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Energy Storage in Electrochemical Cells with Molten Sb Electrodes

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Abstract

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Disciplines

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Energy Storage in Electrochemical Cells with Molten Sb Electrodes

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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 Sb₂O₃ 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 Sb₂O₃ 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-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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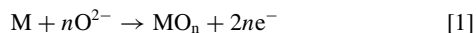
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Renewable energy sources, such as wind or solar energy, could help decrease our dependence on fossil fuels; but they produce intermittent power that may not be available when energy demand is highest. To take full advantage of these energy sources, as well as provide buffering for the electrical grid as a whole, the ability to store electrical energy at times when demand is low for later use when demand is high would be very desirable. Conventional ways to store energy are based primarily on compressed air or elevated water.¹ With compressed air, off-peak power is used to run a compressor. At times of high demand, the compressed air can then be used to drive a turbine. In hydroelectric power plants, energy is stored by pumping water back to higher elevations. Unfortunately, both of these approaches require special geographic conditions, making them infeasible in many cases.

One alternative for energy storage involves electrochemical devices, such as static Li-ion batteries,² metal-air batteries,³ and flow batteries.⁴⁻⁶ With these devices, energy is stored in the form of chemical energy and electricity is generated later by reversing the chemical reaction. An intrinsic advantage of electrochemical energy storage is the direct conversion of chemical energy into electricity with few moving parts. Among the various types of flow batteries, those based on zinc or vanadium redox cycles have received the most attention.^{4,5}

Reversible fuel cells are also a type of flow battery. In the conventional use of reversible fuel cells, surplus electricity would be sent to the cell to electrolyze water to produce H₂; electricity would be generated later by flowing the H₂ back to the cell, which would then be operated in the fuel cell mode.⁷ The low density of gaseous H₂ makes its storage challenging and typically requires that a significant amount of energy be used in compressing the H₂. Several variations on the idea of reversible fuel cells have been proposed to reduce this storage problem. Because H₂O and CO₂ can be electrolyzed with equal efficiency in solid oxide fuel cells (SOFC),⁸⁻¹⁴ Zhan, et al.¹⁴ has suggested electrolyzing mixtures of H₂O and CO₂ to produce syngas, which could in turn be converted to methane, greatly reducing the volume of gas that needs to be stored. In another variation, H₂ produced in the electrolyzer is used to reduce FeO to Fe.¹³ By passing steam over the Fe, H₂ can be generated again for use in the fuel cell.

In this paper, we propose a new type of flow battery based on solid-oxide, O²⁻-conducting electrolytes and molten Sb as one electrode. Previous work from our laboratories has shown that it is possible to operate a fuel cell with molten metals as the fuel, according to the following anode reaction.¹⁵⁻¹⁷



Cells using metals like Sn, In, or Pb exhibit a very high Area-Specific Resistance (ASR) because the respective metal oxides that are formed in Reaction 1 are solids at a typical operating temperature of 973 K and form insulating layers over the electrolyte.^{15,16} Further oxidation is then limited by oxygen transport through this layer and the low solubility of oxygen in the metals (e.g. 0.0233% in liquid Sn at 973 K¹⁸). However, the electrode impedance of an SOFC with molten Sb as the anode can be near zero, in part because Sb₂O₃ is also a liquid at this temperature.¹⁷

Because both Sb and Sb₂O₃ are liquids at typical SOFC operating conditions, it should be possible, in principle, to flow pure Sb from an external tank to the cell during fuel cell operation and flow mixtures of Sb and Sb₂O₃ to the cell during electrolyzer operation. In the present paper, we set out to determine whether electrolysis of Sb₂O₃ is possible and to measure the electrode impedances for Sb-Sb₂O₃ mixtures, information required for the design of a flow battery based on Sb and Sb₂O₃. What we will demonstrate is that the impedances for this system are indeed very low over a wide range of compositions, so that the overpotential losses in a reversible fuel cell based on molten Sb could be low. The high densities of Sb and Sb₂O₃ allow the storage volumes for a reversible fuel cell to also be low, making this a potentially attractive technology.

