

A solid oxide fuel cell operating on hydrogen sulfide (H₂S) and sulfur-containing fuels

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Abstract

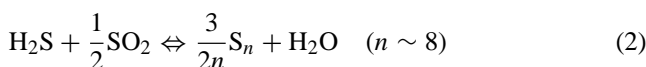
A new class of materials based on La_xSr_{1-x}VO_{3-δ} (LSV) has been studied as the anode for solid oxide fuel cells (SOFCs) operating on H₂S-containing fuels. The LSV-based anodes are chemically and electrochemically stable under SOFC operating conditions. Furthermore, they appear to be active towards the preferential oxidation of H₂S over hydrogen, as suggested by open circuit voltage, impedance spectra, and cell performance measurements using various H₂S and H₂ fuel mixtures. A system with configuration LSV/YSZ/LSM–YSZ showed a maximum power density of 90 mW/cm² at 220 mA/cm² with a 5% H₂S–95% N₂ fuel mixture at 1273 K. This same cell configuration showed a maximum power density of 135 mW/cm² at 280 mA/cm² when the fuel was a 5% H₂S–95% H₂ mixture at 1273 K. Cell performances were stable and showed no significant deterioration during a 48 h period. Impedance measurements showed overall cell resistances decreased with increasing temperature and H₂S content of the fuel. The results are promising due to the drastic improvement in sulfur tolerance compared to the current generation of SOFC anode materials.

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1. Introduction

Each year the US alone produces over 12 million tons of hydrogen sulfide, H₂S, mainly as an industrial by-product in the refining of fossil fuels [1]. Due to the lack of commercial use for H₂S, virtually all of it is converted to sulfur in the Claus Process, where a partial oxidation with air produces elemental sulfur and water [2]. This two-step chemical process may be summarized by:



Reaction (1) is a non-catalytic combustion process usually carried out around 1373 K whereas reaction (2) is a reversible catalytic process carried out over an equilibrium reactor train.

While it is possible to recover low-grade thermal energy from the Claus Process, it would be much more desirable to electrochemically oxidize H₂S in a fuel cell. This would al-

low the direct conversion of the overall reaction free energy of (1) into electricity at efficiency levels as high as 80% for integrated systems. The feasibility of the H₂S//Air SOFC has been shown in the past [3–7]. These devices simultaneously produce electricity, high-temperature steam, and concentrated sulfur dioxide. The SO₂ reaction product may be used in the manufacture of sulfuric acid and sodium hydro-sulfite, both high-volume commodity chemicals.

An additional application for this technology is linked to the ability of SOFC devices to operate on hydrocarbon fuels. If SOFCs could demonstrate stable performance using practical fuels (e.g. liquid hydrocarbons such as diesel and gasoline with sulfur contaminants) they could easily enter the energy market and take advantage of the current energy delivery infrastructure. Typical diesel fuel in the US may contain over 5000 ppmw of sulfur [8], commonly present as H₂S, while most Ni based catalysts can only tolerate H₂S levels <5 ppmw at 1073 K [9–11].

However, one of the major technical challenges towards a viable H₂S//Air SOFC is to identify and develop anode materials that are conductive, chemically and electrochemically stable, and catalytically active in an H₂S-rich environment. The corrosive nature of H₂S renders most conventional SOFC anode materials (Ni, Pt, Ag) useless

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for long-term cell performance even at very low concentrations. The poor performance of traditional metallic anodes with H_2S -containing fuels has led to the investigation of composite oxides as potential electrode materials due to their increased stability and desirable electrical properties.

LSV exhibits slight n-type conduction and is stable over a wide range of oxygen partial pressures (10^{-14} to 10^{-20} atm). Its electrical conductivity at 1073 K has been reported to be 120 S/cm compared to 2.9 S/cm for the undoped lanthanum vanadate [12]. The other end member of this family, SrVO_3 , has a very high conductivity (1000 S/cm) but is unstable at oxygen partial pressures above 10^{-17} atmospheres. Previous work tested LSV in an H_2S removal process via an electrolytic molten carbonate cell [13]. Sour gas (H_2S – CO_2 – H_2 mixtures) was reduced at the cell cathode with sulfide ions migrating across a molten salt membrane. Once these ions reached the anode side of the cell, they were oxidized to form elemental sulfur and were subsequently removed by a N_2 purge stream. The use of a solid electrolyte (instead of a molten salt) was expected to increase anode stability, as there is no exposure to the corrosive nature of the liquid electrolyte.

The performance of an LSV-based anode material in an H_2S //Air SOFC has been characterized as a function of temperature and H_2S content of the fuel. In this paper, we report our recent results using LSV-based anode materials in a SOFC for the oxidation of H_2S and H_2S -containing fuels.

