Evaluation of a molybdenum sulfide reference electrode in hot alkaline solutions

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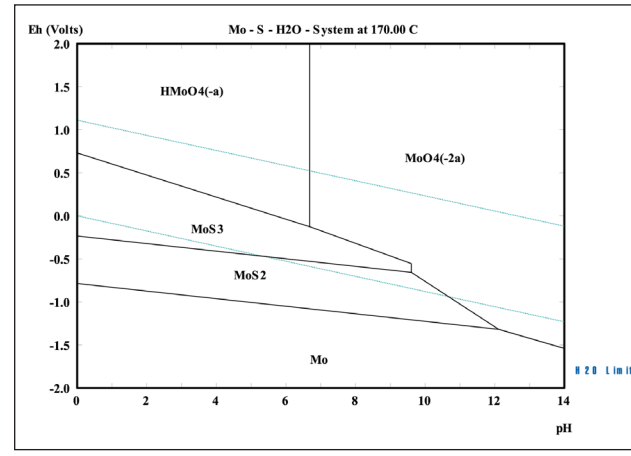
ABSTRACT: This investigation evaluated the applicability of a molybdenum sulfide reference electrode (MSRE) as an internal reference electrode for use in alkaline sulfide solutions over a range of pulp digester liquors at 170°C. The electrode remained stable during the exposure period of two weeks. The experimentally determined half cell potential of the MSRE is E = -0.91 V_{SHE}. The surface of the MSRE was examined by scanning electron microscope (SEM) and electron spectroscopy for chemical analysis (ESCA) to verify the chemical composition of the thin surface film. Based on ESCA studies, the surface film contained molybdenum disulfide and sodium disulfide. During storage of the specimens, sulfide was partly oxidized to sodium sulfite in air. Next to the metallic molybdenum, a mixed molybdenum disulfide and molybdenum hydroxide layer was detected.

Application: The results of this study might help mills in selecting a reference electrode for use with pulp digesters.

In the pulp and paper industry, reliable operation of the digesters is a major concern. The industry uses studies of the corrosion resistance of carbon steels and different grades of stainless steels in hot alkaline sulfide solutions used in digesting pulp chips. In addition, many carbon steel digesters are protected anodically (i.e., the potential of the digester surface is forced to the passive potential range via external current sources) [1,2]. Anodic protection necessitates the use of a reliable reference electrode, because control of potential needs to be rather accurate. Reference electrodes also are used in monitoring corrosion resistance of materials in digesters. The reference electrode should not be "poisoned" by soluble sulfide species. Such an electrode, to be thermodynamically reversible, must almost certainly be a metal/metal sulfide electrode made with an extremely low metal sulfide solubility product. The silver-silver sulfide (Ag-Ag_2S) reference electrode does not work reliably enough in digesting processes because soluble silver complexes, such as polysulfides, form on the surface of the electrode [3]. The upper temperature limit of the Ag-Ag_2S reference electrode appeared to be 25°C [3]. A likely alternative is to use a molybdenum sulfide reference electrode (MSRE), which has been used in anodic protection of kraft digesters [4].

The dissociation constant of molybdenum disulfide (MoS_2) is $K_d(25°C) = 1.156\times10^{-77}$ and $K_d(170°C) = 7.17\times10^{-60}$. The corresponding values for Ag_2S are $K_d(25°C) = 7.246\times10^{-23}$ and $K_d(170°C) = 5.06\times10^{-20}$, respectively [5]. Therefore, molybdenum is a stronger sulfide former than silver and MoS_2 is far more insoluble than Ag_2S. Thus, one would expect MoS_2 to be more stable in pulp digester environments.

