

Solid-state electrochemistry of fluoride ionic conductive materials

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Introduction

Fluorides with the fluorite-type structure exhibit an order-disorder transition accompanied by an increase in ionic conductivity. Among these materials, superionic PbSnF_4 is the highest performance fluoride ion conductor, with a conductivity that reaches 10^{-3} S/cm at room temperature.¹ This exceptionally high fluoride ion conductivity prompted the study of PbSnF_4 for a variety of applications, such as solid-electrolyte batteries, gas sensors, and other electrochemical devices.^{2,3} PbSnF_4 exhibits multiple polymorphic transformations, which has led to a great deal of controversy over its thermal, structural, and electrical properties. Although the structure and polymorphism of PbSnF_4 is largely understood now,⁴ and high F conductivity has been confirmed by multiple methods on samples prepared by a large range of methods, the material is still not widely used for commercial applications. One of the reasons seems to be its limited electrochemical stability in the working potential ranges of devices such as solid-electrolyte batteries or amperometric sensors.

The present study employs classic cyclic voltammetry (in a three electrode configuration), as well as DC polarization methods to establish the stability potential window of PbSnF_4 for different working electrodes, such as Pt and carbon, both in inert (N_2) and reactive atmosphere (F_2). SEM and EDAX techniques are used to image and analyze the electrochemical reaction products.

Experimental

PbSnF_4 powders were prepared according to literature procedures.⁵ A saturated aqueous solution of $\text{Pb}(\text{NO}_3)_2$ or PbF_2 (Sigma-Aldrich) was added drop-wise, under stirring, to a freshly prepared solution of saturated SnF_2 solution, neutral or containing 5% HF, to produce a- PbSnF_4 , and b- PbSnF_4 , respectively. The white precipitate was filtered after about 15 min., washed with distilled water, and dried in a vacuum oven at room temperature. The phase and purity of the produced powders was confirmed by X-ray powder diffraction.

The samples for electrochemical tests were prepared by die-pressing the powders at 50 KPSI into pellets with a thickness of 2-6 mm. Pt or Au electrodes for conductivity tests were evaporated in vacuum, and carbon electrodes were formed by spreading and pressing graphite powder on the side of the pellets. For electrochemical experiments, electrodes were fabricated similarly, or by applying a paste made by mixing PbSnF_4 and Pt powders with isopropanol. Pt mesh disks were used as current collectors, and were spring pressed onto the electrodes. The reference electrode was made from a Sn wire (99.9%, Sigma-Aldrich) in contact with the pressed pellet, with the SnF_2 present in the pellet being the oxidized species of the Sn/ SnF_2 reference electrode.

The conductivity of the produced samples was tested by impedance spectroscopy using a Solartron 1260

impedance analyzer. Samples were heated on a plate between stainless steel contacts at temperature of up to 300 °C, and in a custom made cell at temperatures of up to 200 °C, for experiments having N_2 or F_2 (Matheson – 5% F_2 in N_2) atmospheres. The same cell was used for the electrochemical experiments, connected to an EG&G 271 potentiostat controlled by a Labview application on computer.

Results

Although different PbSnF_4 phases can be obtained by varying synthesis methods, they can also be transformed into one another by heating and cooling cycles. However, small conductivity differences were observed at all temperatures, between samples made from powders prepared from different methods, most likely due to different grain size and, thus, structure of the pellet. The best conductivity was obtained for β - PbSnF_4 samples, and its temperature dependence is shown in Figure 1.

Cyclic voltammetry experiments have shown that PbSnF_4 has a relatively narrow stability window, of about 2 V in inert atmosphere. The cyclic voltammograms obtained with Pt electrodes are shown in Figure 2. At negative potentials, a reducing process starts, and the products are reoxidized on the positive scan. EDAX analysis of the products indicated that a 1:1 Pb-Sn alloy was formed.

In an F_2 containing atmosphere, the material was more stable at oxidizing potentials, and the cathodic current was due to reduction of F_2 at the working electrode. However, even in the presence of F_2 , DC polarization experiments led to the formation of metallic deposits and dendrites that can short the electrodes. The influence of electrode material on the potential stability window was also studied and will be discussed in the presentation.

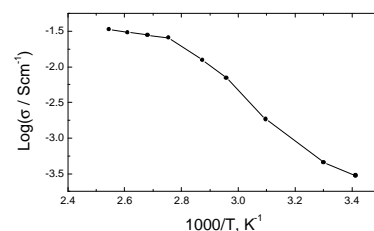


Figure 1. Plot of conductivity data for b- PbSnF_4 prepared by precipitation method.

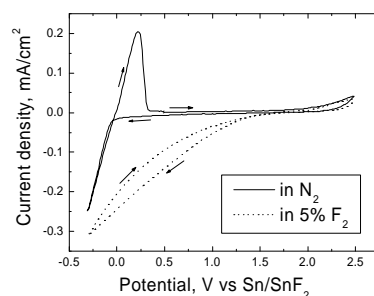


Figure 2. Cyclic voltammograms of an all solid-state cell with a Pt RE and CE, and a Sn/ SnF_2 reference electrode.

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