Energy Storage in Electrochemical Cells with Molten Sb Electrodes

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Energy Storage in Electrochemical Cells with Molten Sb Electrodes

Abstract
An energy-storage concept is proposed using molten Sb as the fuel in a reversible solid-oxide electrochemical cell (SOEC). Because both Sb and Sb$_2$O$_3$ are liquids at typical SOEC operating temperatures, it is possible to flow Sb from an external tank and use it as the fuel under fuel-cell conditions and then electrolyze Sb$_2$O$_3$ during recharging. This concept was tested using a button cell with a Sc-stabilized zirconia electrolyte at 973 K by measuring the impedances under fuel-cell and electrolyzer conditions for a range of stirred Sb-Sb$_2$O$_3$ compositions. The Sb-Sb$_2$O$_3$ electrode impedances were found to be on the order of 0.15 $\Omega cm^2$ for both fuel-cell and electrolyzer conditions, for compositions up to 30% Sb and 70% Sb$_2$O$_3$. The open circuit voltages (OCV) were 0.75 V, independent of oxygen composition. Some features of using molten Sb as an energy-storage medium are discussed.

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An energy-storage concept is proposed using molten Sb as the fuel in a reversible solid-oxide electrochemical cell (SOEC). Because both Sb and SbO2 are liquids at typical SOEC operating temperatures, it is possible to flow Sb from an external tank and use it as the fuel under fuel-cell conditions and then electrolyze SbO2 during recharging. This concept was tested using a button cell with a Sr-stabilized zirconia electrolyte at 973 K by measuring the impedances under fuel-cell and electrolyzer conditions for a range of stirred Sb-Sb2O3 compositions. The Sb-Sb2O3 electrode impedances were found to be on the order of 0.15 Ωcm2 for both fuel-cell and electrolyzer conditions, for compositions up to 30% Sb and 70% Sb2O3. The open circuit voltages (OCV) were 0.75 V, independent of oxygen composition. Some features of using molten Sb as an energy-storage medium are discussed.

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high enough to achieve good electrochemical performance and low enough to minimize the vapor pressure of Sb and Sb₂O₃.

Our earlier studies suggested that Sb and Sb₂O₃ form separate phases at 973 K, with Sb₂O₃ floating to the surface of the mixture due to density differences. Since Sb₂O₃ must be in contact with the electrolyte surface for oxygen to be transferred to the electrolyte, buoyancy forces would prevent electrolysis from occurring with our cell configuration. Furthermore, the static situation in our configuration is very different from that which would be expected in a flow battery, where mixing of Sb and Sb₂O₃ would be expected due to flow in the electrode compartment. Therefore, to mimic the mixing that would be expected in an actual flow battery, we added an alumina stirrer to our design, as shown in Figure 1. The rotation of the stirrer was maintained at approximately 120 rpm in order to ensure reasonable mixing of the phases. This rate of stirring was sufficient to ensure that the V-i polarization curves obtained at a given Sb:Sb₂O₃ ratio were not dependent on the rate at which Sb was oxidized or Sb₂O₃ was reduced.

The electrochemical and impedance measurements in this study were performed using a Gamry Instruments Potentiostat. The relative amounts of Sb and Sb₂O₃ in the electrode compartment were determined by assuming that we started with 100% Sb, using the charge transferred through the electrolyte to determine the overall oxygen content. Unless otherwise stated, the current densities reported in this paper were normalized to the external area of the cathodes. The impedance spectra were performed galvanostatically in the frequency range from 300 kHz to 0.1 Hz with an a.c. perturbation of 1 mA.

### Results

**Experimental.**— The electrochemical performance of a cell with a molten Sb electrode, corresponding to when 40% of the Sb has been oxidized to Sb₂O₃, is shown in Figure 2) for a temperature of 973 K. Figure 2a) is the V-i polarization curve, with positive currents corresponding to fuel-cell operation and negative currents to electrolysis of Sb₂O₃ to Sb. As expected, the potential at zero current (Open Circuit Voltage, OCV) is 0.75 V, equal to the Nernst Potential for the oxidation of Sb to Sb₂O₃. Since the activities for Sb and Sb₂O₃ are equal to unity, this OCV is independent of the Sb:Sb₂O₃ ratio. Equally significant, the V-i relationship is almost linear over the entire range of current densities, implying that the cell impedance is nearly independent of current density and the same under fuel cell and electrolysis conditions.

Figure 2b) is a Nyquist plot of the open-circuit impedance data for the same cell. The total ASR of the cell was 0.47 Ωcm² based on the intercept with the real axis at the lowest frequency, in good agreement with the slope of the V-i relationship in Figure 2a). The ohmic losses, determined from the high-frequency intercept with the real axis, are ~0.26 Ωcm². This resistance is primarily due to the 100-μm ScSZ electrolyte. Based on the reported conductivity of ScSZ, 0.045 S/cm,24 the ohmic losses were expected to be 0.22 Ωcm², which is within the experimental accuracy of our measurements. The non-ohmic portion of the impedance is 0.21 Ωcm² and has contributions from both the anode and cathode. Given that the losses associated with an identical LSF-ScSZ cathode have been reported to be 0.06 Ωcm² under these conditions,25,23 the losses associated with the molten, Sb-Sb₂O₃ electrode must be ~0.15 Ωcm². This is somewhat higher than the value reported for similar cells in an earlier study, 0.06 Ωcm².24 Since this impedance did not change significantly in the absence of Sb₂O₃, as will be discussed shortly, the higher impedance here is not due to the presence of the oxide. It is likely that variations in the roughness of the electrolyte surface could cause changes in the impedance of the molten-metal electrodes, but we did not investigate this.