Figure 1 presents the thermodynamic equilibrium diagram for the molybdenum-sulfide system at 170°C as a function of pH (i.e., Pourbaix diagram). The temperature of 170°C and the sulfide concentration of 50 g/L (0.641 M) represent the upper end conditions for a digester. The pH (T) values of pure sodium hydroxide (NaOH) solutions (100 g/L, 150 g/L, and 200 g/L) at 170°C are 11.29, 11.51, and 11.70, respectively [6]. At this pH, representing the upper end of pH in the cooking process, the disulfide of molybdenum is stable, but only at potentials below the hydrogen equilibrium potential, $E(H_2/H^+)$. In very alkaline conditions, even the disulfide would start to dissolve as molybdate ions. However, the dissociation constant (pK) of MoS_2 is very high, which means that this sulfide is rather stable and fixed [5]. In many cases, the phases, although not exactly thermodynamically stable, still exist in metastable form. In such a case, the metastable equilibrium potential for MoS_2/



1. E-pH diagram of Mo-S-H_2O system (T = 170°C, [Mo] = 10^{-6}M, [S] = 0.0641M).

molybdenum trisulfide (MoS_3)at 170°C, pH (T) = 11.24 and [S^{2-}] = 0.0641M would be predicted to exist at about 0.77 V_{SHE}. Instead of thermodynamic stability of MSRE, the short exposure period (two weeks) was selected for the corrosion problems of polytetrafluoroethylene (PTFE) used in the sensor.

Based on Fig. 1, at the relevant pH range of 9.0 < pH(T) < 11.3, three metastable thermodynamic equilibriums would seem possible for the MSRE: MoS_2/MoS_3, MoS_2/molybdate ion (MoO_4^{2-}), and MoS_3/MoO_4^{2-}.

The goal of this investigation was to determine the applicability of the MSRE as an internal reference electrode for use in alkaline sulfide solutions over a range of liquors. We made sure that the MSRE was functioning reliably and checked the thermodynamic reliability of the electrode by comparing the thermodynamically predicted potentials with those determined experimentally. No stable and reliable reference electrode is available to calibrate the MSRE at T = 170°C and relevant pH. Therefore, the potential of the MSRE was determined indirectly by measuring hydrogen evolution potentials on noble metals.

EXPERIMENTAL

For this study, MSREs were manufactured from a 5-mm-diam rod of 99.9% molybdenum and test pieces 4 mm in length were cut from the rod. The test piece surfaces were sanded with 200 grit silicon-carbide paper and rinsed in ethanol in an ultrasonic bath. Pure molybdenum rod was dipped in saturated sodium sulfide (Na_2S) solution for preparing a thin molybdenum sulfide layer on the electrode surface; analytical reagent grade chemical was used.

Chemical analysis

In describing surface layers on reference molybdenum samples after exposure to Na_2S, we used X-ray photoelectron spectroscopy (XPS). The system is able to generate an X-ray beam of less than 10 µm in diameter together with a scanning electron beam for imaging capability. The negative charge of a sample often is large enough to influence the low energy electrons from the electron flood gun, making it ineffective. To overcome this problem, the ion gun in the XPS has been modified to create an operating mode in which 5–10eV ions are used to neutralize the negative surface charge on insulating samples. A sample neutralizer working at high current (30 µA emission) and low energy (bias 1eV) effectively neutralizes most samples when used with the low energy ion neutralization capability.

A survey spectrum in the energy range of 0–1,100 eV (step size 0.8 eV with pass energy 187 eV) was first acquired showing the detected elements of the sample surface operating in an ultra-high vacuum level (10^{-9}). Two prepared sets of samples were studied during the investigations. These spectra also contain the elements of the carbon-containing contamination layer. The carbon C1S-line (284.01 eV) was used to check the energy scale. Other check-up lines were the sodium Na_2S line at 63.10eV, the molybdenum Mo3p3-line at 394.37 eV, and the oxygen O1s line at 530.45 eV. No shift of C1s-line in the energy scale was observed during the analyses.

