5. According to Jin *et al.* [157] and Li *et al.* [158], these absorptions belong to the different vibration modes of O-H bonds. Since pure BPO₄ (BP1) show much less absorbance at these positions, the amorphous layer in samples of BP2-BP5 are believed to be rich in O-H bonds and could be a source of protons. The general assignment of peaks was listed in Table 3-9 according to Kmecl *et al.* [156].

Table 3-9 Assignments of infrared absorptions of samples investigated.

Wavelength (cm ⁻¹)	Vibration assigned
2500-3700	Stretching modes of PO-H and BO-H bonds
3210 and 1640	Stretching and deformation modes of strongly absorbed water
1085 and 1190	v3(BO ₄) stretching
930	v3(PO ₄) stretching
620 and 550	Deformation absorption bands of
020 414 000	O-B-O and O-P-O(14)

3.4.5. Impedance spectroscopy and conductivity

Figure 3-29 shows a typical impedance response (Cole-Cole plot) of samples with extra phosphorous at 200°C in air.



Figure 3-29: Typical impedance response of samples with extra phosphorus at 200 °C in air.

One 'spike' like response (C~10⁻⁵F/cm) was observed at low frequency corresponding to the charge build-up at the electrodes [86]. This could be due to the dominant ion transportation within the samples since electrodes (carbon black) are not expected to show good electrocatalytic behaviour. We could postulate these samples to be proton conductors since conductivity improves with hydration and protons seem the only likely species that could migrate within the systems if charges and sizes are taken into consideration. The resistance of sample BP1 is beyond the measuring limit of Solartron 1255 which means the conductivity is very low at a dry condition. Although a very high conductivity was observed in humidified BPO₄ at room temperature which involves H_3PO_4 [159], BPO₄ itself is not conductive under dry conditions. Therefore, the high conductivity of samples BP2-BP5 could be attributed to the amorphous layer observed in HRTEM pictures. Figure 3-30 shows the conductivity in the temperature range from 50 °C to 300 °C in different atmospheres. The values are calculated from the Cole-Cole plots at the intercept to the real axis.



Figure 3-30: Conductivity of samples with different B:P molar ratios from 50 $^{\circ}$ C to 300 $^{\circ}$ C in air and in wet 5% H₂ (humidified in water at 20 $^{\circ}$ C).

All samples with extra phosphorous (BP2-BP5) showed remarkable conductivity even for sample BP1 with only 10% excess phosphorous ($\sigma > 10^{-3} \text{ S} \cdot \text{cm}^{-1}$). Like most proton conductors, a wetter atmosphere (humidified at 20 °C) would result in an increase in conductivity compared with ambient conditions. This gives some evidence that water promotes conduction. However, this enhancement is not so obvious compared with other proton conductors like $Zr(HPO_4)_2$ [160] or nano TiO₂ film [33]. For our samples, humidity is not an indispensable factor to maintain high conductivity. Sample BP5 with 40% extra phosphorus (BP5) exhibits a conductivity as high as 8.8×10^{-2} S cm⁻¹ at 300 °C in ambient air. This brings wide potential applications besides fuel cells such as gas sensors [141] and solid electric double layer capacitors [161].

3.4.6. Particle size effect

The effect of particle sizes of BPO₄ on conductivity was also evaluated by comparing samples BP4 and BP6 under different atmospheres. Figure 3-31 shows the conductivity of sample BP4 and BP6 in different atmospheres.



Figure 3-31: Conductivity of samples B:P=1:1.3 prepared by solid state reactions (■, □) and by a solution method (●, ○) in air and in wet 5% H₂ (humidified in water at 20 °C).

Sample BP4 demonstrated a higher conductivity in the whole temperature range under investigation and showed a much better performance beyond 150 °C. This clearly shows a significant considerable influence of BPO₄ particle sizes on conductivity although BPO₄ itself is not a good proton conductor under these conditions. Alberti *et al* [116] and Yaroslavtsev [162] also observed a remarkable increase on conductivity after decreasing the particle sizes of $Zr(HPO_4)_2$ into the nanometer scale. It is believed that smaller particles have much larger surface area which can hold more water and facilitate proton conduction. The small particle size will also give more interfaces between BPO₄ and the amorphous phases which could be the paths for proton conduction.

3.4.7. Stability of proton conductivity

The stability of conductivity is crucial in evaluation of a conductor for practical use. Quite a few unstable proton conductors such as $Cs_2HPW_{12}O_{40}$ [163] and 12-phosphotungstic acid/ionic liquid [164] have been reported although they exhibit remarkably high conductivity at the beginning of test. It is generally thought that two main reasons cause conductivity loss. The first one is the dehydration or decomposition of samples like Nafion and $Zr(HPO_4) \cdot H_2O$ at elevated temperatures. The second one is the leakage of functional parts such as PTFE-H₃PO₄ composites [165]. The stability of samples at high phosphorous loading (BP3-BP5) was evaluated by measuring the

conductivity against time at 250 °C in different atmospheres. Figure 3-32 shows the conductivity measured over 100 hours in air and wet 5% H_2 (humidified at 20 °C).



Figure 3-32: Conductivity of B:P=1:1.2, B:P=1:1.3 and B:P=1:1.4 as a function of time at 250 °C in air and in wet 5% H₂ (humidified in water at 20 °C).

It was found that all samples demonstrated good stability up to 110 hours although some initial deterioration in conductivities occurred and was probably due to the desorption of water since water has an enhancement effect on conductivity as shown above. The conductivity stability of some samples was measured after ageing the sample overnight. After 20 hours, conductivities are stable in either humidified 5%H₂/Ar or air. The conductivity of sample with B:P ratio 1:1.4 is stabilized at 3.6×10^{-2} S/cm in both air and wet 5%H₂/Ar during the measured 115 hours. A decrease in conductivity was observed during the initial overnight aging but finally the conductivity became stable. It is believed that the source of proton conduction is from the phosphorous rich amorphous phase and the amorphous/crystal interface. The unusual stability was thought to come from the favorable interface interactions between the phosphates and amorphous layers.

3.5. Composite of BPO₄-H₃PO₄-PTFE systems

3.5.1. Background

A stable, highly conductive BPO₄-H₃PO₄ composite was successfully developed in the last chapter and possible applications as an electrolyte in fuel cells should be evaluated. However, a high quality membrane electrolyte assembly (MEA) generally requires electrolyte to be of reasonable mechanic strength, proper thickness and crack-free. BPO₄-H₃PO₄ composites are inorganic combinations which are difficult to prepare as a robust, thin membrane. To overcome this problem, organic polytetrafluoroethylene (PTFE) binder was introduced to the composites. Here, BPO₄-H₃PO₄-PTFE organic-inorganic composites were developed and carefully investigated. Fuel cells based on this system were evaluated sequentially.

3.5.2. Experimental

The as-prepared BPO₄ based materials were dispersed in deionized water and were stirred until a homogeneous paste was produced. After that, a calculated amount of PTFE solution (60wt% dispersed in water from Aldrich) was added. The volume ratio of BPO₄:PTFE=50:50 (weight ratio 70:30). The dispersion obtained was then heated at 200°C with continuous stirring in order to remove water until it became solid. The solid obtained was then heated at 300°C for further polymerization and was labeled according to the B: P ratios (1:1.3, 1:1.4, 1:1.5 and 1:1.7) as BPP1, BPP2, BPP3 and BPP4. The final solid state materials were easily pressed into pellets or cast into membranes under different pressures (Figure 3-33). The SiC-H₃PO₄-PTFE composite for conventional PAFCs was prepared according to ref.166. The weight ratio of each component was SiC:H₃PO₄:PTFE=65:33:2.



Figure 3-33: Schematic illustrations of organic-inorganic composites in (a) pellet and (b) membrane.

Crystal structure and phase purity were examined by X-ray diffraction (XRD) analysis of powders on a Stoe STADI/P powder diffractometer. Incident radiation was generated using an Cu_{Ka1} source (λ = 1.54056 Å). The microstructures were examined by JEOL 5600 scanning electron microscope (SEM) and transmission electron microscopy (TEM) JEOL JEM-2011. FTIR (Fourier transform infrared spectrum) was chosen to inspect the interior bonding conditions for all samples. KBr pellets were made for each sample and the IR spectrum was collected on the PERKIN-ELMER Spectrum GX FTIR systems from 400 cm⁻¹ to 4000 cm⁻¹ with a resolution of 4 cm⁻¹. Thermal analysis was carried out on a Rheometric Scientific TG 1000M 1000M+ TA instruments SDT 2960 from room temperature to 300°C (10°C/min). The samples were kept at 300°C for two hours and then cooling down to 25°C (10°C/min) under flowing air at a rate of 20ml/min.

The conductivity measurements were carried out by the a.c. impedance method over the frequency range from 1 MHz to 10 mHz at 100 mV r.m.s. Pellets were used for measurements and were obtained by pressing powders under a pressure of 5×10^3 kg·cm⁻². Both sides of the pellets were dabbed with PTFE bonded carbon which serves as electrodes. Carbon paper was subsequently pressed on as current collector. The pellets were mounted into the tube furnace for impedance measurements. Data were collected from the highest temperature to the lowest after holding for at least one hour at each temperature to reach equilibrium. Different atmospheres were applied to simulate fuel cell conditions.

In order to fabricate a single fuel cell, the BPO₄-H₃PO₄-PTFE membrane was hot pressed at 120°C. Pt/C (E-TEK, 30wt% Pt) was used for both sides with a loading of 0.4mg/cm² for both electrodes for the hydrogen fuel cells. For direct methanol fuel cell, PtRu (E-TEK, 60wt%) was used as anode at a loading of $1.2mg/cm^2$. Pt/C was used as the cathode at a loading of $0.8mg/cm^2$. Wet hydrogen (passed through room temperature water) and wet oxygen were used for the H₂/O₂ fuel cell. 3M methanol was used as the fuel for the direct methanol fuel cells. Carbon paper (Toray-090) was used as current collector. The cell area was $1cm^2$. The fuel cell performance was measured by a Solartron 1287 Electrochemical Interface controlled by electrochemical software CorrWare.

3.5.3. Phase composition, particle sizes and morphology

XRD patterns (Figure 3-34) show the diffraction peaks of PTFE and BPO_4 indicating the samples contain PTFE and BPO_4 . It should be noted that there are some amorphous P-rich phases in the composites which can not be detected by XRD. The particle sizes of BPO_4 in the mixtures were calculated by Debye-Scherrer equation (equation 2.11).



Figure 3-34: X-ray diffraction patterns of BPP1 (a); BPP2 (b); BPP3 (c) and BPP4 (d) respectively. (●) BPO₄ peaks, (▼) PTFE peaks.

According to the results we previously reported, the particle sizes of BPO_4 obtained by solid state reactions were generally less than 30 nm at small B : P ratios. However, the particle sizes of BPO_4 in BPP1 (41 nm) (see table 3-10) in the composites were much larger compared with 15 nm for PTFE-free sample (Figure 3-35).

Samples	B:P ratios	Particle sizes (nm) after solid state reactions	Particle sizes (nm) in the organic- inorganic composites
BPP1	1:1.3	15	41
BPP2	1:1.4	21	24
BPP3	1:1.5	31	30
BPP4	1:1.7	37	37

Table 3-10: Particle sizes of BPO₄ after solid state reactions and in organic-inorganic composites



Figure 3-35: Particle sizes of BPO₄ in different P: B molar ratios after solid state reactions (O) and after adding PTFE (\bullet).

This may be due to the growth of BPO_4 during organic-inorganic composites preparation which involves water. It was also reported that BPO_4 prepared by a solution method exhibits much larger particle size than that prepared by solid state reaction. However, it was found that BPO_4 in sample BPP2 exhibits the smallest particle sizes (~ 24nm) which was very close to that of the PTFE-free sample (~ 21 nm). It seems presence of water is not the only reason for BPO_4 crystal growth. The particle size of BPO_4 in the composite is just slightly larger than the PTFE-free samples when B:P ratio is larger than 1:1.4 indicating the crystal growth in sample B:P 1:1.3 might be related to the completion of solid state reaction. Some residual boric acid or boron oxide in sample may cause the growth of BPO_4 particles in the composite after adding PTFE solution and reactions in sample BP1 seems to be the most incomplete, resulting in a significant growth of particle sizes.

The microstructures of the organic-inorganic composites were examined by SEM and TEM. Figure 3-36 shows the SEM pictures at a magnification factor of 2000.



Figure 3-36: SEM pictures of surface morphologies of BPP1 (a); BPP2 (b); BPP3 (c) and BPP4 (d) at a magnification of 2000.

Apart from some small holes or cracks, all samples maintained a homogeneous form suggesting good dispersions of different components. Figure 3-37 shows the typical TEM pictures at low and high resolutions.



Figure 3-37: Typical TEM images at low resolutions (a) and at high resolutions (b). The scale bars in the images represent 50 nm and 5 nm respectively and the lattice spacing marked corresponds to (101) *d* spacing.

Under low resolution TEM pictures (Figure 3-37a), small particles around 50 nm were observed and they were found to gather together indicating strong interactions between individual particles. Under high resolution TEM pictures, an amorphous layer was observed in addition to the BPO₄ crystals and was well distributed on the surface of BPO₄ implying good interface contact. The amorphous layer was believed to be $H_{3n-2x}P_nO_{4n-x}$ and was acting as a functional part for proton
conduction which has been described above. However, the PTFE particles were hard to be inspected since they became huge granules after polymerizing at high temperatures.

3.5.4. Thermogravimetric, analysis and IR spectroscopic characterizations

TG studies were made to identify thermal stability of the organic-inorganic composites. Figure 3-38 shows the typical TG curves (BPP3) within the temperature range of 25-300°C.



Figure 3-38: Typical TGA curves of organic-inorganic composites from 25°C to 300°C(5°C/min up and down) in air and holding at 300°C for 2 hours.

From the TG curves, it is found that all samples show a continuous weight loss during the heating stage. The observed 1.7wt% weight loss at $25 \sim 100^{\circ}$ C is due to the loss of absorbed water in the composites, after which a gradual weight loss followed by a continuous weight loss (3.5%) were observed till ~ 300°C. This could be attributed to the loss of chemically absorbed water and the condensation of hydroxyl groups in the structure of BPO₄ and the formation of poly phosphoric acid as following:

$$nH_3PO_4 \xleftarrow{\Delta} (HPO_3)_n + nH_2O^{\uparrow}$$
 (3.8)

In the holding stage, in spite of a gradual weight loss (~ 0.5%) corresponding to the continuous condensation of $H_{3n-2x}P_nO_{4n-x}$, a relatively smooth curve was observed, which indicates that the composites were relatively stable up to 300°C. More interestingly, a slow weight increase (~ 0.5%) appeared during the cooling stage which is believed due to the hydrolysis of (HPO₃)_n. The dehydration of the composites is reversible therefore the composites should retain their performance after going to anhydrous conditions. In comparison, the conductivities of most of proton conductors rely on moisture and decrease due to irreversible dehydration [167].

Figure 3-39 shows the IR spectra of different samples and no significant difference was observed in the whole range since phosphorous loading is the only difference between each sample.



Figure 3-39: FT-IR spectrum of BPP1 (a); BPP2 (b); BPP3 (c) and BPP4 (d), respectively.

It is worth noting that the spectra showed systematic increase in strength and width of absorption peaks at $2600 \sim 3500 \text{ cm}^{-1}$ corresponding to the various vibration modes of O-H bond from BPP1 ~ BPP4. More specifically, the absorption around 2900 cm⁻¹ is due to the strong hydrogenbonded hydroxyl groups and absorption in the range of 3600-3900 cm⁻¹ is due to hydrogenbonding-free hydroxyl groups [164]. It has been reported that protons are much more mobile under strong hydrogen-bond hydroxyl groups [164] therefore sample BPP4 should be more conductive since it shows the strongest absorption peaks around 2900 cm⁻¹. Additionally, all samples showed absorption peaks around 1640 cm⁻¹ which could be ascribed to deformation of absorbed water [168]. This is consistent with the weight loss below 150 °C on the TG curves due to the desorption of water since the condensation of hydroxyl attached to phosphorous generally takes place above 150 °C [110].

3.5.5. Impedance spectroscopy and conductivity

Impedance spectra were collected from room temperature up to 300°C under different atmospheres. Figure 3-40 shows the typical impedance response (Cole-Cole plot) at 300°C at ambient conditions.



Figure 3-40: Typical impedance response of organic-inorganic composites at 300 °C in air.

Only one "spike" like response (C ~ 10^{-3} F/cm) was observed at low frequency corresponding to the charge build-up at the electrodes [86]. As was pointed out before, this is due to dominant ion transportation in the composites. The increased capacitance (~ 10^{-3} F/cm compared with ~ 10^{-4} F/cm without PTFE) could come from a better electrolyte-electrode contact in the case of organic-inorganic composites.

The conductivities of the samples at evaluated temperatures and different atmospheres are shown in Figure 3-41.



Figure 3-41: Conductivity of organic-inorganic composites with different B:P molar ratios from 50 °C to 300 °C in air (○) and in wet 5% H₂ (humidified at 20 °C) (●). The abbreviations BPP3 in legend means B: P ratio is 1: 1.3 in PTFE.

A systematic increase in conductivity was observed from samples BPP1 ~ BPP4 which is due to the enhanced phosphorous loading. Like other proton conductors, a wetter atmosphere (humidified at 20°C) leads to an increase in conductivity indicating the presence of water promotes conduction. However, this effect was not obvious at high temperatures and at high phosphorous loading (BPP3) since water was almost eliminated from the systems at high temperatures and the inorganic part itself has an impressive conductivity at anhydrous conditions. The temperature dependence of the conductivity deviated substantially from a linear relationship which implies a non-Arrhenius conduction behavior so the determination of activation energy for

proton transport is not reasonable since the state of the systems (i.e. water content, $H_{3n-2x}P_nO_{4n-x}$ composition) strongly depends on temperature (Figure 3-38). More specifically, BPP1 shows a maximum conductivity at 180°C instead of 300°C; BPP3 has "plateau" conductivity from 110 ~ 280°C and then gradually increase at higher temperatures. It is very complicated to elucidate these diversities above and presumably it is a combination of water effect, phosphorous loading, temperature or PTFE blocking effect etc. It could even be affected by particle sizes since sample BPP2 has a better performance at high temperature which could benefit from the smaller particle sizes as mentioned before.

