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Polarization characteristics of liquid antimony anode with smooth single-crystal solid oxide electrolyte

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HIGHLIGHTS

- Smooth electrolyte for intrinsic reaction kinetics.
- Polarization separation of liquid antimony anode.
- Sb_2O_3 framework for enhancing electrochemical oxidations.
- Polarization reduction by tuning Sb/Sb_2O3 ratio.

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ABSTRACT

A liquid antimony (Sb) anode is examined at 1073 K in solid oxide fuel cells with single-crystal yttria-stabilized zirconia (YSZ) electrolytes. Cells featuring a smooth electrolyte surface (Sa = 0.69 nm) are operated under "battery" mode with dry Ar flow in the anode chamber to characterize the electrochemical oxidation of the metals by oxygen ions while avoiding the effects of the electrolyte surface morphology. The intrinsic anode polarization of the liquid Sb anode is obtained, revealing that the Sb anode polarization was the main cause of performance loss. Because liquid Sb_2O_3 can transfer oxygen ions, the reaction product Sb_2O_3 decreases the anode polarization and enhances the performance by increasing the effective reaction interface. The liquid three-dimensional electrode is formed by discharging. The anode polarization can be reduced by changing the ratio of Sb and Sb_2O_3 in the anode. Using 50% Sb + 50% Sb_2O_3 as the anode, the anode resistance is reduced to 0.8 Ω cm^2, which is comparable to typical porous solid anodes.

1. Introduction

Liquid metal anode solid oxide fuel cells (LMA-SOFCs) are a clean, efficient, and competitive power generation technology for converting the chemical energy of various types of fuel into electricity. In this technology, oxygen from the solid electrolyte is transferred to the liquid metal to form the metal oxide, and the metal oxide can later be reduced by the fuel [1–6].

In past several years, a number of liquid metals have been studied for use as LMA-SOFC anodes. General electric first proposed the liquid Fe anode [7] for high-temperature carbon electrochemical conversion. Jacob et al. [8] used a liquid Cu anode in an LMA-SOFC. Cell Tech Co. developed the liquid tin anode solid oxide fuel cell to lower the cell operating temperature [5,9–13] However, the cell performance is often limited by the formation of an oxide film at the electrolyte interface. The anode polarization loss from the liquid Sn increased dramatically after cell operation, even under a fairly low current. Gorte et al. [14,15] systematically analyzed the electrochemical oxidation performance characteristics of Sn, Bi, In, Pb, and Sb. The cell polarization curves with liquid Sn, In, and Pb operating at 700–800 °C show typical limiting behavior due to the oxide layer formation with low oxygen ion conductivity. For the liquid Bi anode, a Bi_2O_3 oxide layer can also be formed, but its oxygen ion conductivity is relatively high. The liquid Sb anode has shown excellent performance for use in both battery mode for Sb electrochemical reaction with oxygen ions and carbon fuel mode. In one aspect, both Sb and Sb_2O_3 are liquids at typical SOFC operating temperatures, which is beneficial for the transportation of Sb towards the reaction active sites and the transportation of Sb_2O_3 away from the reaction active sites. In

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addition, the liquid Sb_2O_3 is able to conduct oxygen ions with a conductivity of 0.0792 S cm^{-1} at 828 °C [16], which is of the same order of magnitude as the oxygen ion conductivity of yttria-stabilized zirconia (YSZ). Thus, except for the electrochemical oxidation of liquid Sb metal at the electrode/electrolyte interface, as occurs for other liquid metal anodes, liquid Sb can be electrochemically oxidized at the interface between the liquid Sb_2O_3 and liquid Sb phases. This mechanism may extend the electrochemically active area, which is closely related to cell polarization.

Based on the above discussion, the liquid Sb anode is a promising choice for use in a novel liquid metal anode fuel cell. However, the performance of liquid Sb anodes is still limited for multiple reasons, including the mechanism of charge transfer between the liquid electrode and electrolyte surface and the low electrochemical activity of the electrodes. Thus, it is important to understand the performance characteristics of the liquid Sb/electrolyte interface to improve the performance of these anodes.

Many studies have focused on the cell performance characteristics using a liquid Sb anode and novel prototype design development, especially the liquid Sb electrochemical oxidation and the reaction between liquid Sb_2O_3 and solid carbon [17–20]. However, most of the experimental characterizations of liquid Sb anode fuel cells in the literature have used commercially or self-prepared electrolyte layers with different surface roughness. The morphology of the electrode surface significantly affects the liquid metal electrochemical reaction characteristics, and the intrinsic electrochemical reaction rates are obfuscated by interface interactions and transport in rough porous anodes. In addition, the effects of the surface roughness on the cell couple with the effects of the Sb/Sb_2O_3 electrochemically active interface variation due to the composition variation of the liquid metal anode and make the transport and reaction processes within the liquid electrode more complex.

