HIGH TEMPERATURE PROTON CONDUCTORS

Applications and Materials

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1. Liquid and Solid Electrolytes

Most of us are familiar with the use of electrolytes such as the aqueous sulphuric acid in lead accumulators and the alkaline solutions used for electrolytic production of hydrogen. Alkaline fuel cells (AFC), phosphoric acid fuel cells (PAFC) and molten carbonate fuel cells (MCFC) have been around for a few years. All these examples involve liquid electrolytes (although the liquid can be absorbed in a porous support structure). Cells with solid electrolytes may in principle be more compact and sturdy, easier and safer to operate, and less corrosive. Solid electrolytes carrying oxygen or hydrogen ions (or combinations) have particularly broad interest.

Solid oxide fuel cells (SOFC) and related electrolyzers and electrochemical reactors are based upon yttria-stabilised zirconia (YSZ) or other oxygen ion conducting ceramics. The high activation energy of oxygen ion migration requires high operation temperatures (typically 800°C) for sufficient conductivity, leading to severe degradation problems.

At the other end of the temperature scale we find a number of solid protonic conductors. These contain more or less rigidly bonded water, and many may in fact be seen as mixtures of solid and aqueous phases. The charge carriers are thus protons with varying degrees of hydration (H+, H3O+, H5O2+, etc.). Of particular interest are the proton conducting polymers, and the polymer electrolyte fuel cell (PEFC) for vehicles is now rapidly approaching commercialisation.

Polymers and other systems which rely on protonic transport on a network of water are vulnerable to dehydration due for instance to accidental overheating (overload). This leads to irreversible structural and chemical degradation of the electrolyte. As a consequence, polymers must generally be operated below 100°C so that high loads of Pt catalyst are required, and the cells become very expensive. Thus, there is interest in solid protonic conductors with higher operating temperatures, i.e. without water.

Acid salts such as the classical proton conductors KH2PO4 and CsHSO4 contain no water, only structural protons, but the thermal stability is often only marginally better than for systems with water. Furthermore, the materials are often water soluble and mechanically weak, and practical interest has been limited.

Finally, we have materials without water and nominally without protons at all. They
contain protons only as randomly distributed defects, dissolved from some hydrogen-containing component in the surrounding atmosphere. These protons are strongly bonded to anions (typically oxygen ions) in the structure, and elevated temperatures are required to overcome the activation energy of proton jumps. Thus the concentration and conductivity of protons may become too low at high temperatures. But note that the structure is retained during removal of protons, such that these materials survive very high temperatures. In the following a few uses of high temperature proton conductors are mentioned, and thereafter the defect chemistry of such materials is summarised.

2. Applications of High Temperature Proton Conductors

2.1. FUEL CELLS

The principle of H₂/air fuel cells is shown in Figure 1 for a number of different charge carriers. The overall reaction produces water on the anode or cathode side, and many charge carriers require circulation of additional components. Only the high temperature H⁺-ion conductor produces water at the oxidant side and requires no additional component circulation, alleviating in principle the need to circulate and dry the fuel.

The hydrogen fuel cell has been realised with different liquid and solid electrolytes,