



Plasma-spray derived, corrosion-resistive electrolyte for liquid antimony anode direct carbon fuel cell

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HIGHLIGHTS

- Metal supported SOFC prepared by atmospheric plasma spray (APS) technology.
- Direct conversion of solid carbon fuel into power in liquid Sb anode.
- Electrolyte's resistivity against Sb₂O₃ corrosion confirmed in the 120-h long term test.

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ABSTRACT

Direct carbon fuel cells (DCFC) that employ solid oxide electrolytes and liquid antimony (Sb) anodes are efficient electrochemical cells for converting various types of solid carbon fuels directly into power. Though the liquid Sb anode exhibits decent performance, electrolyte corrosion by molten Sb₂O₃ during fuel cell operation has long been an issue. The present study investigates the behavior of scandia stabilized zirconia (ScSZ) electrolytes fabricated through different approaches in liquid antimony anode DCFCs. As for conventional sintered ScSZ electrolyte, we observed severe electrolyte corrosion by molten Sb₂O₃, which agrees with previous reports. In contrast, corrosion or thinning by the oxide was not detected in ScSZ electrolyte prepared with atmospheric plasma spray (APS) technology. Both electrochemical testing and microscopic characterization results suggest that plasma spray is a promising method to prepare robust electrolytes for liquid antimony anode based DCFCs.

1. Introduction

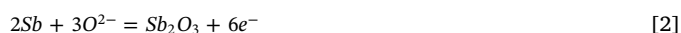
Solid oxide fuel cell (SOFC) is an efficient, high-temperature electrochemical cell capable of converting carbonaceous fuels, such as solid carbon, directly into electricity [1,2]. Such a direct carbon fuel cell (DCFC) isolates solid carbon fuel from air with an ionic conducting ceramic membrane and consumes carbon electrochemically via the following electrode reaction:



One unique advantage of DCFCs is the production of CO₂-rich flue gas free of NO_x or SO_x, allowing for easy carbon capture.

Due to its high efficiency and low emission, considerable efforts have been devoted to DCFC research in recent years [3–5], and progress made in this field has been covered by several recent reviews [6,7,8.] Despite of the above-mentioned advantages of DCFCs, oxidation kinetics of solid carbon fuels at typical operating temperatures of DCFCs

turned out to be very sluggish [9,10]. Oxygen ion transfer from the ionic-conducting electrolyte to the solid carbon fuel is widely recognized as the rate limiting step in cell performance [11]. To overcome this barrier, molten antimony (Sb) metal is employed as a medium to convert solid carbon [12,13]. In this case, the anode reaction is split into two steps. The first step is electrochemical oxidation of Sb-anode at the anode-electrolyte interface:



During this step, metal Sb is oxidized, electrons are released to the external load, and antimony oxide (Sb₂O₃) is produced. The second step is the reduction of Sb₂O₃ by solid carbon fuel into metallic Sb:



The reduction of Sb₂O₃ by carbon is spontaneous and rapid at SOFC working temperature [14].

Since the melting points of Sb and Sb₂O₃ are 904 and 929 K,

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respectively, both species in the anode remain in liquid state during DCFC operation. Under this circumstance, Sb_2O_3 produced can be transported away from the electrochemical reactive sites via diffusion, natural convection, or agitation [15,16], allowing for adequate contact between the liquid Sb and electrolyte and that between Sb_2O_3 and solid carbon.

Although liquid Sb anode exhibits reasonable performance and low impedance (around $0.05 \Omega \text{ cm}^2$ at 700°C [8]), corrosion of the solid electrolyte by the liquid Sb is a critical issue. Thinning effect of the electrolyte by the liquid metal has been previously reported [13,14]. A continuous thinning of electrolyte could lead to collapse of fuel cell, therefore long-term operation of liquid Sb DCFC remains a challenge. Jayakumar et al. [17] reported that the thinning issue on ScSZ electrolyte by liquid metal anode was more severe than that on YSZ electrolyte (yttria stabilized zirconia). The authors attributed this to the smaller radius of Sc^{3+} cation than Y^{3+} cation. Zhou et al. [18] showed that the electrolyte etching can occur in most zirconia based electrolytes regardless of the dopants and become more severe at positions of Sb_2O_3 accumulation. Cao et al. [19] studied liquid Sb anode etching on both zirconia (YSZ) and ceria based (GDC, gadolinia-doped ceria) electrolytes, detecting the corrosion effect in both polycrystalline ceramic electrolytes. In these two cases, Sb was found migrating along grain boundaries in the electrolyte, breaking connections between grains, and damaging the integrity of the electrolytes. This theory was further proved by long-term test carried out on YSZ single crystal electrolyte. The single crystal electrolyte was found resistive against Sb corrosion despite of longer operation time and a large amount of charge being transported. The above-mentioned work also suggests that grain boundaries are weak points in the electrolyte vulnerable to the attack of Sb_2O_3 . Thus, reducing the number of grain boundaries [20,21] or building strong bonds between grains can be a potential solution to resist liquid Sb anode attack on the electrolyte.

Atmospheric plasma spray (APS) technology is known to make robust films by melting feed powder in plasma plume. The molten particles crash on the substrate at high speed, forming splats on the substrate's surface. The bonding of splats to the substrate are so strong that the film deposited is corrosion and wear resistant [22,23]. On the other hand, APS is also considered a promising approach for mass-production of SOFCs [24,25]. In this study, different types of DCFCs were prepared by sintering and APS methods with the same electrolyte material (ScSZ). Both types of cells were discharged at a constant working potential continuously. The etching effect was observed on the sintered electrolyte, but not on plasma sprayed electrolyte. The results of electrochemical test and microscopic characterization suggest APS method is a promising approach to prepare corrosion resistant electrolyte for liquid Sb anode DCFC.