2. Experimental

$\text{La}_{0.7}\text{Sr}_{0.3}\text{VO}_3$ (LSV) powder was synthesized by conventional solid-state reaction. Stoichiometric amounts of

La_2O_3 (Aldrich, 99.9%), SrCO_3 (Aldrich, 99.9+%), and V_2O_5 (Aldrich, 99.6%) were mixed thoroughly by grinding and subsequently calcined at 1473 K for 10 h in 4% H_2 -Ar. The $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ (LSM) cathode was synthesized by a glycine–nitrate combustion process described elsewhere [14]. 8% Ytria stabilized zirconia (YSZ, Alfa Aesar, 99%) was cold-pressed at 250 MPa into cylindrical pellets using a uniaxial die-press. After firing at 1823 K for 5 h, dense YSZ wafers with a 10 mm diameter 250 μm thickness were attained. A slurry consisting of LSM and YSZ (70:30 wt.%), organic binder (V-006, Heraeus), and acetone was applied to one side of the YSZ disc by dip-coating, which was then fired at 1373 K in air for 2 h to form a porous cathode. The LSV ink (a mixture of powder and V-006) was painted to the other side of the YSZ disc by screen-printing. Platinum mesh and wire (Heraeus) were attached to both the anode and cathode electrodes. Then single fuel cells were mounted to an alumina tube and sealed using a ceramic adhesive (Flexbar Autostic). The anode was fired *in situ* under H_2 at 1273 K for 2 h before cell testing. Fig. 1 shows the microstructure for the LSV anode post-firing in H_2 for 2 h.

The experimental apparatus used for cell testing is illustrated in Fig. 2. Certified gas mixtures (10% H_2S -bal. H_2 and 10% H_2S -bal. N_2) were purchased from Airgas. Gas flows (H_2S mixture, H_2 , N_2) were controlled by rotometers calibrated prior to each experimental run. Constant potential was applied to the system using a Perkin-Elmer 273A Potentiostat/Galvanostat. Cell resistances were determined using a Solartron impedance analyzer. Digital multimeters were connected in parallel to the cell to monitor different cell voltages.

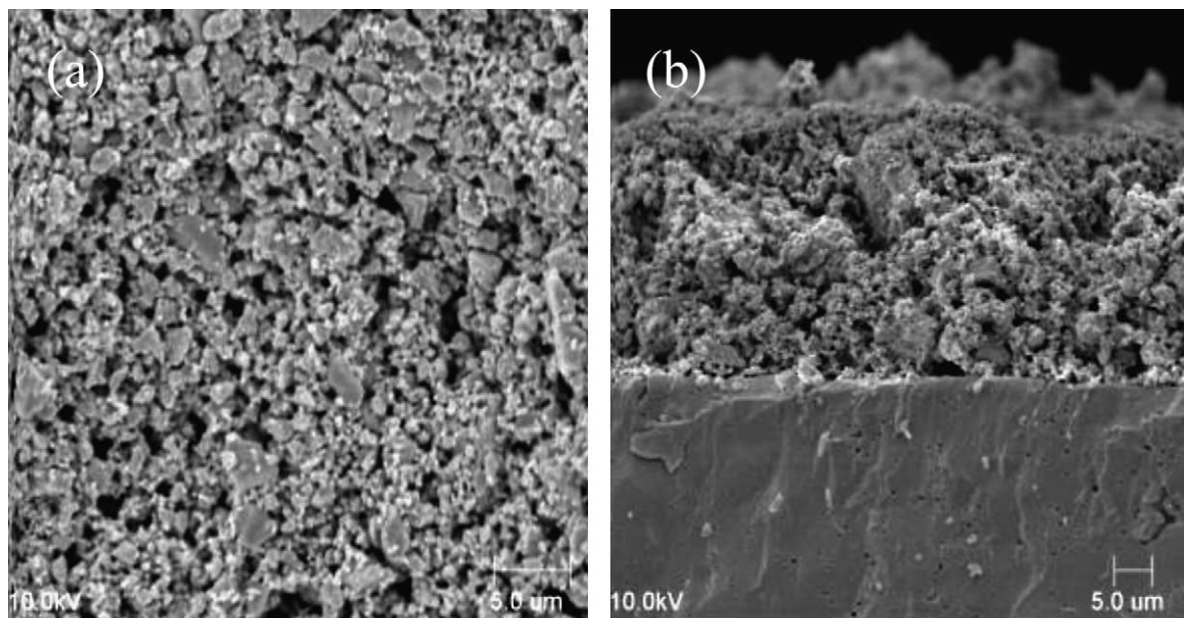


Fig. 1. SEM images of LSV anode after firing in H_2 at 1273 K for 2 h: (a) top view; (b) cross-sectional view over YSZ electrolyte pellet.

