Effect of grain boundary diffusion on electrolyte stability in direct carbon fuel cells with antimony anodes

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ABSTRACT

Direct carbon fuel cells (DCFC) that employ solid oxide electrolytes and molten Sb anodes are promising for the efficient generation of electricity using a range of carbonaceous fuels. The present study examined the etching of yttria-stabilized zirconia (YSZ) and gadolinia-doped ceria (GDC) electrolytes by Sb_2O_3 produced during fuel-cell operation. Migration of Sb along grain boundaries and electrolyte corrosion were observed for both poly-crystalline YSZ and GDC electrolytes; however, corrosion and electrolyte thinning were not observed for a single-crystal YSZ electrolyte, even after long-term operation. These results indicate that Sb migration along grain boundaries plays a significant role in electrolyte corrosion in DCFCs with molten Sb anodes. Several strategies for avoiding this problem are also discussed.

1. Introduction

Since solid oxide fuel cells (SOFC) are based on ceramic electrolytes that are oxygen-ion conductors, it is at least theoretically possible to carry out the electrochemical conversion of any combustible fuel, including solid fuels like coal. The generation of electrical power by a Direct Carbon Fuel Cell (DCFC) would also provide significant benefits if it could be practiced on a large scale. The efficiency could be much higher than that of heat engines, which are subject to Carnot limits; and NO_x emissions would be negligible. If CO_2 sequestration were required, the exhaust gas from the anode would be highly concentrated, allowing for easy CO_2 capture [1,2]. Finally, direct utilization of hydrocarbon fuels would greatly simplify fuel cell operation by eliminating the need for gasification and steam reforming steps [3].

A significant amount of research has gone into finding a practical design for a DCFC and the literature describing this work has been reviewed [4,5]. These studies show that the performance of DCFC is almost always limited by the transfer of oxide ions from the electrolyte to the solid fuel [6,7]. Various approaches have been used to facilitate this transfer, one of the most promising involving the use of molten-Sb electrodes [8]. In this case, the anode reaction can be split into the following two steps:

$$Sb + 3\ O^{2-} \rightarrow Sb_2O_3 + 6\ e^- \tag{1}$$

$$C + 2\ Sb_2O_3 \rightarrow 3\ CO_2 + 6\ Sb \tag{2}$$

The first reaction, Eq. (1), is the oxidation of a portion of the Sb at the electrolyte-anode interface. The resulting Sb_2O_3 is then transported via diffusion, natural convection, or mechanical mixing to the carbonaceous fuel where the carbon is oxidized and the antimony oxide is reduced, Eq. (2). What makes Sb interesting for this application is that the melting temperatures of both the metal (T_{mp} = 630 °C) and its oxide (Sb_2O_3, T_{mp} = 656 °C) are below typical SOFC operating temperatures, allowing for good contact between the metal and the electrolyte and between the oxide and the carbon fuel. Also, the reaction between Sb_2O_3 and carbon is spontaneous and rapid at SOFC temperatures [9].

Although DCFC based on molten Sb can produce high power densities and operate on a wide range of fuels to high conversions, long-term stability remains a problem. Significant thinning of zirconia-based electrolytes has been observed following operation for times on the order of 100 h [10]. Zhou et al. [11] showed that this etching occurred whether the zirconia was stabilized by Sc, Y, or Ca and was most severe at positions of Sb_2O_3 accumulation. However, they also reported that some regions of the electrolytes were unaffected and they were unable to identify the mechanism behind the etching process.

In the present study, we investigated electrolyte etching for molten-Sb anodes using polycrystalline yttria-stabilized zirconia (YSZ), poly-crystalline gadolinia-doped ceria (GDC), and single-crystal YSZ as electrolytes. Etching was observed with both polycrystalline YSZ and GDC electrolytes, but not with single-crystal YSZ, and was shown to be associated with migration of Sb cations along grain boundaries of the

electrolyte. Because Sb migration and electrolyte etching were only observed in regions of current flow within the electrolyte, the process must be electrochemical in nature. Based on the results of this study, methods for preventing electrolyte etching are also suggested.