After screening the spectra for main XP- and auger-electron lines and for possible artifact lines (e.g., Al-satellites, X-ray ghost lines, shake-ups, multiple splitting, energy loss lines, and valence band lines), the lines for the detailed analysis were selected. The selected lines for detailed analysis were Mo3p, Na1s, O1s, and S2p, bearing in mind the line overlap between Mo3d and S2s. The attenuation depth of analyzed electrons is 3–5 nm. Sputtering depth is difficult to approximate beforehand for inhomogeneous mixtures of heavy molybdenum and lighter sodium substances. Therefore, sputtering was performed until pure molybdenum was detected to investigate the surface layer of the molybdenum stub. XPS-spectra nearest to molybdenum metal were studied in detail. The X-ray beam diameter for XPS analyses was approximately 100 µm. Data handling was performed using Shirley background subtraction and peak fitting to explain the shapes of analysis spectra. A possible two-peak identification of a substance would result in probable compound in the thin surface layer or thicker surface deposit. The sputtering energy used was 500 V and the electron spectra were collected with five to 20 sweeps to ensure adequate peak to background ratio, especially for the sulfur S2p peak. The S2p peak was selected because the Mo3d line group overlaps fully with the sulfur S2s line.

Sulfur peak shifts under sputtering and their compensations

We used an argon sputtering gun to gather sputter depth profiles of the surface layers. Sputtering was accomplished at a pressure less than 5×10^{-4} Pa, an emission current of 10 mA, and 0.5 kV of beam energy in an ion gun. Because the sputtering process can cause some chemical damage and broaden the peaks, the 0.5 kV setting was used for MoS_2-reference samples to minimize any spectral distortions caused by the sputtering. Depth profiles were collected using pass energy of 57 eV, which provides sufficient energy resolution to observe chemical shifts, and gives results with adequate sensitivity. To optimize the analysis of the S2p peak on surface layers of MoS_2-reference samples, Al-K_α monochromatic X-rays (1.486 keV) produced with 100W power were chosen, with a take-off angle of 45° for thin layers and 90° for thicker deposits. To ensure reasonable shape and peak-to-background ratio of S2p-peak, we conducted at least 20 averaging sweeps over the energy range 160–180 eV.

SEM morphology studies

Samples were examined with a field emission scanning electron microscope (FE-SEM, Hitatchi 4700) using a 15 kV acceleration voltage, 12 mm working distance, and 10 µA beam current. The qualitative X-ray analyses of the samples were performed with an energy dispersive X-ray analyzer using a 30 mm^2 (135.7 eV) detector. Elements heavier than boron can be detected; elements less than 0.3 w-% might not be detected. We used a correction factor program to estimate quantitative results from the X-ray spectra.

Experimental verification of the MSRE

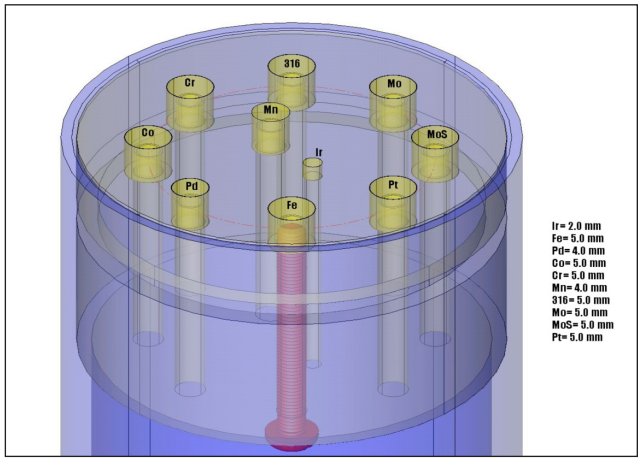
A multispecimen monitoring sensor with internal MSRE was fixed to the lid of the PTFE-coated autoclave using a PTFE cylinder to electrically insulate the sensor from the lid (**Fig. 2**). The sensor had eight places for samples, a place for counter electrode, and a place for a reference electrode (**Fig. 3**). The sensor materials in this study consisted of molybdenum, platinum, and iridium electrodes in addition to the internal MSRE.

The 50-mm-diam sensor tube was made from grade AISI 316 stainless steel. The tube was filled with PTFE and the samples were embedded in PTFE. Each sample had an electric connection wire for electrochemical measurements and all the electric connections were electrically insulated from the sensor body.

We used a potentiostat to perform the electrochemical measurements. The potentiostat was connected to the main current via an isolation transformer that effectively filtered background noise. A thin platinum foil (4 cm^2) served as the counter electrode.