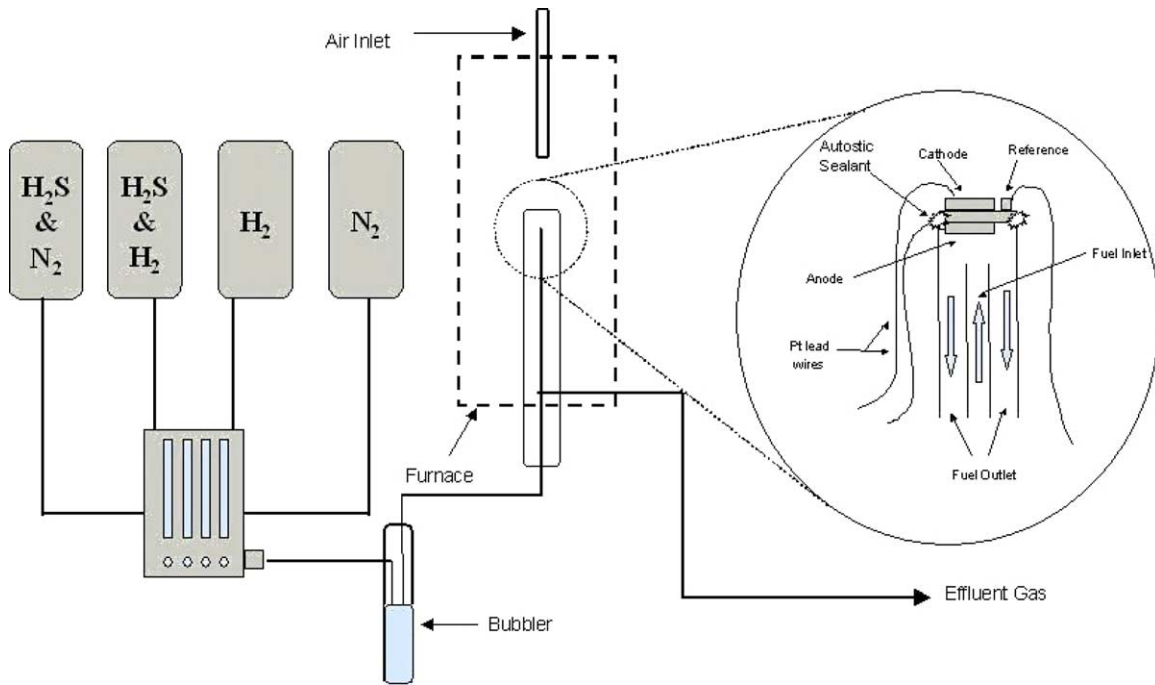
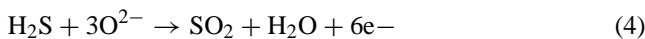
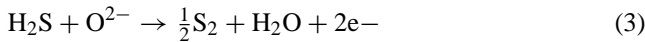


Fig. 2. Experimental apparatus for fuel cell testing.

3. Results and discussion

3.1. Fuel cell reactions and open circuit voltage (OCV)

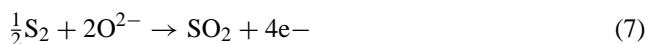
There are several possible cell reactions for the $\text{H}_2\text{S}/\text{Air}$ SOFC. The two main electrochemical processes at the anode side include the partial oxidation of H_2S to sulfur (3) and its complete oxidation to SO_2 (4).



Researchers [4,5] have shown the main oxidation product, particularly at high levels of fuel utilization, is sulfur dioxide. In addition, at the elevated operating temperature of the SOFC, H_2S undergoes thermal decomposition into elemental sulfur and hydrogen (5).



Both reaction products may become oxidized in electrochemical processes (6), (7):



Furthermore, since H_2S and SO_2 will be present at the cell anode they may react in the second step of the Claus Process (2) to form elemental sulfur and water.

The method of Lagrange Undetermined Multipliers was used to minimize the Gibbs free energy of the system (anode side gas chamber) and obtain its equilibrium composition. In summary, this technique takes the feed amounts of

the constituent elements, then considers the user-specified reaction products, and calculates the concentration of each molecular species at which $\delta G/\delta x_i = 0$. The H_2 , H_2S , N_2 , and water inputs are determined from the composition of the feed. The user-specified oxidation products are SO_2 , S_2 , and water. In order to account for the electrochemical processes in the cell, an additional inlet of oxygen was added to the feed, related to the cell current by Faraday's law (8):

$$n \left(\frac{\text{molO}^{2-}}{\text{sec}} \right) = \frac{I}{(z_{\text{O}^{2-}})F} = \frac{I}{2F} \quad (8)$$

Consequently, the O_2 molar feed rate is half that of the oxide ion (O^{2-}) across the cell electrolyte. The detailed description of this method is illustrated elsewhere [15]. Fig. 3 shows the equilibrium gas phase compositions for a 10% H_2S –90% N_2 feed with respect to level of fuel utilization at 1223 K. Our results confirm previous reports that SO_2 is the preferred oxidation product at high levels of fuel utilization. This graph also shows that at low levels of fuel utilization, a significant portion of the sulfur in the system is present as S_2 .

