

An Intermediate-temperature H₂S Fuel Cell with a Li₂SO₄-based Proton-conducting Membrane^{*}

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Abstract A laboratory-scale intermediate-temperature H₂S fuel cell with a configuration of H₂S, (metal sulfide-based composite anode)/Li₂SO₄+Al₂O₃/(NiO-based composite cathode), air was developed and studied for production of power and for desulfurization of a fuel gas process stream. The cell was run at typical temperature (600–650°C) and ambient pressure, but its electrochemical performance may be limited by electrolyte membrane thickness. The membrane and its performance in cell have been characterized using scanning electron microscope (SEM) and electrochemical impedance spectrum (EIS) techniques. Composite anodes based on metal sulfides, Ag powder and electrolyte behaved well and stably in H₂S stream, and composite cathodes based mainly on nickel oxide, Ag powder and electrolyte had superior performance to Pt catalyst. The maximum power density of up to 70mW·cm⁻² and current density of as high as 250mA·cm⁻² were obtained at 650°C. However, the long-term cell stability remains to be investigated.

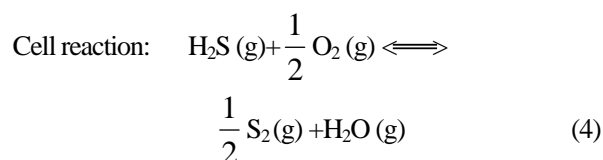
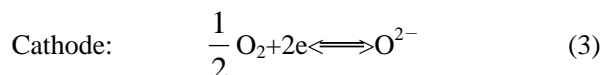
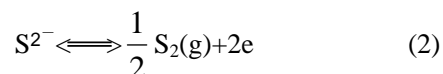
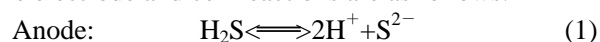
Keywords fuel cell, lithium sulfate, hydrogen sulfide, anode catalyst, cathode catalyst

1 INTRODUCTION

H₂S is a corrosive contaminant in coal gasification and diesel fuel reformat streams, and it must be removed to make each fuel a viable energy source. It can be removed by using the Claus process, in which the chemical energy of the oxidation reaction is either vented or partially recovered as low-grade steam. Fuel cell offers such an economically and environmental desirable technology as to generate high-grade electric power from large amount of chemical energy associating with the oxidation of H₂S^[1–5]. In addition, H₂S is converted with high selectivity to useful chemical raw materials, such as high-purity sulfur.

The feasibility for electrochemically oxidation of H₂S in a fuel cell was first revealed in 1987^[2]. This led to the investigation of alternative electrolytes and anode as well as cathode electrocatalysts for H₂S solid oxide fuel cell (SOFC)^[1–7]. O²⁻ conducting yttria-stabilized zirconia (YSZ) electrolytes (operating temperature above 800°C) were the commonly used electrolyte in H₂S SOFC. More recently, proton-conducting electrolytes have been shown to have some new advantages for H₂S fuel cells operated at temperature below 700°C^[6,7]. The Li₂SO₄-based proton-conducting membrane incorporating Al₂O₃ enhances mechanical property^[1]. Compared with the

H₂S fuel cell with O²⁻ conducting yttria-stabilized zirconia (YSZ) electrolyte, the operating temperature for the H₂S fuel cell with proton-conducting electrolytes was lower, both power and element S (chemical product) were obtained while the H₂S was removed. The electrode and cell reactions are as follows:



The most challenging task for development of H₂S-air fuel cells is development of a proton-conducting membrane with chemical/thermal stability, good mechanical strength and electrical conductivity, and of active and stable electrode catalysts in H₂S stream. Currently, no such membrane and electrode materials are commercially available. In this work, a fuel cell with a Li₂SO₄-based proton-conducting membrane, anode materials based on mainly metal sulfides, and NiO-based cathode materials by admixing Ag

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powder was built and tested. It is found that the electrolyte membrane exhibits good integrity and is promising in conversion of H_2S .

2 EXPERIMENTAL

2.1 Preparation of a membrane

A membrane with a designed composition was prepared using the following procedures^[6]. The appropriate amounts of Li_2SO_4 and Al_2O_3 were weighted and mixed well with a small amount of water. The mixture was in the form of a paste, because the amount of water was insufficient to affect total dissolution. The paste was dried in air, and then ground to powder until the particle size was smaller than $25\mu\text{m}$. An aliquot of the powder was weighted ($0.7\text{--}1\text{g}$), loaded into a mould with a diameter of 2.54cm , and then pressed for about 1 h under around $5\times 10^4\text{N}\cdot\text{cm}^{-2}$ to form a wafer. The wafer so obtained was sintered in air in an oven first at 105°C for $90\text{--}120\text{min}$ and then at 850°C for 360min . The wafer lost approximately 10% (by mass) of its initial mass due to emission of water. Wafers that were to be used as electrolyte disks were first checked for possible pinholes and cracks using an optical microscope. Only disks with no visibly discernable defects were used. All chemical materials used in this work were obtained from Alfa-Aesar, except as otherwise indicated.

