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SOME STUDIES ON A SOLID STATE SULFUR PROBE
FOR COAL GASIFICATION SYSTEMS

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Some Studies on a Solid State Sulfur Probe for Coal Gasification Systems

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Key words: sulfur probe, calcium fluoride sensor for sulfur, galvanic cell, solid electrolyte cell, coal gasification-sulfur control, high temperature sulfur meter.
ABSTRACT

Measurements on the solid electrolyte cell

\((Ar + H_2 + H_2S/\text{CaS} + \text{CaF}_2 + (Pt) // \text{CaF}_2 // (Pt) + \text{CaF}_2 + \text{CaS} / H_2S + H_2 + Ar)\)

demonstrates that the emf of the cell is directly related through the Nernst equation to the difference in sulfur potentials established at the two \(Ar+H_2+H_2S\)/electrode interfaces. The electrodes are designed to convert the sulfur potential gradient across the calcium fluoride electrolyte into an equivalent fluorine potential gradient with the aid of the reaction, \(\text{CaF}_2(s) + 1/2 S_2(g) \rightarrow \text{CaS}(s) + F_2(g)\).

The response time of the probe varies from approximately 9 hr at 990 K to 2.5 hr at 1225 K. The conversion of calcium sulfide and/or calcium fluoride into calcium oxide should not be a problem in anticipated commercial coal gasification systems. Suggestions are presented for improving the cell for such commercial applications.
The ability to continuously monitor the sulfur potential in coal gasification reactors is of crucial importance for efficient gasifier operation and for accurate life prediction of corroding construction materials. From an engineering point of view, in situ solid state sensors that directly measure the sulfur potential are preferable to devices that employ liquid electrolytes or involve sampling of gases for low temperature analytical procedures. Despite the concerted efforts of many laboratories during the last decade to find suitable sulfide electrolytes, analogous to CaO-ZrO$_2$ or Y$_2$O$_3$-ThO$_2$ for oxygen potential measurements, no acceptable material has been identified in which the ionic transport number is higher than 0.99 over a large range of sulfur potentials and temperatures.

The prospect of designing a suitable sulfide electrolyte does not appear promising in the near future because the band gaps in the sulfides are generally narrower than in the corresponding oxides (1). An alternate approach may be to use calcium fluoride (CaF$_2$) as the electrolyte in a solid state cell, in which the electrodes are designed to convert the sulfur potential in the gas into an equivalent fluorine potential.

Calcium fluoride has been found to be a suitable electrolyte at high temperatures and over a large range of fluorine potentials (2-7). Colorless, pure CaF$_2$ contains virtually equal concentrations of interstitial anions and anion vacancies. The fluoride ions are the mobile species, and they migrate as interstitials and vacancies. At very low fluorine potentials or in the presence of calcium vapor, an excess of calcium dissolves in CaF$_2$ according to the reaction

$$\text{Ca(g)} + 2 \text{F}_x + \text{CaF}_2 + 2 \text{e}_x$$

[1]
where \( F^-_x \) is a fluoride ion on a regular anion site, and \( e^-_x \) is an electron substituted for an anion, producing a color (F) center. Wagner (8) has given an analysis of the onset of electronic conduction in \( \text{CaF}_2 \) due to the dissolution of calcium metal. Patterson (9) has also discussed the electrolytic conduction domain for \( \text{CaF}_2 \) at high temperatures. Because of the extreme electronegativity difference between \( \text{Ca}^{2+} \) and \( F^- \) ions and the correspondingly large forbidden bandgap for \( \text{CaF}_2 \), positive hole conduction will not be significant until the fluorine pressure is increased to several atmospheres. The open-circuit emf (E) across the electrolyte is a direct measure of the chemical potential difference, provided the fluorine pressures at the electrodes and the temperatures of operation lie within the electrolytic conduction domain, (that is the transport number of electrons or holes is less than 0.01).

An advantage of the solid electrolyte sensors is that the output is an electric potential that can readily be used to actuate a control circuit. It was, therefore, decided to study the efficiency of the solid electrolyte cell, 

\[
\text{Ar} + \text{H}_2 + \text{H}_2\text{S/\text{CaS} + \text{CaF}_2 + (Pt) // \text{CaF}_2 // (Pt) + \text{CaF}_2 + \text{CaS / \text{H}_2\text{S} + \text{H}_2 + \text{Ar}}
\]

[2]

as a part of our program on the development of a sulfur probe. The experimental results, the limitations of this technique to coal gasification systems, as well as anticipated improvements are presented in this paper.

