Development of an Electrochemical Ion Source for Thermal Ionization Mass Spectrometry

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Abstract:

Thermal ionization mass spectrometry (TIMS) remains the method of choice for many high precision isotope ratio determinations but is handicapped by the use of low efficiency ion emitters. For example, ionization efficiencies from molten glass emitters (Si-gel) used for such elements as Pb, Cr, Ru, and Ag are in the range of 0.05-2%, which limits the sample size and the precision to which isotope ratio determinations for these elements can be made. Our aim is to improve the ionization efficiency of the molten glass ion emitter using electrochemical methods. This work builds on recent observations indicating that many metals doped in borosilicate glasses (eg. Bi, Ag), are emitted from the liquid glass (in vacuo) primarily as the neutral metal atom. Our goal is to increase the proportion of singly charged metal atoms in metal-doped molten glasses via oxidation induced by electrochemical methods and to assess whether such *in situ* oxidation of metal atoms leads to an increase in emitted metal ions.

Our experiments are performed in a vacuum chamber that mimics conditions in the sample chamber of the TIMS. A borosilicate glass sample is placed in a miniature ceramic crucible. The crucible contains working and reference Pt electrodes, and a Pt thermocouple. The entire apparatus is wrapped with a resistively heated Ta wire until temperatures in the glass reach approximately 1400°C, to ensure that the glass is molten. By this method, we have produced simple cyclic voltammograms that suggest that over a 100°C temperature range, the borosilicate glass undergoes a transition from resistive behavior as a solid, to a conductive electrolyte, as a molten liquid glass, as expected. The change is evident as an order of magnitude decrease in resistivity of the glass, as interpreted from the voltammograms. The voltammograms produced for the pure borosilicate glasses represent the baseline against which we will compare the electrochemical characteristics of Pb doped glasses. These experiments are currently underway and are designed to determine the speciation of lead in the glass, and to determine the voltages required to induce cathodic currents in the glass corresponding to ionization to Pb^{+} and Pb^{2+}. By generating a anodic current and an increased concentration of the oxidized species, we hope to ultimately generate a higher intensity ion beam, higher ionization efficiency for low efficiency elements, and higher precision analyses on small sample sizes for the TIMS.

Electrochemistry Background:

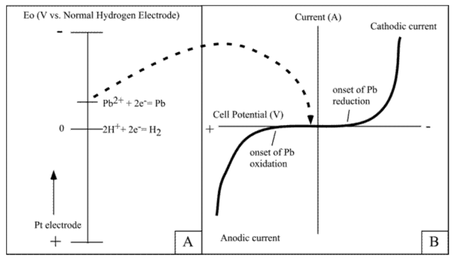
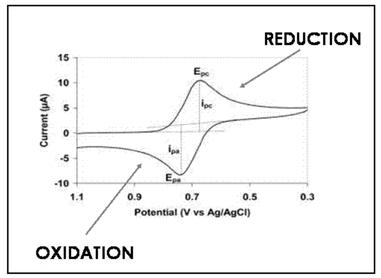


Figure 1. A) A conventional potential diagram for voltage of a Pt electrode relative to a normal hydrogen electrode, showing the hypothetical position of the Pt reduction reaction.

Figure 1. B) A cell potential vs. current diagram showing the hypothetical variation in current associated with reduction and oxidation of Pb.

Figure 2. A typical cyclic voltammogram for a one electron reaction. As one sweeps through a series of potentials, current increases as the potential reaches the oxidation or reduction potential of the analyte in the electrolyte, respectively.



Experimental Set-Up:

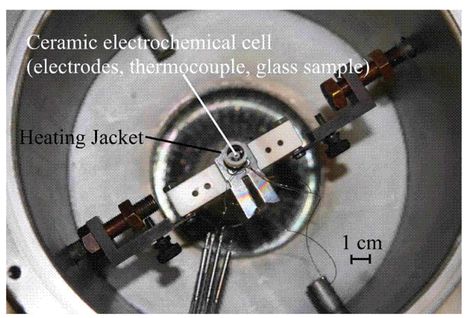
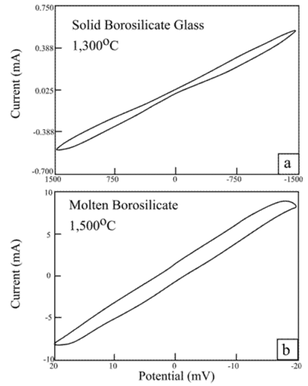


Figure 3. Experiments are performed in a custom-made vacuum chamber. A ceramic electrochemical cell containing electrodes, glass sample, and thermocouple are resistively heated by a Ta heater coil.

Results:



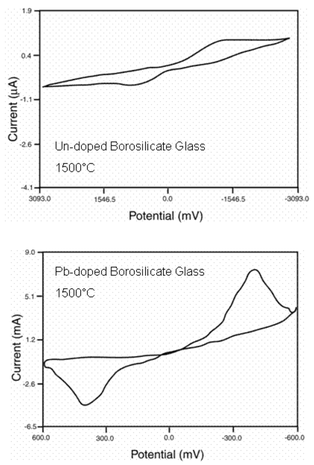


Figure 4. Cyclic voltammograms for solid and molten borosilicate glass. Molten behavior is essential to the glass behaving conductively, rather than resistively, an important initial condition for our experiments. Note the increase in current over 200°C.

Figure 5. Cyclic voltammograms for "un-doped" and "Pb-doped" borosilicate glass. The shape of the un-doped voltammogram appears to be repeatable, whereas work is underway to produce repeatable results for the Pb-doped system.

The Future:

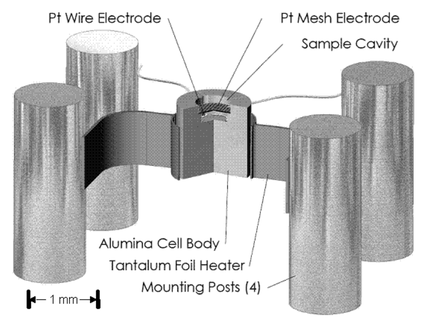


Figure courtesy of D. David (CIRES)

Figure 6. Hypothetical design for the miniaturized electrochemical cell for use in the TIMS. Mounting posts are the filament posts currently used in the mass spectrometer.