The PTFE blocking effect could be simply evaluated by comparing the samples (BPP2) before and after impregnating PTFE (Figure 3-42).



Figure 3-42: Conductivity of samples with B: P = 1:1.4 with and without PTFE in air (\circ) and in wet 5%H₂ (humidified at 20°C) (\bullet).

Although the conductivity decreases almost by a factor of 3 ($0.079 \text{ S} \cdot \text{cm}^{-1} \text{ vs. } 0.026 \text{ S} \cdot \text{cm}^{-1}$) after impregnating PTFE, the mechanical properties of samples (flexibility, density and ductibility etc.) were greatly improved (see Figure 3-33). This gives a lot merits for stabilization and miniaturization of fuel cells since interior resistance of the fuel cells (mainly comes from the electrolyte) could be diminished by thinning the electrolyte which could significantly reduce the volume of single cells and improve the cell efficiency.

3.5.6. Stability of conductivity

The stability of conductivity is another crucial factor in evaluating a conductor for practical use. This was examined by measuring the conductivity against time at 250°C. Figure 3-43 shows the measured conductivity (BPP3 and BPP4) over 150 hours at different atmospheres.



Figure 3-43: Conductivity of BPP3 and BPP4 as a function of time at 250 °C in air (\circ) and in wet 5% H₂ (humidified at 20 °C) (•).

The conductivity is stable for samples with and without impregnating PTFE at a low phosphorous loading (B: P = 1:2, 1:3 and 1:4). Sample BPP4 with very high phosphorous loading (B: P = 1:1.7) with PTFE was not satisfactory. A continuous decrease was observed during the measured 150 hours. The reason for the decrease was not clear and need further investigations. One possible explanation is the leakage or evaporation of phosphorous which is a common problem encountered by phosphoric acid fuel cells (PAFCs) [6,169,170]. Since we maintained the sample at 250°C which is much higher than the operation temperature (200°C) of PAFCs, it is more likely for the phosphorous loading slightly (B: P = 1:1.5), the samples exhibit an attractive stability of conductivity in both air and wet 5% H₂ (humidified at 20°C). The conductivity of sample BPP3 is about 3.2×10^{-2} S/cm. The unusual stability was attributed to the favorable interface contact between phosphates and amorphous layers.



Figure 3-44: Conductivity of the composites (B: P = 1:1.5) by varying the PTFE content. The BPO₄ to PTFE ratio (BP/PTFE) was changed from 4/6 to 7/3.

The conductivity of the composites (B: P = 1:1.5) by varying the PTFE content (weight ratio) was also measured. The BPO₄ to PTFE weight ratio (BP/PTFE) was carefully adjusted from 4/6 to 7/3 and was measured in air and wet 5% H₂ (Figure 3-44). It is obvious that composites with low PTFE content exhibit much higher conductivity in both air and wet 5% H₂ as PTFE itself is not a proton conductor. However, the mechanical strength of the composite membrane is not good enough when the PTFE content is less than 40wt%, so the BP/PTFE ratio was chosen as 6/4 when fuel cells were fabricated.



Figure 3-45: Comparisons of BPO₄-H₃PO₄-PTFE (B:P = 1:1.5, PTFE 40wt%) systems and SiC-H₃PO₄-PTFE (weight ratio of SiC: H₃PO₄: PTFE=65:33:2) systems at different temperatures.

These strong interactions between BPO₄ and H₃PO₄ were confirmed by the comparison with SiC-H₃PO₄-PTFE composites (weight ratio of SiC: H3PO4: PTFE=65:33:2) (Figure 3-45). SiC-H₃PO₄-PTFE composites are the well-known electrolyte for phosphoric acid fuel cells (PAFCs) and were found to be stable at 200°C but unstable at 250°C. The conductivity of SiC-H₃PO₄-PTFE composites decreased from 0.056 S/cm to 4×10^{-4} S/cm after 130 hours. On the contrary, the stability of BPO₄-H₃PO₄-PTFE composites (B:P = 1:1.5, PTFE 40wt%) is good apart from an initial decrease.

It is worth noting that the performance (conductivity, mechanical properties and stability etc.) of the organic-inorganic composites is determined by several factors such as phosphorous loading, PTFE loading and particle sizes. This introduces simplification and maneuverability in designing fuel cells and other electrochemical devices. The further optimization of such composites will be continued in our future work.



Figure 3-46: H_2/O_2 fuel cell performance using BPO₄- H_3PO_4 -PTFE (B:P = 1:1.5, PTFE 40wt%) as the electrolyte (a) and the corresponding impedance at open circuit voltage (b).

Figure 3-46a shows the fuel cell performance of a H₂/O₂ fuel cell based on BPO₄-H₃PO₄-PTFE composites (B:P = 1:1.5, PTFE 40wt%) as electrolyte. The open circuit voltage (OCV) was 0.67 V at 200°C which is lower than the theoretical value for these atmospheres, although this is not that unusual for lower temperature fuel cells. This is due to the polarisation loss at the electrodes. A maximum current density of 1.9 A/cm² was observed at 200°C. The maximum power density was 320 mW/cm² at a voltage of 0.31 V. When the operating temperature increased to 225 and 250°C, the maximum power density is slightly lower compared to that at 200°C. The impedance spectra of the cell (recorded at OCV) at different temperatures is shown in Figure 3-46b. The series resistance of the cell was only 0.19 Ω cm² at 200°C with an overall resistance 0.51 Ω cm². Therefore the electrode polarisation resistance is $0.32 \ \Omega \text{cm}^2$. The overall resistance is slightly higher than the resistance from the I-V curve in Figure 3-46a because it was measured under OCV. Under polarisation, steam will be produced by the fuel cell which will affect both the series and polarisation resistance. The series resistance increases slightly indicating that, the formation of polyphosphoric acid was not fully suppressed in the presence of BPO₄ which is consistent with the conductivity measurements showing that the conductivity at 250°C is lower than that in 200°C (Figure 3-45a). No significant changes were observed in the overall resistance and fuel cell performance when the temperature increased to 250°C. The catalytic activity of Pt/C electrodes may be enhanced at higher temperature but the coarsening, agglomerating and dissolving of the Pt catalyst also become serious. In our experiments, no obvious benefit was achieved on the H_2/O_2 fuel cell when the operating temperature was above 200°C. Better CO tolerance is expected at higher temperatures however, which needs further investigation.



Figure 3-47: Performance of direct methanol fuel cell at different temperatures (a) and the OCV of the cells at different operating temperatures (b).

The direct methanol fuel cell is very promising for portable and transport applications [171]. Most direct methanol fuel cells are based on polymer proton conducting electrolytes. Here we tried methanol as fuels for our fuel cells based on BPO₄-H₃PO₄-PTFE composites. Direct methanol/biomethanol fuel cells can be used for stationary power generation or for auxiliary power unit (APU). Figure 3-47a shows the performance of a direct methanol fuel cell based on the BPO₄-H₃PO₄-PTFE composite electrolyte. Clearly, the performance of the cell increases with operating temperature. This is mainly due to the improvement of the catalytic activity at the anode as indicated by the improvement in OCV. The Pt/C cathode should behave similarly to the H₂/O₂ fuel cell as the reaction is unchanged (Figure 3-46a). A maximum current of 300mA/cm² and power density of 40mW/cm² at 275°C were observed when 3M methanol was used in the cell. The OCV of the cell also increased at higher temperature (Figure 3-47b). Therefore, it has been demonstrated that higher temperatures (above 200°C) are more favorable for such fuel cells when methanol is used as the fuel.

3.6 Conclusions

Al(H₂PO₄)₃ synthesised here showed a comparable proton conductivity with AlH₂P₃O₁₀ and AlH₃(PO₄)₂•3H₂O. However, the conductivity was greatly improved even after introducing 0.7% more H₃PO₄. The Al(H₂PO₄)₃-H₃PO₄ composite demonstrated a stable conductivity during measured 100 hours at 175°C and withstood several thermal cycles. Pure SnP₂O₇ synthesised by our method is not a good proton conductor, high conductivity was only achieved when excess amount of H₃PO₄ was used during material synthesis. Solid State ³¹P NMR confirmed the residual phosphoric acid within the composites. A thin amorphous layer could be observed under HRTEM for these samples with non-stoichiometric P:Sn ratios. The remarkable high conductivity for SnP₂O₇-H₃PO₄ was probably attributed to the residual acid rather than SnP₂O₇ itself. The composites exhibited a stable conductivity at 250°C in the measured time scale. Based on this observation, nano-sized BPO₄-H₃PO₄ composites were developed. The composite showed a similar microstructure and presented a high conductivity independent of humidity. Stable conductivity was also achieved for more than 100 hours at 250°C.

Thin, soft membranes can be developed after introducing PTFE into the BPO₄-H₃PO₄ systems. The BPO₄-H₃PO₄-PTFE systems showed practical stable proton conductivity for an extended temperature range (room temperature to 300° C). Fuel cells based on BPO₄-H₃PO₄-PTFE composites as electrolyte exhibited a maximum power density 320mW/cm² and a maximum current density of 1.9 A/cm² at 200° C. Increasing operating temperature was not beneficial to the fuel cell performance when H₂ was used as fuel but can improve the fuel cell performance when methanol was used as fuels. A maximum current of 300mA/cm² and power density of 40mW/cm² at 275° C were observed when 3M methanol was used in the cell.

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4.1. Introduction

In chapter 3, we have investigated several systems that phosphoric acid was maintained by the strong interactions between phosphate surface and amorphous acid layer. A similar idea on stabilizing acid was to insert acid into the internal structures to gain additional connections between acid and matrix. Heteropolyacids and their salts have internal open structures which might be suitable for trapping acid molecules. Therefore, a careful investigation of these materials after introducing phosphoric acid would be interesting. In this chapter, proton conduction of $H_3PW_{12}O_{40}$ -x H_3PO_4 (x=1-3) hybrids have been investigated.

4.2. Anhydrous proton conductors based on $H_3PW_{12}O_{40}$ -x H_3PO_4 (x=1-3) hybrids

4.2.1. Background

Heteropolyacids and their salts are generally considered as one of the most acidic materials in solids. Their internal structure, known as Keggin structure $(XM_{12}O_{40}^{n-})$, is illustrated in Figure 4-1 which shows the structure of $H_3PW_{12}O_{40}$ ·6 H_2O .



Figure 4-1: Schematic structure illustration of H₃PW₁₂O₄₀·6H₂O

It has a central atom which generally has a high valence such as Si⁴⁺ and P⁵⁺ and peripheral atoms like Mo and W which are symmetrically located around the centre atoms by sharing oxygen atoms in the coordination corners. This specific structure which is called primary structure or Keggin ion usually has a radius around 5~6 Å; however, considerable space ~23 Å between these ions can form by joining the primary structures together which is known as secondary structures [172]. The unusual space between Keggin ions gives access to many ionic and molecular species such as Cs⁺, NH₄⁺ or water molecules, which in return, imparts the materials with various useful properties. Heteropolyacids as well as their salts have been widely applied as one of the most effective catalysts in the organic industry such as amidation of alcohols [173]. alkylation [174, 175] and one-pot synthesis of dihydropyrimidin-2(1H)-ones [176]. Their exceptionally high proton conductivity (~0.1 S/cm) at room temperature gives rise to other potential applications such as fuel cells [177], gas sensors [141] and solid electric double layer capacitors [160]. Among the numerous heteropolyacids and their salts, dodecatungstophosphoric acid (H₃PW₁₂O₄₀·29H₂O) exhibits the highest proton conductivity 0.18 S/cm at room temperature and under proper humidity [178]. More importantly, the compound is environmentally benign and has now become commercially available so that wide applications have been launched [172]. Staiti et al. reported an output electrical power of 738mW/cm² by using $H_3PW_{12}O_{40}$ as solid electrolyte at 23°C [179]. Although the fuel cell performance was remarkably high, it suffered from dissolution of electrolyte at cathode since a huge amount of water could be generated which remained in liquid state due to the relatively low operation temperature. There are two strategies to overcome this problem. One is to use H₃PW₁₂O₄₀ solution as an alternative electrolyte. The other is to increase operating temperature above the boiling point of water so that water can be removed from the system in the form of gas as long as it is produced. For the formal strategy, Giordano et al. used a $H_3PW_{12}O_{40}$ solution with concentration of 60% as electrolyte and obtained a fuel cell peak power of 700 mW/cm² with lifetime of more than 300 hours at 25°C [180]. However, their fuel cells required continuous feed of electrolyte otherwise dilution and leakage may occur. For the latter strategy, as H₃PW₁₂O₄₀·29H₂O per se is not a good conductive material above 40°C due to dehydration [181], other proton conductive materials were introduced. Jang et al. combined partially sulfonated polyimides and heteropolyacid together into organic-inorganic composite membranes which presented reasonable conductivity near 100°C [182]. Li et al. embedded phosphotungstic acid (PWA) into sulfonated polyethersulfone Cardo (SPES-C) and the composites obtained showed impressive conductivity $(6.7 \times 10^{-2} \text{ S cm}^{-1})$ at 110°C [183]. However, the composites mentioned above generally demand humidified conditions otherwise degradation of conductivity will occur. This requirement would greatly complicate the systems as an additional humidifier has to be introduced during applications. Recently, Kim et al. prepared an anhydrous proton conductor based on phosphotungstic acid and ionic liquid [1-butyl-3methylimidazole][bis-(fluoromethanesulfonyl) amide] ([BMIM][TFSI]). The hybrids showed an

interesting conductivity of 0.04 S/cm at 60°C and > 10^{-3} S/cm above 100°C under anhydrous conditions [180]. In this chapter, $H_3PW_{12}O_{40}-H_3PO_4$ solid hybrids were synthesised and their conductivity was investigated under ambient conditions in a temperature range from room temperature up to 180°C. It is believed that phosphoric acid can interact with phosphotungstic acid and 'replace' some water molecules in the internal structure which could improve the conductivity in relatively dry conditions.

4.2.2. Experimental

 $H_3PW_{12}O_{40}$ - xH_3PO_4 (x = 1-3) hybrids were synthesized by a simple solution method. Calculated amounts of $H_3PW_{12}O_{40}$ · xH_2O and H_3PO_4 were dissolved in deionised water to form transparent solutions. Samples with $H_3PW_{12}O_{40}$ · xH_2O/H_3PO_4 molar ratio1:0, 1:1, 1:2 and 1:3 were labelled as HPP0, HPP1, HPP2 and HPP3 respectively. The solutions were then heated up to 200°C in order to evaporate excess water. Continuous agitation was applied during evaporation until white powders were obtained. The powders were collected and dried at 90°C for 2 hours before property characterisation.

Crystal structure and phase purity were examined by X-ray diffraction (XRD) analysis of powders on a Stoe STADI/P powder diffractometer. Incident radiation was generated using a Cu_{Ka1} source ($\lambda = 1.54056$ Å). X-POW software was used to perform least square refinement of the lattice parameters. Solid state ³¹P NMR analysis was performed on a 400MHz Bruker Avance III spectrometer, both magic angle spinning (MAS) and proton decoupling were applied for the elimination of broadening effects. The microstructures were examined by JEOL 5600 scanning electron microscope (SEM). Fourier transform infrared spectra (FT-IR) were collected on the PERKIN-ELMER Spectrum GX FTIR systems using KBr pellets for each sample. The spectra were collected from 400 to 4000 cm⁻¹ with a resolution of 4 cm⁻¹. Thermal analysis was carried out on a Rheometric Scientific TG 1000M 1000M+ TA instruments SDT 2960 with a heating rate of 5°C/min under flowing argon at a rate of 20ml/min.

The conductivities of as-prepared pyrophosphates in air (water content 0.084%) and wet 5% H₂ (water content 3% by volume) were measured by a.c. impedance over the frequency range 1 MHz to 100 mHz at 100 mV r.m.s. Data were collected using a Schlumberger Solartron 1255 Frequency Response Analyzer coupled with a 1287 Electrochemical Interface. The total systems were controlled by Z-plot electrochemical impedance software and impedance data were analysed using Z-view software. Pellets (13mm in diameter and 2~3mm in thickness) were used for measurements and were obtained by pressing powders under a pressure of 1×10^3 kg·cm⁻². PTFE bonded carbon (Carbot Vulcan 72R) was coated on both sides of the pellets which served as electrodes. Carbon paper (Torory TGPH-090) was subsequently pressed on as current

collector. The pellets were mounted on a sample holder then put into furnaces for measurements at various temperatures. Data were collected from the highest temperature to the lowest on cooling after holding at least one hour at each temperature.

A fuel cell based on HPP3 was fabricated. The electrolyte was composed of 50wt% HPP3 and 50%wt PTFE which served as a binder. The electrolyte was hot pressed at 100° C with a thickness of 1mm. Pt/C (E-TEK, 30wt% Pt) was used for both sides with a Pt loading of 0.4mg/cm² for both electrodes. Carbon paper (Toray-090) was used as current collector and the cell area was 1cm².

4.2.3. Phase composition, thermal stability and morphology

All samples prepared contain a single phase with cubic symmetric according to the X-ray diffraction patterns (Figure 4-2).



Figure 4-2: X-ray diffraction patterns of as-prepared samples, part of the patterns were zoomed in for inspection.

