



Sulfur-Tolerant Materials for the Hydrogen Sulfide SOFC

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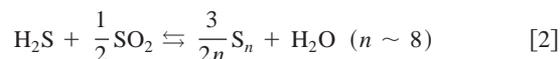
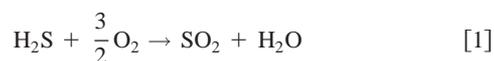
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This study examined sulfur tolerant materials for solid oxide fuel cells (SOFCs) operating on H₂S and H₂S containing fuels, focusing on the stability and electrochemical performance of perovskite-type materials in a H₂S atmosphere under SOFC operating conditions ($P = 1 \text{ atm}$, $T > 800^\circ\text{C}$). Preliminary results indicate anodes of the general form La_xSr_yVO_{3-δ} are stable and active toward the electrochemical oxidation of H₂S. In particular, an SOFC using La_{0.7}Sr_{0.3}VO₃ as the anode has shown good performance at H₂S levels of 10%, over 5000 times greater than the H₂S tolerance level of contemporary Ni-based systems. The results are promising due to the drastic improvement in sulfur tolerance compared to the current generation of SOFC anode materials. © 2004 The Electrochemical Society. [DOI: 10.1149/1.1788613] All rights reserved.

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Each year the United States alone produces over twelve 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 noncatalytic combustion process usually carried out around 1100°C. Reaction 2 is a reversible catalytic process carried out over an equilibrium reactor train, limiting the practical sulfur recovery of the entire process to around 95%.

While it is possible to recover low-grade thermal energy from the Claus process, it is much more desirable to electrochemically oxidize H₂S in a fuel cell. This allows the direct conversion of the overall reaction free energy of Reaction 1 into electricity at efficiency levels as high as 80% for integrated systems. The feasibility of using H₂S as the fuel for a solid oxide fuel cell (SOFC) has been proven to produce electricity, high-temperature steam, and concentrated sulfur dioxide simultaneously.³⁻⁸ 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 fuels in the U.S. may contain up to 5000 ppmw of sulfur, commonly present as H₂S.¹

Unfortunately, H₂S has a catastrophic effect on typical anode materials for SOFC devices. Sulfur poisoning is responsible for severe degradation in fuel cell stability and electrochemical performance. Consequently, the search for sulfur-tolerant materials is one of the most investigated topics in contemporary SOFC research. This goal is complicated by the corrosive nature of H₂S that renders most conventional SOFC anode materials useless for long-term cell performance even at very low concentrations.⁹⁻¹¹

Our main research goal was to develop new anode materials for SOFCs operating with sulfur-containing fuels. We have characterized the performance of novel ceramic materials in an H₂S atmosphere as well as the effect of process variables (time, temperature, etc.) on the sulfur poisoning effect. Our work is ultimately aimed at achieving the electrochemical oxidation of H₂S at the fuel cell anode in an efficient and reliable SOFC system. In this article, we report our recent results using LSV-based anodes for the oxidation of H₂S and H₂S-containing fuels in a SOFC.

The experimental apparatus used for cell testing is illustrated in Fig. 1. The setup consists of two concentric tubes (96% alumina) with the cell serving as a “cap” to the outer tube. The entire setup is placed inside a Thermolyne high-temperature tubular furnace during cell testing. Gastight seals between the air and fuel sides are achieved using Aremco 503-VFG ceramic adhesive. A second alumina tube immediately above the cell cathode provides a steady flow of air to the cell.

Certified gas mixtures (10% H₂S-90% H₂ and 10% H₂S-90% N₂) used in the experimental runs were purchased from Airgas. Gas flows (H₂S mixtures, H₂, N₂) were controlled by rotometers calibrated prior to each experimental run. Electrolyte disks (1 cm diam, 250 μm thick) were prepared by dry pressing 8% mol yttria-stabilized zirconia (YSZ) pellets and subsequent firing at 1500°C for 5 h. The cathode material Sm_{0.5}Sr_{0.5}CoO₃-Ce_{0.9}Gd_{0.1}O_{1.95} (SSC-GDC) was screen printed on the YSZ disks and fired at 950°C for 4 h. After firing the effective cathode area was approximately 0.25 cm². A small pseudoreference electrode was screen printed on the cell during cathode preparation to assist the electrochemical measurements. The La_{0.7}Sr_{0.3}VO₃ (LSV) anode material was screen printed on the opposite side of the disk and fired *in situ* at 1000°C before current was drawn from the cell. This procedure is necessary because both anode and cathode are unstable in oxidizing and reducing environments, respectively. The detailed preparation for the electrode powders and slurries is not included with this paper in the interest of simplicity.

Platinum gauze (52 mesh) was used as the current collector. The Pt lead wires were attached to each current collector (or YSZ pellets for the blank cell runs) using Pt paste. Constant potential was applied using a Perkin-Elmer 273A potentiostat/galvanostat. Cell resistances were determined using the current interrupt method using a Tektronix 5111A oscilloscope as well as a Solartron impedance analyzer. Digital multimeters were connected in parallel to the cell to monitor different cell voltages.

