



Review article

A review on synthesis and characterization of solid acid materials for fuel cell applications



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H I G H L I G H T S

- Solvent-induced precipitation is the fastest method to produce solid acids.
- Solvent-induced precipitation produces polycrystalline solid acid powder.
- Isothermal evaporation technique produces single crystals solid acid.
- Decomposition is observed in solid acids heated lower than $0.3\text{ }^{\circ}\text{C min}^{-1}$.
- Humidification is required to maintain long term fuel cell performance.

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Solid acids emerged as an electrolyte material for application in fuel cells due to their high protonic conductivity and stability at high temperatures between $100\text{ }^{\circ}\text{C}$ and $250\text{ }^{\circ}\text{C}$. This paper gives an overview of the different solid acid materials and their properties, such as high protonic conductivity and thermal stability, in relation to phase transitions and mechanisms of proton transport. Various solid acid synthesis methods including aqueous and dry mixing, electrospinning, sol-gel, impregnation and thin-film casting will be discussed, and the impact of synthesis methods on the properties of solid acids will be highlighted. The properties of solid acids synthesized as either single crystals and or polycrystalline powders were identified via X-ray diffraction, nuclear magnetic resonance, thermal analyses, optical microscopy and infrared spectroscopy. A selection of electrolyte-electrode assembly methods and the performance of solid acid fuel cell prototypes are also reviewed.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs), also known as hydrogen fuel cells, are fuel cells that require hydrogen and air to produce electricity based upon a simple reaction, the reverse of the electrolysis of water as given by the following equation:



The most important component of a PEMFC is the electrolyte-electrode assembly (EEA) where chemical reactions take place and electricity is produced. A perfluorosulphonic acid polymer membrane named Nafion[®] was developed by Dupont and has been used as commercial membrane in PEMFCs thanks to its stability and high protonic conductivity, ranging from $9 \times 10^{-3}\text{ S cm}^{-1}$ to $1.2 \times 10^{-1}\text{ S cm}^{-1}$ [1,2] at PEMFC operating temperatures from $80\text{ }^{\circ}\text{C}$ to $100\text{ }^{\circ}\text{C}$ [3]. However, keeping Nafion[®] hydrated to facilitate proton conduction requires an external humidification system during operation, which increases operating costs because of the additional complexity of the system. Furthermore, the operation temperature of a PEMFC with a Nafion[®] membrane cannot exceed $100\text{ }^{\circ}\text{C}$ to keep the membrane hydrated, so other issues arise related to the low operating temperature, such as anode catalyst

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inefficiency and catalyst intolerance to carbon monoxide [4].

Recently, alternatives to polymer membranes have been developed. A solid acid, caesium hydrogen sulphate, CsHSO₄ was first introduced by Haile et al. [4] as an electrolyte material that does not require hydration, an appealing property for application in fuel cells. This solid acid enables fuel cells to operate at higher temperatures and eliminates the issues of catalyst inefficiency and intolerance to carbon monoxide that are associated with low-temperature PEMFCs. It also allows the use of cheaper alternative catalysts such as non-platinum alloy and transition metal oxides [5]. Without costly temperature and humidity control hardware, solid acid fuel cell systems are much less complex [4].

Solid acids are proton conducting materials produced by combining any monovalent alkali metal cations or divalent earth metal cations with tetrahedral oxyanions. Caesium dihydrogen phosphate, CsH₂PO₄ (CDP), and caesium hydrogen sulphate, CsHSO₄ (CHS), are relatively well-characterized solid acids with high proton conductivity values of $2.2 \times 10^{-2} \text{ S cm}^{-1}$ at 240 °C [6] and $4 \times 10^{-2} \text{ S cm}^{-1}$ at 200 °C [7], respectively. Solid acids are usually white powdery substances and are also known as acid salts due to their properties, which are transitional from those of acids and salts, such as conductive due to the protons from the 'acid' structure but brittle like a salt [8,9]. Solid acids are generally soluble in water at room temperature and ductile at temperatures above 125 °C [4]. The property of solid acids that attracts the most attention is the high proton conductivity, also known as superprotonic property, where the conductivity increases by 2–3 orders of magnitude when heated to temperatures between 100 °C and 250 °C, which is accompanied by a phase transition [2]. The superprotonic behaviour of solid acids is closely related to the proton transport mechanism and phase transition of the material.

This review categorize solid acids into three classes that are single-salt solid acids, mixed-salt solid acids and solid acid composites. We highlight the properties of the solid acids including their thermal stability, conductivity values at superprotonic temperatures and proton transport mechanisms. We compile various solid acid synthesis methods and identify the impacts of synthesis methods on solid acid production and properties. The techniques used to characterize solid acid materials such as X-ray diffraction analysis, nuclear magnetic resonance spectroscopy, thermal analyses, electrochemical impedance spectroscopy, optical microscopy and Fourier transform infra-red spectroscopy are highlighted in this review. The performance of several solid acid fuel cell prototypes produced in other studies are summarized in this review along with the factors that affect fuel cell performance, including electrolyte-electrode assembly (EEA) methods, protonic conductivity of the electrolyte, thickness of the EEA, catalyst loading and humidification of fuels.

