Molten Metal Electrodes in Solid Oxide Fuel Cells

Molten metal electrodes in solid oxide fuel cells (SOFCs) are electrochemically characterized for their possible use in direct carbon oxidation and energy storage. Molten alloys with 50-mol% In-Sb, Sn-Sb, Sb-Bi, and Sb-Pb were examined as anodes for solid oxide fuel cells at 973 K. The cells were operated in the battery mode, without added fuel, in order to understand the oxidation characteristics of these alloys at electrolyte interfaces. Cells using 50-mol% In-Sb and Sn-Sb mixtures exhibited open-circuit voltages (OCV) of 1.0 and 0.93 V, values that are identical to that of cell with pure In and Sn respectively. Also similar to the pure In and Sn anodes, the impedances of these cells were initially low but increased dramatically after drawing a small amount of charge, implying formation of In$_2$O$_3$ and SnO$_2$ layers at the electrolyte interface. The 50-mol% Sb-Bi cell had an OCV of 0.73 V initially, close to the OCV observed with pure Sb. The OCV remained constant until a charge identical to that required for oxidation of all the Sb had been passed, after which the OCV dropped to 0.43 V, similar to the value for pure Bi. SEM analysis of the cell after conversion of the Sb showed two distinct phases, with metallic Bi at the bottom and Sb$_2$O$_3$ at the top. The electrochemical oxidation of 50-mol% Sb-Pb alloys exhibited an OCV that changed continuously with conversion, from 0.73 V initially to 0.67 V following the addition of charge corresponding to oxidation of 120% the Sb. The total cell impedance remained low for this entire period. EDS measurements on the sectioned Sb-Pb cell suggested that both Sb and Pb were oxidized simultaneously to form a mixed oxide of Pb and Sb.

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 OCVs were 0.75 V, independent of oxygen composition. Some features of using molten Sb as an energy-storage medium are discussed.

The use of molten neat Ag and alloyed Ag-Sb for direct-carbon anodes in SOFCs has been examined at 1273 K. For Ag, an OCV typical of that expected for carbon oxidation, 1.12 V, was observed when charcoal was mixed with the molten metal. However, the anode impedance was very high, ~100 $\Omega$cm$^2$. The nature of the electrode losses was investigated by measuring the voltage-current characteristics of a cell with Ag but no carbon at the electrode, while ramping the voltage under fuel cell and electrolysis conditions. The results indicate that the cell potential is governed by the dissolved oxygen concentration in the Ag at the electrolyte interface. Using this and a model of carbon oxidation within the molten Ag, it is determined that the impedance of the electrode is limited by diffusion of oxygen in the Ag phase, due to the low solubility of oxygen in molten Ag. With Ag-Sb alloy with added charcoal, the OCV at 973 K was 0.75 V, the potential associated with equilibrium between Sb and Sb$_2$O$_3$, due to the low solubility of oxygen in the Sb phase. The implications of these results for using molten-Ag electrodes for direct-carbon fuel cells are discussed.