2. Experimental

Three different types of electrolyte-supported, button cells were prepared for the present study. Cells with polycrystalline YSZ electrolytes (8 mol% Y_2O_3) were fabricated using tape casting methods described in earlier studies [12,13]. For these cells, YSZ tapes, with and without pore-formers, were laminated and then fired at 1450 °C for 4 h to form bilayer wafers with one side dense and the other 60% porous. The porous layer was impregnated with aqueous solutions of the nitrate salts of lanthanum, strontium and iron, then calcined to 850 °C to form a 35-wt% $La_{0.8}Sr_{0.2}FeO_3$ (LSF) cathode, using methods described in detail elsewhere [14]. The electrolyte layers in these cells were 1 cm in diameter and 125 μm thick, while the cathode layers had a diameter of 0.67 cm and were 50 μm thick.

Preparation of the GDC-based DCFC used procedures described by Si et al. [15]. A 0.5-mm thick, 1-cm diameter, GDC pellet was prepared by pressing GDC powder ($Ce_{0.8}Gd_{0.2}O_{1.9}$, Fuel Cell Materials, USA) in a die and then sintering at 1475 °C for 10 h. An LSCF ink (($La_{0.6}Sr_{0.4}$)$_{0.95}$($Co_{0.2}Fe_{0.8}$)$O_{3-\delta}$, solid loading: 62–72 wt%, Fuel Cell Materials, USA) was then printed onto one side of the sintered GDC pellet and fired to 1100 °C for 3 h to serve as the cathode. The reactive area of the GDC cell was 0.96 cm^2.

A YSZ single crystal ($Y_{0.13}Zr_{0.87}O_{1.935-\delta}$, crystal orientation < 100 > , MTI Corp., USA), with a thickness of 0.5 mm, was also employed as the electrolyte for a molten-Sb DCFC. For this cell, the cathode was formed by screen printing a slurry containing LSM ($La_{0.8}Sr_{0.2}$)$_{0.98}MnO_{3-\delta}$ from Praxair Inc.) and YSZ (8 mol% Y_2O_3-92 mol% ZrO_2, Tosoh Corp.) powders, in a 1:1 weight ratio and dispersed in alpha-terpineol (96% Alfa Aesar). The components of the slurry were ball milled for 72 h to achieve a homogeneous fluid. The screen-printed, LSM-YSZ layer was sintered at 1100 °C for 2 h and had a surface area of 0.35 cm^2.

Identical testing procedures were used for each DFCF. Each button cell was sealed onto one end of an alumina tube with a ceramic adhesive (Ceramabond 552, Aremco), with the cathode side situated on the outside of the tube. A silver current-collecting wire was attached to the cathode with silver paste (SPI Supplies). 20 g of Sb metal (100 mesh powder, 99.5%, Alfa Aesar) was loaded into the alumina tube and allowed to contact the surface of the fuel cell disk.

The current collector for the anode side consisted of two 0.5-mm diameter Re wires (Alfa Aesar, USA) that were submerged into the molten Sb. To achieve stable operation, only the lower 5 mm of the Re wires were exposed to the Sb, while the other parts were shielded by an alumina tube. This was done to avoid having the Re metal come in contact with Sb_2O_3. Lastly, glass wool was inserted at the top opening of the alumina tube to minimize reaction between the air and Sb. The test system was then placed into a vertical tube furnace, with a K-type thermocouple placed next to the fuel cell to monitor the temperature. All electrochemical tests in the present research were performed at 700 °C. All fuel-cell tests were performed in battery mode, i.e. without any combustible fuel being added to the Sb. This simplified operation allowed us to focus on the chemistry at the Sb-electrolyte interface.

A Gamry Instruments potentiostat was used to discharge the fuel cell at a constant potential and to measure impedance spectra. Current values during the discharge test were recorded as a function of time and integrated in order to determine the amount of charge that was transferred through the electrolyte.