2.2 Preparation of MEA (membrane-electrodes assembly)

To prepare a MEA, the cathode catalyst in paste form was screen-printed first onto one side of the membrane. Then the anode catalyst in paste form was screen-printed onto the other side of the membrane. The thicknesses of anode and cathode catalysts are about $30\text{--}40\mu\text{m}$. The effective contacting area of electrodes with membrane is 1cm^2 . The whole assembly was put in an oven and then heated in nitrogen atmosphere, first at 230°C for 30min and then at 750°C for another 30min . The MEA was then cooled down to room temperature slowly under nitrogen.

The anode and cathode materials used were a Mo-Ni-S-based composite anode, either Pt paste or a NiO-based composite cathode. The metal sulfide-based composite anode and the NiO-based composite cathode in this research were prepared from the

mass ratio 70% ($\text{MoS}_2 + \text{NiS}$) ($\text{MoS}_2 : \text{NiS} = 1 : 1$, mass ratio), 10% Ag ($<12\mu\text{m}$) and 20% electrolyte, and from the mass ratio 70% NiO ($<10\mu\text{m}$, Aldrich Company) as well as 10% Ag and 20% electrolyte, respectively. Details of the preparation of a fuel cell test station (the MEA assembly) are in Ref. [7].

2.3 Measurements of fuel cell performance

Cell performance was determined using pure H_2S as the fuel and air as the oxidant. The cell open circuit voltage (OCV) was monitored as a function of time on stream. Data were recorded with a Gamry electrochemical measurement system (PC4-750). Initial electrical performance data were evaluated to determine cell integrity. Typically, a cell that had no leaks showed a steady OCV value after about 30min on stream. OCV that fluctuated, or that had a persistently low value ($0.5\text{--}0.6\text{V}$), indicated possible leaks in the cell, and that MEA assembly was discarded.

After a steady OCV was achieved, electrochemical impedance spectrum (EIS) measurements were performed to determine cell resistance. The frequency region was $0.2\text{--}100\,000\text{Hz}$ and a stimulating alternating current (AC) signal of 5mV was imposed onto OCV. Potentiodynamic measurements were conducted to determine the cell current-voltage performance in their compensation mode using the Gamry system at a scanning rate of $1\text{mV}\cdot\text{s}^{-1}$ ^[7,8].

3 RESULTS AND DISCUSSION

3.1 Phase transformation of membrane

EIS technique was used to study the variation of the membrane electric resistance with temperature. Fig.1 shows the resistance of given membrane thickness *versus* the temperature for membranes with different ratios of Li_2SO_4 over Al_2O_3 : 3 : 2 (mass ratio) and 3 : 1. Some change of membrane resistance (increase in electrical conductance) occurred as a result of increasing ratio of Li_2SO_4 over Al_2O_3 . However, higher ratios of Li_2SO_4 over Al_2O_3 resulted in the decrease of mechanical strength. An abrupt change in the cell resistance occurred about 575°C , irrespective of the mass ratio of Li : Al. The increase in resistance with decreasing temperature is small above 575°C . Below 575°C , the electrical resistance increased dramatically with reduction in temperature. This indicates that 575°C is the lowest operating temperature appropriate for the present Li_2SO_4 -based proton-conducting membranes. This phenomenon is attributed to the

Li₂SO₄ phase transformation known to occur at 577°C. Li₂SO₄ is in the cubic α -phase above 577°C, which has high proton conductivity, while in the monoclinic β -phase below 577°C with low proton conductivity, as described by Peterson and Winnick^[5]. As seen in Fig.1, a hysteresis phenomenon was observed at around 575°C with elevating temperature while no such phenomenon was observed with reducing temperature. The hysteresis implied a slower transformation rate from β -phase to α -phase while the reverse process was relatively rapid. Fig.2 gives the scanning electron microscope (SEM) image of the membrane with the mass ratio 75%Li₂SO₄ : 25% Al₂O₃ prior to electrochemical experiments. The membrane showed a strongly integrated surface, although a few particles and cracks could be still seen, which indicated a need for further improvement in membrane preparation.

