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# Liquid antimony anode direct carbon fuel cell fueled with mass-produced de-ash coal

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ABSTRACT

A liquid antimony (Sb) anode DCFC (direct carbon fuel cell) is fabricated on a smooth single crystal YSZ (Yttria Stabilized Zirconia) electrolyte substrate with porous Pt cathode to reveal the intrinsic reaction kinetics of electrochemical oxidation of liquid Sb and the reduction reaction characteristics of $Sb_2O_3$ with the reaction mass-produced Taixi de-ash coal fuel. The reduction kinetics of $Sb_2O_3$ with the de-ash coal is obtained using a temperature programmed reaction testing system. The reaction kinetics of the $Sb_2O_3$ with the de-ash coal can be enhanced by decreasing the coal particle size, and by adding de-ash coal into the anode chamber. The $Sb_2O_3$ accumulation at the interface between anode and electrolyte lead to the increase of ohmic resistance. While effective reaction active sites increase when the mole content of oxygen ion conductor $Sb_2O_3$ increase at the earlier stage of the cell discharging processes which further decrease the electrode polarization. The Si and Fe in the ash possibly accumulate at the interface between anode and electrolyte.



## 1. Introduction

Fuel cell is a clean, efficient and competitive power generation technology, which could convert fuel directly into electricity [1–3]. A hydrogen fueled PEMFC (Proton exchange membrane fuel cell) could exhibit satisfying performance on power generation and environment protection [4,5] under relatively mild working temperature (<100 °C). But when the fuel becomes less electrochemically active, such as carbon fuel, one should raise the operation temperature of the fuel cell to activate the reaction. SOFCs (solid oxide fuel cell) mainly work between 600 and 1000 °C is an ideal device for direct carbon power generation. An SOFC fueled by carbon fuel makes a SO-DCFC (solid oxide direct carbon fuel cell). The anode where the carbon is oxidized to produce electricity is a vital part of the whole power generating system, and there are mainly three types of anodes for SO-DCFC: Porous solid anode [6–8], molten carbonate anode [9,10] and liquid metal anode [11]. When compared to the porous solid anode, liquid metal offers better contacting condition between carbon fuel and electrode which promotes the SO-DCFC's performance. As the liquid metal could serve as a good electronic conductor, the liquid metal anode meets less problem than the molten carbonate anode when it comes to current collection. And what makes the liquid metal anode more fascinating is that a SO-DCFC utilizing a liquid metal anode can keep producing electricity for a couple of time without carbon supplement. This would decrease performance fluctuation brought by carbon fuel transportation.

A number of liquid metals have been studied as the liquid metal anode, such as Sn [12,13], In Refs. [14], Bi [15], Ag [16], Sb [17–20]. Due to a non-oxygen-ion conducting layer formed at the interface between anode and electrolyte, the performance of liquid Sn [12,13] and In Ref. [14] anode decreased sharply at battery mode. Although $Bi_2O_3$ is an oxygen ion conductor, the OCV (open circuit voltage) of liquid Bi [15] is quite low. For liquid Ag, AgO decomposes when temperature is higher than 250 °C which avoid the metal oxide layer formation. However, the impedance of liquid Ag anode was high, ~100 Ω $cm^2$ [16]. But for Sb, both Sb and $Sb_2O_3$ are liquids at typical SOFC operating temperatures, which is beneficial for the transport of Sb towards the reaction active sites and the transport of $Sb_2O_3$ away from the reaction active sites, the liquid Sb anode showed excellent performance both under the “battery mode”, in which the metallic Sb is electrochemically oxidized by oxygen ions, and under the carbon fuel mode [15,16].

Raymond J. Gorte [17] used rice starch, carbon black and sugar char as fuel for liquid Sb anode DCFC, which suggested that the amount of ash in the carbon fuel, the carbon fuel density and the

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initial reaction temperature were very important for the liquid Sb anode DCFC as the carbon fuel should contact the liquid Sb and the carbon oxidation should be thermo-dynamically favored. Recently, Chung-Hwan Jeon et al. [21] and Lee Injae [22] showed the feasibility of using de-ash coal in a porous-solid-anode SO-DCFC, since it has low ash content. In order to use de-ash coal as fuel in liquid Sb anode DCFC, the performance characteristics of liquid Sb anode SO-DCFC fuel with de-ash coal is necessary. Meanwhile, Shenhua Ningxia Coal Industry Group of China has successfully achieved mass production of Taixi de-ash coal (600,000 ton/year) using the skimping-floatation method. As shown in Fig. 1, the de-ash coal can be obtained by this novel coal washing system developed by Shenhua Ningxia Coal Industry Group of China. The de-ash coal can then be fed into the anode chamber of the liquid Sb anode DCFC (direct carbon fuel cell). The coal added in would reduce the $Sb_2O_3$ produced during fuel cell operation while power and heat can be generated cleanly and efficiently. For further consideration, syngas can also be produced at a certain operating conditions, which indicates the possibilities of developing an advanced power-gas co-generation system based on the liquid Sb anode DCFC technology.