To determine how losses in the molten Sb-Sb₂O₃ electrode varied as the oxygen content increased, V-i polarization curves were measured as a function of the extent of Sb oxidation, with data for a few representative concentrations reported in Figure 3 and a summary of all the results in Figure 4. The V-i and impedance data were measured starting with pure Sb metal in the anode compartment. We then drew current through the electrolyte to oxidize an equivalent of 10% of the original Sb, after which V-i and impedance measurements were again performed. This was repeated until the performance of the cell became poor. Where possible, impedance data were taken under both fuel-cell (0.2 A/cm²) and electrolysis (~0.1 A/cm²) conditions.

In the absence of Sb₂O₃, Figure 3a), the V-i relationship in the fuel-cell region is similar to that shown in Figure 2a) but it was
not possible to draw current in the electrolysis region. This is not surprising since there can be no electrolysis in the absence of Sb₂O₃. The V-i relationship and the electrode impedance in the fuel-cell region were the same as when 40% of the Sb had been oxidized to Sb₂O₃. The OCV with the pure Sb electrode was also still 0.75 V, implying that even small amounts of oxygen in the molten electrode are sufficient to establish the equilibrium Nernst Potential. At 90% conversion of the Sb, the magnitude of the slope of the V-i relationship is significantly higher. As shown in Figure 4a), the ohmic losses in the cell at this level of Sb conversion were high, greater than 1.1 Ωcm². At this point, the molten, Sb-Sb₂O₃ mixture is no longer sufficiently conductive. Given that the only electrical contact with the molten electrode was from a rhenium wire dipped into the bath, it is perhaps surprising that the ohmic losses were not higher at this level of conversion. The OCV at this high conversion was very close to 0.75 V, highlighting the fact the Nernst Potential does not change with conversion when the reactant and product are both present as separate phases on the microscopic scale.

The electrode losses as a function of Sb conversion are summarized in Figure 4, with the ohmic losses given in Figure 4a) and the non-ohmic losses in Figure 4b). First, even at 10% conversion of the Sb, the electrode impedance for electrolysis mode is close to that observed for fuel-cell mode. This is important in demonstrating that Sb₂O₃ can be efficiently converted to Sb. Considering the losses at high conversion, the impedances for both fuel-cell and electrolysis operation are nearly independent of Sb conversion up to about 70% conversion of Sb. Only at higher conversions do the ohmic losses increase precipitously. The non-ohmic losses in the fuel-cell mode also increased dramatically at this same level of conversion. In part, the non-ohmic losses are coupled to the ohmic losses when the electrode is not sufficiently conductive, since the electrode processes cannot occur without efficient transfer of electrons. It is therefore interesting to notice that the non-ohmic losses in the electrolysis mode did not increase significantly at high Sb conversions.

Theoretical considerations.— In any energy-storage system, the efficiency needs to be considered. Obviously, the efficiency of a cell can be improved by obtaining better electrodes and thinner electrolytes. However, there are theoretical limits to the efficiency that can be achieved in an electrochemical device that are determined by thermodynamics. The theoretical efficiency of a fuel cell or electrolyzer is given by ΔG/ΔH. For systems based on H₂-H₂O reactions, the theoretical efficiency can be so close to unity that overpotential losses in the cell completely dominate the process. This is not true in the Sb-Sb₂O₃ system, for which ΔG/ΔH is 0.65 at 973 K.

In the fuel-cell mode, 35% of the energy will be generated as heat, even for an ideal cell with no losses. Adiabatic operation would not be possible because the temperature rise in the Sb-Sb₂O₃ mixture would be hundreds of degrees, even for modest conversions. Fortunately, molten-metals have very high thermal conductivities, so that this heat can be easily recovered for use in other applications or potentially stored. In electrolysis mode, a significant fraction of the energy required to convert Sb₂O₃ to Sb must be added as heat, or else the molten mixture will cool. One of the effective ways of providing the heat for electrolysis is to use the polarization losses from the cell. The thermoneutral voltage for an electrolyzer is ΔH/(-nF), which is 1.2 V for the Sb-Sb₂O₃ system.

One very attractive aspect of an energy storage system based on Sb-Sb₂O₃ conversion is the relatively small storage volume and high energy density. The theoretical Sb storage volume for 1 MW-h of energy storage is only approximately 160 liters. The theoretical energy density of molten Sb is ~1020 Wh/kg, which is at least two orders of magnitude higher than that of the reactants used in vanadium redox flow battery.

Conclusions

What we have demonstrated here is that an energy storage system based on Sb and Sb₂O₃ is a viable alternative. Attractive features include the low volume requirements for energy storage, the low cell losses that are achievable in this system, and the fact that there is no electrode required on the fuel side of the fuel cell/electrolyzer. As in any energy storage device, thermal management issues would need to be dealt with.

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