**Experimental**

**Materials.**—High purity \( \text{Ar}+\text{H}_2+\text{H}_2\text{S} \) gas mixtures and their analysis were obtained from Matheson. A slight decrease in the \( \text{H}_2\text{S} \) concentration of the gases was observed over extended periods of storage, presumably due to the reaction of \( \text{H}_2\text{S} \) with the storage tank. Correction factors for gas ratios

4
were obtained by periodically observing the ion intensity ratios of H$_2$S to H$_2$

in a mass spectrometer. For the electrolyte, optical grade single crystals

of CaF$_2$, in the form of discs of 1.5 cm in diameter and 0.2 cm thick, were

obtained from Harshaw Chemical Company. High purity anhydrous CaF$_2$ and CaS

powders were supplied by Apache Chemical Company and Ventron Corporation.

Fine platinum powder and porous platinum sheet were obtained from Johnson and

Mathey Company. The electrode pellets were made by double end compression of

an intimate mixture of fine powders of CaF$_2$, CaS, and Pt in the molar ratio

1.5 : 1 : 0.2. The pellets were sintered in evacuated silica capsules at

1225 K for 12 hr.

Apparatus.—A schematic diagram of the apparatus is shown in Fig. 1. A
disc of CaF$_2$ electrolyte was spring loaded against an alumina tube with a gold

'0' ring between them to obtain a gastight joint. The alumina tube was held

firmly in a water cooled brass head, to which the springs were attached.

Since gold softens at the high temperatures used in these experiments, low
tension springs were sufficient to produce a gastight joint. Thus, the ceramic

components of the assembly were not subjected to high applied stresses. Elec-
trode pellets containing CaF$_2$+CaS+Pt were spring loaded on either side of the

electrolyte, with a thin porous platinum sheet sandwiched between the pellet

and the electrolyte. Platinum leads, flame sprayed with alumina, were spot

welded to the porous platinum sheets. At the low sulfur potentials used in

the experiments, no chemical attack on the platinum was observed in the hot
zone of the furnace. At the cooler end, however, there was some evidence of
reaction between platinum and H$_2$S gas. Therefore, in this region, the plat-
inum leads were protected by an alumina sheath closed on both ends by alumina
cement.
The cell was designed to provide two separate gastight compartments around the two electrode pellets. Separate gas streams with differing sulfur potentials were passed through these compartments. The test gas was admitted to the system at the lower end of the reaction tube and flowed past the outer electrode pellet at a rate of 250 ml min⁻¹. The reference gas was passed around the inner electrode at a flow rate of 100 ml min⁻¹. The two gas streams were isolated in the reaction tube and escaped through different ports in the brass head. The escaping gases were bubbled through two 25 cm high columns of NaOH solution to remove H₂S and HF. The exit gases were further scrubbed before being pumped through the fume exhaust system.

The entire cell assembly, attached to the brass head, was lowered into a vertical alumina reaction tube. The cell was electrically shielded by connecting a platinum foil, wrapped around the reaction tube, to ground. The reaction tube was heated by a Kanthal resistance furnace. Temperatures of the furnace and of the cell were measured by two separate Pt-Pt (13% Rh) thermocouples. The furnace temperature was controlled to ±1 K by use of a stepless current-compensating controller.

Procedure.—The test cell was assembled as shown in Fig. 1, and the reaction tube was evacuated by a mechanical pump to a pressure of 0.5 Nm⁻² and then backfilled with purified argon. The argon purification train consisted of magnesium perchlorate (to absorb the residual moisture), and copper turnings at 700 K and titanium turnings at 1100 K (to remove residual oxygen). The cell was heated to 500 K, evacuated, and refilled with argon. The temperature of the cell was then raised to 1225 K. The reference gas was introduced into the inner gas compartment of the cell, while argon flow was
maintained through the outer reaction tube. Gastightness of the 'O' ring seal was checked by analyzing the argon stream exiting from the reaction tube for traces of H₂S. After ensuring that the test cell was leaktight and the two gas streams were isolated, the test gas was introduced into the reaction tube. Cell voltage was monitored using a Keithly digital voltmeter with an internal impedance of 10¹² Ohms. After the start of the experiment, approximately 5 hr were required to obtain a steady emf.

Two procedures were followed during the investigations: (i) During isothermal runs, cell temperature was kept constant at 1073 K or 1173 K and the steady, reversible emf corresponding to different test gases was measured, and (ii) For two selected test gases, the temperature dependence of the steady, reversible emf was measured.