In this study, the mass-produced de-ash coal from Shenhua Ningxia Coal Industry Group of China was directly used as the fuel of DCFC. The reduction kinetics of $Sb_2O_3$ with Taixi de-ash coal was obtained using a TPR (temperature programmed reaction) testing system. A liquid Sb anode direct carbon fuel cell was fabricated on a single crystal YSZ (Yttria Stabilized Zirconia) electrolyte substrate. IV (Current-voltage) characteristic curves and EIS (electrochemical impedance spectroscopy) were measured to evaluate the cell performance.

## 2. Experimental procedures

### 2.1. Liquid Sb anode fuel cell preparation

A round single crystal smooth YSZ substrate with a diameter of 25 mm made of 13 mol%$Y_2O_3$ ($Y_{0.13}Zr_{0.87}O_{1.935-\delta}$, Crystal orientation <100>, Hefei Kejing Materials Technology Limited Company, China) was used as the electrolyte. The maximum roughness of the electrolyte surface is kept below 156 nm, and the thickness of the YSZ pellet is 500 μm. The platinum cathode of the cell was made from platinum paste (MC-Pt100, Grikin Advanced Materials Limited Company, China) by the method of screen printing. The as printed Pt paste layer was dried at 100 °C in air for 15 min, and then a temperature of 800 °C was set for cathode calcination. The post-calcination cathode is 16 mm in diameter and 15 μm in thickness.

The cell was placed at the bottom end of a vertical alumina tube, fixed by an alumina plate with 3 springs. A platinum mesh was used as current collector on the cathode. While on the anode side, a $Ni_{20}Cr_{80}$ ring was utilized as the current collector and also work as an antimony metal electrode holder above the electrolyte. The metallic antimony and the solid carbon fuel would be added into the anode chamber during the cell operation through the top of the alumina tube. In this study, 10 g antimony (99.5%, Sinopharm Chemical Reagent Limited Company, China) was added to the upper surface of the YSZ electrolyte. The thickness of the liquid metal thin layer should be around 7.5 mm according to the approximate calculation based on the density of the liquid Sb at 800 °C (6.34 g $cm^{-3}$) [23]. The fuel cell preparation is described in more details in our previous work [24].

### 2.2. Characteristics of Taixi de-ash coal

Taixi de-ash coal (Shenhua Ningxia Coal Industry Group Co. Ltd, China) was used as fuel for liquid Sb anode DCFC in this study. The proximate and ultimate analysis of the Taixi de-ash coal is shown in Table 1. The proximate analysis was carried out based on the standard of GB/T212 of China. The ultimate analysis was carried out based on the standard of GB/T476 of China. The sulfur in the coal was analyzed based on the standard of GB/T214 of China. The results shows that the weight percentage of the ash is lower than 3%, and fixed carbon in the de-ash coal is around 88.79%. Further, the specific surface area was 0.1836 $m^2$ $g^{-1}$ tested by BET (Brunauer-Em- mett-Teller method). The ash composition was shown in Table 2, which was analyzed based on the standard GB/T1574 of China.

### 2.3. Experimental testing setup

A test system was built for this liquid antimony anode fuel cell. The polarization curves were measured using the four-probe method with an electrochemical workstation (IM6ex, Zahner-Elektrik GmbH, Germany). EIS (Electrochemical impedance spectroscopy) test was performed with amplitude of 20 mV, with frequency ranging from 100 kHz to 0.1 Hz. The ohmic resistance of the cell was estimated from the high frequency intercept of the EIS curve. A K-type thermocouple was placed next to the fuel cell as a temperature monitor.

During the experiments, the button cell was heated to 800 °C from room temperature, shielded in Ar. As soon as the fuel cell reaches the temperature steady state, the Ar gas flow rate in the anode chamber was increased, and the cathode gas was switched to air. And the Sb powder was added. The parameters of cell testing are presented elsewhere [24].

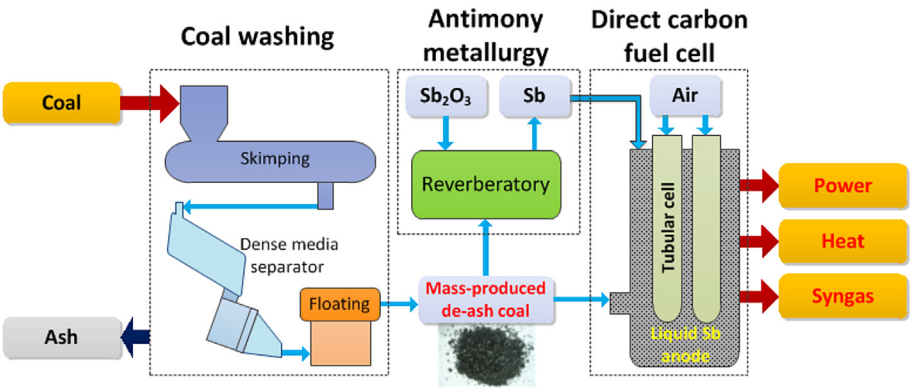


**Fig. 1.** Technology roadmap for liquid Sb anode DCFC using de-ash coal.