2. Experimental procedure

2.1. Preparation of sintered cell

The sintered electrolyte was prepared from a commercially available ScSZ powder ($(\text{Sc}_2\text{O}_3)_{0.10}(\text{CeO}_2)_{0.01}(\text{ZrO}_2)_{0.89}$, Fuel Cell Materials, USA). The powder was first pressed in a die and then sintered at 1450°C for 6 h; the sintered electrolyte was $170 \mu\text{m}$ thick. The cathode of LSM-YSZ ($(\text{La}_{0.80}\text{Sr}_{0.20})_{0.95}\text{MnO}_3 \cdot (\text{Y}_2\text{O}_3)_{0.08}(\text{ZrO}_2)_{0.92}$, Fuel Cell Materials, USA) was made by screen printing of its ink comprising of LSM-YSZ and alpha-terpineol (96% Alfa Aesar) at a weight ratio of 1:1 after being ball milled for 12 h. The printed cathode was calcined at 1150°C for 2 h. Effective area of the cathode was 0.785 cm^2 .

2.2. Preparation of plasma sprayed cell

Preparation of plasma sprayed cell started from stainless steel powder. Tape cast SUS 441 (gas atomized powder, Jiangsu Vilory Advanced Materials Technology Co., Ltd., China) sheets with a

thickness of 1.8 mm were sintered at 1300°C under reducing atmosphere containing 5 vol % of H_2 . The porous stainless-steel discs, with a porosity of $20.1 \pm 2\%$, served as substrates for plasma sprayed cells.

Cathode scaffold was first sprayed to the substrate by an SG-100 spray gun (Praxair Surface Technology, USA) at a power of 24 kW and a feed rate of 8 g min^{-1} . To do so, a mixed powder of 90 wt % ScSZ ($(\text{Sc}_2\text{O}_3)_{0.10}(\text{CeO}_2)_{0.01}(\text{ZrO}_2)_{0.89}$, Siemens) and 10 wt % PMMA (Poly (methyl methacrylate), Acros Organics, USA) as pore former was fed into the APS system. The torch was intentionally ran at a low power level to maintain the scaffold's porosity. The as-sprayed sample with a thickness of $20 \mu\text{m}$ was first heated up to 600°C for 2 h to remove the pore former, and then submerged into aqueous solution containing nitrates of lanthanum, strontium, cobalt and iron. The impregnated samples were then calcined at 850°C for 2 h to obtain infiltrated LSCF ($(\text{La}_{0.6}\text{Sr}_{0.4})_{0.95}(\text{Co}_{0.2}\text{Fe}_{0.8})\text{O}_3$)-ScSZ composite cathode layer. Detailed information of cathode infiltration is given elsewhere [26].

The ScSZ electrolyte layer was prepared by the same APS system, but without pore former in the ScSZ feedstock. The plasma torch was held 80 mm away from the substrate, and the torch power was 28 kW to melt the ceramic powder at a powder feed rate of 8 g min^{-1} . The sprayed electrolyte layer was $\sim 100 \mu\text{m}$ thick. The torch power for electrolyte layer spraying is higher than that of cathode scaffold spraying, because the ScSZ particles need to be fully melt. Only in this way, can we achieve a highly dense electrolyte layer.

2.3. Electrochemical test and characterization of fuel cells

Similar testing procedures were used for both types of DCFCs. Each button cell was first sealed onto one end of an alumina tube with a ceramic adhesive (Ceramabond 552, Aremco). For the plasma sprayed cell, the effective reaction area was 1.26 cm^2 , which was calculated based on inner radius of the alumina tube. Cathode side of the fuel cells situated on the outside of the tube. Silver wires were attached to the cathode with a silver paste to serve as the current collector. A 20 g of Sb metal powder (100 mesh, 99.5%, Alfa Aesar) was loaded into the alumina tube and contact directly with the ScSZ electrolyte. A 2.5 g of activated charcoal (C-1102, Multivita, USA) was loaded on the top of the metal, serving as fuel to support for long-term operation. The current collector for the liquid Sb anode were two Re wires (diameter: 0.5 mm, Alfa Aesar), both were submerged into the molten Sb. To achieve stable operation, only the lower 5 mm of Re wires were exposed to the Sb, while the rest parts were shielded in alumina tube to avoid Sb_2O_3 corrosion. When the cells were ready for the tests, a glass wool was inserted into the opening at the top of the alumina tube to minimize oxygen transport into the anode chamber. The test assembly was then fixed 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 .

A Solartron electrochemical working station (consisting of a 1470 multichannel potentiostat and a 1255B frequency response analyzer) was used to perform the electrochemical tests. Each cell subject to test was shorted (discharged at 0 V) to achieve a maximized current, and the current during the discharge test was recorded as a function of time. The recorded current was then integrated over time, from which the amount of charge transferred through the electrolyte was determined. Electrochemical impedance spectroscopy (EIS) was measured on cells at open-circuit condition. The Ohmic resistance of the cell was taken from the high frequency intercept on the real axis, while non-ohmic resistance of the cell was estimated from the "length" of the impedance arc on the real-axis.

Open circuit potentials (OCP) of the cells were always 0.75 V at 700°C for both types of electrolytes, which are very close to the theoretical value. After electrochemical tests, the tested cells were removed from the alumina tube for SEM (scanning electron microscope, Zeiss Ultra plus) characterizations. The sintered cell was broken up to take cross-sectional SEM images. The plasma-sprayed cell was cut, mounted

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