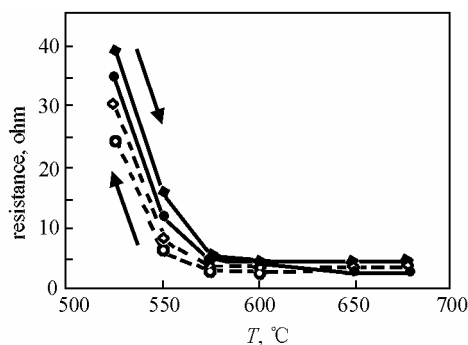


Figure 1 Resistance of membrane vs. temperature for various ratios of Li₂SO₄ : Al₂O₃

(thickness of membrane: 1mm)

Li₂SO₄ : Al₂O₃(mass ratio) : ○ 3 : 1(temp. down);

● 3 : 1(temp. up); ◇ 3 : 2(temp. down); ◆ 3 : 2(temp. up)

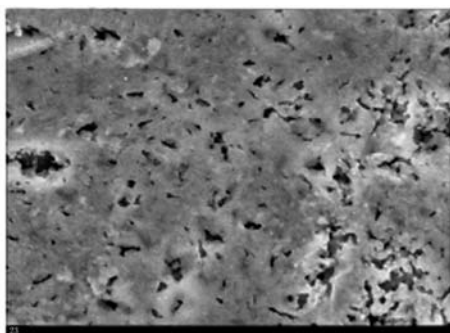


Figure 2 SEM image of membrane with Li₂SO₄ : Al₂O₃=3 : 1

3.2 Effect of membrane thickness

The most convincing evidence indicating the effect of membrane thickness on performance of fuel

cell is the comparison of membrane thickness used in the cell. Fig.3 demonstrates the cell performance of three different membrane thicknesses, 0.7, 1.0 and 1.4mm with metal sulfide-based composite anode and NiO-based composite cathode, respectively. A membrane twice as thick would diminish remarkably current and power densities if all other parameters were held the same. The membrane electric resistance nearly decreased by half for a membrane half as thick (from 1.4mm to 0.7mm), enabling about double the fuel cell performance under the given operating conditions, suggesting smaller membrane thickness is preferred for better cell performance. However, further reduction of membrane thickness might lead to gas (air or H₂S) leakage and degrade the long-term period performance of fuel cells. The reasonable value for membrane thickness is approximately 0.7mm in this work.

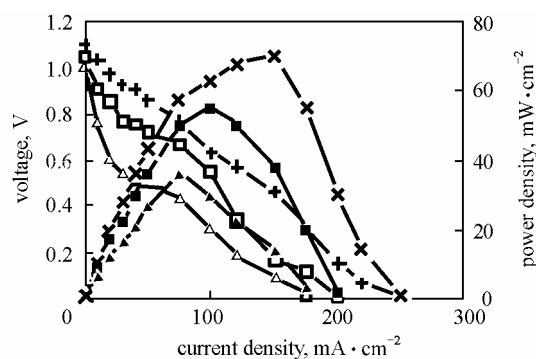


Figure 3 Cell performance with different thicknesses of membrane with Li₂SO₄ : Al₂O₃=3 : 1 at 650°C

△, □, + current vs. voltage;

▲, ■, × current vs. power density

thickness, mm: △ 1.4; □ 1; + 0.7; ▲ 1.4; ■ 1; × 0.7

3.3 Electrode over potential and stability results

3.3.1 Cathode over potential

Our results with Pt catalyst as cathode and metal sulfide-based composite catalyst as anode were discouraging because the electrode showed higher over potential (0.6V, current density 250mA·cm⁻²), as shown in Fig.4, although as anode catalyst it was very successful in the earlier H₂-O₂ fuel cell studies. The over potential (less than 0.3V, current density 250mA·cm⁻²) of NiO-based composite cathode was much lower than that of Pt cathode at the same current output. In other words, the NiO-based composite cathode had higher current density at the same over potential. This was the evidence that nickel oxide might be a suitable cathode candidate.