In this study, a liquid Sb anode solid oxide fuel cell is fabricated on a smooth single-crystal YSZ electrolyte substrate with a porous Pt cathode to investigate the intrinsic reacting kinetics of the electrochemical oxidation of liquid Sb. Polarization curves and electrochemical impedance spectroscopy (EIS) are used to evaluate the cell performance. The polarization of each cell component (anodic, cathodic, and electrolyte) is determined from specific experiments using a symmetric cell for polarization curves and EIS measurements. The discharge curves are used to analyze the effect of the reactant consumption and product accumulation on the cell performance. Scanning electron microscopy (SEM) is used to characterize the liquid Sb and electrolyte interface before and after the testing, and a novel reaction mechanism for liquid Sb electrochemical oxidation processes is proposed and discussed.

2. Experimental

2.1. Liquid Sb fuel cell preparation

A 25-mm diameter single-crystal smooth YSZ substrate with 13 mol% Y_2O_3 (<100> crystal orientation, Hefei Kejing Materials Technology Co., Ltd., China) was used as the electrolyte. The roughness of the electrolyte surface Ra is maintained at 0.69 nm, which is polished by chemical method. And the thickness of the electrolyte is 500 μm. The cathode was prepared from platinum paste (MC-Pt100, Grikin Advanced Materials Co., Ltd., China) by screen printing. The Pt paste layer was dried at 100 °C in air for 15 min. The calcination temperature for the cathode composite was set at 800 °C. Fig. 1a shows the surface morphology of the YSZ single crystal obtained by scanning electronic microscopy (SEM) (JSM-6460, JEOL, Japan), and Fig. 1b shows the YSZ surface roughness obtained by 3D profilometry (Phase Shift MicroXAM-3D, AEP Technology, USA).

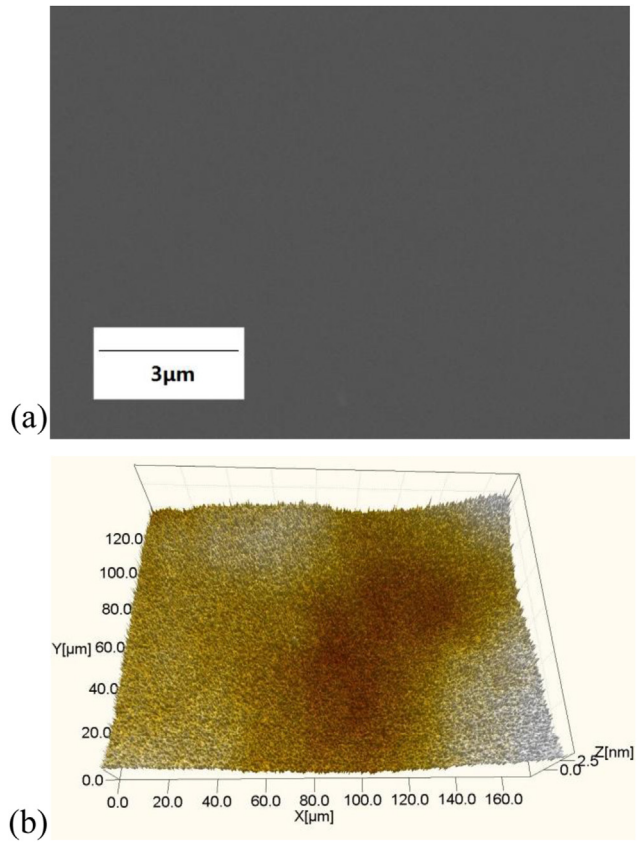

Fig. 1. Surface morphology characteristics of single-crystal YSZ electrolyte: (a) SEM images, (b) 3D profilometer images.

The cell was placed on the end of an alumina tube. An alumina plate was pressed to the button cell and fixed to three springs. A sealing glass ring was placed between the alumina tube and the button cell. On the cathode side, a platinum mesh was used as the current collector. On the anode side, a $Ni_{20}Cr_{80}$ ring was used as a current collector and to hold the antimony metal electrode above the electrolyte. The alumina tube was then set vertically to keep the liquid metal in contact with the single-crystal YSZ electrolyte. The antimony metal powder and carbon fuel powder can be added into the anode chamber during the cell operation by mounting the alumina tube. In this study, 2.0 g of antimony (99.5%, Sinopharm Chemical Reagent Co., Ltd., China) was added on top of the electrolyte. The thickness of the liquid metal anode should be 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}) [21].

2.2. Experimental testing setup

A liquid Sb anode fuel cell experimental testing setup was constructed for cell performance testing, as shown in Fig. 2.

The polarization curves were measured by the four-probe method using an electrochemical workstation (IM6ex, Zahner-Elektrik GmbH, Germany). Electrochemical impedance spectroscopy (EIS) was performed with an amplitude of 20 mV from 0.1 Hz to 100 kHz. The ohm resistance of the cell was estimated from the high-frequency intercept of the impedance curve. The measurements were initiated 30 min after the temperature of the system had stabilized. A K-type thermal couple was used to measure the temperature next to the button cell. The Ar gas for the anode