Small peak shifts towards low diffraction angles were observed for samples containing H_3PO_4 (Figure 4-2), suggesting enlarged unit cells. The symmetry and lattice parameter of each sample is listed in Table 4-1, together with some hydrated forms of $H_3PW_{12}O_{40}$ reported.

Sample	Symmetry	a (Å)	b (Å)	<i>c</i> (Å)	α (°)	β (°)	γ (°)	Ref
HPP0	Cubic	12.1581(6)	-	-	90	90	90	-
HPP1	Cubic	12.16161(18)	-	-	90	90	90	-
HPP2	Cubic	12.15818(20)	-	-	90	90	90	-
HPP3	Cubic	12.1663(3)	-	-	90	90	90	-
$H_{3}PW_{12}O_{40}$	Cubic	12.13(4)	-	-	90	90	90	184
H ₃ PW ₁₂ O ₄₀ ·6 H ₂ O	Cubic	12.1507(2)	-	-	90	90	90	185
H₃PW₁₂O₄₀·1 4H₂O	Anorthic	14.075(4)	14.121(4)	13.525(3)	112.0 1(2)	109.6 2(2)	60.89 (2)	184
H ₃ PW ₁₂ O ₄₀ ·2 1H ₂ O	Orthorho mbic	20.91(6)	13.13(15)	19(35)	90	90	90	186
H ₃ PW ₁₂ O ₄₀ ·2 9H ₂ O	Cubic	23.328(2)	-	-	90	90	90	184

Table 4-1: Cell parameters calculated from X-ray powder diffraction patterns together with parameters reported in the literatures.

The symmetry for $H_3PW_{12}O_{40}$ • xH_2O were found to be closely related to the hydration levels: cubic for x=0, 6, 29 and slightly lower symmetry for other values. Introducing H_3PO_4 has little change in symmetry but only slightly expands the unit cells, indicating the secondary structure of Keggin ions was maintained. However, the increase of unit cell parameters is not monotonic after adding H_3PO_4 , with HPP2 slightly small, probably due to the complicated interactions between Keggin ions and H_3PO_4 molecules.

Thermal analysis was carried out to investigate the hydration level of the hybrids. For HPP0, a plateau was identified between 100-150°C, corresponding to hexahydrate of $H_3PW_{12}O_{40}$ [187]. All weight changes were recorded based on this plateau (Figure 4-3).



Figure 4-3: Thermogravimetry analysis (TGA) of as-prepared samples in Ar atmosphere, data was ploted against the plateau of $H_3PW_{12}O_{40}$ •6 H_2O (dashed line) between 100-150°C.

Irrespective of the weight loss before the plateau due to absorbed water, weight loss afterwards changes systematically. The increased weight loss could come from the polymerization of H_3PO_4 into polyphosphoric acid or evaporation of H_3PO_4 molecules. The water content for sample HPP0 was calculated to be 6.83 H_2O per $H_3PW_{12}O_{40}$ formula unit, in agreement with the slightly larger unit cell parameters calculated by XRD (*a* = 12.1581(6) Å for HPP0, *a* = 12.1507(2) Å for $H_3PW_{12}O_{40}$ ·6H₂O) (Table 4-1). The water content within the hybrids (HPP1-HPP3) was difficult to determine precisely, due to the coexistence of H_3PO_4 , but was approximately 6, 9 and 8.5 H_2O per $H_3PW_{12}O_{40}$ formula unit for HPP1, HPP2 and HPP3.

The morphologies of the hybrids and commercial $H_3PW_{12}O_{40}$ ·x H_2O were examined by SEM. Figure 4-4 shows the pictures taken under a magnification of 2000.



Figure 4-4: SEM pictures of morphologies of (a) HPP0; (b) HPP1; (c) HPP2 and (d) HPP3 at a magnification of 2000.

In contrast to HPP0 where particles are irregularly shaped, highly symmetrical particles were observed in the hybrids. Clear 3-fold and 4-fold rotation axis were observed for individual particles which are evident signs of cubic symmetry. Obviously, particles were better shaped in HPP2 and HPP3 which contain more phosphoric acid during preparation, suggesting that phosphoric acid plays an assistant role during crystallization. This is quite different from the reported ionic liquid [BMIM][TFSI], in which case, particles of the hybrids remain unshaped and tend to become smaller at higher loadings [180].

4.2.4. Solid state ³¹P NMR spectra

More detailed investigations of local interactions between $H_3PW_{12}O_{40}$ and H_3PO_4 concerning internal chemical environment were carried out by ³¹P MAS NMR, Figure 4-5.



Figure 4-5 Solid state ³¹P NMR of samples prepared, data was collected with H decoupling and magic angle spinning (MAS) rate of 13 kHz for HPP0, 12 kHz for HPP1, 12 kHz for HPP2 and 5 kHz for HPP3. Peaks were labelled according to their positions as P1 to P4.

From their appearance, the NMR spectra suggest four types of phosphorous corresponding to four different chemical environments. Here we nominate different phosphorous according to their chemical shift, increasing from P1 to P4. The large differences in chemical shift between P1, P2 (<-6 ppm) and P3, P4 (>-17 ppm) suggest these four types of phosphorous could be subcategorized into two groups. A careful investigation of $H_3PW_{12}O_{40}\bullet H_2O$ (0<n<6) by ³¹P MAS NMR had already been conducted by Uchida *et al.* [188]. It was found that the chemical shift of $H_3PW_{12}O_{40}\bullet H_2O$ systematically increased with the hydration level of $H_3PW_{12}O_{40}$ and $H_3PW_{12}O_{40}\bullet H_2O$ gave the largest chemical shift at -15.6ppm which belongs to the phosphorus inside the Keggin ion. Here two isolated peaks were observed for sample HPP0 with chemical shift of -17.6 ppm (P3) and -18.5 ppm (P4) which could be due to the co-existence of two different hydrates of $H_3PW_{12}O_{40}\bullet H_2O$ (TGA gives an average value of n=6.83) [189]. Similar peaks were also observed for sample HPP1 but with a much stronger P3 peak, one possible explanation is

the relatively low hydration level for HPP2 as confirmed by TGA. Whilst in HPP2 and HPP3, P3 peak was not observed, suggesting only one type of secondary structure remained. Introducing H₃PO₄ gives rise to P1 (ca. -2.6ppm) and P2 (ca. -5ppm) peaks and if we recall the chemical shift of pure H_3PO_4 to be zero. These two peaks then confirmed the strong attractions between H_3PO_4 and $H_3PW_{12}O_{40}$, in which manner, the chemical surroundings of $H_3PW_{12}O_{40}$ were modified to some extent. Similar work has been done by Deleplanque et al. where two peaks at -1.7ppm and -4.6ppm were observed by introducing trimethylphosphine molecules to H₃PW₁₂O₄₀ and were attributed to the formation of trimethylphosphonium ion (TMPH $^{+}$) [189]. Furthermore, as P2 (ca. -5ppm) peak has slightly higher chemical shift compared with P1 (ca. -2.6ppm). If we presume P1 peak as loosely bonded acid such as acid remains on the surface, P2 could be the indication that H_3PO_4 is more strongly bonded to Keggin ions $PW_{12}O_{40}^{3-}$ as would be the case for inside the open structures. The missing P2 peak for HPP1 could be due to the low loadings of H₃PO₄ that may only enough to be settled on the surface of $H_3PW_{12}O_{40}$ crystallites. Although it is very premature to draw such conclusions based on these observations, interactions between H₃PO₄ and $H_3PW_{12}O_{40}$ are clear. Figure 4-6 shows the intensity and chemical shift of NMR peaks for all samples.



Figure 4-6: Intensity (a) and chemical shift (b) of P1-P4 peaks as a function of H₃PO₄/PWA ratios

4.2.5. IR spectra

Infrared spectra of as-prepared samples were plotted in Figure 4-7, together with spectrum of 85wt% H₃PO₄ for comparisons.



Figure 4-7: FT-IR spectra of (a) HPP0; (b) HPP1; (c) HPP2; (d) HPP3 and (e) 85wt.% H₃PO₄, respectively.

Spectra for the hybrids were found have great similarity to the spectrum of HPP0 (free of H_3PO_4), suggesting a good maintenance of Keggin structures and good compatibility between $H_3PW_{12}O_{40}$ and H_3PO_4 molecules. The major differences between hybrids and HPP0 lie in wavenumber range 1100 ~ 1300 cm⁻¹ and 2600 ~ 3000 cm⁻¹. For the range 1100 to 1300 cm⁻¹, hybrids exhibit an increased broad shoulder peak corresponding to the vibrations of various phosphoric species $(HPO_4^{2-} and H_2PO_4^{-})$ as were also observed in 85wt% H₃PO₄. However, the peak position is slightly red shifted to the low wavenumbers compared with 85wt% H₃PO₄ (Figure 4-7e). This could be explained as the strong interactions between phosphate species and Keggin ions, in which manner, the vibrations of phosphate species were confined. For the range of 2600 ~ 3000 cm⁻¹, broad absorption peaks were observed and became stronger for hybrids with more phosphoric acid. Peaks in these regions generally belong to the stretching of hydrogen bonding O-H groups in which protons are expected to be more mobile and easier to migrate [135,136]. One factor worth mentioning is that absorption peak at 975 cm⁻¹ was broadened progressively with increasing phosphoric acid. The peak was assigned as the vibration of terminal W=O, upon which dioxonium ions $(H_5 O_2^+)$ were bonded at hexahydrated state [135]. Similar phenomenon was also observed for the peaks at 525, 795 and 887 cm⁻¹ which were assigned to v_s (W-O-W)

and v_{as} (W-O-W), respectively [135]. This could also be interpreted as the interactions between phosphoric acid and Keggin ions such as the formation of hydrogen bonds so that the symmetry of the Keggin ions was lowered consequently. Other weak absorption peaks at 596 cm⁻¹ and 1079 cm⁻¹ could be assigned to δ (O-P-O) and v_{as} (PO) respectively [135].

4.2.6. Conductivity

The conductivities of the hybrids and HPP0 in air (water content 0.084%) are shown in Figure 4-8. The values are calculated from the Cole-Cole plot according to the intersection of the response with the real axis.



Figure 4-8: Conductivity in air of hybrids together with HPP0 for comparisons

For sample HPP0, conductivity undergoes a sharp decrease above 40°C from 3.37×10⁻³ S/cm to 1.72×10⁻⁶ S/cm due to the dehydration. Nevertheless, conductivity of hybrids was greatly improved although a decrease was also observed at higher temperature. It can be noticed that the conductivity increased systematically with an increase of phosphoric acid and HPP3 exhibited a conductivity of 4.3×10⁻² S/cm at nearly 120°C which is, to the best of our knowledge, the highest value ever reported among the phosphotungstic acid and their hybrids under the same conditions. Therefore, it can be realized that phosphoric acid plays a vital role in the conduction of protons and can significantly improve the conductivity at high temperatures.

Conductivity at humidified conditions was also measured for comparison (Figure 4-9). 5% H_2 in argon was applied which was humidified at 20°C (water content 3%).



Figure 4-9: Conductivity of HPP3 in air ($^{\bigcirc}$) and in wet 5% H₂ (humidified at 20°C) ($^{\bigcirc}$)

It is clear that the hybrids (HPP3) exhibit higher conductivity under humidified conditions, implying water promotes conduction which is similar to other proton conductors. However, the conductivity undergoes a decrease and remains in the same range both in air and wet 5% H₂ above 120°C due to the rapid dehydration above the temperatures (Figure 4-3). It is believed that water is still playing an important role proton transfer in both $H_3PW_{12}O_{40}\cdot xH_2O$ and the $H_3PW_{12}O_{40}-H_3PO_4$ hybrids.

4.2.7. Fuel cell performance

The fuel cell performance based on hybrid $H_3PW_{12}O_{40}$ - $3H_3PO_4$ -PTFE (weight ratio $H_3PW_{12}O_{40}$ - $3H_3PO_4$ /PTFE=1/1) is shown in Figure 4-10. The fuel cell was operated at room temperature with 5% H_2 /Ar as fuels.



Figure 4-10: Fuel cell performance of Pt/C $\|$ HPP3/PTFE $\|$ Pt/C using wet H₂ as fuels, wet air as oxidant at room temperatures.

The open circuit voltage (OCV) of the fuel cell is 0.67V which is lower than the theoretical value, probably due to the leakage of fuels as pin holes could exist within the electrolyte. The fuel cell exhibit a peak power density of 2.7mW/cm² at 0.3V. The large resistance was mainly attributed to the unoptimised electrodes.

4.3. Anhydrous proton conductors based on $(NH_4)_3PW_{12}O_{40}-xH_3PO_4$ (x=1-10) hybrids

4.3.1. Background

Although $H_3PW_{12}O_{40}$ -x H_3PO_4 (x=1-3) hybrids exhibit improved conductivity at elevated temperatures, their solubility in the water become a serious problem during fuel cell operations. Heteropolyacid salts with large cations (Cs⁺, Rb⁺, K⁺ and NH₄⁺) are insoluble in water and could be an alternative. Caesium based heteropolyacid salts such as Cs₂HPW₁₂O₄₀ have been investigated, their conductivity (<10³S/cm) is found to be highly dependent on humidity and inadequate for practical applications [162]. Ammonium based heteropolyacid salts such as (NH₄)₃PW₁₂O₄₀ were systematically investigated by Gregg *et al.* about 30 years ago [190]. The salts showed selectivity in catalyzing alkylation of ammonia with methanol above 400°C [191] and reduction of NO₂ at a low temperature (150°C) [192,193]. Their surface area is remarkably high (over 100 m² g⁻¹), considering the heavy molecular weight (~2931). Inumaru and Ito et al. discovered the "Epitaxial Self Assembly" phenomenon of (NH₄)₃PW₁₂O₄₀ and categorized $(NH_4)_3PW_{12}O_{40}$ to be a "Sponge Crystal" in order to highlight the original porosity coming from the residual spaces between the constituent nanocrystallites [194, 195]. More importantly, Mikhailenko et al. investigated the electrical properties of (NH₄)₃PW₁₂O₄₀ in dry Ar, 100% RH and in the presence of liquid water [196]. They found that the conductivity of $(NH_4)_3PW_{12}O_{40}$ was improved by several orders of magnitude on introducing liquid water (10⁻⁵-10⁻⁴ S cm⁻¹ in dry Ar and 3.3-8.0×10⁻² S cm⁻¹ mixed with 10% water). However, they measured the conductivity of $(NH_4)_3PW_{12}O_{40}$ only in the temperature range from ambient up to 60°C whereas the conductivity at higher temperature range is still unknown. In this section, we investigated the electrical properties of (NH₄)₃PW₁₂O₄₀ from room temperature up to 450°C and by synthesizing (NH₄)₃PW₁₂O₄₀-xH₃PO₄ (x=1-10) hybrids, the conductivity of (NH₄)₃PW₁₂O₄₀-xH₃PO₄ has been improved significantly.

4.3.2. Experimental

 $(NH_4)_3PW_{12}O_{40}-H_3PO_4$ composites were synthesized by precipitation method: calculated amounts of H₃PO₄ (Aldrich) and NH₄HCO₃ (Aldrich) were mixed up and dissolved with deionized water to form a transparent solution. The solution was then dripped into H₃PW₁₂O₄₀ solution (0.1mol/L) under vigorous agitations in order to obtain homogeneous mixtures. White precipitations were produced immediately and the mixtures were heated at 200°C to evaporate excess water. The white powders finally obtained were labeled as NP0, NP3, NP5 and NP10 according to the molar ratios of NH₄HCO₃/ H₃PW₁₂O₄₀/ H₃PO₄ = 3/1/0, 3/1/3, 3/1/5 and 3/1/10. The powders were dried at 90°C for 12 hours and collected for measurements. Crystal structure and phase purity were examined by X-ray diffraction (XRD) analysis of powders on a Stoe STADI/P powder diffractometer. Incident radiation was generated using a $Cu_{K\alpha 1}$ source ($\lambda = 1.54056$ Å).

The microstructures were examined by JEOL 5600 scanning electron microscope (SEM) and transmission electron microscopy (TEM) JEOL JEM-2011. Fourier transform infrared spectrum (FT-IR) was chosen to inspect the interior bonding conditions for all samples. KBr pellets were made for each sample and the IR spectrum was collected on the PERKIN-ELMER Spectrum GX FTIR systems from 400 cm⁻¹ to 4000 cm⁻¹ with a resolution of 4 cm⁻¹. Thermal analysis was carried out on a Rheometric Scientific TG 1000M 1000M+ TA instruments SDT 2960 with heating and cooling rate of 5°C/min under flowing air at a rate of 20mL/min.

The conductivity measurements were carried out by the a.c. impedance method over the frequency range from 1 MHz to 10 mHz at 100 mV r.m.s. Pellets were used for measurements and were obtained by pressing powders under a pressure of 3×10^3 kg·cm⁻² (diameter 13mm, thickness 4-5mm).

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 pellets were mounted into furnaces for impedance measurements. Data were collected from the highest temperature to the lowest on cooling after holding at least one hour at each temperature to reach equilibrium. Air and wet 5% H_2 (humidified at 20°C) were applied to create different atmospheres and to evaluate conductivity.

4.3.3. Phase composition, thermal stability and morphology

All samples obtained here were white powders. X-ray powder diffraction (XRD) analysis shows similar diffraction patterns (Figure 4-11) which belongs to cubic symmetries (Pn-3m (224)). The calculated lattice parameters were listed in Table 4-2.



Figure 4-11: X-ray diffraction patterns of (a) NP0; (b) NP3; (c) NP5 and (d) NP10 respectively. The indexed peaks were labeled according to calculations.

