

600 nm. The transmission of the NESA glass substrate was 80% at 600 nm. The poor transparency of the film could be ascribed to surface roughness and the existence of pores, as noted⁹ for the films prepared from the 0.1 mol/liter electrolyte. The absorption edge is 375 nm, which corresponds to the optical bandgap energy of 3.3 eV. Although ZnO films prepared from 0.01 or 0.2 mol/liter zinc nitrate electrolyte exhibited lower transmittances in the visible light region, the optical bandgap energy was constant at 3.3 eV. The bandgap energy of 3.3 eV is consistent with the characteristic value for undoped ZnO films prepared by sputter deposition.⁷

In conclusion, ZnO films of good quality have been grown by potentiostatic cathodic deposition at -0.7 V vs. Ag/AgCl reference electrode onto NESA glass from aqueous 0.03 to 0.1 mol/liter zinc nitrate electrolytes at 335 K. The optimum range of electrolyte concentration had been found.

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A Hydrogen Sulfide Fuel Cell Using a Proton-Conducting Solid Electrolyte

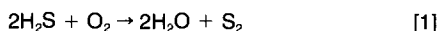
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ABSTRACT

A proton-conducting solid-state electrolyte composed of Li_2SO_4 has been tested in a medium temperature ($\sim 700^\circ\text{C}$) fuel cell with H_2S as the fuel. Proton conductors are preferred over oxide-ion conductors for the elimination of SO_2 as a possible product of the oxidation of H_2S . This electrolyte, Li_2SO_4 , had been previously used with H_2 as the fuel; its thermodynamic stability in H_2S makes it a natural choice for this application. Here we report, with first, crudely prepared electrolytes, open-circuit voltages of above 1 V, with short-circuit current densities of above 10 mA/cm².

Hydrogen sulfide (H_2S) is a noxious gas which is produced at a rate of greater than 10 million tons annually. This production comes mainly as the result of desulfurization of sour fuels. Typically, these cleaning processes involve sorbent scrubbing from which concentrated H_2S streams are evolved upon regeneration of the sorbent. The standard method of handling these streams is to partially oxidize the hydrogen sulfide in "Claus" reactors to elemental sulfur and water



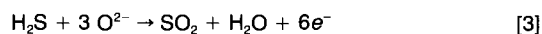
The energy from this highly exothermic reaction is recovered in the steam produced; however, it is clear that recovery as electrical energy would be preferable.

While it has been recognized for some time that H_2S is potentially oxidizable in a fuel cell, it is also known that this gas is a powerful poison in most of the standard cells (e.g., phosphoric acid, molten carbonate, methanol). For this reason, its use was unexploited until the late 1980s when Pujare *et al.*¹ demonstrated that a zirconia-based electrolyte at 1000°C could not only tolerate high levels of H_2S , but also actually could operate with it as a fuel. Other studies have shown that lower temperatures of operation are possible² and that other materials, such as metal sulfides or thio-spinels, could replace platinum which initially was used for the anode material.³

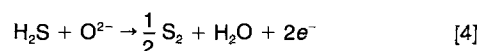
Although the cathode half-cell reaction in all of these experiments was the reduction of oxygen (in air), the half-cell reactions occurring at the anode remained unresolved. With these oxide conducting electrolytes, oxygen reduction occurs by



After transport through the electrolyte, these oxide ions can then react with H_2S at the anode to produce either sulfur dioxide (SO_2) or sulfur (S_2)

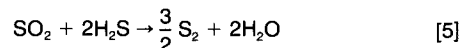


or



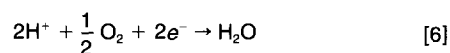
Thermodynamically, neither of these reactions is favored over the other; the equilibrium voltages at 700°C are 0.774 and 0.789 V, respectively. The second of these, reaction 4, is preferable since elemental sulfur, produced as a gas at temperatures above 450°C , can be condensed and recovered. On the other hand, sulfur dioxide, formed in reaction 3, is, in itself, toxic and would require further treatment.

The early experiments,^{2,3} run at high fuel rates, were unable to resolve which of the two anode half-cell reactions were occurring because, at low fuel utilization, SO_2 is reduced by the excess H_2S in a reaction that also occurs in the Claus process

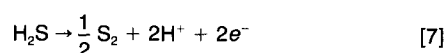


As a result, the lack of effluent SO_2 is insufficient evidence for reaction 4. At high utilization, the obvious choice for commercial operation, reaction 4 is required.