The open circuit voltage of the $\text{H}_2\text{S}/\text{Air}$ SOFC is a function of reactions occurring at each electrode as well as the concentration of the species in the feed. The theoretical open circuit voltages for a cell based on YSZ can be obtained from the Nernst equation since the ionic transport number of the electrolyte is nearly unity [16]. Assuming ideal gas behavior, if sulfur is the product in the electrochemical oxidation of H_2S by (3), the Nernst equation takes the form (9):

$$E = E^0 - \frac{RT}{2F} \ln \left(\frac{P_{\text{S}_2}^{1/2} P_{\text{H}_2\text{O}}}{P_{\text{H}_2\text{S}} P_{\text{O}_2}^{1/2}} \right) \quad (9)$$

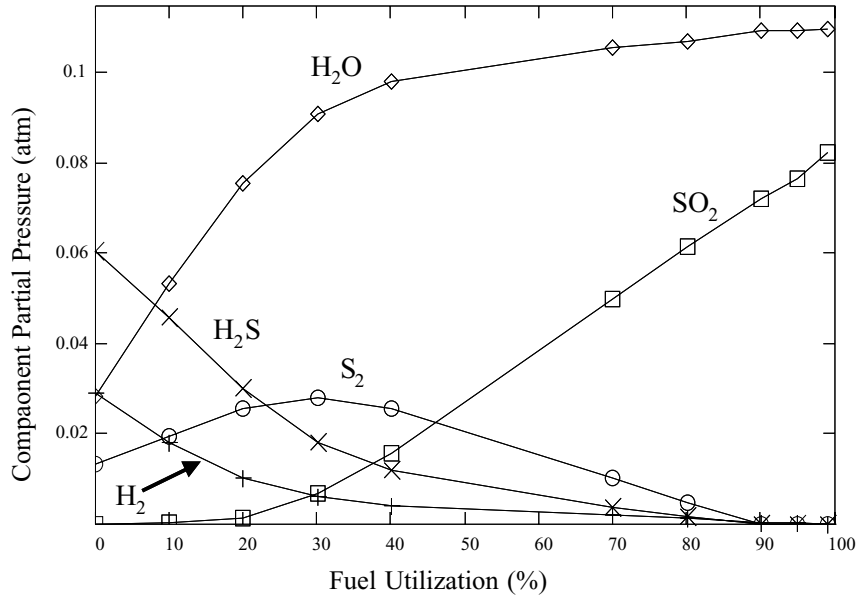


Fig. 3. Gas phase partial pressures at equilibrium vs. level of fuel utilization for a 10% H₂S-bal. N₂ fuel mixture at 1223 K. N₂ is not shown in the graph.

If sulfur dioxide is the main product (4), then the Nernst equation is given by (10):

$$E = E^0 - \frac{RT}{6F} \ln \left(\frac{P_{SO_2} P_{H_2O}}{P_{H_2S} P_{O_2}^{3/2}} \right) \quad (10)$$

Since more than one electrochemical oxidation is possible in the system, the theoretical OCV is a combination of the different reactions taking place at the anode surface.

Fig. 4 shows the theoretical open circuit voltage as a function of cell operating temperature for two different fuel mixtures: (a) 5% H₂S–95% N₂; (b) 5% H₂S–95% H₂. These

values were calculated using the Nernst equation in conjunction with the equilibrium gas phase compositions from our Gibbs Free Energy model. Therefore, the calculated Nernst potential for the fuel mixture should be the same regardless of what reaction is used (3, 4, 6, 7) to compute it.

The observed experimental open circuit potentials are also included in this figure for comparison. The equilibrium model and experimental data are in good agreement when the fuel was a 5% H₂S–95% N₂ mixture. As expected, the additional amount of H₂ in the fuel gas for case (b) causes an upward shift in the experimental and theoretical OCV values. However, the experimental open circuit potentials for