Results

Response time.—Composition of the test gases and the reference gas and the emf obtained at 1073 K and 1173 K are shown in Table I. Generally, the response time of the cell at 1225 K, after a small change in temperature or gas composition, was 2.5 hr, while at a lower temperature of 990 K the response time was approximately 9 hr. The cell emf was insensitive to moderate increase in the flow rate of the test gas and/or the reference gas. However, when the flow rate of one of the streams was increased by factors greater than two, while keeping the flow rate of the other stream constant, significant changes in the emf were noted — about 20 mV during the transient period, and about 15 mV during the steady state period. The changes were, however, not always reproducible. When the flow rates of both streams were changed simultaneously by the same amount, the cell emf remained virtually
constant. It is likely that a substantial increase in the flow of gas through one stream may have resulted in differential cooling, thus creating a thermal gradient across the electrolyte. Changes in emf resulting from the presence of a steady state thermal gradient are quantitatively related to the partial entropy of fluorine in the gas phase, as discussed by Fitzner, Jacob, and Alcock (10).

Reversibility of the emf was checked by passing small currents (5µA) through the cell in either direction for 2 min. It was found that the emf returned to the steady value before the titration in approximately 30 min. After several days of use, the electrode pellets became fragile and fractured easily.

Calculation of sulfur potentials.—Experimental emfs obtained at 1073 K and 1173 K for different test gases are compared in Fig. 2 with known values calculated from the difference in sulfur potential between the test gas and the reference gas. The emf developed across a CaF₂ electrolyte can be related through the Nernst equation to the partial pressure of fluorine (fluorine potential) across the electrolyte, provided the ionic transport number is close to unity:

\[
E = \frac{\Delta \mu_{F_2}^R - \Delta \mu_{F_2}^T}{nF} = \frac{RT}{nF} \ln \frac{P_{F_2}^R}{P_{F_2}^T}
\]

where \(E\) is the emf, \(\Delta \mu_{F_2}^R\) and \(\Delta \mu_{F_2}^T\) are the fluorine potential at the reference and the test electrodes, \(F\) is the Faraday constant, \(n\) is the number of electrons (=2) involved in the transfer of one molecule of \(F_2\) gas between the two electrodes, \(R\) is the gas constant, \(T\) is the absolute temperature, and \(P_{F_2}\) is the fluorine partial pressure. The gas phase containing Ar+H₂+H₂S
establishes a partial pressure of sulfur (sulfur potential) over the electrode, depending on the ratio of \( \text{H}_2 \) to \( \text{H}_2\text{S} \), by virtue of the reaction,

\[
\text{H}_2(g) + \frac{1}{2} \text{S}_2(g) + \text{H}_2\text{S}(g)
\]

\[ [4] \]

\[
\frac{1}{2} \Delta \mu_{\text{S}_2} = RT \ln \frac{P_{\text{S}_2}^{1/2}}{P_{\text{H}_2\text{S}} P_{\text{H}_2}} = \Delta G^0_4 + RT \ln \left( \frac{P_{\text{H}_2\text{S}}}{P_{\text{H}_2}} \right)
\]

\[ [5] \]

where \( \Delta G^0_4 \) is the standard Gibbs' free energy change for reaction [4]. The sulfur potential established by the gas phase, when in contact with the electrode pellet consisting of CaS and CaF₂, fixes a fluorine potential through the reaction

\[
\text{CaF}_2(s) + \frac{1}{2} \text{S}_2(g) \rightarrow \text{CaS}(s) + \text{F}_2(g)
\]

\[ [6] \]

\[
\Delta \mu_{\text{F}_2} = \frac{1}{2} \Delta \mu_{\text{S}_2} - \Delta G^0_6
\]

\[ [7] \]

where \( \Delta G^0_6 \) is the standard Gibbs' free energy change for reaction [6]. The platinum in the electrode pellet acts as a catalyst for the reaction. Since there is no ternary compound or significant solid solubility in the CaF₂-CaS system, the condensed phases in the electrode pellets are present at unit activity. Combining equations [3] and [7], an expression is obtained relating the emf to the difference in the sulfur potential between the electrodes;

\[
E = \frac{\Delta \mu_{\text{S}_2}^R - \Delta \mu_{\text{S}_2}^T}{2nF} = \frac{RT}{2nF} \ln \frac{P_{\text{S}_2}^R}{P_{\text{S}_2}^T}
\]

\[ [8] \]

Equation [8] may also be expressed in terms of the ratio of \( \text{H}_2\text{S} \) to \( \text{H}_2 \) in the gas phase over the two electrodes;
The measured emfs, as shown in Fig. 2, do not deviate by more than 2.5 mV from that calculated using equation [9]. Deviations from theoretical values have the same sign at different temperatures for each test gas. Thus, it is likely that these deviations arise from small errors in gas analysis.