Sample	Symmetry	a (Å)	b (Å)	c (Å)	V (Å ³)
NP0	Cubic	11.6729(19)	-	-	1590.5(5)
NP0 after TG	Tetragonal	5.2858(13)	-	3.8720(9)	108.18(6)
NP3	Cubic	11.7033(18)	-	-	1603.0(4)
NP5	Cubic	11.7140(22)	-	-	1607.4(5)
NP5 after TG	Cubic	11.630(24)	-	-	1573.0(56)
NP10	Cubic	11.718(3)	-	-	1609.0(7)

Table 4-2: Cell parameters calculated from X-ray powder diffraction patterns

As expected, the lattice parameters and lattice volume were enhanced by introducing phosphoric acid. This can be explained by the interaction of phosphoric acid molecules and heteropolyanions where phosphoric anions were assumed to participate in building up the integrity through certain effects such as hydrogen bonding and enlarge the crystal lattice correspondingly. However, this enhancing effect of phosphoric acid toward lattice parameters was limited, as can be seen from Figure 4-12, as lattice parameters and volume reached a plateau after sample NP5 and a considerable amount of phosphoric acid was speculated to remain outside.



Figure 4-12: Cell parameters of all samples: (a) cell parameter *a* and (b) cell volume *V* respectively.

This was confirmed by the XRD background (Figure 4-11) where background noise increased when the phosphoric acid loadings were increased, an indication of decreased crystallinity. According to Inumaru [194], the particles of $(NH_4)_3PW_{12}O_{40}$ were composed of $(NH_4)_3PW_{12}O_{40}$ nanocrystallites which self-assembled with the aligned crystal orientations. The microporosity of $(NH_4)_3PW_{12}O_{40}$ comes from the residual space between these nanocrystallites. It is very likely that the additional phosphoric acid can be maintained inside the micropores by hydrogen bonds or capillary effects.

Thermal analysis was carried out to investigate the dehydration and stability of these composites. For sample NP0, the analysis was continued from room temperature up to 800° C. The results were shown in Figure 4-13(I) and (II).



Figure 4-13: TGA curves of pure (NH₄)₃PW₁₂O₄₀ (I, II) from 25°C to 800°C (5°C/min up and down) in air and holding at 800°C for 30 minutes and hybrids NP3 (IIIa,IVa), NP5(IIIb,IVb) and NP10 (IIIc,IVc) respectively. (I,III) Mass loss against time and (II, IV) Mass loss against temperature

According to Belanger *et al.* [192], ammonia was not released from the solid until the temperature is beyond 400°C and considerable amount of ammonium was only released at a temperature higher than 550°C. Therefore, the weight loss observed below 500°C in Figure 4-13(I) and (II) could be reasonably attributed to the loss of water. The thermgravimetric curves showed a two step progress at this temperature range. The first step is a linear loss from room temperature up to around 118°C, a weight loss of 1.48% was observed corresponding to 2.5 H₂O molecules per (NH₄)₃PW₁₂O₄₀ unit. The weight loss at this region was generally believed as the desorption of physically absorbed water due to the hydrophilic properties of (NH₄)₃PW₁₂O₄₀. The second one is from 118°C to 500°C where 1.07% weight loss was observed and corresponded to 1.8 H₂O molecules per (NH₄)₃PW₁₂O₄₀ unit. The thermgravimetric curve at this region presented a smoother slope which could be ascribed to the loss of strongly absorbed water inside the internal structures. As the temperature kept increasing, a sharp loss took place and ended up around 612°C. If ammonium was completely removed from the solid, a weight loss less than 1.7% should be observed theoretically. The experimental value (2.54%) was significantly larger than the theoretical one, suggesting a decomposition of other constituents such as oxygen. XRD patterns of samples after TG analysis confirmed these observations (Figure 4-14a).



Figure 4-14: X-ray diffraction patterns of (a) NP0, (b) NP5 and (c) NP10 after TGA analysis respectively.

The diffraction patterns were attributed to a pure $W_{12}PO_{38.5}$ (PDF card 00-041-0369) with slightly enlarged unit cells and a theoretical weight loss 2.6% can be calculated which is very close to the experimental value (2.54%).

The $(NH_4)_3PW_{12}O_{40}-H_3PO_4$ composites exhibited substantially different thermgravimetric curves at temperatures below 300°C (Figure 4-13(III) and (IV)). The corresponding weight loss below 100°C and from 100°C to 300°C are listed in Table 4-3.

Sample	Weight loss below 100°C	Weight loss between 100°C and 300°C	Total weight loss
NP0	0.98%	0.99%	1.97%
NP3	2.34%	2.53%	4.87%
NP5	0.23%	3.24%	3.57%
NP10	1.22%	5.62%	6.84%

Table 4-3: Weight loss of all samples in different temperature regions

It can be seen from the table that weight loss below 100°C was quite different from NP0 to NP10 due to different extent of hydration during the preparation process. However, the weight loss between 100°C and 300°C increased systematically. This weight loss could mainly come from the dehydration of phosphoric acid since only 0.99% was observed for pure $(NH_4)_3PW_{12}O_{40}$ whereas more than 2.53% was found in the composites. It has been realized that phosphoric acid could condense into pyrophosphoric acid in a temperature of 175°C or even lower [197], therefore, the accelerated weight loss above 150°C for all composites could mainly be attributed to the condensation of phosphoric acid. Another aspect worth mentioning is the stability of $(NH_4)_3PW_{12}O_{40}$ in the presence of phosphoric acid at high temperature. XRD patterns in Figure 4-14b and c revealed that the composites were unstable at high acid loadings (NP5 and NP10). At high H_3PO_4 content (NP10), the phase was poly-crystallized after TG analysis. The slight changes in lattice parameter (NP5) (Table 4-2) before and after TG analysis were probably due to the evaporation of H_3PO_4 .

The morphologies of the composites and pure $(NH_4)_3PW_{12}O_{40}$ were examined by SEM and TEM. Figure 4-15 shows the pictures taken at a magnification of 2000.



Figure 4-15: SEM pictures of (a) NP0; (b) NP3; (c) NP5 and (d) NP10 at a magnification of 2000.

Homogeneous spherical particles were observed for all samples. The particle sizes were approximately in the range of 100nm~500nm which were consistent with the value reported [190]. According to Inumaru's observation, the particles under SEM conditions were composed of nanocrystallites that self-assembled together in the same orientations and the morphologies of these particles were highly sensitive to the preparation temperatures: with spherical particles in the low temperatures (~20°C) and symmetric particles at higher temperatures (~90°C). In addition, they attributed this phenomenon to the various surface energy and/or growth rates between crystal planes. This speculation could be partly true due to the small constituent nanocrystallites (4~6nm) and exceptionally high surface energy that could be envisaged. However, in our point of view, there could be another factor that might govern the outer shape of $(NH_4)_3PW_{12}O_{40}$ which is the hydrogen bonds. According to Okuhara et al., Caesium based heteropolyacid salts like Cs3- $_{x}PW_{12}O_{40}$ were not observed to have such an epitaxial growth phenomenon [198] and the particle dimensions calculated through XRD were significantly smaller (24nm for $Cs_3PW_{12}O_{40}$) than (NH₄)₃PW₁₂O₄₀ (>150nm) prepared at the same conditions. This observation could not be explained by surface energies since the constituent nanocrystallites were of the same dimensions (<10nm) and M₃PW₁₂O₄₀ (M=Cs, NH₄, Rb, K) shared the same crystal structures. Therefore, other factors could trigger the epitaxial growth of (NH₄)₃PW₁₂O₄₀ and hydrogen bonds are wellknown for their direction and strength. It is likely that protons in ammonium formed hydrogen bonds such as N-H...O-W and lead to the translation and rotation of Keggin ions during the local
dissolution-reprecipitation process. Figure 4-16 shows the TEM pictures of NP10 where spherical particles with diameters varied from 150nm-500nm were observed.



Figure 4-16: TEM pictures of sample NP10 at low resolutions.

Inumaru found that the BET surface area and micropore volume of $(NH_4)_3PW_{12}O_{40}$ decreased significantly at a high precipitation temperature due to the rearrangements and formation of rigid dodecahedra. It can be seen from Figure 4-16 that the particles remained spherical after aging at 100°C for 2 hours and no rigid dodecahedra were observed.

4.3.4. IR spectra

Figure 4-17 shows the infrared absorption spectra of pure $(NH_4)_3PW_{12}O_{40}$ and all composites.



The spectra of 85 wt% phosphoric acid are also shown for comparison. It can be seen that the composites and pure (NH₄)₃PW₁₂O₄₀ exhibit only minor differences, implying the structure of the Keggin ions are preserved in the presence of phosphoric acid. The main differences between pure (NH₄)₃PW₁₂O₄₀ and the composites lie in the range 1100 cm⁻¹~1300 cm⁻¹ and 2600 cm⁻¹ ¹~3300 cm⁻¹. Pure (NH₄)₃PW₁₂O₄₀ shows almost no absorption in these two ranges. The composites show a broad shoulder adsorption peak from 1100 cm⁻¹ to 1300 cm⁻¹ corresponding to vibrations of different phosphoric species (HPO₄²⁻ and H₂PO₄⁻) and relatively stronger absorptions at 2600 cm⁻¹~ 3300 cm⁻¹ due to the O-H vibrations [135]. These absorptions could come from the additional phosphoric acid if we compare them with 85 wt% phosphoric acid where much stronger and broader absorptions appeared around the same ranges. Park et al pointed out that hydroxyl groups that have absorption around 2900 cm⁻¹ have higher proton mobility compared with the ones at higher wavenumber [136]. Therefore, it is clear that introducing phosphoric acid into (NH₄)₃PW₁₂O₄₀ significantly enhances the intensities of absorption peaks at this region. Another factor worth noticing is that absorption peaks at wavenumber 525 cm⁻¹, 795 cm⁻¹, 887 cm⁻¹ and 975 cm⁻¹ were broadened progressively with increasing phosphoric acid and could be assigned to vibration mode v_s (W-O-W) and v_{as} (W-O-W), and v(W=O) [199]. This

phenomenon could be evidence of interactions between phosphoric acid and oxygen ions in the Keggin structure such as the formation of hydrogen bonds therefore the symmetry of the Keggin ions was consequently lowered. The weak absorption peaks at 596 cm⁻¹, 1400cm⁻¹ and 1079 cm⁻¹ could be assigned to δ (O-P-O), ν_{as} (PO) and deformation vibration of the ammonium ions respectively [135,177].

4.3.5. Conductivity

The conductivity of pure $(NH_4)_3PW_{12}O_{40}$ under different atmospheres was shown in Figure 4-19. The values are calculated from the Cole-Cole plots obtained by a.c. impedance spectra at the intersection to the real axis Figure 4-18.



Figure 4-18: Impedance spectroscopy of pure (NH₄)₃PW₁₂O₄₀ under different atmospheres.



Figure 4-19: Conductivity of NP0 in air ($^{\bigcirc}$) and in wet 5% H₂ (humidified at 20°C) ($^{\bigcirc}$)

The pure $(NH_4)_3PW_{12}O_{40}$, however, was not a good ionic conductor even in wet 5% H₂ and did not obey Arrhenius behavior. The reason for this could be the continuous loss of water and decomposition of $(NH_4)_3PW_{12}O_{40}$ at high temperatures [192,196]. According to Mikhailenko *et al.*, mechanisms had been proposed for the explanations of proton transport in $(NH_4)_3PW_{12}O_{40}$. They attributed the conductivity to the transport of hydrated protons which was developed in the vicinity of NH_4^+ sites in $(NH_4)_3PW_{12}O_{40}$ structures. In our experiment, $(NH_4)_3PW_{12}O_{40}$ showed a much better conductivity in wet 5% H₂ than in air which provides evidence of proton conduction. More specifically, the differences between wet 5% H₂ and air were enlarged from room temperature to 220°C due to the thermal activation and subsided above 220°C probably due to the dehydration [192]. Since the ammonium was not expected to release from $(NH_4)_3PW_{12}O_{40}$ below 400°C, additional hydrogen bonds might be formed between ammonium ions and water molecules that promote the proton conduction, however, it can not be ruled out that the a.c. conductivity of $(NH_4)_3PW_{12}O_{40}$ is due to other ions such as NH_4^+ as well.

The composites, however, exhibited a much better performance on conductivity in air (Figure 4-20).



The highest conductivity is 0.14 S/cm for NP10 at 170°C which is almost 4 orders of magnitude higher than NP3 under the same conditions. It is postulated that phosphoric acid in NP3 was discretely distributed in the so-called "spongy crystal" of (NH₄)₃PW₁₂O₄₀ where continuous channels for proton conduction may not be fully established. However, in the case of sample NP10 where a huge amount of phosphoric acid was added, those internal space and channels inside crystals could be fully filled and connected well with each other therefore a high conductivity was achieved. The decreased conductivity at high temperature was attributed to the decomposition of Keggin structures in the presence of phosphoric acid which could become a drawback of these composites applied at high temperatures.

4.4. Conclusions

 $H_3PW_{12}O_{40}$ - xH_3PO_4 hybrids synthesized here have a cubic symmetry with enlarged unit cells. Solid state ³¹P NMR suggested strong interactions between H_3PO_4 and $H_3PW_{12}O_{40}$. The conductivity of the hybrids showed a systematic increase with the increase of phosphoric acid. Although the decrease of conductivity was still observable at high temperatures due to the dehydration, the hybrids demonstrated much higher conductivity than pure $H_3PW_{12}O_{40}$ • xH_2O under ambient conditions. A fuel cell based on $H_3PW_{12}O_{40}$ - $3H_3PO_4$ hybrids exhibited a peak power density of 2.7mW/cm² at 0.3V at room temperatures. To overcome the solubility problem encountered at $H_3PW_{12}O_{40}-3H_3PO_4$ hybrids, $(NH_4)_3PW_{12}O_{40}-xH_3PO_4$ hybrids were also synthesised. The hybrids also had an enlarged unit cell and phosphoric acid was believed to be preserved in the micropores of $(NH_4)_3PW_{12}O_{40}$. Although $(NH_4)_3PW_{12}O_{40}$ per se is not a good proton conductor, $(NH_4)_3PW_{12}O_{40}-xH_3PO_4$ hybrids exhibited a improved conductivity and the highest conductivity 0.14S/cm was achieved at 170°C for $(NH_4)_3PW_{12}O_{40}-10H_3PO_4$ hybrids in air. Such high conductivity could give rise to broad potential applications such as fuel cells and worthy of future study.

CHAPTER 5 Barium zirconate based systems

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5.1. Introduction

Perovskites were firstly discovered in the Ural mountain of Russia by Gustav Rose in 1839 and were named after Russian mineralogist L.A. Perovski (1792-1856). They have the same type of crystal structure as strontium titanium oxide (SrTiO₃). The general chemical formula for perovskites is ABX₃, where A and B are two cations with different atom sizes and X is an anion bonded to both. An ideal structure for perovskite has cubic symmetry with A and B type atoms in 12-fold and 6-fold coordination (Figure 5-1). Changes in atom sizes usually lead to structure distortion and a lowered symmetry. Perovskite oxides usually found to exhibit various extraordinary properties such as superconductivity [200], giant magnetoresistance (GMR) [201], ferroelectricity [202] and catalytic activity [203,204,205] etc. probably due to their specific structures.



Figure 5-1: Overview of perovskite structure based on BaZrO₃.

Perovskite oxides based on SrCeO₃ have been recognized to exhibit predominant proton conduction under hydrogen containing atmospheres at elevated temperatures many years ago [69]. Thereafter, numerous perovskite oxides with similar compositions have been synthesized and investigated such as CaZrO₃ [70,71,72], BaCeO₃ [73,74,75,76]. Their chemical compositions can be written as $AB_{1-x}M_xO_{3-\delta}$, where M is some trivalent elements like rare earth elements and δ is the oxygen deficiency per perovskite primitive unit cell and A is divalent and B is tetravalent in

this cell. Among perovskite oxides investigated, cerate-based oxides generally present the highest proton conductivity but suffer from decomposition under atmospheres containing CO_2 or H_2O below 500°C [77,78]. Great efforts have been devoted to partially substitute cerium with zirconium in the hope to improve the stability or by introduction of other elements such as Gd. Nd or Co [206, 79, 80,207]. It has been found that the stability of these partially replaced cerates depends strongly on the zirconium content [79]. In other words, complete replacement of cerium for zirconium is expected to exhibit the highest stability under atmospheres containing CO₂ and H₂O therefore allowing hydrocarbon fuels to be utilized. Although zirconates such as doped BaZrO₃ demonstrate similar conducting behavior to cerates in terms of formation and mobility of protonic charge carriers [81], their conductivity is usually one order of magnitude lower than cerates [82]. This is attributed to the highly refractory properties of zirconates with low rates of grain growth under typical sintering conditions which limit the overall proton transport [81]. This explanation has been confirmed by annealing the zirconates at high temperature (~2200°C) where the grain boundary conductivity was improved by nearly two orders of magnitudes [208]. However, high temperature sintering should be avoided due to loss of barium at high temperature which is one factor that leads to a diminished conductivity [209]. Besides, from a technological point of view, high sintering temperatures introduce difficulties and unfavorable cost in manufacturing the materials since other auxiliary materials such as electrodes in fuel cells can hardly sustain such a high temperatures, never mind the likelihood of interfacial reaction [210]. Introducing zinc oxide into the B sites is an efficient way in improving sintering conditions while conductivity is still unsatisfactory compared with cerates. Here, we tried to improve the conductivity by aliovalent doping of barium zirconates. As there is already a huge amount of doping at B site and too much doping will decrease the conductivity, we tried to dope different elements on the A site.