Experimental

All of the electrochemical studies were conducted using button cells made by methods that are described in other papers.¹⁹⁻²¹ The cells were constructed using a bilayer structure of the electrolyte material, scandia-stabilized zirconia (ScSZ, 10 mol% Sc₂O₃), with one side dense and the other porous. The dense electrolyte layer was 1-cm in diameter and 100-μm thick, while the porous layer was 0.67-cm in diameter and 50-μm thick. Composite cathodes were formed from the porous layer by infiltration of 40-wt% La_{0.8}Sr_{0.2}FeO₃ (LSF), using an aqueous solution of La(NO₃)₃, Fe(NO₃)₃, and Sr(NO₃)₂ in the proper molar ratios, followed by calcination to 1123 K.^{22,23} There was no additional treatment to the anode side of the electrolyte other than adding 6 g of powdered Sb (99.5%, Alfa Aesar).

For electrochemical testing, the button cells were attached to an alumina tube using a ceramic adhesive (Aremeco Ceramabond 552). The tube was then mounted vertically in a tubular furnace so that the molten metal would be in contact with the anode side of the electrolyte by gravity, while the cathode was simply exposed to air. Silver wire and silver paste were applied to the cathode for current collection, and a rhenium wire (0.5-mm diameter) was dipped into the molten metal for the current collector on the anode side. Rhenium was chosen as a current collector because of its insolubility in Sb metal. We chose to conduct the electrochemical measurements at 973 K, a temperature

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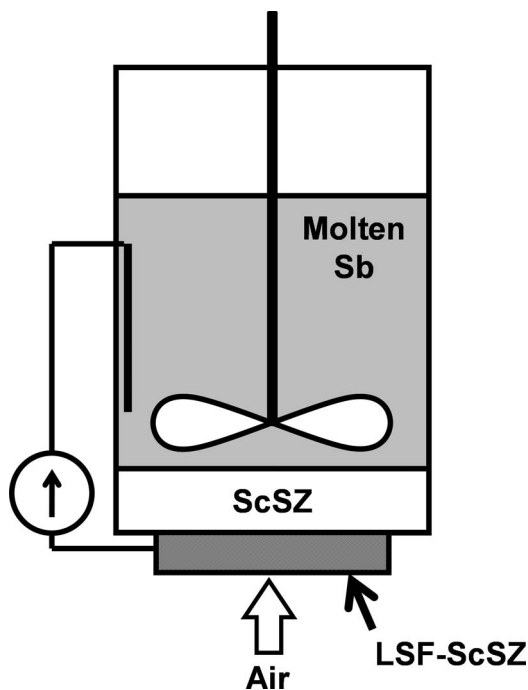


Figure 1. A diagram of the electrochemical cell using an alumina stirrer for mixing of the molten Sb anode.

high enough to achieve good electrochemical performance and low enough to minimize the vapor pressure of Sb and Sb_2O_3 .

Our earlier studies suggested that Sb and Sb_2O_3 form separate phases at 973 K, with Sb_2O_3 floating to the surface of the mixture due to density differences.¹⁷ Since Sb_2O_3 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 Sb_2O_3 would be expected due to flow within 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: Sb_2O_3 ratio were not dependent on the rate at which Sb was oxidized or Sb_2O_3 was reduced.

The electrochemical and impedance measurements in this study were performed using a Gamry Instruments Potentiostat. The relative amounts of Sb and Sb_2O_3 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 Sb_2O_3 , 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 Sb_2O_3 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 Sb_2O_3 . Since the activities for Sb and Sb_2O_3 are

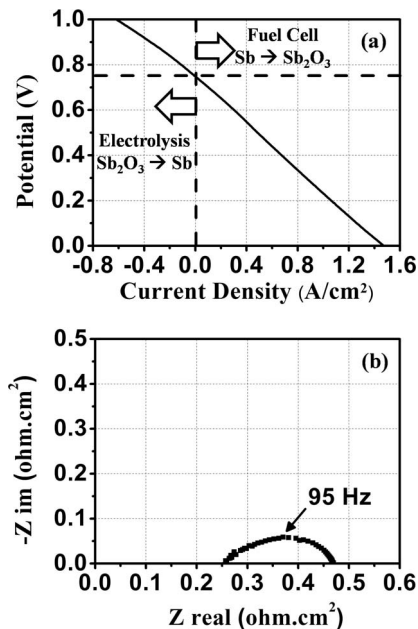


Figure 2. Performance of the cell with 60% Sb and 40% Sb_2O_3 at 973 K: (a) V-i polarization curve obtained by ramping from 1 V to 0 V at 10 mV/s; (b) Impedance data for this same cell and open-circuit conditions.

