Effects of interface roughness on a liquid-Sb-anode solid oxide fuel cell

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ABSTRACT

Liquid Sb anodes are examined at 1073 K in solid-oxide fuel cells with single-crystal yttria-stabilized zirconia (YSZ) electrolytes. Two types of cells with different anode—electrolyte interface morphologies are operated in "battery" mode, with dry Ar flow in the anode chamber, to characterize the effects of the interface roughness on the electrochemical oxidation of the metals with oxygen ions. When the effects of the electrolyte surface morphology are minimized by using an extremely smooth (Ra = 0.69 nm) anode —electrolyte interface, the intrinsic exchange current density is found to be 1.5 mA cm^{-2} by fitting the Tafel equation. When the surface roughness is increased to Ra = 540 nm, the effective contact area of the liquid Sb anode increases by 33% compared to the smooth cell. The product Sb_2O_3 can increase the effective reaction boundary by acting as an oxygen ion conductor. However, the accumulation of Sb_2O_3 at the interface weakens the effect of the surface morphology.

1. Introduction

Solid carbon, such as biomass or coal, can be used as fuel to directly generate electricity in fuel cells based on electrolytes that transfer oxygen ions [1–5]. A major challenge in making the direct carbon fuel cells (DCFC) practical is the necessity of fabricating low-impedance anodes that allow the facile transfer of oxygen from the electrolyte to the surface of the solid fuel [6–9]. One of the possible technical routes is the use of electrodes based on liquid metals, which could also serve for energy storage [10–14].

In liquid-metal-anode direct carbon fuel cells (LMA-DCFCs), the metal reacts with oxygen ions at the electrolyte interface, and the metal oxide is in turn reduced by the carbonaceous fuel in a separate step [15–17]. To determine the performance characteristics of the liquid-metal-and-oxygen-ion reaction at the anode—electrolyte interface, Gorte et al. [18,19] studied several metals with low melting points, such as Sn, Sb, In, Bi, and Pb, in fuel cells operated in battery mode without fuel. They concluded that the phase state and the oxygen ion conductivity were key impact factors. For a liquid metal with a solid metal oxide that does not behave as an oxygen ion conductor at a working temperature of 600 °C–1000 °C, such as Sn, a solid metal oxide formed that caused a sharp degradation in performance. In contrast, a liquid antimony anode, whose metal oxide is liquid at the working temperature, did not suffer performance degradation like that of Sn. Furthermore, the product Sb_2O_3 can transfer oxygen ions with a conductivity 0.0792 S cm^{-1} at 828 °C [20]. However, at present, most studies have used traditional ceramic yttria-stabilized zirconia (YSZ) electrolytes [21,22], which have various types of surface morphology that can

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have very important effects on the liquid—solid reaction as a result of differences in the effective contact area, the product separation from the electrolyte, and the product distribution.

In this paper, we use the current—voltage testing (IV) characteristic curves and electrochemical impedance spectroscopy (EIS) methods to investigate the effects of the electrolyte surface roughness on the performance of a liquid Sb anode in a fuel cell with a single-crystal YSZ electrolyte and a porous platinum cathode operating in battery mode. Scanning-electron-microscopy (SEM) tests were carried out for the characterization of the liquid Sb and the electrolyte interface before and after the testing, and a novel reaction mechanism for liquid-Sb electrochemical oxidation processes was proposed and discussed.

2. Experimental

2.1. Cell fabrication

The electrolyte and cathode of the liquid-metal-anode DCFC used in this study were prepared from a single-crystal YSZ electrolyte substrate with 13 mol% Y_2O_3 (crystal orientation <100>, Hefei Kejing Materials Technology Limited Company, China) with a 25 mm diameter and a 500 μm thickness. Two types of electrolyte were chosen with different surface roughnesses, Ra = 0.69 nm and Ra = 540 nm. Fig. 1 shows the surface morphology of the two electrolytes obtained by using a three-dimensional profilometer (Phase Shift MicroXAM-3D, AEP Technology, USA). The cathode of the cell was manufactured from platinum paste (MC-Pt100, Grikin Advanced Materials Limited Company, China) by the screen-printing method. The Pt-paste layer was dried at 100 °C in air for 15 min. The final calcination temperature for the cathode composite was 800 °C. The cathode diameter is 16 mm, and the cathode thickness is 15 μm.