5.2. Potassium doped barium zirconate

5.2.1. Background

Proton conductivity of perovskite oxides was found to be strongly affected by the basicity of the constituent oxides due to the dominant effect of basicity in water uptake capacity [211], as introducing highly basic alkaline oxides should improve the conductivity. Patnaik *et al* [212] did some early fundamental work on A-site potassium doped barium zirconates, finding that the A-site potassium doped barium zirconates showed a significantly higher conductivity than A-site undoped barium zirconates where the yttrium dopant contents on the B-site are approximately equal. However, some impurities (ZrO₂) remained in their samples and pure A-site potassium doped barium zirconates were not synthesized successfully in their work. One possible reason is

that the limit for potassium doping at the A-site is lower than 10%. Here, samples in the series $Ba_{1-x}K_xZr_{1-y}Y_yO_{3-\delta}$ (x \leq 0.15, y \leq 0.2) with and without zinc doped have been synthesized. The conductivity of the samples in different atmospheres has also been investigated.

5.2.2. Experimental

All samples were synthesized by conventional solid state reaction methods. Calculated amounts of BaCO₃, ZrO₂, Y₂O₃, K₂CO₃, ZnO were mixed according to the desired compositions. The oxides were preheated at 500°C prior to weighing in order to remove the adsorbed water and gases. The mixtures were then planetary ball milled in a zirconia container with zirconia balls in the presence of acetone to ensure thorough mixing. The finely ground materials were fired at 1400°C for 10 hours. For samples without zinc, the fired powders was subsequently ground using a mortar and pestle before pressing into pellets under a pressure of 500 MPa. The pellets were fired at 1450°C again for another 10 hours before conductivity measurements. For samples with zinc, a specific amount of zinc oxides was mixed together with as-fired powders, ball-milled for 30 minutes and pressed into pellets in a diameter of 13mm before firing at 1300 °C for 10 hours.

Crystal structure and phase purity were examined by X-ray diffraction (XRD) analysis of powders on a Stoe STADI/P powder diffractometer. Incident radiation was generated using a Cu_{Ka1} source ($\lambda = 1.54056$ Å). The step size for data collection is 0.02 degree and 1000 seconds per step. Vaseline was used to stick the sample in the holder. X-POW software was used to perform least square refinement of the lattice parameters of the samples. Thermal analysis was carried out on a Rheometric Scientific TG 000M+ and TA instruments SDT 2960 with heating and cooling rate of 5°C/min under flowing dry Ar, dry and wet 5% H₂/Ar (humidified in water at 20°C) at a rate of 20mL/min. The microstructure of the pellets was inspected by scanning electron microscope (SEM) on a JEOL 5600 SEM with a Mica energy dispersive X-ray spectroscopy (EDS) analysis system. An Agilent 7500a inductively coupled plasma mass spectroscopy (ICP-MS) for element distribution analysis.

Conductivity was investigated by a.c. impedance method over the frequency range from 1 MHz to 0.1Hz at 100 mV r.m.s. using a Schlumberger Solartron 1255 Frequency Response Analyzer coupled with a 1287 Electrochemical Interface controlled by Zplot electrochemical impedance software. Pellets obtained above were coated with conductive platinum paste on both sides serving as electrodes and were then fired at 900°C to ensure good ohmic contact. Measurements were performed from 200 to 850°C on cooling under ambient air, wet 5% H₂/Ar (humidified at 20°C in water), dry 5% H₂/Ar (desiccated at 20°C in 98% H₂SO₄). Accordingly, the steam vapour pressures are 8.4×10^{-4} , 3.0×10^{-2} and 1.3×10^{-6} atm for air, dry and wet 5% H₂, respectively [213].

Pellets were maintained at 850°C for at least 12 hours in each atmosphere and impedance data were collected at 50°C steps after one hour dwell at each step for equilibrium.

5.2.3. Phase composition

X-ray powder diffraction was carried out on each of the prepared samples. Patterns for samples without zinc are shown in Figure 5-2.



Figure 5-2: X-ray diffraction patterns of samples prepared. +, vaseline peak; \forall YSZ peaks; \downarrow second phase.

Single phase perovskite oxides were formed after doping 5% potassium at the A-sites and 10% yttrium at B-site; second phase or YSZ (yttrium stabilized zirconium) emerged when 10% or more potassium was introduced, implying the upper limit of solid solution formation on the A-sites for potassium is between 5 ~ 10%. This could be a reason why Patnaik *et al.* did not obtain a pure potassium doped BaZrO₃ as more than 10% potassium was used [212]. The unit cell parameter of Ba_{0.95}K_{0.05}Zr_{0.9}Y_{0.1}O_{3-δ} (4.2065(7) Å) is close to the reported value for BaZr_{0.9}Y_{0.1}O_{3-δ} [214] (4.2044 Å) which is plausible due to the similar average ionic radius of Ba²⁺ (1.6 Å) and K⁺ (1.6 Å) at 12 coordination [215]. However, the experimental density of Ba_{0.95}K_{0.05}Zr_{0.9}Y_{0.1}O_{3-δ} pellets fired at 1450°C only reached 60% of its theoretical density (calculated using lattice parameters from

XRD data) due to the refractory properties of Barium Zirconates. Dense pellets were not obtained even when the sintering temperature was increased to 1600°C indicating that potassium is not an efficient sintering aid for barium zirconates.

5.2.4. Thermogravimetric test and water uptake

Thermogravimetric studies were carried out by recording the weight change against temperature in different atmospheres (dry and wet 5% H_2 (humidified at 20 °C)). Samples for TG studies were pre-treated in dry Ar at 900 °C for 5 hours to eliminate water and the temperature was controlled from 900 °C to 20 °C at a cooling rate of 5 °C/min. Figure 5-3 shows the weight changes in different atmospheres.



Figure 5-3: TGA patterns of $Ba_{0.95}K_{0.05}Zr_{0.9}Y_{0.1}O_{3-\delta}$ in dry and wet 5% H₂, the samples were pretreated in dry Ar at 900 °C for 5 hours. The flow rate of gas was controlled at 20ml/min and the cooling rate is 5 °C /min.

In dry 5% H₂, the as-prepared sample shows a weight change less than 0.25% from 900 $^{\circ}$ C to 20 $^{\circ}$ C. This weight change can be arising from the buoyancy since density of the gas is changed with temperature. On the contrary, almost 0.35% weight increase was observed in wet 5% H₂. The additional 0.1% weight change could be attributed to the absorption of water molecules when

samples were exposed to moisture. This is nearly 0.02 water molecules per formula unit correspondingly. Compared with $BaZr_{0.9}Y_{0.1}O_{3-\delta}$ where no significant water change was observed [214], introducing potassium even with 5% is an effective way to improve the water uptake.

5.2.5. Conductivity

The conductivities of as-prepared samples under various atmospheres are shown in Figure 5-4.



Figure 5-4: Conductivity of $Ba_{0.95}K_{0.05}Zr_{0.9}Y_{0.1}O_{3-\delta}$ in differently atmospheres.

The values were calculated from the Cole-Cole plots obtained by a.c. impedance spectra (not shown). For the conductivity in air, a linear relationship versus reciprocal temperature was observed indicating a single activation process. The activation energy is 0.86eV calculated from the slope. According to Iwahara *et al.* [82], these perovskite-type ceramics exhibit p-type electronic (hole) conduction under oxidizing atmospheres by the following equation:

$$O_2 + 2V_0^{\bullet\bullet} \longleftrightarrow 4h^{\bullet} + 2O_0^{\times} \tag{5.1}$$

However, in a wet reducing atmosphere, the Arrhenius plots of conductivity shows a different linear trend with large deviations at high temperatures. The activation energy from 300°C to 600°C is 0.61eV. The ceramics were believed to become a proton conductor in the presence of water vapor and hydrogen by equation:

$$H_2O(g) + O_0^* + V_0^{\bullet\bullet} \longleftrightarrow 2(OH)_0^{\bullet} \tag{5.2}$$

However, in dry 5% H₂, the conductivity was significantly lower than that in air and wet 5% H₂. It was found that the conductivity of potassium doped samples in wet reduced atmospheres at 600° C was improved substantially (from 5.78×10^{-5} S/cm to 1.5×10^{-4} S/cm after doped 5% potassium) [214]; however, the conductivity is still lower than similar compounds containing cerium [216]. The conductivity in air is p-type electronic dominant [210].

5.2.6. Addition of ZnO

The poor conductivity of $Ba_{0.95}K_{0.05}Zr_{0.9}Y_{0.1}O_{3-\delta}$ was probably due to the low density where grain boundary resistance dominates the conduction process and the low defect concentration that only 10% of zirconium was replaced by yttrium. To improve the sinterability and conductivity, zinc oxide and additional yttrium were introduced. In previous work, it was found that barium zirconates can be well sintered at 1325°C by introducing 4% mol ratio ZnO at B site [212]. In this experiment, the ZnO content was fixed at 0.04mol at the B-sites and the yttrium content was varied correspondingly. Figure 5-5 shows the XRD patterns with stoichiometric formula $Ba_{0.95}K_{0.05}Zr_{0.8}Y_{0.16}Zn_{0.04}O_{3-\delta}$ and $Ba_{0.95}K_{0.05}Zr_{0.85}Y_{0.11}Zn_{0.04}O_{3-\delta}$.



Figure 5-5: X-ray diffraction patterns of samples with zinc added. The powders were fired at 1300 °C for 10 hours after ZnO was added.

It was found that introducing 5% more yttrium leads to the separation of Y_2O_3 from the perovskite structure therefore the upper limit of yttrium solid solution in B site lies between 11% and 16% after introducing 4% Zn at B site. The unit cell parameter for $Ba_{0.95}K_{0.05}Zr_{0.85}Y_{0.11}Zn_{0.04}O_{3-\delta}$ is 4.2116(5) Å which is slightly lower than $Ba_{0.97}Zr_{0.8}Y_{0.16}Zn_{0.04}O_{3-\delta}$ (4.2220(4) Å) [210]. The experimental density of $Ba_{0.95}K_{0.05}Zr_{0.85}Y_{0.11}Zn_{0.04}O_{3-\delta}$ reaches 92% of its theoretical density confirming the improved sintering conditions after zinc doping.

Figure 5-6 shows the SEM pictures of $Ba_{0.95}K_{0.05}Zr_{0.85}Y_{0.11}Zn_{0.04}O_{3-\delta}$ pellet (surface) fired at 1300 °C for 10 hours. The particle size is around 500nm on average with some larger than 1 micron. Some small pinholes can still be observed in the closely packed particles since the experimental density only reached 92% of the theoretical one.



Figure 5-6: SEM pictures of $Ba_{0.95}K_{0.05}Zr_{0.85}Y_{0.11}Zn_{0.04}O_{3-\delta}$ pellet fired at 1300 °C for 10 hours.

The element distribution was inspected by ICP-MS and EDS techniques, although ICP-MS indicated a deficiency of potassium at the pellet surface, EDS analysis of the cross-section in SEM (Figure 5-7) and Figure 5-8) showed a uniform distribution of all elements, including potassium across the cross-section of the pellet.





Figure 5-7 EDS analysis (element mapping) of cross-section of $Ba_{0.95}K_{0.05}Zr_{0.85}Y_{0.11}Zn_{0.04}O_{3-\delta}$ pellet.

From the EDS profile (line scanning), the depth resolution was estimated as < 5 μ m hence the material was essentially homogeneous (Figure 5-8).



Figure 5-8: EDS linear scanning of $Ba_{0.95}K_{0.05}Zr_{0.85}Y_{0.11}Zn_{0.04}O_{3-\delta}$ pellet cross section, the element content was calculated according to the area of each spectrum (scanning time was 30 minutes).

Typical impedance spectra of $Ba_{0.95}K_{0.05}Zr_{0.85}Y_{0.11}Zn_{0.04}O_{3-\delta}$ at low temperatures (200 °C) in dry and wet 5% H₂/Ar are shown in Figure 5-9. All impedance data can be well fitted using equivalent circuit present (Figure 5-9).



Figure 5-9: Complex impedance diagrams for Ba_{0.95}K_{0.05}Zr_{0.85}Y_{0.11}Zn_{0.04}O_{3-δ} at 205 °C in dry and wet 5% H₂. Equivalent circuit that was used to calculate the resistance was inserted in the diagrams.

Through out the entire frequency range, only two depressed semicircles can be separated. The first high frequency semicircle (geometrical capacitance $\sim 3 \times 10^{-9}$ Fcm⁻¹) could be assigned to the grain boundary response and the second low frequency semicircle (geometrical capacitance $\sim 1 \times 10^{-6}$ Fcm⁻¹) is a typical response of electrode process [86]. The bulk response, however, could not be clearly separated from the impedance spectra through the whole temperature range (200°C ~ 800°C), as it is probably masked by that from grain boundary. It is clear that Ba_{0.95}K_{0.05}Zr_{0.85}Y_{0.11}Zn_{0.04}O_{3- \overline{o}} exhibits lower grain boundary and total resistance in wet 5% H₂ than in dry 5% H₂ indicating proton conduction.

Figure 5-10 shows the Arrhenius plot of total conductivity for $Ba_{0.95}K_{0.05}Zr_{0.85}Y_{0.11}Zn_{0.04}O_{3-\delta}$ as a function of temperature in different atmospheres.



Figure 5-10: Conductivity of $Ba_{0.95}K_{0.05}Zr_{0.85}Y_{0.11}Zn_{0.04}O_{3-\delta}$ in differently atmospheres.

The values were calculated from fitting of the impedance spectra using the equivalent circuit provided (Figure 5-9). The total conductivity, in all three atmospheres, was improved significantly (more than one order of magnitude) as compared with samples without zinc. The effect of doping potassium at the A site can be evaluated by comparing samples with and without zinc. A typical total conductivity in wet 5% H₂ for Ba_{0.95}K_{0.05}Zr_{0.85}Y_{0.11}Zn_{0.04}O_{3-δ} is 2.2×10^{-3} Scm⁻¹ at 600 °C which is two times higher than Ba_{0.97}Zr_{0.8}Y_{0.16}Zn_{0.04}O_{3-δ} (1×10⁻³ Scm⁻¹) reported [210]. The grain boundary and bulk conductivity (calculated by subtracting grain boundary resistance from total resistance) below 400°C in wet and dry 5% H₂ were plotted together with total conductivity for comparisons (Figure 5-11).



Figure 5-11: Bulk, grain boundary and total conductivity of $Ba_{0.95}K_{0.05}Zr_{0.85}Y_{0.11}Zn_{0.04}O_{3-\delta}$ between 200 °C and 300 °C in wet (a) and dry (b) 5% H₂.

It can be seen that bulk conductivity is significantly higher than that for grain boundary at lower temperature and the total conductivity was dominated by grain boundary at low temperatures. The activation energy between 200 °C and 300 °C calculated from the slope is listed in Table 5-1. The values obtained for bulk in wet and dry 5% H₂ are 0.29(2)eV and 0.31(1)eV while for grain boundary; the energy is 0.79(2)eV and 0.74(3)eV respectively. It can be noticed that the activation energy for bulk conduction is significantly lower than the values reported, one possible explanation could be the A-site doping which may alleviate the proton-dopant trapping effect.

Table 5-1: activation energy of $Ba_{0.95}K_{0.05}Zr_{0.85}Y_{0.11}Zn_{0.04}O_{3-\delta}$ between 200 °C and 300 °C in different atmospheres.

Bulk		Grain boundary	Total
Wet 5% H_2	0.29(2)eV	0.79(2)eV	0.76(1)eV
Dry 5% H_2	0.31(1)eV	0.74(3)eV	0.72(4)eV

The stability of conductivity in wet 5% H_2 /Ar was investigated by measuring the conductivity in two cycles both from highest (850°C) to lowest (200°C). Figure 5-12 shows the results. There is no significantly difference between these two cycles suggesting good reproducibility of conductivity.



Figure 5-12: Total conductivity of $Ba_{0.95}K_{0.05}Zr_{0.85}Y_{0.11}Zn_{0.04}O_{3-\delta}$ in wet 5% H₂ for two cycles.

The fuel cell performance based on $Ba_{0.97}Zr_{0.8}Y_{0.16}Zn_{0.04}O_{3-\delta}$ electrolyte has been evaluated. Pellets that were used as electrolyte were sintered at 1400°C for 10 hours. The thickness of the electrolyte is 1 mm and platinum paste was used as the electrodes with an effective area 0.2 cm². Wet 5% H₂ and air were used as fuels and oxidant respectively. Figure 5-13 shows the fuel cell (Pt/Ba_{0.95}K_{0.05}Zr_{0.85}Y_{0.11}Zn_{0.04}O_{3-\delta}/Pt) performance in different temperatures.



Figure 5-13: Fuel cell performance for Pt/ $Ba_{0.95}K_{0.05}Zr_{0.85}Y_{0.11}Zn_{0.04}O_{3-5}$ /Pt under humidified 5% H₂/air conditions at different temperatures

The OCV (open circuit voltage) is 0.81V, 0.85V and 0.88V at 718°C, 653° C and 586° C, respectively. The OCV is lower than the theoretical values and is decreased with increasing temperature. This could be due to the introduction of p-type electronic conduction after doping with potassium [212]. The fuel cell gives a maximum power density 7.7mWcm⁻² at 718°C and an electrode polarization resistance $4\Omega \cdot \text{cm}^2$ (Figure 5-14).



Figure 5-14: Complex impedance diagrams under open circuit conditions at different temperatures.

The calculated conductivity of $Ba_{0.95}K_{0.05}Zr_{0.85}Y_{0.11}Zn_{0.04}O_{3-\delta}$ in fuel cell, according to a.c. impedance is 0.006 Scm⁻¹, 0.005 Scm⁻¹ and 0.003 Scm⁻¹ for 718°C, 653°C and 586°C, respectively. The conductivity for the electrolyte measured separately, however, is about 30% lower, probably implying extension of electrode activity beyond the small Pt-painted region in the fuel cell.