The first experimental run was aimed at understanding the stability and catalytic contribution (toward H₂S oxidation) of the Pt current collector used in all subsequent runs. Figure 2 compares the performance of two cells, one using only Pt mesh (blank) and the second our novel LSV material as anodes at 1273 K. The blank cell

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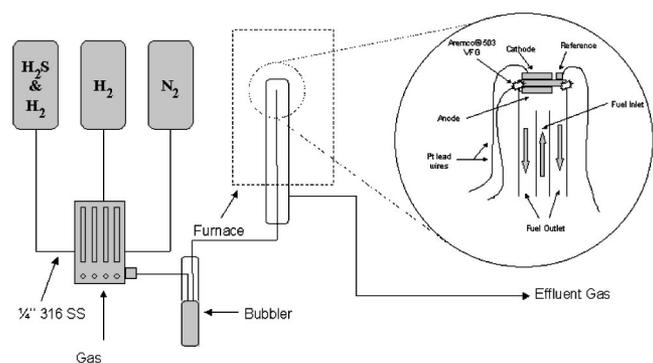


Figure 1. Experimental apparatus for cell testing.

experienced an abrupt drop in performance (total resistance increased by a factor of three after 12 h of operation) attributable to the reversible formation of PtS at the anode surface confirmed by scanning electron microscopy (SEM) and X-ray diffraction (XRD) measurements. 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.⁸ Even though the metallic sulfide phase is electronically conductive under these conditions, this conversion promotes the delamination of the Pt anode from the electrolyte.

In pure H₂, 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 an H₂S/H₂ mixture. Under these feed conditions, the LSV system initially increased and subsequently maintained a constant performance for over 2 days. In stark contrast, the performance of blank cell dropped significantly after 8 h and ultimately to zero after 22 h. Consequently, prior to measuring performance, cells were allowed to operate at a constant 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 testing.

The choice of anode material, strontium-doped lanthanum vanadium oxide, LSV, exhibits slight n-type conduction and is stable over a wide range of oxygen partial pressures (10⁻¹⁴-10⁻²⁰ atm).¹² Its electrical conductivity at 800°C has been reported at 120 S/cm compared to 2.9 S/cm for the undoped lanthanum vanadate. The other end member of this family, SrVO₃ has a very high conductiv-

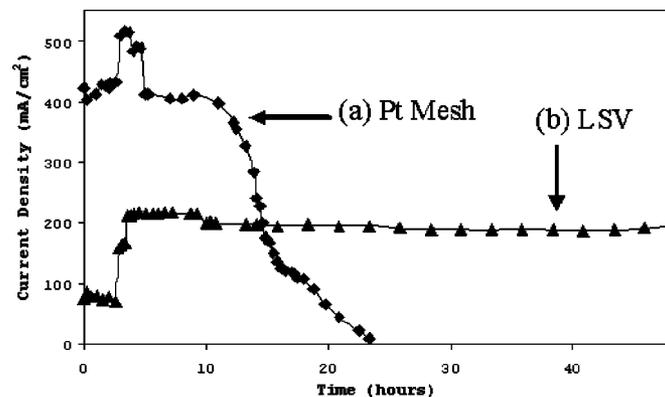


Figure 2. Performance of two cells with different anodes (a) a blank cell Pt mesh/YSZ/SSC-GDC and (b) LSV/YSZ/SSC-GDC. Cells were operated at $V_{\text{applied}} = 0.5$ V, $T = 1273$ K, $P = 1$ atm, fuel flow = 40 sccm. (Note the significant drop and increase in cell performance for the blank and LSV anodes, respectively, once the H₂S containing fuel is introduced at $t = 2$ h.)

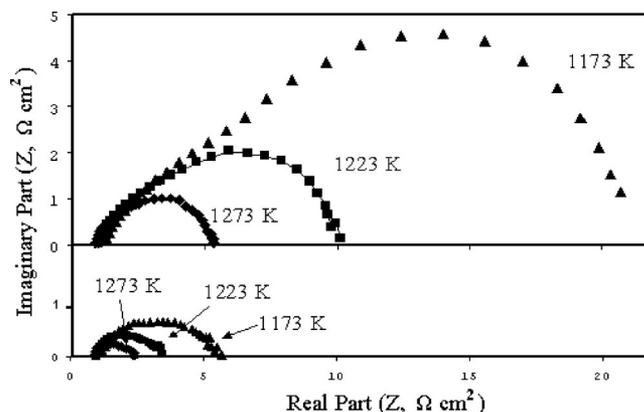


Figure 3. Impedance spectra of a cell with configuration LSV/YSZ/SSC-GDC when the anode was exposed to (a) pure H₂ fuel and (b) 10% H₂S Bal. H₂.

ity (1000 S/cm) but is unstable at oxygen partial pressures above 10⁻¹⁷ atmospheres. LSV has been tested previously in the catalytic oxidation of H₂S, implying good stability in an H₂S atmosphere. Similarly, our group has tested LSV in an H₂S removal processes using an electrolytic molten carbonate cell.¹³ Hydrogen sulfide was reduced at the cell cathode with sulfate ions migrating across a molten salt membrane. The use of a solid electrolyte instead of a molten salt is expected to increase anode stability, as it is no longer exposed to the corrosive nature of the liquid electrolyte.

