

A Comparison of Molten Sn and Bi for Solid Oxide Fuel Cell Anodes

A. Jayakumar, J. M. Vohs, and R. J. Gorte, Chemical & Biomolecular Engineering, University of Pennsylvania, Philadelphia, PA 19104

Summary

Molten Sn and molten Bi were examined, in the absence of added fuel, for use in direct-carbon solid oxide fuel cells (SOFC). For both metals, the open-circuit voltages (OCV) were close to that expected based on their oxidation thermodynamics, ~ 0.93 V for Sn and ~ 0.48 V for Bi. With Sn, the cell performance degraded rapidly due to formation of a SnO_2 layer at the YSZ interface. With Bi, the OCV anode impedance at 973 K was less than $0.25 \Omega\text{cm}^2$ and remained constant until essentially all of the Bi had been oxidized to Bi_2O_3 . Some implications of these results for Direct Carbon Fuel Cells are discussed.

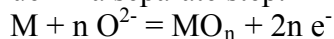
Keywords

Direct Carbon Fuel Cells; Molten Anodes.

Introduction

It is theoretically possible to convert solid carbonaceous fuels, including biomass or coal, directly into electricity using fuel cells based on electrolytes that transfer oxygen ions. A major challenge in making these Direct Carbon Fuel Cells (DCFC) practical is the requirement of fabricating low-impedance anodes that allow facile transfer of oxygen from the electrolyte to the surface of the solid fuel.

The approach that we have taken for transferring oxygen from the electrolyte to the solid fuel involves the use of anodes composed of liquid metals, such as Sn or Bi. For these anodes, the metal reacts at the electrolyte interface via the reaction below and the metal oxide, MO , is in turn reduced by the carbonaceous fuel in a separate step.



For cells using Sn anodes, it has been reported that this type of fuel cell can be operated in a “battery” mode by simply allowing the metallic Sn to be consumed and then be regenerated later [1]. However, while the concept has been demonstrated with liquid-Sn anodes, there is very little fundamental information available to show what limits the performance of these electrodes and how one might improve them.

In the present paper, we set out to investigate metal oxidation in a fuel cell with a yttria-stabilized zirconia (YSZ) electrolyte, using Sn or Bi as the anode. With Sn, we will show that a critical issue that will limit performance is the formation of a SnO_2 oxide film at the electrolyte interface due to the very low solubility of oxygen in molten Sn. The performance of the Sn-based electrodes appears to be limited by the low ionic conductance of this SnO_2 layer. With molten Bi, the electrochemical reaction is facile, probably due to the fact that the oxide is a good ionic conductor; however, the critical issue with Bi is its lower open-circuit potential.

Results & Conclusions

Two important factors were identified as affecting the performance of molten metal anodes for SOFC: the thermodynamic oxidation potential of the metal and the tendency for the oxide to form a film at the electrolyte interface. For operation of cells in the “battery” mode, where the metal is oxidized, the oxidation potential determines the open-circuit voltage that can be achieved. Oxide films at the YSZ interface can effectively block charge transfer at the electrolyte interface if the oxide is a poor ionic conductor.

With Sn, the V-i characteristics of the cell showed a strong, time-dependent behavior when current was drawn. The data show that the current increased and reached a maximum as the potential was lowered from open-circuit but the current then began to decrease. The decrease in current was not reversed by increasing the potential but was instead related to the amount of charge that had been drawn from the cell. Once this charge had been transferred, the only way to restore the low impedance of the cell was to expose the anode to flowing H₂.

We postulated that the results were due to formation of a dense SnO₂ layer at the electrolyte interface. Once this layer is formed, oxidation of additional Sn is limited by transport of oxygen through the SnO₂ layer and the low solubility of oxygen in liquid Sn. In order to confirm that cell deactivation was due to formation of an oxide layer at the YSZ interface, we allowed a cell to deactivate by drawing current at 800°C, cooled the cell to room temperature, broke it, and examined the YSZ interface using SEM and EDX. These measurements confirmed the formation of an oxide layer.

Bi has a similar melting temperature to that of Sn (545 K versus 505 K), so that it was of interest to examine the characteristics of a cell with a molten Bi anode. We again operated the cell in a “battery” mode, with dry He flowing into the anode compartment after reducing the Bi, so that the electrochemical oxidation of the metal could be studied. The V-i plot for Bi was very different. First, in agreement with expectations based on the Bi oxidation thermodynamics, the OCV was only 0.48 V. Second, the V-i polarization plot was a straight line that exhibited complete reversibility when the potential was ramped up or down. Impedance measurements indicated negligible electrode losses with the Bi. Furthermore, it was possible to draw current until essentially all of the Bi was oxidized.

Additional experiments were carried out using graphite together with the molten Bi in the anode. While it was possible to electrochemically oxidize the graphite, the kinetics were too slow to change the open circuit potential. Clearly a catalyst will need to be added in order to make this design practical.

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References

- (1) T. Tao, M. Slaney, L. Bateman, and J. Bentley, *ECS Transactions*, **7**, 1389 (2007).