Experiments were performed in 2.5M NaOH with Na_2S additions up to 5 g/L (= 0.0641 M) at 170°C. The highest sulfide concentration tested was 0.0641 M; low sulfide concentration (e.g., 5 g/L), is the most critical for MoS_2 stability. Stabilization of the open circuit potential of platinum was used as a sign of reaching stable test conditions (when potential of platinum changed less than 0.05 mV/s). Cyclic polarization curves (sweep rate 1 mV/s) with noble metal electrodes (platinum and iridium) were measured to determine potentials of hydrogen (and oxygen) generation in the test solution at a temperature of 170°C. Potentiodynamic curves (sweep rate 1 mV/s) were measured for molybdenum to clarify the effect of sulfide on the stability of the MSRE.

2. The autoclave, the lid of the autoclave, and the sensor fixed to the lid.



3. Schematic figure of the designed sensor.

RESULTS

Surface analysis

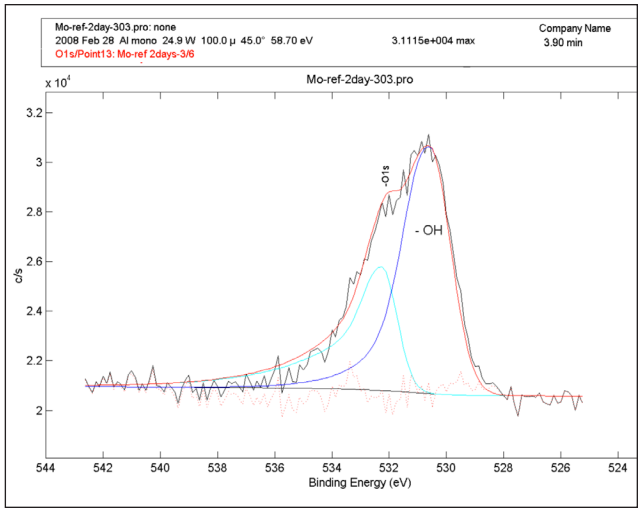
We exposed the molybdenum rod samples to saturated Na_2S solution and then stored the samples in plastic Petri dish sample containers for seven days. The sample sets were analyzed within days after their preparation. The sample containers were kept dry in an excavator in the laboratory. During transport from preparation to analysis, excess humidity was collected in a hydroscopic gel protecting the samples from atmospheric moisture. After exposure to saturated Na_2S, the MoS_2 reference electrodes showed only slight formation of a surface layer. In pre-analysis screening of the samples with a stereo microscope, the sample surfaces showed markings from the grinding of the test pieces, and slight surface coloring resulting from the exposure experiment. The surface coloring was barely visible to the unaided eye, and the grinding marks seemed to be less sharp in the sample with three days of exposure in Na_2S than the corresponding marks in the one-day exposure. In SEM-screening of the molybdenum sulfide reference sample and sputtered samples, the surfaces were clean from environmental contaminations such as chlorides or silicates.

Electron spectroscopy for chemical analysis (ESCA) showed high carbon C1s line associated to the surface contamination layer, which was removed by repeated argon sputtering. On the sixth cycle the carbon C1s line had reduced to the level of the pure molybdenum reference material. In studying the topmost oxide of the sample, more detailed investigation was focused to the sixth sputtering depth.

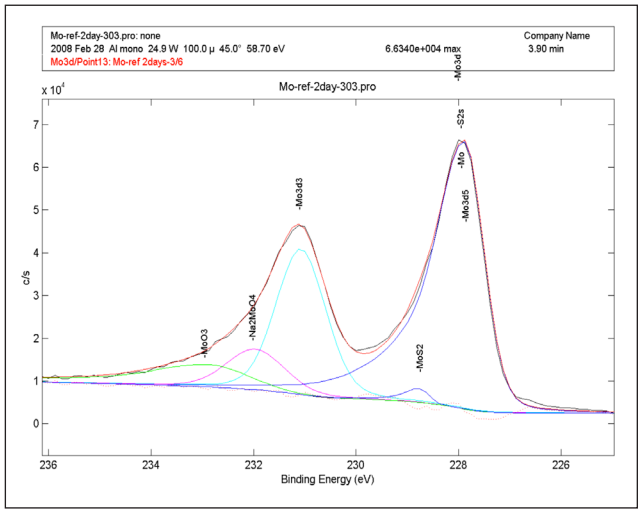
The O1s depth profiling and peak at the sixth sputtering depth suggest presence of hydroxide near the molybdenum surface (**Fig. 4**).