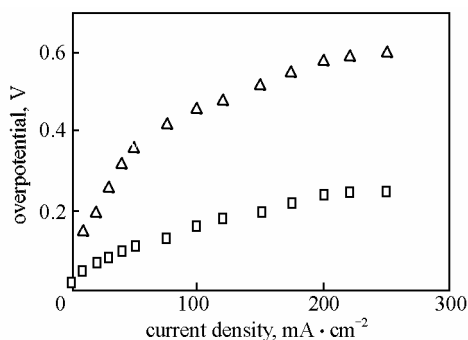


Figure 4 Current-overpotential curves of Pt and NiO-based composite cathode catalysts with metal sulfide-based composite anode at 650 °C

($\text{Li}_2\text{SO}_4 : \text{Al}_2\text{O}_3 = 3 : 1$; thickness of membrane: 1mm)
cathode: \triangle Pt catalyst; \square NiO-based catalyst

3.3.2 Anode over potential and stability

A bimetallic Ni-Mo-S anode catalyst has been reported^[6,8]. Use of Mo-Ni-S as the anode catalyst in H_2S -air fuel cell gave better cell performance than Mo-S only. Fig.5 depicted the relationship of over potential of metal sulfide-based composite catalyst as anode with current density. Compared with that of cathode, the anode over potential was smaller. Therefore, the limitation of over potential and cell performance was in the cathode side. Fig.5 also shows the performance of metal sulfide-based composite catalyst as anode and NiO-based composite catalyst as cathode at different on-stream time. It indicated that the metal sulfides as anode materials were quite stable in H_2S stream. In addition, our experiment and XRD analysis suggested no significant sign of damage and also no sign of detachment after running continuously 24h at 650 °C. This was further evidence that the metal sulfides might be a suitable anode candidate for the H_2S fuel cell.

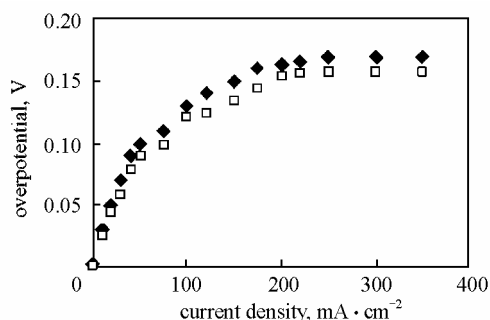


Figure 5 Current-overpotential curves of metal sulfide-based composite anode with NiO-based composite cathode at 650 °C

($\text{Li}_2\text{SO}_4 : \text{Al}_2\text{O}_3 = 3 : 1$; thickness of membrane: 1mm)
running time, h: \blacklozenge 24; \square 4

3.4 Fuel cell performance

Figure 6 exhibits the relationship of current density and voltage as well as power density with a cell configuration of H_2S , (metal sulfide-based composite anode)/ $\text{Li}_2\text{SO}_4 + \text{Al}_2\text{O}_3$ /(NiO-based composite cathode), air at 600 and 650 °C, respectively. The maximum current density was $100 \text{ mA} \cdot \text{cm}^{-2}$ at 600 °C, and was $250 \text{ mA} \cdot \text{cm}^{-2}$ at 650 °C, respectively. The maximum power densities achieved from Fig.6 were $30 \text{ mW} \cdot \text{cm}^{-2}$ at 600 °C and $70 \text{ mW} \cdot \text{cm}^{-2}$ at 650 °C, respectively. At 600 °C, the current-power density curves demonstrated a steep drop in cell potential in the high current range, which was characteristic of mass-transport limitation^[8]. However, this effect was greatly reduced when the temperature was increased to 650 °C. These observations were consistent with a mechanism in which sulfur was generated more rapidly at active sites than it was removed by desorption and transport at 600 °C, which limited the ability of H_2S fuel to access the triple-phase boundary, the reaction zone. At 650 °C, the rate of desorption and transport of sulfur from the vicinity of the active sites was increased, which thereby enhanced mass transport of H_2S to the active sites.

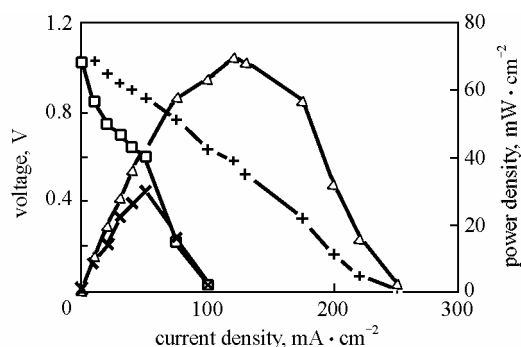


Figure 6 Current density vs. voltage and power density curves at 600 °C and 650 °C

($\text{Li}_2\text{SO}_4 : \text{Al}_2\text{O}_3 = 3 : 1$; thickness of membrane: 0.7mm)

\square , + current vs. voltage;
 \times , \triangle current vs. power density
temperature, °C: \square 600; + 650; \times 600; \triangle 650

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