The open circuit potentials (OCP) were always 0.73 V at 700 °C, regardless of the type of electrolyte. This value is very close to the theoretical Nernst potential for the oxidation of Sb to Sb_2O_3 [8,10]. After testing, the cells were cooled to room temperature and removed from the alumina tube to facilitate SEM (scanning electron microscope)

analysis. Cross-sectional SEM images of the cells were collected using a Quanta 600 FEG ESEM (FEI, USA). The elemental distributions through the electrolyte were measured using Energy-Dispersive X-ray Spectroscopy (EDS).

3. Results and discussion

The performance of a cell with a sintered polycrystalline YSZ electrolyte was investigated by continuously discharging at 700 °C at a constant 0.3 V potential for 20 h, resulting in 11.4 kC of charge being extracted from the molten Sb anode. The current density for this cell is reported as a function of time in Fig. S1 and the results are consistent with previous reports for similar cells [11,12]. The current density decreased from ~ 490 mA cm^{-2} to ~ 400 mA cm^{-2} over the first five hours of operation and then gradually increased throughout the remaining duration of the test, reaching 480 mA cm^{-2} after 20 h on stream. Impedance spectra were also collected at the beginning and end of the test (see Fig. S2) and showed that the ohmic component of the Area Specific Resistance (ASR), which is due to transport of oxygen ions through the electrolyte, decreased from 0.71 Ω cm^2 to 0.64 Ω cm^2. As discussed in previous work, this result is consistent with thinning of the electrolyte during operation of the cell [11].

Cross-sectional SEM images and EDS elemental maps of the YSZ electrolyte, obtained after this cell test, were used to assess the structural and compositional changes that occurred during cell discharge. As shown in Fig. 1, two separate regions were selected for analysis: Region 1 is in the middle of the cell where the current density during operation is highest, and Region 2 is outside the area covered by the cathode where there would be minimal ion transport within the electrolyte during operation. Fig. 2a displays the SEM image of the central Region 1. An area without Sb attachment was selected to give a clearer view of the electrolyte interface. This image shows that the thickness of the YSZ electrolyte is 100 μm, which is 25 μm less than the electrolyte thickness (125 μm) prior to testing, demonstrating electrolyte corrosion during cell operation. It is also noteworthy that there is a clear difference in the crystalline morphology of the YSZ layer near the surface exposed to the Sb and in the bulk of the electrolyte (denoted by the white dashed line in the right corner of Fig. 2a). This difference shows that microscopic, structural changes have occurred in the interfacial region of the polycrystalline YSZ electrolyte. This change is revealed in more detail in image Fig. 2b which shows a close-up of the electrolyte. Note that the grain morphology of YSZ bulk (shown both in the lower part of Fig. 2b and c) is very different from that in the interfacial region (shown in the upper part of Fig. 2b).

EDS was used to map the elemental composition of the electrolyte in the white framed part of Fig. 2b. EDS data for O, Y, Zr, and Sb in this region are presented on the right side of Fig. 2b.

Note that the distributions of Y and Zr are similar, with regions in the upper portion of each map corresponding to individual YSZ grains. It is also noteworthy that Sb is distributed throughout the near-surface region of the electrolyte. There are subtle differences, however, in the Sb distribution compared to that of Y and Zr. The Sb is much more localized to specific areas. The Sb appears to be primarily at grain boundaries in the YSZ layer, as denoted by the white arrows in Sb map
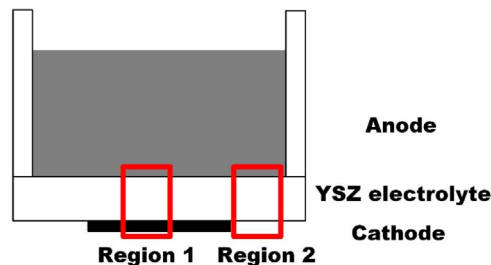

Fig. 1. Schematic diagram of the molten Sb anode DCFC.