After background subtraction and peak fitting of known substances, the contour of the molybdenum Mo3d line group (**Fig. 5**) would suggest a layer containing molybdenum, sodium molybdate (Na_2MoO_4), molybdenum oxide or hydroxide together with some MoS_2. At this depth the sodium Na_1S line is still present. The Na_2S exposure was performed in an atmosphere with as little oxygen as possible, but after exposure the sample collected oxygen from the laboratory air.

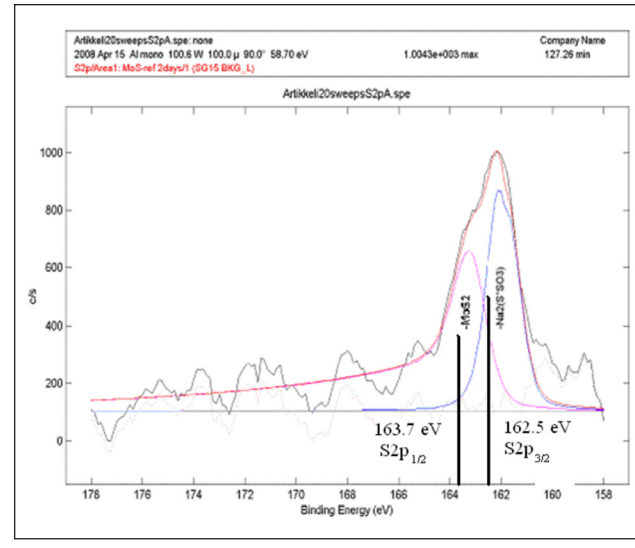
The contour of the sulfur S1s line near the metal surface (**Fig. 6**) suggests the presence of MoS_2 and oxidized sodium disulfide (i.e., sodium thiosulfate [$Na_2S_2O_3$]).



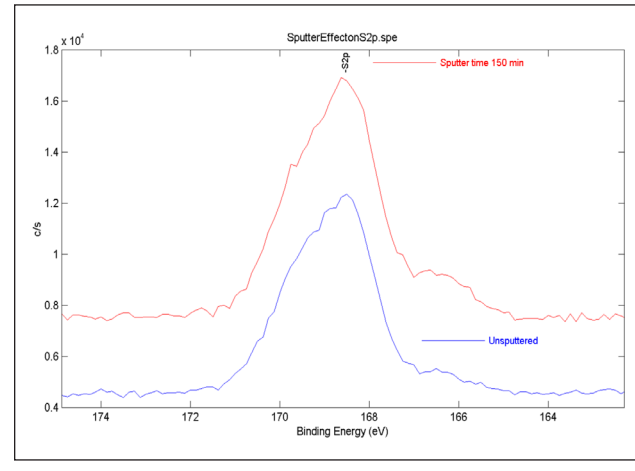
4. Oxygen (O1s) of MoS-ref sample near the metal surface.



5. Mo3d peak near the metal surface.



6. Sulfur S2p peak near the metal surface.



7. Sulfur S2p peak as unsputtered and after 150 min sputtering time; 20 sweeps over energy range 160–180 eV.

A detailed study of molybdenum oxygen O1s, Mo3d, and sulfur S2p lines suggests the presence of MoS_2 and possibly MoS_3 near the metal surface, either as a thin layer or a mixture of sulfides and hydroxide. Sodium also might be present near the metal surface as oxidized sodium disulfide (i.e., $Na_2S_2O_3$,), which typically supports the presence of MoS_3. Molybdenum in some degree might have been oxidized to MoO_3 or, together with sodium, to Na_2MoO_4 (Fig. 5).

Shift of the peak under ESCA analysis

Sulfur S2p line was monitored during sputtering. The sulfur S2p line did not experience any significant shift or fluctuation in the overall line contour after 150 min sputtering with argon at 500 V (**Fig. 7**).