Impedance spectroscopy was used to determine the effect of H₂S concentration on the interfacial polarization resistances at different operating temperatures. Figure 3 shows the impedance spectra when the SOFC anode was exposed to (a) pure H₂ and (b) 10% H₂S-90% H₂ gas mixture. The interfacial resistances decreased in the presence of the H₂S containing fuel, supporting the results from the LSV stability testing, where a noticeable increase was seen in cell performance in the presence of H₂S.

Previous studies indicate that LSV would not be a suitable SOFC anode candidate because it could potentially form a nonconductive Sr₃V₂O₈ structure at very low oxygen partial pressures.¹³ It is believed the migrating ions from the cathode side of the cell would readily react with the LSV compound, creating an insulating layer for electronic transport (between the cell anode and electrolyte) and hindering efficient cell performance. This conversion explains the poor performance of LSV when pure H₂ was used as the fuel.

However, our preliminary results suggest H₂S promotes the (reversible) formation of a conductive vanadium sulfide phase, instead of the insulating Sr₃V₂O₈ compound. This change appears to occur very rapidly, as the resistance of the LSV anode quadrupled only 5 min after removing the H₂S impurity from fuel. Furthermore, the opposite would occur when H₂S was introduced to a pure H₂ fuel stream in an identical amount of time. The detailed phase analysis of LSV used to devise this hypothesis will be presented in a subsequent paper. Similar observations (in the presence of H₂S) have been reported recently for a comparable perovskite anode.¹⁴

Figure 4 compares the performance of two cells with different fuels, one with 10% H₂S-90% H₂ and the second with 10% H₂S-90% N₂ as the fuel at 1273 K. Both setups converted H₂S to SO₂, as confirmed by mass spectrometry (MS). Even though more fuel is available for the first cell, its performance is almost identical to that of the second, implying that the level of fuel utilization for the second cell is over ten times greater than that of the first. This is further confirmed by the observation that a cell supplied with 80 sccm of a 10% H₂S-90% N₂ fuel mixture performed much better than the same cell supplied with 8 sccm of a 10% H₂S-90% H₂ mixture. These results seem to suggest that LSV is

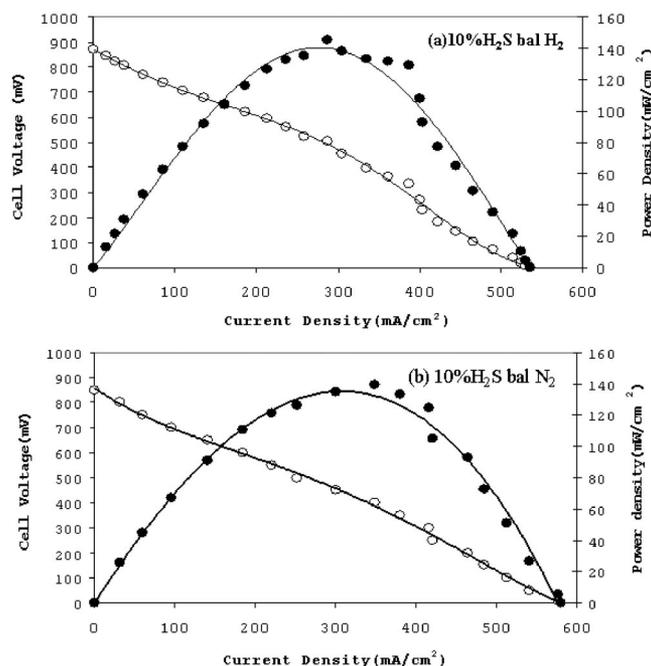


Figure 4. Cell voltage (open symbols) and power density (closed symbols) as a function of current density for a cell with configuration LSV/YSZ/SSC-GDC when the fuel was (a) 10% H₂S in H₂ and (b) 10% H₂S in N₂. ($T = 1273$ K, $P = 1$ atm, fuel flow = 75 sccm.)

very active toward the electrochemical oxidation of H₂S and would be an excellent anode for SOFCs operating on H₂S and H₂S containing fuels. Future testing will address the exact causes for this somewhat strange behavior as well as the relationships between fuel utilization, H₂S thermal cracking, and oxidation products from the cell.

The LSV anode material has shown very promising results for SOFC devices operating with sulfur containing fuels. Our preliminary results have shown that LSV is stable under the presence of H₂

and H₂S. This anode material has shown stable electrochemical performance over time periods of 48 h. Furthermore, this material appears to promote the specific electrochemical oxidation of H₂S. Cell performance was almost identical for fuel mixtures of 10% H₂S in H₂ and 10% H₂S in N₂, suggesting H₂S is selectively oxidized even under the presence of an alternate fuel (H₂). This conclusion is supported by our impedance results, which showed overall cell resistances drop (by an average factor of four) once the transition was made from pure H₂ to an H₂S containing fuel mixture. Future work will focus on determining the reasons for this behavior and optimizing cathode materials in an attempt to maximize cell performance.

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