A Direct H_2S/Air Solid Oxide Fuel Cell

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We wish to report recent work performed in our laboratory on the direct electrochemical oxidation of H_2S using a solid oxide fuel cell possessing the configuration:

$$H_2S,W/CuFe_2S_4/ZrO_2(8^{w}/o\ Y_2O_3)/$$
$$La_{0.89}Sr_{.10}MnO_3/Pt,O_2(Air)$$

This cell utilized the thiospinel $CuFe_2S_4$ as the anode electrocatalytic site for promoting H_2S oxidation. The thiospinel used in this work was prepared by direct chemical reaction between intimately mixed stoichiometric quantities of the finely dispersed powdered elements (purities > 99.9%) in a sealed ampoule. This solid-state reaction mixture was heated at 700°C for three days to promote reaction, with the resulting black crystalline reaction product possessing good electronic conductivity.

The fuel cell assembly was fabricated using a closed one end yttria stabilized zirconia tube (Corning, OD 0.9cm, ID 0.6cm) giving a resultant solid electrolyte thickness of 0.15cm. The oxygen reduction electrode was initially introduced onto the lower closed end of the $ZrO_2(8^{w}/o\ Y_2O_3)$ tube as a $5^{w}/o$ suspension in ethylene glycol/citric acid of $La(C_2H_3O_2)$, $SrCO_3$ and $MnCO_3$ of appropriate composition. A Pt wire (0.25mm) current collector was initially tightly coiled in this region. Decomposition of the electrocatalyst precursor was achieved by heating the tube assembly to 800°C in air for 1h followed immediately by heating the half-cell assembly to 1250°C for 1h to form the $La_{0.89}Sr_{.10}MnO_3$ oxygen electrode. In most cases good adhesion was found between the finally sintered fuel cell cathode, the solid electrolyte tube and the Pt current collector.

The thiospinel electrocatalyst used at the anode was initially prepared into a paste comprising 1g $CuFe_2S_4$ (< 325 mesh) 0.1g carbowax 1000 (Alltech) and 3 to 4 drops of water. A coiled tungsten wire current collector (0.25mm diameter, 99.9% Aldrich) was initially introduced into the lower ≅5cm of the solid electrolyte tube maximizing its initial superficial mechanical contact to the inside wall. The thiospinel containing paste was then painted over the coiled W current collector region ensuring that contact was simultaneously achieved both to the W and solid electrolyte. The thiospinel electrocatalyst was now cured under Ar for 1h at each of the following respective temperatures: i) 100°C for water removal, ii) 200°C for carbowax 1000 removal, and iii) at 800°C for removal of residual volatiles. H_2S (Matheson 99.5%) was now introduced into the anode compartment at 900°C via a copper tube whose outlet was in close proximity to the thiospinel electrocatalyst region. The initial fuel cell open-circuit potential (OCP) became 1.04V. The overall cell resistance of ≅10Ω was dominated by that of the solid electrolyte. The current-potential curve for this cell is shown in Figure 1 together with the projected IR-free curve (since the cell was dominated by solid electrolyte resistance losses). The geometric area of the thiospinel anode was not known with any precision but was < 10cm^2. The thiospinel appeared to possess good stability in this cell although no exhaustive study was performed to address this issue. It is of interest to note that several thiospinels might in principle be prepared <u>in situ</u> at the anode from initially deposited oxide spinels (AB_2O_4) via the general reaction[1]:

$$AB_2O_4 + 4H_2S \longrightarrow AB_2S_4 + 4H_2O \qquad (1)$$

For internally reformed methane fuel cells containing significant concentrations of H_2S at the anode and utilizing oxide spinel anodes, an equilibrium in reaction (1) above may prove a convenient strategy for achieving fuel cell sulfur tolerance. The question remains as to what might be the H_2S oxidation reaction. The overall reaction

$$H_2S + 3/2O_2 \longrightarrow SO_2 + H_2O \qquad (2)$$

at 900°C would possess a theoretical OCP of only 0.56V and the reaction

$$H_2S + 1/2O_2 \longrightarrow H_2O + S \qquad (3)$$

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occurs at -0.26V. The higher than expected OCP observed experimentally suggested the possibility of some internal reforming mechanism to give H_2 which subsequently became anodized. Furthermore the overall reaction

$$S + O_2 \longrightarrow SO_2 \qquad (4)$$

occurs at a theoretical potential 0.97V at this temperature, close to that for H_2. Additionally SO_2 present in the anode compartment will be expected chemically reduced by H_2S via the overall reaction:

$$2H_2S + SO_2 \longrightarrow 3S + 2H_2O \qquad (5)$$

resulting in the essential conversion of H_2S to sulfur and electricity. Similar observations of higher than expected OCPs for H_2S oxidation in solid oxide type fuel cells have recently been discussed[2] using Au, Pt or Ni as electrocatalysts, where the active electrocatalytic sites for H_2S oxidation were considered colored F-centers introduced into the solid electrolytic surface.

These preliminary experimental observations were intended to merely show the potential utility of this approach for direct H_2S oxidation and for achieving sulfur tolerance in solid oxide methane fuel cells. No effort has yet been directed towards cell optimization incorporating such electrode components.

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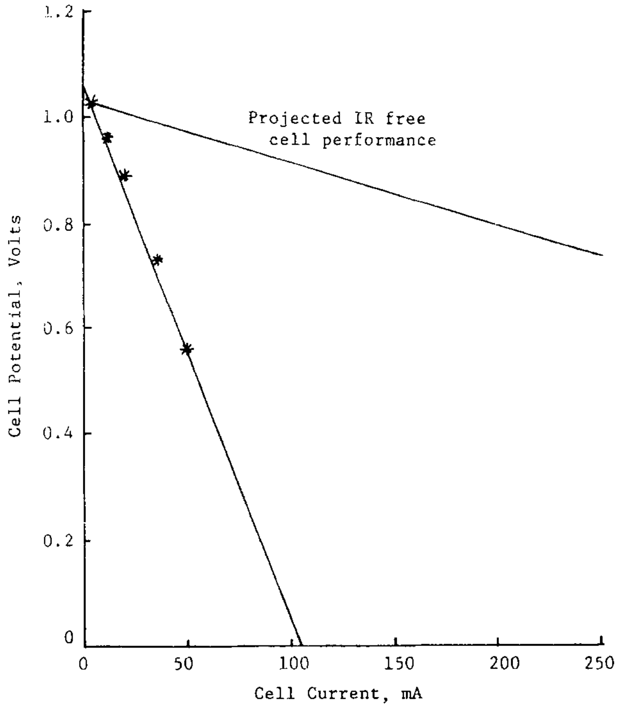

Figure 1.
Current-potential load curve for the fuel cell

$$H_2S,W/CuFe_2S_4/ZrO_2(8^{w}/o\ Y_2O_3)/$$
$$La_{0.89}Sr_{.10}MnO_3/Pt,O_2(air)$$

at 900°C.

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