equal to unity, this OCV is independent of the Sb: Sb_2O_3 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 $0.47 \Omega\text{cm}^2$ 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 $\sim 0.26 \Omega\text{cm}^2$. 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 $0.22 \Omega\text{cm}^2$, which is within the experimental accuracy of our measurements. The non-ohmic portion of the impedance is $0.21 \Omega\text{cm}^2$ 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 $0.06 \Omega\text{cm}^2$ under these conditions,^{22,23} the losses associated with the molten, Sb- Sb_2O_3 electrode must be $\sim 0.15 \Omega\text{cm}^2$. This is somewhat higher than the value reported for similar cells in an earlier study, $0.06 \Omega\text{cm}^2$.¹⁷ Since this impedance did not change significantly in the absence of Sb_2O_3 , 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- Sb_2O_3 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/cm^2) and electrolysis (-0.1 A/cm^2) conditions.

In the absence of Sb_2O_3 , Figure 3a), the V-i relationship in the fuel-cell region is similar to that shown in Figure 2a) but it was

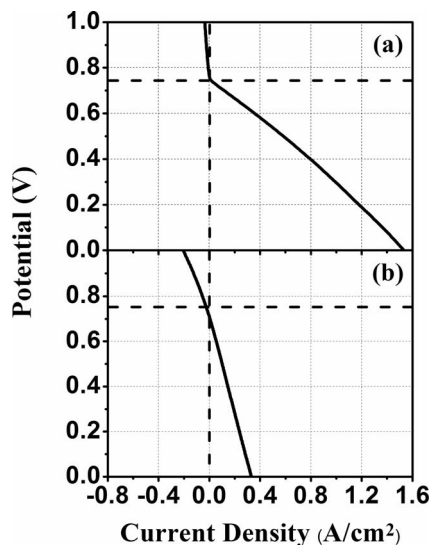


Figure 3. V-i polarization curves taken at 973 K for (a) 100% Sb and 0% Sb_2O_3 (b) 10% Sb and 90% Sb_2O_3 .

not possible to draw current in the electrolysis region. This is not surprising since there can be no electrolysis in the absence of Sb_2O_3 . 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 Sb_2O_3 . 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 $1.1 \Omega\text{cm}^2$. At this point, the molten, Sb- Sb_2O_3 mixture is no longer sufficiently conductive. Given

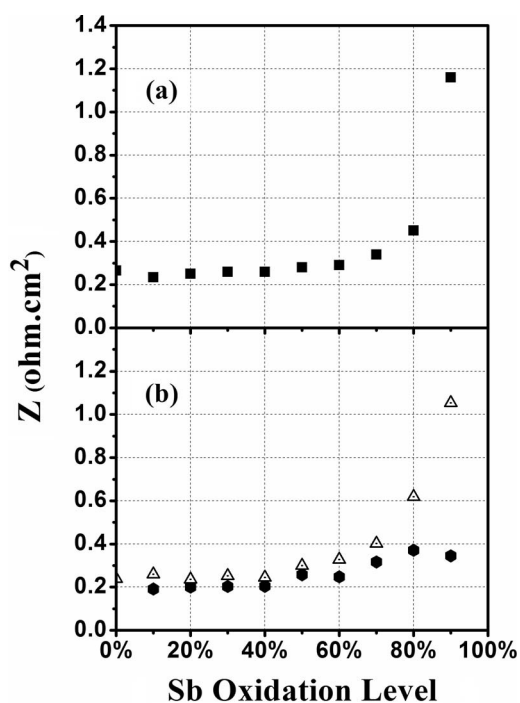


Figure 4. Measured impedances as a function of the extent to which Sb had been oxidized: a) Ohmic resistances at 0.2 A/cm^2 ; b) Non-ohmic impedances measured at -0.1 A/cm^2 (electrolysis mode, Δ) and 0.2 A/cm^2 (fuel cell mode, \bullet).

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 Sb_2O_3 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 $\Delta G/\Delta H$. For systems based on H_2 - H_2O 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- Sb_2O_3 system, for which $\Delta G/\Delta H$ 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- Sb_2O_3 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 Sb_2O_3 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 $\Delta H/(-nF)$, which is 1.2 V for the Sb- Sb_2O_3 system.

One very attractive aspect of an energy storage system based on Sb- Sb_2O_3 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 $\sim 1020 \text{ Wh/kg}$, which is at least two orders of magnitude higher than that of the reactants used in vanadium redox flow battery.^{25,26}

Conclusions

What we have demonstrated here is that an energy storage system based on Sb and Sb_2O_3 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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