2. Solid acid materials and properties

Solid acids are classified according to the cation-oxyanion combinations and supporting materials such as oxides and polymers. The simplest form of solid acid is the single-salt solid acid, M_aH_b(XO₄)_c, where M is a monovalent or divalent metal cation, XO₄ is a tetrahedral oxy-anion, and a, b, and c are integers [9]. Previous studies as reviewed by Dupuis [2] have focused mostly on solid acids from Group I monovalent alkali metal cations Li⁺, Na⁺, K⁺, Rb⁺ and Cs⁺, transition metal cations Tl⁺ and ammonium (NH₄⁺) in combination with sulphate (SO₄²⁻), phosphate (PO₄³⁻), selenate (SeO₄²⁻) or arsenate (AsO₄³⁻) tetrahedral oxy-anions.

A common behaviour that has emerged in the literature on Group I monovalent alkali metal dihydrogen phosphates is that larger cations stabilize the superprotonic behaviour of the solid acid [2]. The melting or decomposition temperature of the solid

acid increases from the smallest cation Li⁺ to the largest cation Cs⁺, with larger cations such as Rb⁺ and Cs⁺ exhibiting superprotonic conductivity at intermediate temperatures before they undergo melting. However, small cations such as K⁺, Na⁺ and Li⁺ do not exhibit the superprotonic behaviour because they melt at much lower temperatures compared with CDP and rubidium dihydrogen phosphate, RbH₂PO₄ (RDP) [2,9]. There have been discrepancies in the high temperature behaviour of solid acid CDP as compiled by Haile et al. [6]. Many studies [10–23] concluded that CDP is superprotonic at high temperatures, while others [24–26] disagreed due to observation of dehydration or decomposition of the solid acid at high temperatures.

Mixed- or multiple-salt solid acids are synthesized by mixing or combining more than one cation, oxyanion or both to achieve the desired properties of a PEMFC electrolyte. These mixed-salt solid acids are often, but not limited to, mixed MHXO₄-MH₂ZO₄ compounds (where X = S, Se; Z = P, As; M = Li, Na, K, NH₄, Rb, Cs) [27]. Mixed solid acids are also known as binary solid acid composites and exhibit properties superior to single-salt solid acids such as a wider temperature range for superprotonic conductivity and higher protonic conductivity at lower temperatures due to lower activation enthalpy [23,28–30]. Partial substitution with larger cations or tetrahedral oxy-anions increases hydrostatic pressure and induces superprotonic behaviour in solid acids [23].

The mechanical and thermal stability of solid acids can be enhanced by mixing oxide materials such as silica (SiO₂), zirconia (ZrO₂), titania (TiO₂) and alumina (Al₂O₃) with the solid acids. Also known as heterogeneous doping of solid acids, this mixing produces disordered systems at the interface of the solid acids and oxide materials, which enhances proton transport within the solid acid composite. Ponomareva et al. [31] found that heterogeneous doping of CHS with SiO₂ increases the proton conductivity of the (1-x)CsHSO₄/xSiO₂ composite in the low temperature region compared with pure CHS. A similar trend was observed for hydrogen sulphate solid acids with Rb and K cations. The conductivity of the solid acid increases by 1–3.5 orders of magnitude when mixed with hygroscopic oxides in the order Al₂O₃ < TiO₂ < SiO₂ [32]. High temperature thermoplastics such as perfluorinated polymers, polybenzimidazole (PBI), fluoroelastomers and polytetrafluoroethylene (PTFE) can also be added as binders to produce more flexible, less brittle solid acid electrolytes [33].

2.1. Proton transport mechanism

Proton transport within a medium is generally modelled by two different competing mechanisms, the vehicle transport mechanism and the Grotthus transport mechanism. In the vehicle transport mechanism, protons are being transported via the translational motion of a carrier molecule, such as the water molecule, H₂O [34]. The hydrogen ion attaches to a water molecule to produce a hydronium ion, H₃O⁺. The hydronium ion diffuses and the unprotonated water molecule counter diffuses which then enables the hydrogen ion to be transported across the medium. The diffusion rate of the proton carriers will determine the conductivity of the material [27,34]. Vehicle transport mechanism is usually described for proton transport in polymer membranes such as Nafion[®], where water is required to move protons across the membrane, indicating crucial hydration requirement for polymer membranes and the limitation of operating temperatures to less than 100 °C. Other than polymer membranes, the vehicle transport mechanism is also present in acidic aqueous solutions, acidic phosphates and phosphonates, heteropolyacids, water-containing compounds such as particle hydrates and xerogels, protonic β-aluminas and hydrated acidic polymers, as compiled by Kreuer [34].

The Grotthus transport mechanism consists of structural or

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