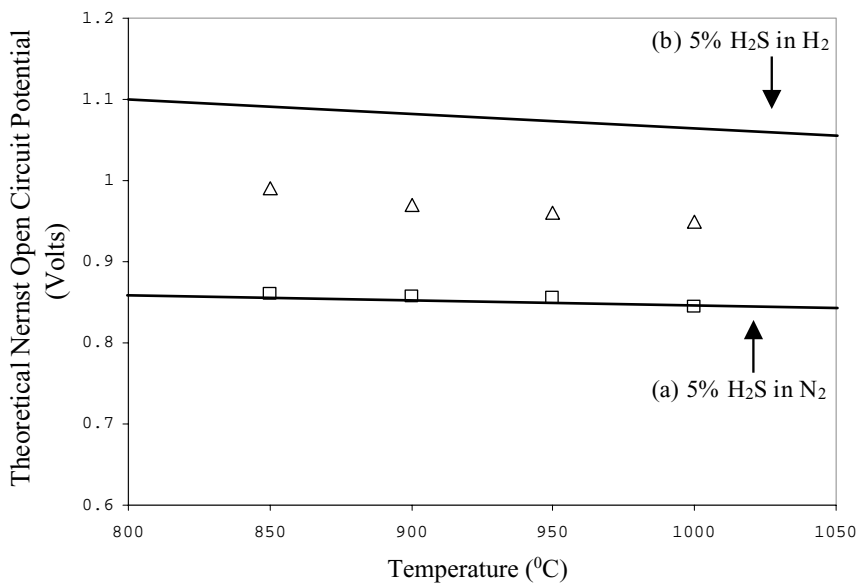


Fig. 4. Theoretical OCV calculations as a function of temperature for: (a) 5% H₂S-bal. N₂; (b) 5% H₂S-bal. H₂ and fuel mixtures. Experimental values are included for comparison: (a) squares; (b) triangles.

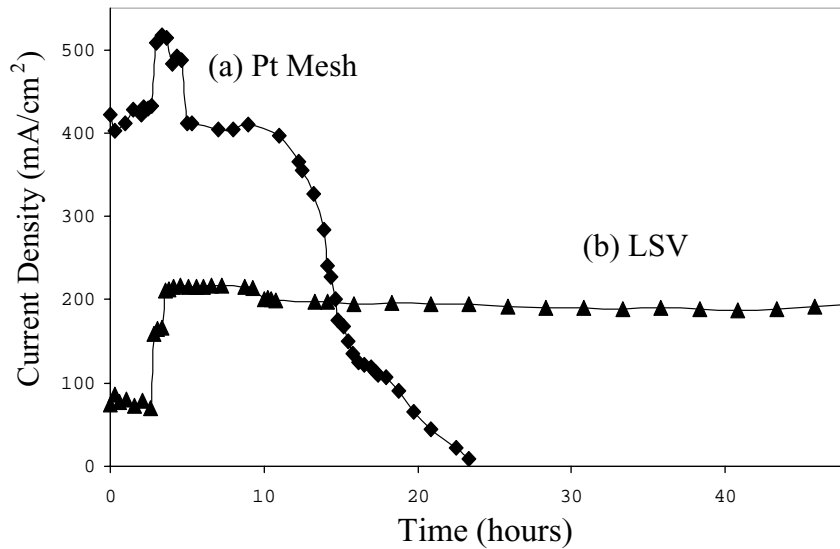


Fig. 5. Stability testing for two cells with different anodes (a) a blank cell Pt/YSZ/LSM–YSZ, and (b) LSV/YSZ/LSM–YSZ. Cells were operated at $V_{\text{cell}} = 0.44$ V, $T = 1273$ K, $P = 1$ atm, fuel flow = 14 sccm. Pure H_2 was the fuel for the first 2 h before changing to a 5% H_2S –95% H_2 mixture.

this fuel composition were only 90% of the OCV predicted by our model. We believe this deviation may be caused by the preferential adsorption of sulfur species onto the LSV anode. DC polarization and impedance measurements showed that the presence of H_2S in the fuel stream had a significant (positive) effect on the electrochemical performance of the LSV anode. The quick response times after introduction (and before removal) of H_2S to the fuel stream suggest an adsorption process at the electrode surface is responsible for the significant improvements in cell performance. This increased concentration of sulfur species would shift the experimental OCV towards the value predicted by (9) or (10). The equilibrium model is unable to account for this behavior, as it assumes the concentration of each species at the anode/electrolyte interface is the same as the bulk gas concentration.

As current is drawn from a fuel cell to obtain electrical work, the equilibrium cell potential is reduced by various irreversible losses in the system [16]. Under polarization conditions, the voltage across a cell has contributions from the electrode potentials as well as the over-potentials given by (11):

$$E_{\text{cell}} = \Delta E_{a-c} - \eta_{\text{ACT}} - \eta_{\text{CONC}} - IR_{\text{total}} \quad (11)$$

where E_{cell} is the measured cell potential, ΔE_{a-c} the open circuit voltage (assuming the cathode is the greater positive potential), η_{ACT} the activation over-potential (sum of both electrodes), η_{CONC} the concentration polarization (of both electrodes), and η_{IR} the IR drop across the cell. By minimizing these irreversible losses it becomes possible to make E_{cell} closer to ΔE_{a-c} , thus increasing overall cell performance. In traditional SOFC power systems, H_2S poisoning is responsible for increasing the interfacial resistance (R_{total}) and reducing the catalytic activity (greater η_{ACT}) by a variety of methods [10,16].