The variation of the emf of the cell with temperature and with two test gases (3 and 4 in Table I) is shown in Fig. 3. Again, measured temperature dependence is in agreement with the theoretical value given by the derivative of equation [9] with respect to temperature.

$$\frac{dE}{dT} = \frac{R}{nF} \ln \left( \frac{\frac{P_{H_2S}}{P_{H_2}}}{\frac{P_{H_2S}}{P_{H_2}}} \right)_T$$

Discussion

The activity of calcium at the electrodes, during the present investigation, can be evaluated by considering the reaction,

$$\text{CaS(s) + H}_2(g) \rightarrow \text{H}_2\text{S(g) + Ca(s)}$$

The activity of calcium, \(a_{\text{Ca}}\), is given by

$$a_{\text{Ca}} = \left( \frac{P_{H_2}}{P_{H_2S}} \right) \exp \left( - \frac{\Delta G^0_{11}}{RT} \right)$$

where \(\Delta G^0_{11}\) is the standard Gibbs' free energy change for reaction [11]. It can readily be shown from known thermodynamic data that the activity of calcium varies from \(9.5 \times 10^{-19}\) to \(6.0 \times 10^{-17}\) at 1113 K over the range of test gas composition (gases 1 and 4, respectively, Table I). Wagner (8) has suggested that
the electronic transport number of CaF$_2$ is $10^{-2}$ when the activity of calcium is $6 \times 10^{-6}$ at 1113 K. It is apparent, therefore, that the electronic transport number is much less than $10^{-2}$ and contributes very little to the results of the present study.

The exact factors affecting the slow response time of galvanic cells based on a CaF$_2$ electrolyte have not yet been determined. Clearly, the kinetics of the electrode reaction [6] may be rate controlling, or the transport of ions in CaF$_2$ may be slow, such that the composition gradient across the electrolyte cannot readjust rapidly after a perturbation in the chemical potential at the electrode. Additionally, since the fluorine potentials are low ($F_2^- = 10^{-24}$ to $10^{-28}$ Nm$^{-2}$), gas phase polarization at the electrolyte-electrode interface may be the rate limiting step. This latter possibility seems rather improbable, however, because sufficient concentration of HF gas should be created by the reaction of H$_2$S with CaF$_2$ to transport the fluorine potential to the electrolyte surface.

Electrical current techniques, such as voltage recording after a galvanostatic pulse or impedance measurement at low frequencies, can be used to determine whether the kinetics of the electrode reaction is responsible for the slow response of the cell (13). Heyne and Engelson (14) have recently suggested that for oxygen probes containing calcia-stabilized zirconia as the electrolyte, the uptake or release of oxygen by the electrolyte, when the partial pressure of oxygen in the ambient atmosphere is altered, is the main reason for the sluggishness in response and variation with time of the emf developed. If a similar mechanism is valid for CaF$_2$, a reduction in the thickness of the electrolyte or doping, to increase the effective diffusion coefficient, may accelerate the response of the probe to changes in sulfur potential. Another alternative is to use β-alumina as the electrolyte (15).
β-alumina has much higher conductivity than CaF₂, especially at lower temperatures. Further, the electrodes would be redesigned to convert the sulfur potential gradient into an equivalent sodium potential gradient.

Although systematic studies on the catalytic behavior of platinum or other materials have not been undertaken, it was found in preliminary experiments that approximately 0.2 moles of platinum per mole of CaO is the optimum amount of catalyst in the electrode pellets. To use the cell for sulfur potentials higher than those studied in this investigation, a more suitable catalyst than platinum is needed. Platinum readily forms sulfides at higher sulfur potentials (12). Transition metal sulfides that do not react with CaS and in which cations exist in multivalent states may prove to be good catalysts.