Using a proton conductor instead, water is produced at the cathode



and hydrogen ions at the anode



Thus, there is no opportunity for SO_2 production; sulfur is the only possible anode product. This concept was first revealed by Kirk⁴ in 1992, but successful experiments with proton conducting solid electrolytes were not reported until 1994.⁵ These did, in fact, pro-

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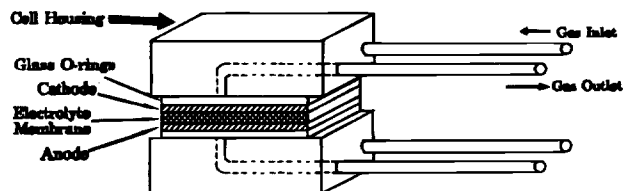


Fig. 1. Fuel cell design.

duce electrical energy as predicted, but suffered from gradual degradation of the electrolyte. The proton and mixed-ion conducting cerates, ytterbia-doped strontium cerate ($\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_3$) and samaria-doped barium cerate ($\text{BaCe}_{0.9}\text{Sm}_{0.1}\text{O}_3$), respectively, converted to their nonconductive sulfate forms, SrSO_4 and BaSO_4 .

However, a recent work by Heed *et al.*⁶ utilized solid alkali-metal sulfates, which are proton conductors at intermediate temperatures (400 to 800°C), as the electrolyte in a fuel cell. While these experiments were run only with hydrogen (H_2) as the fuel, the extension to H_2S seemed reasonable; these sulfates are thermodynamically stable in the presence of hydrogen sulfide. This communication relates some initial experimental results obtained using a lithium sulfate electrolyte with H_2S as the fuel.

Anhydrous lithium sulfate was ground up and heated at 250°C for a period of 30 min before being pressed uniaxially at 13,000 psi in a 1.25 in. diam die. The resulting electrolyte was greater than 2 mm thick, and the density was between 75 and 80% of theoretical density. The membrane was then fired at 500°C for 24 h. Platinum paste (Engelhard 6926) was applied to both faces and sintered during heat up for the fuel cell run. The area of the electrodes exposed to the gases was estimated to be 1.7 cm^2 .

The electrolyte was contained between MACOR housings as shown in Fig. 1. It was necessary to operate this fuel cell at a temperature above 575°C in order to obtain the highly conductive α -phase of lithium sulfate, which is cubic in nature, as opposed to the low temperature, low conductivity, monoclinic β -phase. A hydrogen sulfide/nitrogen mixture (10,200 ppm H_2S , balance N_2) was used as the fuel, and air was passed through the cathode compartment. Pure hydrogen preceded hydrogen sulfide as the fuel in order to have a reasonable basis for comparison and to insure that every-

thing was operating properly. Open-circuit potential and short-circuit current were monitored. The cell resistance was estimated using an ac bridge.

With an open-circuit potential of 1.1 V, a maximum short-circuit current density of 12 mA/cm^2 was obtained at a temperature of 725°C. This high open-circuit potential, as compared with the standard potential, is due to the Nernstian effect of very low product concentrations at both electrodes. The cell resistance was measured to be in the range of 2 to 3 Ω . Furthermore, postmortem analysis of the electrolyte with x-ray diffraction showed that no conversion of the electrolyte had occurred.

Even though the current densities obtained in these preliminary experiments were far below those reported by Heed,⁶ the fact that H_2S performed as well as H_2 gives reason to expect that more sophisticated experiments (*e.g.*, denser, thinner electrolytes, more adherent electrode films) will yield far better results. Future experiments also will utilize ceramic electrodes applied as powder during initial membrane preparation.

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Defect Generation during Epitaxial CoSi_2 Formation Using Co/Ti Bilayer on Oxide Patterned (100)Si Substrate and Its Effect on the Electrical Properties

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ABSTRACT

Self-aligned formation of epitaxial CoSi_2 , using a Co/Ti bilayer, on linear oxide (SiO_2) patterned (100)Si substrates has been investigated. Rapid thermal annealing (RTA) at 550°C resulted in lateral encroachment of silicide at the Si under the edge of the oxide. After RTA at 900°C, even though an epitaxial CoSi_2 layer was formed on the Si substrate, defects such as lateral encroachment and void were generated under the edge of the oxide. It was found that such defects yield device failures due to deterioration of the gate oxide and the shallow junction.

There has been a continuous demand for improvement in the metallurgical aspects of self-aligned silicide (salicide) with the miniaturization of very large scale integration (VLSI) devices. Recently, it was reported that epitaxial CoSi_2 layers successfully form on (100)Si substrates using Co/refractory bilayers, such as Co/Ti,¹⁻³ Co/Ta,^{4,5} and Co/Zr.⁶ Such a technique has been the subject of intensive study because of its potential benefit as a silicide contact in VLSI technology. Thus far, the studies were conducted exclusively on laterally unconfined films, that is, on blank Si

wafers, and the primary concern was focused mainly on the epitaxial crystallinity of CoSi_2 and its low electrical resistivity. In its practical applications to VLSI, however, the silicide layer has to be confined to an exposed Si area having an oxide (SiO_2) sidewall spacer around the polycrystalline silicon (poly-Si) gate. Therefore, it is of utmost importance to confirm the crystalline nature of the silicide on the oxide patterned substrate. In this paper, we report the results of an investigation of the epitaxial growth of CoSi_2 on such a substrate. Electrical properties of the VLSI device which had such an epitaxial CoSi_2 silicide on the exposed area of source/drain junctions also have been discussed.

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