

Deformation of Cesium Hydrogen Sulfate for Fuel Cell Application

Christopher K. Lee

Walnut High School, Walnut, CA

Mentors: Sossina Haile, Mikhail Kislitsyn, California Institute of Technology

Cesium hydrogen sulfate (CHS) is a solid acid that has been demonstrated as a promising fuel cell electrolyte; however, its poor mechanical strength may undermine fuel cell stability. The mechanical properties of CHS were investigated to characterize plastic deformation, and thus to guide the development of improved composites. Creep deformation was studied under 0.3 MPa-1.0 MPa stress at a temperature range of 120-160 °C. At temperatures above the superprotonic phase transition (SPT), creep activation energy is 200 ± 10 kJ/mol and appears to be limited by cesium ion diffusion. Furthermore, the activation energy above and below the transition differed, confirming that the SPT alters the rate of deformation. Stress exponents at different temperatures were determined and shown to change from $n \sim 1$ to $n \sim 2$ upon SPT.

Introduction

Alternative fuels, such as hydrogen and ethanol, have received widespread attention since the rise of oil prices. Although any substitution for oil has its setbacks—whether it is high cost, lack of infrastructure or premature technologies—the success of any alternative energy requires inexpensive components, minimal environmental harm and higher efficiencies. Fuel cells have the potential to exceed existing automobiles engine efficiencies and use environmentally-friendly fuels. In this project, a thorough understanding of the mechanical properties of cesium hydrogen sulfate (CHS) was completed, which led to methodical approach to engineer a nanocomposite electrolyte material with improved properties. Fuel cells based on this technology may have widespread use in the energy demanding future.

A fuel cell is a device that converts chemical energy into electrical energy through a series of controlled, electrochemical reactions, generating electricity, water and minimal heat. The fuel cell system has no moving parts and replaces relatively inefficient combustion reactions with electrochemical reactions as seen in Fig. 1. Thus,

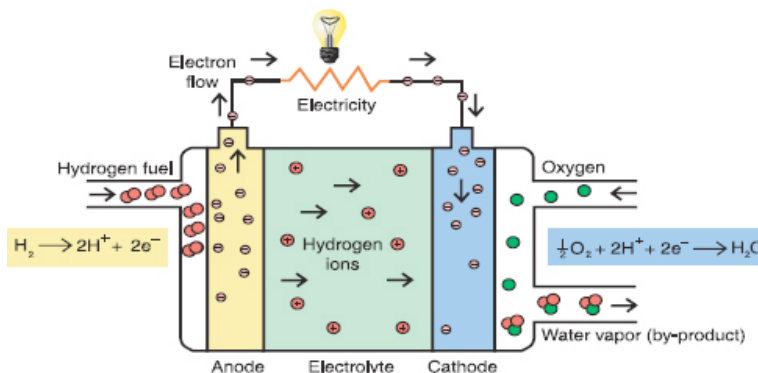


Figure 1: Diagram of a typical proton conducting fuel cell¹

waste heat and friction are minimized or avoided, resulting in higher efficiencies². Electrolytes, such as solid acids, are the membranes that separate fuel and oxidant and are impermeable to gases but conductive for specific, charged species.

Solid acids are intermediates between normal salts (e.g. Cs_2SO_4) and normal acids (e.g. H_2SO_4) that exhibit unique properties, the most intriguing being their ability to conduct protons as reported by Baranov *et. al.* in the 1980s³. Few useful applications of these materials were found until 2001,

when Haile *et. al.* fabricated a solid acid fuel cell based on CHS as an electrolyte, which resulted in a plethora of development by other scientists, including papers devoted to the electrochemical, thermodynamic, and phase behavior of solid acids and their application as fuel cells⁴⁻⁷.

The potential of solid acid electrolyte may exceed other existing fuel cell technologies for the following reasons: 1) solid acids are simple salts that are drastically less expensive than existing electrolytes^{1, 8}; 2) they operate at intermediate temperatures (150 °C – 250 °C) where Pt catalysts are more efficient; and 3) the ionic conduction mechanism is simple and requires few or no exterior systems to operate. Development of solid acid materials may advance current fuel cell technology.

Cesium Hydrogen Sulfate as a Fuel Cell Electrolyte

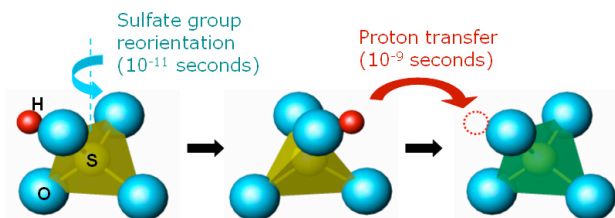


Figure 2: Mechanism of solid acid proton transport^{8, 9}

Among the many types of solid acids compounds, those containing cesium ions (e.g. CsHSO_4 , and CsH_2PO_4) are of most interest due to higher proton conductivity created by unique phase transition behaviors. Chisholm *et. al.*

investigated the mechanism for proton transport (Fig. 2) with a molecular dynamics study⁹. Each HSO_4 group forms a tetrahedron with a sulfur atom in the center and an oxygen atom at each of the four corners. The hydrogen is bonded to one of the oxygen and is conducted as a proton. At room temperature, all the HSO_4 groups have a fixed orientation with hydrogen-bonded networks. Above 141 °C, CHS undergoes a phase transition from a monoclinic to tetragonal structure upon which disorder sets, hydrogen bonds weaken and the HSO_4 groups undergo rapid reorientation. For every ~ 100 reorientations, neighboring HSO_4 groups align to transfer a proton between one another. In this way, protons can be conducted through the solid acid. The temperature above which this conduction process occurs is called the “superprotonic phase transition” temperature (SPT) upon which the