5.3. Lathanum doped barium zirconate

5.3.1. Background

It has been reported that $BaZr_{0.9}Y_{0.1}O_{2.95}$ has two variants, both with the cubic perovskite structure. The β -form exhibits a slightly larger unit cell and demonstrates significant higher proton conductivity than the α -form. Neutron diffraction suggests that the difference coming from a small cross substitution of Y atom onto the A-sites in the case of the β -form. It is anticipated that donor doping at the A-sites may reduce the defect association and enhance the conductivity [217]. La presents the same charge as Y in the oxides and has a larger ionic radius that favors the substitution onto the A-sites, so doping La might be a novel approach to increase conductivity.

5.3.2. Experimental

Lanthanum doped Barium Zirconate was synthesized by the conventional solid state reaction method and by sol-gel method. For conventional method, calculated amounts of BaCO₃, ZrO₂, Y₂O₃, La₂O₃ were mixed according to the desired compositions. The oxides were preheated at 500°C prior to weighing in order to remove the adsorbed water and gases. The mixtures were then ball milled in the presence of acetone to ensure thorough mixing. The finely ground materials were fired at 1300°C for 10 hours. After that, a specific amount of zinc oxide was mixed together with as-fired powders, ball-milled for 30 minutes and pressed into pellets in a diameter of 13mm before firing at 1400 °C for 10 hours. For sol-gel method, a calculated amount of Ba(NO₃)₃, La(NO₃)₃•6H₂O, ZrO(NO₃)₂ and Y(NO₃)₃•6H₂O were dissolved in ethylene glycol. Citric acid was used as a chelating agent and for full chelation, the molar ratio of citric acid to the sum of cation were kept at 2:1. The solution was then continuously agitated using magnetic stirring at 1300 °C for 10 hours. White powders were collected and subsequently ground using a mortar and pestle before pressing into pellets under a pressure of 500 MPa. The pellets were fired at 1500°C again for another 10 hours before conductivity measurements.

Crystal structure and phase purity were examined by X-ray diffraction (XRD) analysis of powders on a Stoe STADI/P powder diffractometer. Incident radiation was generated using a Cu_{Ka1} source (λ = 1.54056 Å). X-POW software was used to perform least square refinement of the lattice parameters of samples. Thermal analysis was carried out on a Rheometric Scientific TG 1000M 1000M+ TA instruments SDT 2960 with heating and cooling rate of 5°C/min under flowing dry Ar, dry and wet 5% H₂/Ar (humidified in water at 20°C) at a rate of 20ml/min. The conductivity measurements were carried out by the a.c. impedance method over the frequency range from 1 MHz to 0.01Hz at 100 mV r.m.s. Pellets obtained above were dabbed with conductive platinum paste on both sides serving as electrodes and were then fired at 900°C to ensure good ohmic contact. Measurements were performed from 200 to 850° C on cooling under ambient air, wet 5% H₂/Ar (humidified at 20°C in water), dry 5% H₂/Ar or dry O₂ (desiccated at 20°C in 98% H₂SO₄). Accordingly, the steam vapour pressure are 8.4×10^{-4} , 1.3×10^{-6} , 3.0×10^{-2} and 1.3×10^{-6} atm for air, dry O₂, dry and wet 5% H₂/Ar, respectively [213]. Pellets were maintained at 850° C for at least 12 hours in each atmosphere and impedance data were collected at 50° C steps after one hour dwell at each step for equilibrium.

5.3.3. Phase composition

X-ray powder diffraction was carried out on each of the prepared samples. Samples synthesized by different methods were compared. Figure 5-15 shows XRD patterns for $Ba_{0.95}La_{0.05}Zr_{0.8}Y_{0.2}O_{3-\delta}$ obtained by solid state reactions and a sol-gel process.



Figure 5-15: XRD patterns of $Ba_{0.95}La_{0.05}Zr_{0.8}Y_{0.2}O_{3-\delta}$ synthesized by different methods. The samples were only fired at 1300°C for 10 hours.

Both samples were fired at 1300° C for 10 hours. In the case of solid state reactions, impurity peaks corresponding to Ba₃Y₄O₉ were identified, indicating incomplete reactions. For the sample obtained by the sol-gel process, XRD patterns confirmed a single phase is present with cubic

symmetry (*a* = 4.2170(24) Å, *V* = 74.99(8) Å³). This large discrepancy suggested that sol-gel process can favor the reactions and accelerate the formation of $Ba_{0.95}La_{0.05}Zr_{0.8}Y_{0.2}O_{3-\delta}$. Besides, the peaks in sample prepared by sol-gel process are much broader than by solid state reaction, implying much smaller particles obtained.

After adding a calculated amount of ZnO and firing at 1400°C for 10 hours, Rietveld refinement (performed using general structure analysis system (GSAS)) of the XRD data shows the sample prepared by solid state reactions as cubic in the space group Pm-3m (Figure 5-16). Atomic positions and isotropic temperature factors are listed in Table 5-2.



Figure 5-16: Rietveld refinement plot of the XRD data of Ba_{0.95}La_{0.05}Zr_{0.8}Y_{0.16}Zn_{0.04}O₃₋₅.

Atom	Site	Occupancy	х	Y	Z	U _{iso} (Å ²)
Ва	1a	0.95	0	0	0	0.0078(4)
La	1a	0.05	0	0	0	0.0078(4)
Zr	1b	0.8	0.5	0.5	0.5	0.0022(6)
Y	1b	0.16	0.5	0.5	0.5	0.0022(6)
Zn	1b	0.04	0.5	0.5	0.5	0.0022(6)
0	3c	1	0	0.5	0.5	0.0089(17)

Table 5-2: Refinement results of Ba_{0.95}La_{0.05}Zr_{0.8}Y_{0.16}Zn_{0.04}O_{3-δ}

The refinements converged with good R-factors and χ^2 (R_p =6.60%, R_{wp} =8.80%, χ^2 =3.199). The unite cell parameter (a = 4.2179(1) Å and V = 75.037(1) Å³) is slightly larger than the values for sol-gel process (a = 4.2170(24) Å, V = 74.99(8) Å³). The relative density of pellets prepared by

different methods was listed in Table 5-3. The pellet by sol-gel process has a poor density (3.39 g/cm³) which is only 56% of the theoretical one (6.09 g/cm³). However, the pellet prepared by solid state reaction possess a density of 5.76 g/cm³ which is 95% of the theoretical one (6.05 g/cm³). Therefore, sol-gel process can produce single phase at a lower temperature but the sinterability of these powders are not as good as when ZnO is added.

Table 5-3: Unit cell parameters and relative density of samples prepared by different methods

Sample	Preparation method	аÅ	VÅ ³	Relative density
$Ba_{0.95}La_{0.05}Zr_{0.8}Y_{0.2}O_{3\cdot\delta}$	Sol-gel process	4.2170(24)	74.99(8)	56%
$Ba_{0.95}La_{0.05}Zr_{0.8}Y_{0.16}Zn_{0.04}O_{3\cdot\delta}$	Solid state reactions	4.21795(12)	75.042(4)	95%

5.3.4. Thermogravimetric test, water uptake and morphology

Thermogravimetric studies were carried out by recording the weight change against temperature. Samples for TG studies were pre-treated in dry Ar at 900 °C for 2 hours to eliminate water and the temperature was controlled from 900 °C to 20 °C at a cooling rate of 5 °C/min. Figure 5-17 gives the weight change of samples prepared by different methods.



Figure 5-17: TGA cooling curves of samples prepared by different methods at wet 5% H₂/Ar.

In the case of sol-gel samples, TGA studies shows almost a 0.6wt% weight increase from 900 °C to 20 °C, corresponding to 0.09 water molecules per formula unit and the main weight increase was observed between 400°C to 700°C. However, for samples prepared by solid state reactions, only less than 0.2wt% weight increase was observed, corresponding to less than 0.03 water molecules per formula unit. This big difference in water absorption might be due to different particle sizes. The sol-gel method generally produced small and loosely contacted particles with large surface area, favorable for water absorption so that absorption equilibrium can be easily established. On the contrary, large and aggregated particles were usually found in solid state reactions, especially after adding the sintering aid ZnO, where water absorption was to some extent retarded. For comparison, samples prepared by solid state reactions were ball milled for two days in order to reduce particle sizes and the TGA was again carried out in the same conditions (Figure 5-17). The total weight change was improved significantly, from less than 0.2wt% before ball milling to almost 0.85% afterwards; therefore, it is beneficial to reduce particle sizes in order to enhance water absorption. However, it is noteworthy that weight increase in this case mainly took place below 100°C which was generally attributed to the physically absorbed water. The weight increase above 100°C was still less than in the samples prepared by sol-gel method. Adding ZnO might modify the composition and affect the water absorption, but this effect should be limited as only 4mol% ZnO at the B-sites was introduced. Another explanation could be the formation of a dense phase in the shell of each particle after adding ZnO which prevents the diffusion of molecules.

Figure 5-18 shows SEM pictures of pellets synthesized by different methods. Figure 5-18a is the cross section of $Ba_{0.95}La_{0.05}Zr_{0.8}Y_{0.2}O_{3-\delta}$ prepared by the sol-gel method. Pinholes and aggregates of particles can be identified, attributing to a low density. A relatively dense and uniform cross section was observed for samples prepared by solid state reactions, suggesting a good sinterability after adding 4mol% ZnO at B-sites (Figure 5-18b).



Figure 5-18: SEM pictures of (a) $Ba_{0.95}La_{0.05}Zr_{0.8}Y_{0.2}O_{3-\delta}$ synthesized by sol-gel method and (b) $Ba_{0.95}La_{0.05}Zr_{0.8}Y_{0.16}Zn_{0.04}O_{3-\delta}$ by solid state reactions.

5.3.5. Conductivity

Figure 5-19 and 5-20 show the bulk, grain and total conductivity for sol-gel prepared samples as a function of temperatures in different atmospheres. Bulk and grain boundary elements here show classical pF cm⁻¹ and nF cm⁻¹ geometric capacitance values so that they can be easily separated from impedance spectra. The conductivity in all atmospheres gives a nonlinear trend and is an indication of complex conduction processes in all atmospheres (Figure 5-20). In air, the grain boundary conductivity is higher than that of the bulk above 550°C (Figure 5-21a) which is consistent with that reported for $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ [210]. The conductivity in dry 5% H₂ is significantly lower than in air and wet 5% H₂ (Figure 5-20). This is due to poor grain boundary conductivity in dry 5% H₂ which is more than two orders of magnitude lower than the bulk conductivity below 600°C (Figure 5-19), consistent with small particle size with extensive intergrain regions.



Figure 5-19: Impedance spectroscopy of $Ba_{0.95}La_{0.05}Zr_{0.8}Y_{0.2}O_{3-\delta}$ in different atmospheres at $400^{\circ}C$.

However, this is not the case in wet 5% H₂ where the grain boundary conductivity exceeds the bulk conductivity above 450°C (Figure 5-21c). The bulk, grain boundary and total conductivity after equilibrating in wet 5% H₂ are all higher than those in dry 5% H₂ indicating a significant improvement of conductivity in the presence of steam due to enhanced proton conduction (Figure 5-20). The total conductivity in wet 5% H₂ at 840°C is 1.23×10^{-4} S/cm which is almost one order of magnitude higher than in dry 5% H₂ at 840°C (1.68×10^{-5} S/cm). The grain boundary conductivity at 515°C is 1.48×10^{-4} S/cm, 4.34×10^{-5} S/cm and 4.35×10^{-5} S/cm in wet 5% H₂, dry 5% H₂ and in air respectively.



Figure 5-20: Total conductivity of $Ba_{0.95}La_{0.05}Zr_{0.8}Y_{0.2}O_{3-\delta}$ (sol-gel process) in different atmospheres.



Figure 5-21: Bulk, grain boundary and total conductivity of $Ba_{0.95}La_{0.05}Zr_{0.8}Y_{0.2}O_{3-\delta}$ (sol-gel method) in (a) air, (b) dry 5% H₂ and (c) wet 5% H₂.

For samples prepared by solid state reactions, conductivity was calculated through impedance spectroscopy which was measured at dry O_2 , wet 5% H_2 and dry 5% H_2 atmospheres (Figure 5-23). The samples show a different response in different atmospheres, probably due to the different charge species generated. In dry oxygen, it has been reported that electron holes are the main conducting species in Y doped BaZrO₃ under dry O_2 which shows the lowest resistance at 568°C (Figure 5-22) [218]. While in wet and dry atmospheres, protons become the dominant species and the resistance increases. The conduction mechanisms and species not only rely on the atmosphere but also change with temperature: in wet 5% H_2 , the dominant conducting species could change from protons to oxygen ions if the temperature is increased (Figure 5-22).



Figure 5-22: Impedance spectroscopy of $Ba_{0.95}La_{0.05}Zr_{0.8}Y_{0.16}Zn_{0.04}O_{3-\delta}$ in different atmosphere at $568^{\circ}C$.



Figure 5-23: conductivity of $Ba_{0.95}La_{0.05}Zr_{0.8}Y_{0.16}Zn_{0.04}O_{3-\delta}$ (solid state reactions) in different atmospheres

Figure 5-24 shows the bulk, grain and total conductivity as a function of temperature. In dry O_2 and dry 5% H₂, the total conductivity shows a linear relationship versus reciprocal temperature suggesting single activation process (Figure 5-23). The calculated activation energy is 0.93eV and 0.84eV in dry O_2 and dry 5% H₂ respectively. In wet 5% H₂, the total conductivity shows two linear relationships versus reciprocal temperature. One is between 618°C and 781°C where resistance is dominated by the grain boundary (Figure 5-24c). The other lies between 199°C and 254°C where bulk resistance is the main contribution to the total resistance (Figure 5-24c). The activation energy for these two temperature range is 0.63eV and 0.87eV respectively. Similar to Ba_{0.95}La_{0.05}Zr_{0.8}Y_{0.2}O₃₋₆ prepared by sol-gel method, the grain boundary resistance dominates the total resistance (Figure 5-24b) in dry 5% H₂; while in dry O_2 , bulk and grain boundary resistance are comparable (Figure 5-24a). The bulk conductivity for Ba_{0.95}La_{0.05}Zr_{0.8}Y_{0.16}Zn_{0.04}O₃₋₆ prepared by sol-gel method, the Signe Sig
great improvement can be attributed to the difference in relative density and additions of ZnO that favors sintering. The grain boundary conductivity at 515° C is 7.7×10^{-4} S/cm and 8.4×10^{-3} S/cm in wet 5% H₂ and dry 5% H₂ which are all higher than Ba_{0.95}La_{0.05}Zr_{0.8}Y_{0.2}O₃₋₅ prepared by a sol-gel process at the same measuring conditions.



Figure 5-24: bulk, grain boundary and total conductivity of $Ba_{0.95}La_{0.05}Zr_{0.8}Y_{0.16}Zn_{0.04}O_{3-\delta}$ (solid state reactions) in (a) air, (b) dry 5% H₂ and (c) wet 5% H₂.



Figure 5-25: Conductivity versus reciprocal temperature for Y doped Barium zirconates with similar compositions, (\Box) bulk and (\circ) total conductivity for Ba_{0.95}La_{0.05}Zr_{0.8}Y_{0.16}Zn_{0.04}O_{3-δ} in wet 5% H₂ (*P* (H₂O)=0.03atm).

The bulk and total conductivity of Ba_{0.95}La_{0.05}Zr_{0.8}Y_{0.16}Zn_{0.04}O₃₋₅ in wet 5% H₂ are plotted together with other similar compositions that were measured in reducing atmosphere [218, 210, 214, 211, 209]. The water partial pressure is also shown for comparisons. The bulk conductivity of Ba_{0.95}La_{0.05}Zr_{0.8}Y_{0.16}Zn_{0.04}O₃₋₅ are very close to the value of Ba_{0.97}Zr_{0.77}Y_{0.19}Zn_{0.04}O₃ reported [210], but the total conductivity is lower, which is due to contribution of grain boundary resistance. The reported conductivity of BaZr_{0.9}Y_{0.1}O₃ and BaZr_{0.8}Y_{0.2}O₃ varied a lot even if they were measured under the same conditions. The different synthetic methods or conditions may produce the same material with different morphologies (relative density, particle size) that result in different electrical properties. The comparison could be more plausible if the material was obtained in the same conditions. The bulk conductivity of Ba_{0.95}La_{0.05}Zr_{0.8}Y_{0.16}Zn_{0.04}O₃₋₅ still show a comparable value with Ba_{0.97}Zr_{0.77}Y_{0.19}Zn_{0.04}O₃ obtained in the same synthetic procedures [210]. The benefits of introducing lanthanum at the A-sites may not be so obvious as deficiency of barium is one factor that leads to the diminishing conductivity [210]. In the meantime, introduction of La³⁺ at the A-

sites will also decrease the oxygen vacancy concentration, thereby less proton defects can be formed (equation 5.2), possibly leading to a lower proton conductivity.

5.4. Conclusions

Doping potassium at the A-site can improve the water uptake of barium zirconates. The upper limit of solid solution formation on the A-sites for potassium is between 5 ~ 10 %. Introducing extra potassium leads to the formation of a second phase or YSZ impurities. Adding 4mol% ZnO at B-sites can significantly improve the sintering conditions and $Ba_{0.95}K_{0.05}Zr_{0.85}Y_{0.11}Zn_{0.04}O_{3-\delta}$ exhibited a conductivity of 2.2×10^{-3} Scm⁻¹ in wet 5% H₂ at 600°C. Fuel cells using $Ba_{0.95}K_{0.05}Zr_{0.85}Y_{0.11}Zn_{0.04}O_{3-\delta}$ as electrolyte reached a maximum power density of 7.7mWcm⁻² when platinum was used as cathode and anode. β -form barium zirconates can be synthesised by doping 5% La at the A-sites and pure $Ba_{0.95}La_{0.05}Zr_{0.8}Y_{0.2}O_{3-\delta}$ can be obtained by sol-gel process at a relatively lower temperatures (1300°C). Adding ZnO significantly assists sintering. However, the La doped barium zirconates only exhibit comparable conductivity with undoped ones, The benefits of introducing lanthanum at A-sites may not be so important as a result of barium deficiency.