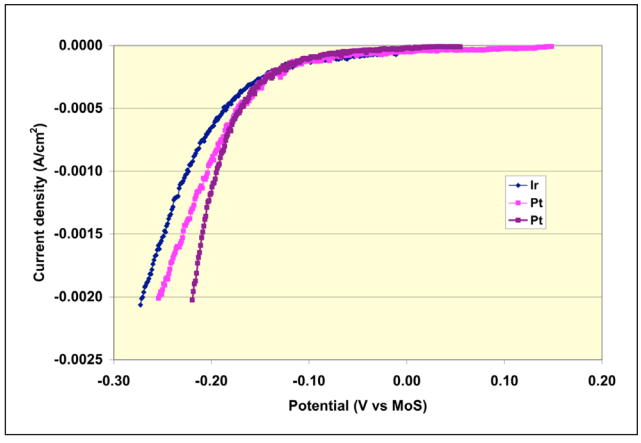
After 150 min of sputtering, the X-ray analysis in SEM could still detect some sodium and oxygen on the surface. Probably because of the phase-selective nature of the sputtering process, the surface was torn away unevenly, leaving a rough surface on the sample.

Voltammetry

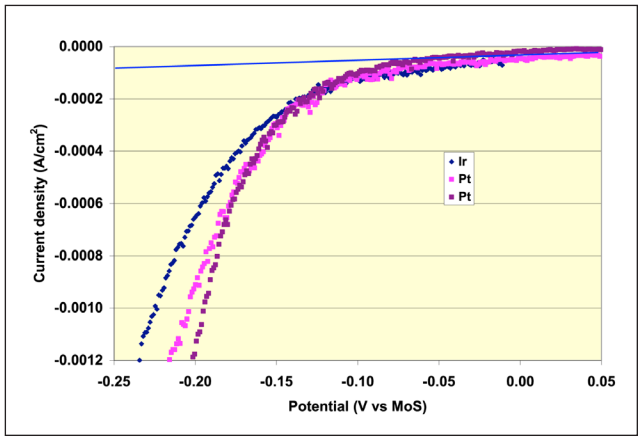
Figure 8 shows the polarization curves of platinum and iridium versus MSRE.

Hydrogen gas evolution on platinum and iridium starts roughly at potential -0.075 ±0.02 V versus the MSRE (Fig. 8). At pH(T) = 11.24, the H_2/H^+ -equilibrium potential is $E_o(H_2/H^+) = -0.988\ V_{SHE}$. The experimentally determined half cell potential for MSRE at 170°C is therefore $E_{oMSRE}(170°C) = -0.988\ V_{SHE} + 0.075\ V = -0.91 \pm 0.02\ V_{SHE}$. This value is about 0.15 V more negative than that estimated, based on the E-pH diagram in Fig. 1, for equilibrium between MoS_2 and MoS_3. We estimated the experimental error of measurements to involve errors in the T, pH, and E values. The temperature was measured with an accuracy of ±1°C and the pH of solution with an accuracy of ±0.1 unit. The voltage signal could be measured within 0.01 V. The half cell potential could be measured with an accuracy of 2 × 0.2 × 0.01 V = 0.004 V.

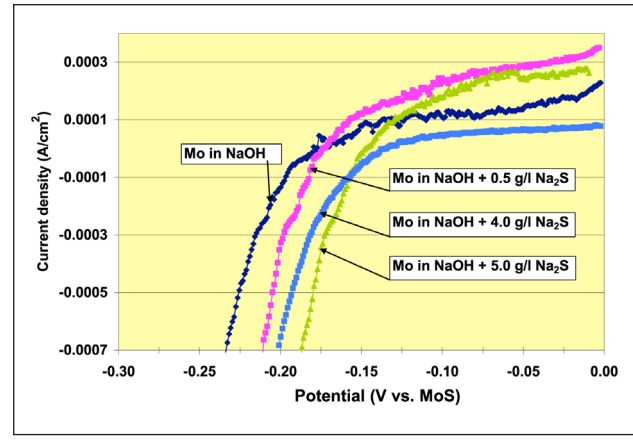
Hydrogen evolution on pure molybdenum requires a