After cathode-layer preparation, the cell was placed on the end of an alumina tube. An alumina plate was fixed in place against the button cell with three springs. A glass sealing ring was placed between the alumina tube and the button cell. On the cathode side, a platinum mesh was used as a current collector. On the anode side, a $Ni_{20}Cr_{80}$ ring was used as a current collector and also to hold the antimony metal electrode above the electrolyte. The alumina tube was then placed vertically to keep the liquid metal in contact with the single-crystal YSZ electrolyte. Antimony metal powder and carbon fuel powder could be added into the anode chamber during cell operation through the mount of the alumina tube in the middle. In this study, 2.0 g of antimony (99.5%, Sinopharm Chemical Reagent Limited Company, China) was added. The anode diameter is 16 mm, and the thickness of the 2 g liquid Sb anode is approximately 1.5 mm according to an estimate based on the inner diameter of the current collector ring (16 mm) and the density of the liquid Sb at 800 °C (6.34 g cm^{-3}) [23].

2.2. Experimental setup

A direct-carbon-fuel-cell experimental setup has been built for cell-performance testing, as shown in Fig. 2.

The polarization curves were measured with an electrochemical workstation (IM6ex, Zahner-Elektrik GmbH, Germany) using the four-probe method. Electrochemical impedance spectroscopy was performed using amplitude of 20 mV over a frequency range from to 100 kHz 0.1 Hz. The ohmic resistance of the cell was estimated from the high-frequency intercept of the impedance curve. The measurements were initiated while the temperature was changing and continued for 30 min, until the system was stable. A K-type thermal couple was used to monitor the temperature next to the button cell. The Ar gas for the anode chamber and the air for the cathode chamber were controlled by mass flow controllers.

During the experimental tests, the button cell was heated to 800 °C from room temperature over 10 h using shielding Ar gas with a flow rate of 35 mL min^{-1} for both the anode and cathode chambers. The platinum paste was then sintered for 30 min at 800 °C. Next, the anode Ar-flow rate was increased to 50 mL min^{-1}, and the cathode gas flow was switched to air at 200 mL min^{-1}. Finally, 2.0 g Sb was introduced into the anode chamber through the alumina tube in the middle. In this experiment, the anode gas-flow rate was 50 mL min^{-1}, much less than the cathode gas-flow rate of 200 mL min^{-1}, because the cathode chamber was much larger.

2.3. Experimental characterization of the polarization of each cell component

To determine each polarization loss experimentally for the liquid-Sb-anode fuel cell, a symmetric cell was used to estimate the cathode polarization. The symmetric cathode was printed in the same way as described previously for a single button cell on a single-crystal YSZ substrate with the same surface morphology as the liquid Sb fuel cell cathode on both sides. The total ohmic resistance was determined by EIS tests of the symmetric cell from the high-frequency intercept of the impedance curve. The cathodic polarization was determined by subtracting the ohmic polarization from the measured polarization and then dividing by two. The anodic polarization was then estimated by subtracting the ohmic polarization, the cathodic polarization and the leak overpotential from the total polarization of the single cell. Considering that the electrodes are good conductors, it is reasonable to assume that the resistance determined from EIS measurements at high frequency (the high-frequency intercept of the impedance curve) includes only the ohmic resistances of the contact and the electrolyte. The polarization due to both the contact and electrolyte resistances was then calculated from the value of the resistance determined from the EIS measurement.

3. Results and discussion

3.1. Liquid Sb anodes in their initial states

Fig. 3(a) presents the IV performance of the liquid Sb anodes with both rough and smooth electrolyte surfaces operated in battery mode. The open circuit voltage (OCV) of the smooth cell was 0.75 V, while the OCV of the rough cell was 0.70 V; both were comparable to the theoretical OCV of 0.738 V