CHAPTER 6 Conclusions and Future Work

Phosphoric acid is excellent proton conductor for the intermediate temperature ranges (100~300°C) and can be transformed into relevant salts or introduced into other organic/inorganic systems for the development of novel proton conductors.

Al(H₂PO₄)₃ was synthesised and showed a comparable proton conductivity with AlH₂P₃O₁₀ and AlH₃(PO₄)₂•3H₂O which is in the range of 10⁻⁶~10⁻⁷ S/cm. However, the conductivity can be greatly improved after introducing even 0.7% more H₃PO₄. The Al(H₂PO₄)₃-H₃PO₄ composite demonstrated a stable conductivity measured during 100 hours at 175°C and withstood several thermal cycles. Pure SnP₂O₇ synthesised by our method is not a good proton conductor, high conductivity was only achieved when excess amount of H₃PO₄ was used during synthesis. Solid State ³¹P NMR confirmed the residual phosphoric acid within the composites even with samples which underwent high temperature treatment. A thin amorphous phase was observed under HRTEM conditions for these samples with non-stoichiometric Sn:P ratios. The remarkable high conductivity for SnP₂O₇-H₃PO₄ composites was probably attributed to the residual acid rather than SnP₂O₇ itself. The composites exhibited a stable conductivity at 250°C in the measured time scale. Based on this observation, nano-sized BPO₄-H₃PO₄ composites and presented a high conductivity independent of humidity. Stable conductivity was also observed for more than 100 hours at 250°C.

Thin, soft membrane can be fabricated after introducing PTFE into the BPO₄-H₃PO₄ systems. The BPO₄-H₃PO₄-PTFE organic-inorganic systems showed practical stable proton conductivity for an extended temperature range (room temperature to 300° C). Fuel cells based on BPO₄-H₃PO₄-PTFE composites as electrolyte exhibited a maximum power density 320mW/cm² and a maximum current density of 1.9 A/cm² at 200° C. Increasing operating temperature was not beneficial to the fuel cell performance when H₂ was used as fuel but can improve the fuel cell performance when methanol was supplied as fuels. A maximum current of 300mA/cm² and power density of 40mW/cm² at 275° C were observed when 3M methanol was used in the cell.

 $H_3PW_{12}O_{40}$ - xH_3PO_4 hybrids were also synthesized and exhibited cubic symmetries. The unit cell was slightly enlarged when phosphoric acid was introduced. Solid state ³¹P NMR suggested residual phosphoric acid and the strong interactions between H_3PO_4 and $H_3PW_{12}O_{40}$. The conductivity of the hybrids showed a systematic increase with an increase of phosphoric acid. Although the decrease of conductivity was still observable at high temperatures due to the dehydration, the hybrids demonstrated much higher conductivity than pure $H_3PW_{12}O_{40}$ • xH_2O_{40}

under ambient conditions. A fuel cell based on $H_3PW_{12}O_{40}-3H_3PO_4$ hybrids exhibited a peak power density of 2.7mW/cm² at 0.3V at room temperatures. To overcome the solubility problem encountered with $H_3PW_{12}O_{40}-3H_3PO_4$ hybrids, $(NH_4)_3PW_{12}O_{40}-xH_3PO_4$ hybrids were synthesised. The hybrids also had an enlarged unit cell and phosphoric acid was believed to be preserved in the micropores of $(NH_4)_3PW_{12}O_{40}$. Although $(NH_4)_3PW_{12}O_{40}$ per se is not a good proton conductor, $(NH_4)_3PW_{12}O_{40}-xH_3PO_4$ hybrids exhibited a improved conductivity and the highest conductivity 0.14S/cm was achieved at $170^{\circ}C$ for $(NH_4)_3PW_{12}O_{40}-10H_3PO_4$ hybrids in air. Such high conductivity could give rise to broad potential applications such as fuel cells and worthy of future study.

Persovskites based on $BaZrO_3$ have demonstrated good stability over $BaCeO_3$, which undergoes decomposition in the presence of CO_2 or moistures. The conductivity, however, is significantly lower due to the refractory nature of $BaZrO_3$. Introducing other element such as potassium and lanthanum at A-sites was investigated.

Doping potassium at the A-site can improve the water uptake of barium zirconates. The upper limit of solid solution formation on the A-sites for potassium is between 5 ~ 10 %. Introducing extra potassium leads to the formation of second phase or YSZ impurities. Adding 4mol% ZnO at B-sites can significantly improve the sintering conditions and $Ba_{0.95}K_{0.05}Zr_{0.85}Y_{0.11}Zn_{0.04}O_{3-\delta}$ exhibited a conductivity of 2.2×10^{-3} Scm⁻¹ in wet 5% H₂ at 600°C. Fuel cells using $Ba_{0.95}K_{0.05}Zr_{0.85}Y_{0.11}Zn_{0.04}O_{3-\delta}$ as electrolyte reached a maximum power density of 7.7mWcm⁻² when platinum was used as cathode and anode.

β-form barium zirconates can be synthesised by doping 5% La at the A-sites and pure $Ba_{0.95}La_{0.05}Zr_{0.8}Y_{0.2}O_{3-\delta}$ can be obtained by sol-gel process at a relatively lower temperatures (1300°C). Adding ZnO significantly assists sintering. However, the La doped barium zirconates only exhibit comparable conductivity with undoped ones, The benefits of introducing lanthanum at the A-sites may not be so important as a result of barium deficiency.

Our future work will focus on optimization of the existing proton conducting systems such as $BPO_4-H_3PO_4-PTFE$ organic-inorganic systems and manufacture of fuel cell stacks. We will also continue our previous work on developing novel proton conductors. Several organic and inorganic materials such as acceptor doped Ba_2YNbO_6 and organic-inorganic $BPO_4-H_3PO_4-PBI$ systems will be investigated and their potential applications will also be explored.

Reference

[2] L.R. David, Handbook of Chemistry and Physics, 76th edition

[3] W.R. Groves, Philos. Mag. 14 (1839) 127-130

[4] C. Yang, P. Costamagna, S. Srinivasan, J. Benziger, A.B. Bocarsly, Journal of Power Source 103 (2001) 1-9

[5] T. Uda, D.A. Boysen, C.R.I. Chisholm, S.M. Haile, Electrochemical and Solid-State Letters, 9 (6) A261-A264

[6] N. Sammes, R. Bove, K. Stahl, Current Opinion in Solid State and Materials Science 8 (2004) 372-378

[7] J.H. Hirschenhofer, D.B. Stauffer, R.R. Engleman, M.G. Klett, Fuel Cell Handbook Fourth Edition.

[8] Q.F. Li, R.H. He, J.O. Jensen, N.J. Bjerrum, Chem. Mater. (2003) 15 4896-4915

[9] M. Ghouse, H. Abaoud, A. Al-Boeiz, M. Abdulhaidi, Applied Energy 60 (1998) 153-167

[10] B.C.H. Steele, Nature 400 (1999) 619-621

[11] A. Atkinson, S. Barnett, R.J. Gorte, J.T.S. Irvine, A.J. Mcevoy, M. Mogensen, S.C. Singhal, J. Vohs, Nature Materials 3 (2004) 17-27

[12] H. Iwahara, Solid State Ionics 77 (1995) 289-298

[13] K. D. Kreuer, Chem.Mater. (1996) 8 610-641

[14] Van Grotthuss, C. J. D. Ann, Chim. (1806) 58 54

[15] K. D. Kreuer, A. Rabenau, W. Weppner, Angew. Chem. Int. Ed. Engl. 21 (1982)

[16] K. D. Kreuer, S. J. Paddison, E. Spohr, M. Schuster, Chem. Rev. (2004) 104 4637-4678

[17] M. Eigen, L. De Maeyer, Proc. R. Soc. (London), Ser. A (1958) 247 505

[18] M. Eigen, Angew. Chem. (1963) 75 489

[19] P. Colomban, Proton conductors solid, membranes and gels-materials and devices,

Cambridge University Press, New York (1992).

[20] T. Dipel, K. D. Kreuer, J. C. Lassegues, D. Rodriguez, Solid State Ionics (1993) 61 41

[21] K. D. Kreuer, S. J. Paddison, E. Spohr, M. Schuster, Chem. Rev. (2004) 104 4637-4678

[22] A. L. Laskar, S. Chandra, Superionic Solid and Solid Electrolytes Recent Trends (1989) ISBN: 0-12-437075-6

[23] J. Maier, Angew. Chem. Int. Ed. Engl (1993) 32 313-335

[24] I. A. Stenina, I. Y. Pinus, A. I. Rebrov, A. B. Yaroslavtsev, Solid State Ionics 175 (2005) 445 [25] A. B. Yaroslavtsev, Solid State Ionics 176 (2005) 2935-2940

[26] A.R. West, Solid State Chemistry and Its Applications, John Wiley & Sons Ltd. (1984)

[27] P.S. Nicholson, M. Nagai, K. Yamashita, M. Sayer and M. F. Bell, J. Am. Ceram. Soc. 15 (1985) 317-326.

[28] T. Tsurumi, H. Ikawa, M. Ishimori, K. Urabe and S. Udagawa, Solid State Ionics 21 (1986) 31-35.

[29] A. Matsuda, Y. Nono, T. Kanzaki, K. Tadanaga, M. Tatsumisago, T. Minami, Solid State Ionics 145 (2001) 135-140

[30] Y. Piffard, M. Dion, M. Tournoux, H. Aribart, Solid State Ionics 7 (1982) 81

[31] U. Chowdhry, J. R. Barkley, A. D. English, A. W. Sleight, Mater. Res. Bull. 17 (1982) 917

[32] N. Knudsen, E. Krogh Anderson, I. G. Krogh Anderson, E. Skou, Solid State Ionics 28/30 (1988) 627

[33] M. T. Colomer, Adv. Mater. (2006) 18 371-374

[34] M. Yamada, D-L. Li, I. Honma, H-S. Zhou, J. AM. CHEM. SOC (2005) 127 13092-13093

[35] H. Ikawa, in: Ph. Colomban (Ed.), Proton Conductors, Cambridge Univ. Press, Cambridge, 1992, p. 190

[36] E. Krogh Andersen, I. G. Krogh Andersen, E. Skou, Solid State Ionics 27 (1988) 181

[37] M. Casciola, u. Costantino, Solid State Ionics 20 (1986) 69

[38] G. Alberti, M. Casciola, S. Cavalaglio, R. Vivani, Solid State Ionics 125 (1999) 91-97

- [39] O. Nakamura, T. Kodama, I. Ogino, Y. Miyake, Chemistry Letters, 1 17-18 (1979)
- [40] T. Kasuga, M. Nakano, M. Nogami, Adv. Mater. (2004) 14 1490-1492

^[1] B.C.H Steele, A. Heinzel, Nature, 414, 345-352

[41] S.M. Haile, C.R.I. Chisholm, K. Sasaki, D.A. Boysen, T. Uda, Faraday Discuss, (2007) 17 17-39
[42] S.M. Haile, D.A. Boysen, C.R.I. Chisholm, R.B. Merle, Nature, 410, 910-913

[43] R.B. Merle, C.R.I. Chisholm, D.A. Boysen, S.M. Haile, Energy & Fuels, (2003), 17, 210-215 [44] T. Matsui, T. Kukino, R. Kikuchi, K. Eguchi, Electrochemical and Solid-State Letters, 8(5) A256-A258 (2005)

[45] R. Borup, J. Meyers, B. Pivovar, Y.S. Kim, R. Mukundan, N. Garland, D. Myers, M. Wilson, F. Garzon, D. Wood, P. Zelenay, K. More, K. Stroh, T. Zawodzinski, J. Boncella, J.E. McGrath, M.

Inaba, K. Miyatake, M. Hori, K. Ota, Z. Ogumi, S. Miyata, A. Nishikata, Z. siroma, Y. Uchimoto, K. Yasuda, K-I. Kimijima, N. Iwashita, Chem. Rev. (2007) 107 3904-3905

[46] M.A. Hickner, H. Ghassemi, Y.S. Kim, B.R. Einsla, J.E. McGrath, Chem. Rev. (2004) 104 4587-4612

[47] L. Li, J. Zhang, Y.X. Wang, Journal of Membrane Science 226 (2003) 159-167
[48] C. Yang, S. Srinivasan, A.B. Bocarsly, S. Tulyani, J.B. Benziger, Journal of Membrane Science 237 (2004) 145-161

[49] R.H. He, Q.F. Li, G. Xiao, N.J. Bjerrum, Journal of Membrane Science 226 (2003) 169-184 [50] Y.-L. Ma, J.S. Wainright, M.H. Litt, R.F. Savinell, Journal of The Electrochemical Society, (2004) 151 (1) A8-A16

[51] Y.L. Ma, J.S. Wainright, M.H. Litt, R.F. Savinell, Journal of The Electrochemical Society 151 (1) A8-A16 (2004)

[52] P. Krishnan, J.S. Park, C.S. Kim, Journal of Membrane Science 279 (2006) 220-229
[53] A. Bozkurt, W.H. Meyer, Journal of Polymer Science: Part B: Polymer Physics, 39 1987-1994 (2001)

[54] L.S. Ng, A.A. Mohamad, Journal of Power Sources 163 (2006) 382-385

[55] S.C. Yap, A.A. Mohamad, Electrochemical and Solid-State Letters 10 (6) A139-A141 (2007) [56] K. Tadanaga, H. Yoshida, A. Matsuda, T. Minami, M. Tatsumisago, Solid State Ionics 176 (2005) 2997-2999

[57] F. Bauer, M. willert-Porada, Journal of Power Sources 145 (2005) 101-107

[58] Y.-Z. Fu, A. Manthiram, Journal of The Electrochemical Society 154 (1) B8-B12 (2007)

[59] Z.-G. Shao, H-F. Xu, M-Q. Li, I.-M. Hsing, Solid State Ionics 177 (2006) 779-785

[60] P. Choi, N. H. Jalani, R. Datta, Journal of The Electrochemical Society 152 (8) A1548-A1554 (2005)

[61] Y-T. Kim, K. H. Kim, M-K. Song, H-W. Rhee, Current Applied Physics 6 (2006) 612-615

[62] M.Y. Jang, Y. Yamazaki, Journal of Power Sources 139 (2005) 2-8

[63] U. Costantino, M. Casciola, G. Pani, D. J. Jones, J. Roziere, Solid State Ionics 97 (1997) 261-267

[64] S. Reichman, A. Ulus, E. Peled, Journal of The Electrochemical Society 154 (3) B327-B333 (2007)

[65] Y. Jin, J-C. Diniz da Costa, G. Q. Lu, Solid State Ionics 178 (2007) 937-942

[66] C.S. Ramya, S. Selvasekarapandian, T. Savitha, G. Hirankumar, R. Baskaran, M.S.

Bhuvaneswari, P.C. Angelo, European Polymer Journal 42 (2006) 2672-2677

[67] M-Q, Li, H-M. Zhang, Z-G. Shao, Electrochemical and Solid-State Letters 9 (2) A60-A63 (2006)

[68] M. I. Ahmad, S. M. J. Zaidi, S. U. Rahman, Desalination 193 (2006) 387-397

[69] H. Iwahara, T. Esaka, H. Uchida, N. Maeda, Solid State Ionics 3/4 (1981) 359.

[70] T. Higuchi, S. Yamaguchi, K. Kobayashi, S. Shin, T. Tsukamoto, Solid State Ionics 162-163 (2003) 121.

[71] S. Yamaguchi, K. Kobayashi, T. Higuchi, S. Shin, Y. Iguchi, Solid State Ionics 136-137 (2000) 305.

[72] K. Kabayashi, S. Yamaguchi, Y. Iguchi, Solid State Ionics 108 (1998) 355.

[73] S. Yamaguchi, N. Yamada, Solid State Ionics 162-163 (2003) 23.

[74] M. Oishi, K. Yashiro, K. Sato, J. Mizusaki, N. Kitamura, K. Amezawa, T. Kawada, Y.

Uchimoto, Solid State ionics 179 (2008) 529.

[75] S. Yamaguchi, K. Nakamura, T. Higuchi, S. Shin, Y. Iguchi, Solid State Ionics 136-137 (2000) 191.

[76] N. Zakowsky, S. Williamson, J.T.S. Irvine, Solid State Ionics 176 (2005) 3019.

[77] S.V. Bhide, A.V. Virkar, J. Electrochem. Soc. 146 (12) (1999) 4386.

[78] S.V. Bhide, A.V. Virkar, J. Electrochem. Soc. 146 (6) (1999) 2038.

[79] K. Katahira, Y. Kohchi, T. Shimura, H. Iwahara, Solid State Ionics 138 (2000) 91.

[80] C.D. Zuo, S.W. Zha, M.L. Liu, M. Hatano, M. Uchiyama, Adv. Mater. 18 (2006) 3318.

[81] K.D. Kreuer, St. Adams, W. Munch, A. Fuchs, U. Klock, J. Maier, Solid State Ionics 145 (2001) 295.

[82] H. Iwahara, Y. Asakura, K. Katahira, M. Tanaka, Solid State Ionics 168 (2004) 299.

[83] J.D. Atwood, Inorganic Reactions and Methods, Formation of Ceramics (Inorganic Reactions and Methods). New York: Wiley-VCH

[84] L.E. Smart, E.A. Moore, Solid State Chemistry (third edition) An introduction, Taylor & Francis Group, LLC (2005)

[85] E. Barsoukov, J.R. Macdonald, Impedance Spectroscopy Thery, Experiment, and Applications Second Edition, John Wiley & Sons, Inc

[86] J.T.S. Irvine, D.C. Sinclair and A. R. West, Advance Materials (1990) 3 133-138

[87] M.C. Verbraeken, Ph.D thesis.