3.2. Stability of electrode materials

The first full cell experimental run was aimed at understanding the stability and performance contribution of the Pt mesh current collector used in all future tests. Fig. 5 compares the performance of two cells: one using only Pt mesh (blank) and the second our LSV material as anodes at 1273 K. For this experiment, the mesh and lead wires were attached to the YSZ/LSM–YSZ pellet using Pt paste. The ‘blank’ cell experienced an abrupt drop in performance (total resistance increased by a factor of 3 after 12 h of operation) attributable to the reversible formation of PtS at the anode surface. This material was concentrated at the union point between the lead wire and Pt mesh current collector, supporting previously reported observations that the electrochemical oxidations at the anode surface accelerate the formation of PtS [7]. Even though this metallic sulfide phase is electronically conductive, the conversion process causes the delamination of the anode from the YSZ electrolyte. Differences in microstructure and thermal expansion coefficients between the metallic form and the sulfide are responsible for this process.

In pure H_2 , the performance of the blank anode was far superior to LSV, but a noticeable change occurred once the fuel was changed (after 2 h) to a 5% H_2S –95% H_2 mixture. With the latter feed, the LSV/YSZ/LSM–YSZ configuration initially increased, and subsequently maintained its performance for over 2 days. In stark contrast, the performance of the blank cell dropped significantly after 8 h and ultimately to zero after 22 h. Consequently, prior to measuring performance in all subsequent experimental runs, cells were allowed to operate at a working voltage of 0.5 V for 8 h (after the transition from open circuit conditions). If there was no noticeable decline in output after this time period, the cell was deemed adequate for performance testing.