Typical compositions of the raw gases in some coal gasification processes are shown in Table II. It can readily be shown that under the conditions of coal gasification, the conversion of CaS to CaO, according to the scheme,

$$\text{CaS}(s) + \text{H}_2\text{O}(g) \rightarrow \text{CaO}(s) + \text{H}_2\text{S}(g)$$  \[13\]

is not thermodynamically favorable. However, the reaction of \(\text{H}_2\text{S}(g)\) with CaF₂,

$$\text{CaF}_2(s) + \text{H}_2\text{S}(g) \rightarrow \text{CaS}(s) + 2 \text{HF}(g)$$  \[14\]

will result in a partial pressure of HF in the immediate neighborhood of the electrode that can vary from \(2.8\times10^2 \text{ Nm}^{-2}\) to \(80 \text{ Nm}^{-2}\). Since all the gas passing through the probe is not saturated in HF, the average HF concentration in the exit gas is estimated to be approximately 200 ppm, and therefore must be scrubbed for the removal of HF. Additionally, for commercial application, the probe must be designed in such a way as to prevent particulate material in the gas from depositing on the electrodes of the sensor.
Conclusion

The theory, design and operation of a solid state sulfur probe based on CaF$_2$ electrolyte has been demonstrated. The cell responds to changes in sulfur potential in a manner predicted by the Nernst equation. Further research is needed to determine the main reason for the slow response of the cell. The rate limiting steps may be either the kinetics of electrode reactions or the rate of transport through the electrolyte. If the reaction kinetics is rate controlling, suitable catalysts may be developed to overcome the problem. If the slow transport of ions in the electrolyte is the reason for the sluggish response, a cell based on β-alumina electrolyte may be more suitable.

Acknowledgements

The authors thank Dr. Ian Finnie, University of California, Berkeley, and Mr. A. V. Levy, Lawrence Berkeley Laboratory, for their support and encouragement.
REFERENCES

Table I. Composition of the test gas mixtures and the corresponding cell emfs

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<tr>
<th>Test gas Number</th>
<th>H₂ (%)</th>
<th>H₂S (%)</th>
<th>Ar (%)</th>
<th>emf (1073 K)</th>
<th>emf (1173 K)</th>
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<tr>
<td>1</td>
<td>40.6</td>
<td>8.3</td>
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<td>-34</td>
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<td>2</td>
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<td>55.1</td>
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</tr>
<tr>
<td>5*</td>
<td>25.2</td>
<td>2.52</td>
<td>72.28</td>
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</table>

*Reference gas
Table II. Composition of raw gases in various coal gasification processes

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<td>$\text{N}_2$</td>
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<td>0.4</td>
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<tr>
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<td>6</td>
<td>7</td>
<td>12</td>
<td>13</td>
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</table>

Compositions are given in vol. %
FIGURE CAPTIONS

Fig. 1. Schematic diagram of the apparatus used for testing the CaF$_2$ electrolyte based sulfur probe.

Fig. 2. Variations of the emf with H$_2$S/H$_2$ ratio of the test gas at 1073 K and 1173 K; — theoretical values [9].

Fig. 3. The temperature dependence of the reversible emf with test gases 3 and 4 passing through the cell; — theoretical values [10].
Fig. 1. Schematic diagram of the apparatus used for testing the CaF$_2$ electrolyte based sulfur probe.
Fig. 2. Variations of the emf with $\frac{H_2S}{H_2}$ ratio of the test gas at 1073 K and 1173 K; — theoretical values [9].
Fig. 3. The temperature dependence of the reversible emf with test gases 3 and 4 passing through the cell; -- theoretical values [10].
Measurements on the solid electrolyte cell

\[
(\text{Ar} + \text{H}_2 + \text{H}_2\text{S}/\text{CaS} + \text{CaF}_2 + \text{Pt} + \text{Pt}) \rightarrow \text{CaF}_2 (\text{Pt}) + \text{CaF}_2 + \text{CaS} + \text{H}_2 + \text{Ar}
\]

shows that the emf of the cell is directly related through the Nernst equation to the difference in sulfur potentials established at the two Ar + H\textsubscript{2} + H\textsubscript{2}S/electrode interfaces. The electrodes are designed to convert the sulfur potential gradient across the calcium fluoride electrolyte into an equivalent fluorine potential gradient with the aid of the reaction, CaF\textsubscript{2}(s) + 1/2 S\textsubscript{2}(g) \rightarrow CaS(s) + F\textsubscript{2}(g). The response time of the probe varies from approximately 9 hr at 990 K to 2.5 hr at 1225 K. The conversion of calcium sulfide and/or calcium fluoride into calcium oxide should not be a problem in anticipated commercial coal gasification systems. Suggestions are presented for improving the cell for such commercial applications.