[88] http://www.purdue.edu/REM/rs/sem.htm

[89] http://www4.nau.edu/microanalysis/Microprobe-SEM/Signals.html

[90] http://en.wikipedia.org/wiki/Energy-dispersive_X-ray_spectroscopy

[91] http://astronomy.nmsu.edu/jlevans/seminarSpr07/transmission_electron_microscope.png

[92] A.D. Cross, An introduction to practical infra-red spectroscopy (1964) Butterworth & CO. (Publisher) Ltd. London

[93] K.D. Kreuer, Chem. Mater. (1996) 8 610-641

[94] K.D. Kreuer, Solid State ionics 125 (1999) 285-302

[95] M. Davies, Infra-red Spectroscopy and Molecular Structure, Elsevier Publishing Company (1963)

[96] Y.-I, Park, J.-D. Kim, M. Nagai, Journal of Materials Science Letters 19 (2000) 1591-1594 [97] M. Davies, Infra-red Spectroscopy and Molecular Structure, Elsevier Publishing Company (1963)

[98] K.J.D. MacKenzie, M.E. Smith, Multinuclear Solid-State NMR of Inorganic Materials, Elsevier Science Ltd. (2002)

[99] R.B. Merle, C.R.I. Chisholm, D.A. Boysen, S.M. Haile, Energy & Fuels, (2003), 17, 210-215 [100] D.A. Boysen, S.M. Haile, H. Liu, R.A. Secco, Chem. Mater. 15 (2003) 727.

[101] D. Yoire, Bull. Soc. Chim. Fr. (1961) 2277.

[102] R. Baies, V. Pralong, V. Caignaert, B. Raveau, Materials Research Bulletin 41 (2006) 1170. [103] S.K. Rishi, B.M. Kariuki, N.J. Checker, J. Godber, A.J. Wright, ChemComm (2006) 747

[104] M. Tsuhako, K. Hasegawa, T. Matsuo, I. Motooka, M. Kobayashi, Bulletin of the Chemical Society of Japan 48 (1975) 1830.

[105] A. Matsuda, T. Tezuka, Y. Nono, K. Tadanaga, T. Minami, M. Tatsumisago, Solid State Ionics 176 (2005) 2899.

[106] Z.Y. Kanene, Z.A. Konstant, V.V. Krasnikov. Inorg. Mater. 21 (1985) 1354.

[107] A.K. Pathak, T. Mukherjee, D.K. Maity, J. Phys. Chem. A 112 (2008) 3399

[108] H.-J. Han, D.-P. Kim, Journal of Sol-Gel Science and Technology 26 (2003) 223

[109] Z.-Y. Li, Y. Liu, H.-T. Liu, P. He, Q. Zhang, J.-H. Li, Solid State Ionics 177 (2006) 1281.

[110] Y. Tanaka, S. Takano and M. Miyayama, Journal of the Ceramic Society of Japan, (2003) 111, 323

[111] S.-W. Chuang, S. L.-C. HSU, J. Polym. Sci. Part A Polym. Chem 44 (2006) 4508.

[112] Y. Aihara, A. Sonai, M. Hattori, K. Hayamizu, J. Phys. Chem. B 110 (2006) 24999.

[113] Y. Aihara, A. Sonai, J. Power Sources 163 (2006) 60.

[114] J. Otomo, T. Tamaki, S. Nishida, S. Wang, M. Ogura, T. Kobayashi, C.-j. Wen, H.

Nagamoto, H. Takahashi, J. Appl. Electrochem. 35 (2005) 865.

[115] M. Casciola, F. Marmottini, A. Peraio, Solid State Ionics 61 (1993) 125.

[116] G. Alberti, M. Casciola, Solid State Ionics 97 (1997) 177.

[117] K.-H. Yoon, B.-D. Yang, J. Power Sources 124 (2003) 47.

[118] R.-H. Song, S. Dheenadayalan, D.-R. Shin, J. Power Sources 106 (2002) 167.

[119] M. Neergat, A. K. Shukla, J. Power Sources 102 (2001) 317.

[120] M. Nagao, T. Kamiya, P. Heo, A. Tomita, T. Hibino, M. Sano, J. Electrochem. Soc. 153 (8) A1604-A1609 (2006)

[121] P. Heo, M. Nagao, T. Kamiya, M. Sano, A. Tomita, T. Hibino, J. Electrochem. Soc. 154 (1) B63-B67 (2007)

[122] S.W. Tao, Solid State Ionics, 180 (2009) 148–153.

[123] R. Lan, S.W. Tao,, J. Alloys Compd., 486 (2009) 380–385.

[124] X.X. Xu, S.W. Tao, J.T.S. Irvine, Solid State Ionics, (2009) 180 343-350

[125] L. Korosi, S. Papp, V. Meynen, P. Cool, E. F. Vansant, I. Dekany, Colloids and Surfaces A: Physicochem. Eng. Aspects 268 (2005) 147-154

[126] C. H. Huang, O. Knop, D. A. Othen, F. W. D. Woodhams, R. A. Howie, Can. J. Chem. 53 (1975) 79

[127] R. K. B. Gover, N. D. Withers, S. Allen, R.L. Withers, J.S.O. Evans, J. Solid State Chem. 166 (2002) 42

[128] P.S. Attidekou, P.A. Connor, P. Wormald, D.P. Tunstall, S.M. Francis, J.T.S. Irvine, Solid State Ionics 175 (2004) 185-190

[129] M. Behm, J.T.S. Irvine, Electrochimica Acta, 47 (2002) 1727-1738

[130] R.K. Brow, R.J. Kirkpatrick, G.L. Turner, Journal of Non-crystalline solids, 116 39-45 (1990)

[131] G. Alberti, M. Casciola, U. Costantino, A. Peraio, T. Rega, J. Mater. Chem. (1995) 5(11) 1809-1812

[132] J. Chen, M. Liu, H. Pan, S. Lin, X. Xin, Journal of Solid State Chemistry 159 130-133 (2009)
 [133] A. Tarafdar, A. B. Panda, N. C. Pradhan, P. Pramnanik, Microporous and Mesoporous
 Materials 95 (2006) 360-365

[134] H-N Kim, S. W. Keller, T. E. Mallouk, Chem. Mater. (1997) 9 1414-1421

[135]N. Zouari, M. Mnif, H. Khemakhem, T. Mhiri, A. Daoud, Solid State Ionics 110 (1998) 269-275

[136] N. Essayem, A. Holmqvist, P.Y. Gayraud, J.C. Vedrine, Y. Ben Taarit, Journal of Catalysis 197 273-280 (2001)

[137] Y.-I. Park, J.-D. Kim, M. Nagai, Journal of Materials Science Letters 19 (2000) 1591-1594 [138] S.W. Tao, Solid State Ionics, 180 (2009) 148–153.

[139] M. Nagao, A. Takeuchi, P. Heo, T. Hibino, M. Sano, A. Tomita, Electrochemical and Solid State Letters 9 (3) A105-A109 (2006)

[140] A. Tomita, N. Kajiyama, T. Kamiya, M. Nagao, T. Hibino, Journal of The Electrochemical Society 154 (12) B1265-B1269 (2007)

[141] X. Chen, C. Wang, E.A. Payzant, C. Xia, D. Chu, Journal of The Electrochemical Society, 155 (12) B1264-B1269 (2008)

[142] P. Staiti, M. Minutoli, F. Lufrano, Electrochim. Acta 2002 47 2795-2800

[143] S.D. Mikhailenko, J. Zaidi and S. Kaliaguine, J. Chem. Soc., Faraday Trans., (1998) 94 1613-1618

[144] S.D. Mikhailenko, S.M.J. Zaidi, S. Kaliaguine, Catalysis Today 67 (2001) 225-236

[145] Z. H. Li, Y. C. Wu, P. Z. Fu, S. L. Pan, C. T. Chen, Journal of Crystal Growth 270 (2004) 486-490

[146] I. S. Mulla, V. A. Chaudhary, K. Vijayamohanan, Sensors and Actuators A 69 (1998) 72-76 [147] H. L. Goltz, J. B. Moffat, Journal of Catalysis 22 (1) 81 (1971)

[148] J. B. Moffat, A. S. Riggs, Journal of Catalysis, 42 (3) 388-397 (1976)

[149] M. giorgini, P. F. Marconi, G. Monzani, R. Simula and R. Tartarelli, Journal of Catalysis, 24 (3) 521-528 (1972)

[150] J. B. Moffat, J. F. Neeleman, Journal of Catalysis, 31 (2) 274-277 (1973)

[151] M. Schmidt, B. Ewald, Y. Prots, R. Cardoso-Gil, M. Armbruster, I. Loa, L. Zhang, Y. X.

Huang, U. Schwarz, R. Kniep, Zeitschrift Fur Anorganische Und Allgemeine Chemie 630 (5) 655-662 (2004)

[152] S. Sato, M. Hasegawa, T. Sodesawa, F. Nozaki, Bulletin of The Chemical Society of Japan 64 (2) 516-522 (1991)

[153] C. Keary, J. B. Moffat, Journal of Colloid and Interface Science 154 (1) 8-16 (1992)

[154] A. Adamczyk, M. Handke, Journal of Molecular Structure 555 (2000) 159-164

[155] R. D. Shannon and C. T. Prewitt, Acta Cryst. B25 (1969) 925.

[156] P. Kmecl, P. Bukovee, Acta Chim. Slov. 46 (2) 161-171 (1999)

[157] Y. G. Jin, S. Z. Qiao, J. C. Diniz da Costa, B. J. Wood, B. P. Ladewig, G. Q. Lu, Advance Functional Materials 17 3304-3311 (2007)

[158] Y. M. Li, K. Hinokuma, Solid State Ionics 150 (2002) 309-315

[159] S. D. Mikhailenko, J. Zaidi, S. Kaliaguine, Journal of the Chemical Society-Faraday Transactions 94 (11) 1613-1618 (1998)

[160] G. Alberti, M. Casciola, A. Connadio, P. Piaggio, M. Pica, M. Sisani, Solid State Ionics 176 (2005) 2893-2898

[161] A. Matsuda, H. Honjo, K. Hirata, M. Tatsumisago, T. Minami, Journal of Power Sources 77 (1) 12-16 (1999)

[162] A. B. Yarslavtsev, Solid State Ionics, 176 (2005) 2935-2940

[163] T. Kukino, R. Kikuchi, T. Takeguchi, T. Matsui, K. Eguchi, Solid State Ionics 176 (2005) 1845-1848

[164] J-D. Kim, S. Hayashi, T. Mori, I. Honma, Electrochimica Acta 53 (2007) 963-967

[165] Y. I. Park, J. D. Kim, M. Nagai, Journal of materials Science Letters 19 (2000) 1591-1594

[166] R.-H. Songa, S. Dheenadayalanb, D.-R. Shin, *J. Power Sources* **2002**, *106*, 167–172.

[167] J-H. Park, Physical Review B 69 054104 (2004)

[168] P. Kmecl and P. Bukovee, Acta Chim. Slov. (1999) 46 (2) 161-171

[169] EG&G Services Parsons, Inc. Fuel Cell Handbook Fifth Edition October 2000 U.S.A ISBN No. 0-89934-368-6

[170] T. Kenjo, Y. Ogawa, Solid State Ionics 76 (1995) 29-34

[171] V. Neburchilov, J. Martin, H. J. Wang, J. J. Zhang, J. Power Sources 2007, 169, 221-238.

[172] A. Corma, Chem. Rev. 1995 95 559-614

[173] H. Firouzabadi, N. Iranpoor, A. Khoshnood, Catalysis Communications 9 (2008) 529-531

[174] T. Okuhara, N. Mizuno, M. Misono, Advances in Catalysis 41 1996 113-252

[175] B.M. Devassy, G.V. Shanbhag, F. Lefebvre, W. Bohringer, J. Fletcher, S.B. Halligudi,

Journal of Molecular Catalysis A: Chemical 230 (2005) 113-119

[176] M.M. Amini, A. Shaabani, A. Bazgir, Catalysis Communications 7 (2006) 843-847

[177] J.-Deok, Kim, S. Hayashi, T. Mori, I. Honma, Electrochimica Acta 53 (2007) 963-967

[178] D.P. Padiyan, S.J. Ethilton, K. Paulraj, Cryst. Res. Technol. 35 2000 87-94

[179] P. Staiti, S. Hocevar, N. Giordano, Int. J. Hydrogen Energy 22 1997 809-814

[180] N. Giordano, P. Staiti, S. Hocevar, A.S. Arico, Electrochimica Acta 41 (1996) 397-403

[181] J.-D. Kim, S. Hayashi, T. mori, I. Honma, Electrochimica Acta 53 (2007) 963-967

[182] W.-B. Jang, S. Choi, S. Lee, Y. Shul, H. Han, Polymer Degradation and Stability 92 (2007) 1289-1296

[183] L. Li, Y.-X. Wang, Journal of Power Sources 162 (2006) 541-546

[184] U. Mioc, R. Dimitrijevic, M. Davidovic, Z. Nedic, M. Mitrovic, P.H. Colomban, J. Mater. Sci. 29 3705 (1994)

[185] A. Kremenovic, A. Spasojevic-de Bire, F. Bouree, P. Colomban, R. Dimitrijevic, M. Davidovic, U.B. Mioc, Solid State Ionics 150 431 (2002)

[186] A. Hardwick, P. Dickens. R. Slade, Solid State Ionics 13 345 (1984)

[187] L. Marosi, E. Escalona-Platero, J. Cifre, C. Otero-Arean, J. Mater. Chem. 10 1949 (2000)

[188] S. Uchida, K. Inumaru, M. Misono, J. Phys. Chem. B (2000) 104 8108-8115

[189] J. Deleplanque, R. Hubaut, P. Bodart, M. Fournier, A. Rives, Applied Surface Science 255 (2009) 4897-4901

[190] S.T. Gregg, M.M. Tayyab, J. Chem. Soc. , Faraday Trans., I 74 (1978) 348

[191] M. Nasikin, R. Nakanura, H. Niiyama, Chemistry Letters, 209-212 (1993)

[192] R. Belanger, J.B. Moffat, Applied Catalysis B: Environmental 13 (1997) 167-173

[193] R. Belanger, J.B. Moffat, Langmuir, (1996) 12 2230-2238

[194] K, Inumaru, Catalysis Surveys from Asia, 10 151-160 (2006)

[195] T. Ito, K. Inumaru, M. Misono, Chem. Mater. 13 824-831 (2001)

[196] S.D. Mikhailenko, S. Kaliaguine, J.B. Moffat, Solid State Ionics 99 (1997) 281-286

[197] S.-W. Chuang and S. L.-C. HSU, J. Polym. Sci. Part A Polym. Chem, 2006, 44, 4508.

[198] T. Okuhara, Applied Catalysis A: General, 256 (2003) 213-224

[199] N. Essayem, A. Holmqvist, P.Y. Gayraud, J.C. Vedrine, Y. Ben Taarit, Journal of Catalysis 197 273-280 (2001)

[200] R.J. Cava, B. Batlogg, R.B. van Dover, D.W. Murphy, S. Sunshine, T. Siegrist, J.P.

Remeika, Physical Review Letters (1987) 58 16 1676-1679

[201] S. Jin, T.H. Tiefel, M. Mccormack, R.A. Fastnacht, R. Ramesh, L.H. Chen, Science (1994) 264 5157 413-415

[202] R.E. Cohen, Nature (1992) 358 6382 136-138

[203] S.W. Tao, J.T.S. Irvine, Nature Materials (2003) 2 5 320-323

[204] S.W. Tao, J.T.S. Irvine, J. Electrochem. Soc. 151 (2) A252-A259 (2004)

[205] J.C. Ruiz-Morales, J. Canales-Vazquez, C. Savaniu, D. Marrero-Lopez, W.Z. Zhou, J.T.S. Irvine, Nature (2006) 439 7076 568-571

[206] K.H. Ryu and S.M. Haile, Solid State Ionics 125 (1999) 355.

[207] M.A. Azimova, S. McIntosh, Solid State Ionics 180 (2009) 160.

[208] S.B.C. Duval, P. Holtappels, U.F. Vogt, E. Pomjakushina, K. Conder, U. Stimming, T. Graule, Solid State Ionics 178 (2007) 1437.

[209] P. Babilo, T. Uda, S.M. Haile, J. Mater. Res. 22 (2007) 1322.

[210] S.W. Tao, J.T.S. Irvine, J. Solid State Chem. 180 (2007) 3493.

[211] K.D. Kreuer, Solid State Ionics 97 (1997) 1.

[212] A.S. Patnaik, A.V. Virkar, J. Electrochem. Soc. 154 (7) (2006) A1397.

[213] D.R. Lide, Handbook of Chemistry and Physics, 76th ed., CRC Press, 1995-96

[214] C.D. Savaniu, J. Canales-Vazquez, J.T.S. Irvine, J. Mater. Chem. 15 (2005) 598.

[215] R.D. Shannon, C.T. Prewitt, Acta Cryst. B25 (1969) 925.

[216] S.W. Tao, J.T.S. Irvine, Adv.Matr. 18 (2006) 1581

[217] A.K. Azad, C. Savaniu, S.W. Tao, S. Duval, P. Holtappels, R.M. Ibberson, J.T.S. Irvine,

Journal of Materials Chemistry (2008) 18 3414-3418

[218] K. Nomura, H. Kageyama, Solid State Ionics 178 (2007) 661-665

Associated Publications

Proton conductivity of $Al(H_2PO_4)_3-H_3PO_4$ composites at intermediate temperature Xiaoxiang Xu, Shanwen Tao, John T.S. Irvine

(Solid State Ionics 180 (2009) 343–350)

Proton conductivity of potassium doped barium zirconates Xiaoxiang Xu, Shanwen Tao, John T.S. Irvine

(Journal of Solid State Chemistry 183 (2010) 93–98)

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