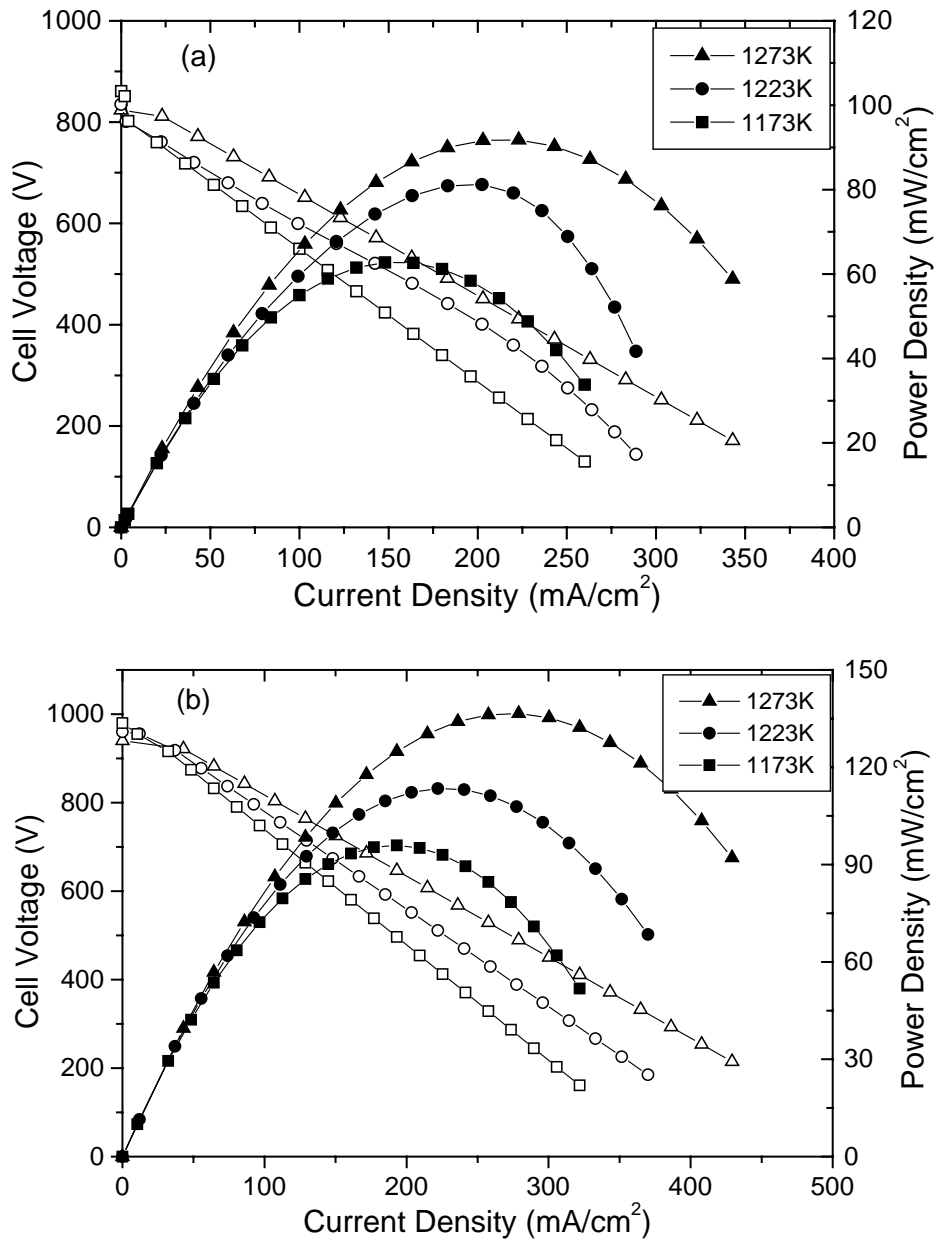


Fig. 6. Cell voltage (closed symbols) and power density (open symbols) as a function of current density at different operating temperatures for cells with configuration LSV/YSZ/LSM-YSZ when the fuel was: (a) 5% H₂S in N₂; (b) 5% H₂S in H₂.

3.3. Fuel cell performance

Shown in Fig. 6 are the I - V characteristics at different operating temperatures for cells using the LSV exposed to (a) a 5% H₂S-bal. N₂ and (b) a 5% H₂S-bal. H₂ fuel mixture. It is interesting to note that the performance of both cells was similar, even though much more fuel is available for the second. These observations suggest that H₂S was preferentially oxidized at the LSV anode even in the presence of a large amount of H₂. The effect of electrolyte thickness and lead wires on cell performance at 1273 K is shown in Fig. 7. Curve (a) represents the performance for a cell based on

250 μ m YSZ (as measured without any corrections). Curves (b) and (c) are the projected powers with IR correction for lead wires with cells based on 250 μ m YSZ electrolyte and 10 μ m YSZ electrolyte, respectively.

In all runs involving H₂S-N₂ fuel mixtures, there was a noticeable amount from sulfur deposition in the exit line of the cell. According to our thermodynamic calculations, at zero current (OCV) nearly 25% of sulfur in the system is in the form of S₂. This fraction increases until reaching a maximum at a fuel utilization of 30%, over three times the maximum level achieved in our experiments. S₂ is a vapor at the operating temperature of the SOFC, but condenses to a

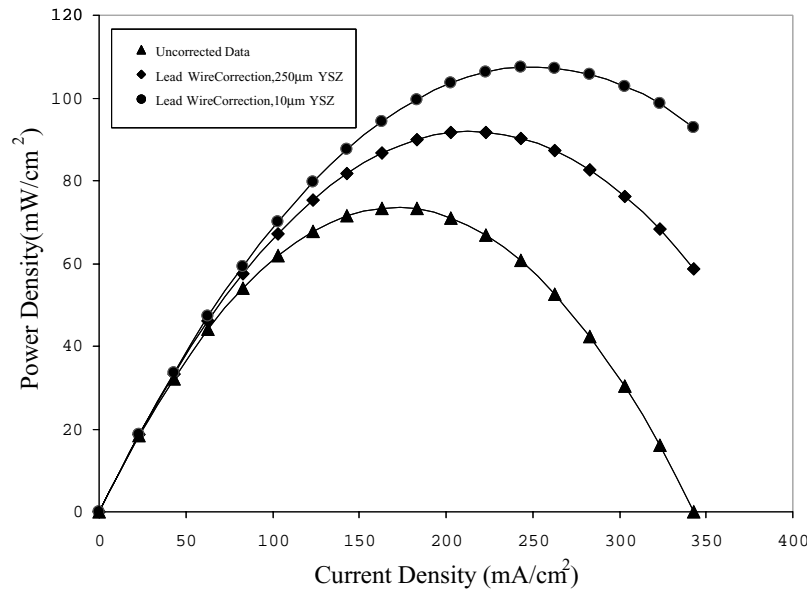


Fig. 7. Projected cell power density as a function of current density for a 5% H_2S -bal. N_2 fuel mixture at 1223 K: (a) uncorrected data; (b) projection for a 250 μm YSZ electrolyte with IR correction for cell lead wires ($\sim 2 \Omega$); (c) projection for a 10 μm YSZ electrolyte with IR correction for cell lead wires.

solid around 723 K. Thus, a small condenser at the exit line of the cell had to be included as part of the design to prevent the obstruction of fuel flow. As expected, sulfur deposition was not a problem for H_2 - H_2S fuel mixtures as the presence of hydrogen in the feed shifts the equilibrium of (5) to the left.

3.4. Interfacial polarization resistances

Impedance spectroscopy was used to determine the effect of operating temperature and H_2S concentration of the fuel on the interfacial resistances for cells using LSV as an anode. Fig. 8 compares the impedance spectra of the SOFC under exposure to (a) pure H_2 and (b) 10% H_2S -90% H_2 gas mixture. Cell resistances were reduced by two thirds once the fuel was changed to a H_2 - H_2S mixture. This rapid tran-

sition was fully reversible, as the fuel streams were shifted on multiple occasions for each experiment. Fig. 9 shows the effect of H_2S concentrations in the fuel for a cell with configuration LSV/YSZ/LSM-YSZ operating at 1223 K. The bulk resistances (ohmic drop from electrolyte and lead wires) have been removed from this figure. The interfacial resistances decreased with increasing H_2S content of the fuel and this behavior was consistent over several fuel cycles. Similar observations in the presence of H_2S have been recently reported for a comparable perovskite anode [6]. Both results suggest that sulfur-containing compounds are formed at the electrode, which significantly reduce the interfacial polarization resistance. Identification of the phases formed on the anode surface and the corresponding interpretation of this phenomenon will be reported in a subsequent communication.

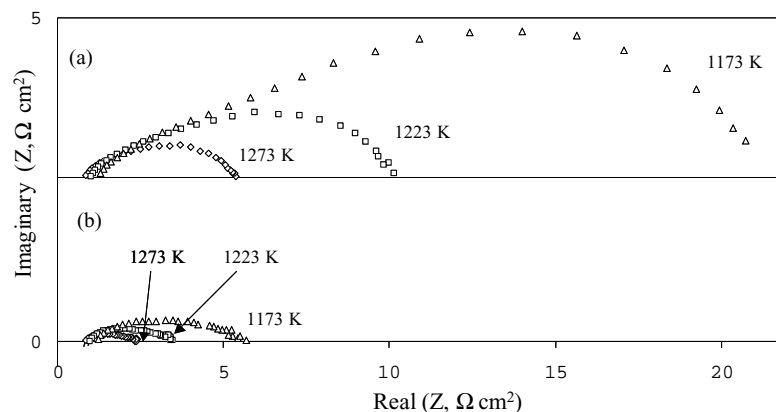


Fig. 8. Impedance spectra of a cell with an LSV anode when exposed to: (a) pure H_2 fuel; (b) 10% H_2S -bal. H_2 at different operating temperatures.

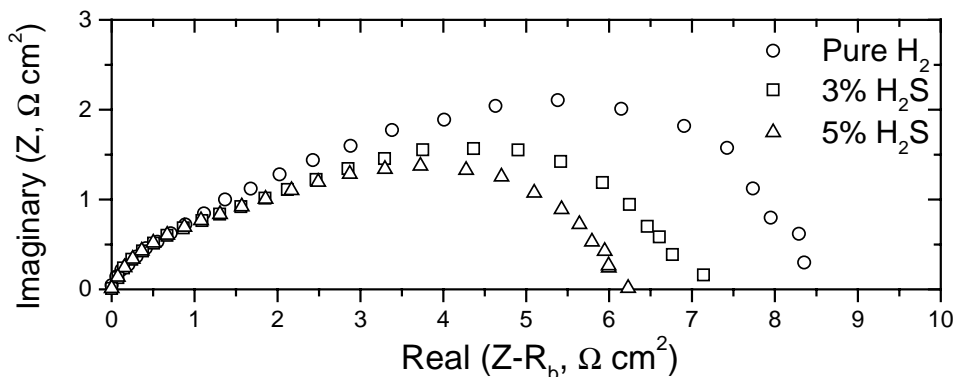


Fig. 9. Impedance spectra of a cell with a LSV anode when exposed to: (a) pure H_2 fuel; (b) 3% H_2S -bal. H_2 ; (c) 5% H_2S -bal. H_2 .

4. Conclusions

LSV has shown very promising results for SOFCs operating with H_2S and sulfur-containing fuels. Even though its electrochemical performance in H_2 is poor, LSV cells have shown stable operation with H_2S and H_2S -containing fuels. The overall reasons for this behavior are only partly understood, but are consistent with observations for similar perovskites under the presence of H_2S . Cell performances were very similar for fuel mixtures of 5% H_2S in H_2 and 5% H_2S in N_2 , suggesting H_2S is preferentially oxidized even under the presence of an alternate fuel. Future work will focus on determining the reasons for its electrochemical behavior and optimizing anode composition and microstructure in an attempt to improve cell performance.

Acknowledgements

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