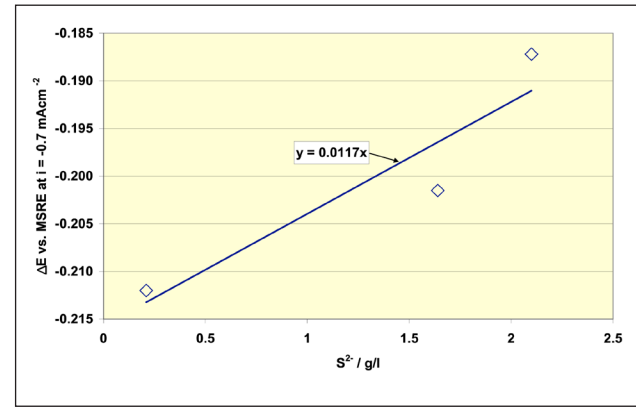
8a. Cathodic polarization curves (1 mV/s) of platinum and iridium versus MSRE in 2.5 M NaOH at 170°C. Repeated measurement is shown by platinum.



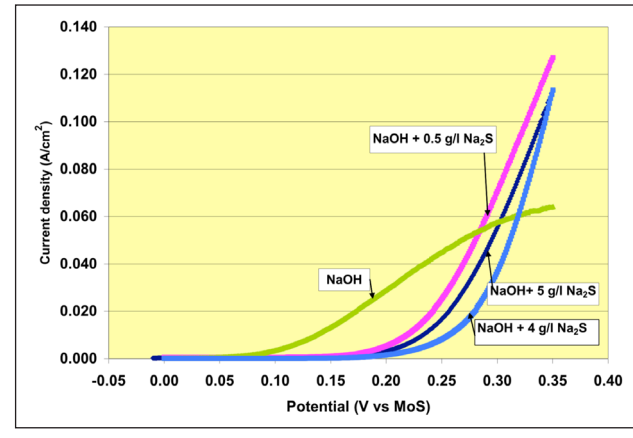
8b. A detail of cathodic polarization curves (1 mV/s) of platinum and iridium vs. MSRE in 2.5 M NaOH at 170°C. Repeated measurement is shown by platinum.



9. Cathodic polarization curves (1 mV/s) of molybdenum vs. MSRE in 2.5M NaOH and 2.5M NaOH + Na_2S solutions at 170°C.



10. Effect of sulfide concentration on the MSRE equilibrium potential. The scatter in data is R2 = 0.9845.



11. Anodic polarization curves of molybdenum in 2.5M NaOH and in 2.5M NaOH + Na_2S solutions at 170°C.

slightly higher overpotential than that on platinum and iridium (data measured in 2.5M NaOH) (**Fig. 9**). Hydrogen evolution starts on pure molybdenum at about E = -0.15 V versus MSRE. Addition of sulfide into the solution results in an apparent shift of hydrogen evolution potential towards higher potentials. As the Na_2S additions are not expected to change the pH of the solution, this shift is interpreted as a change in the equilibrium potential of the MSRE itself. **Figure 10** shows the magnitude of the shift as a function of the sulfide concentration. The slope is roughly 12 mV/dec of sulfide. However, the relationship of MSRE may not be linear, if three or more substances involved to the half-cell reaction. A similar situation might occur if the activity coefficient changed in concentrated solutions.

Figure 11 shows the anodic polarization curves of molybdenum in 2.5M NaOH with and without Na_2S additions. The increase of current in 2.5M NaOH at about 0.075 V versus MSRE is probably the result of molybdenum dissolving as MoO_4^{2-}. In the presence of sulfide, a thin MoS_2 film will cover the metal surface, effectively preventing dissolution. Based on data in Fig. 11, the upper limit of the MSRE is approximately 200 mV versus molybdenum sulfide. The increase of current density at about +0.200 V versus MSRE in presence of sulfide coincides with the equilibrium potential for formation of polysulfide [5] and thus most probably is not connected to dissolution of the film on molybdenum.

DISCUSSION

In saturated solution, the amount of oxidized sulfur substances is very low compared to the disulfide amount. Thus, we assume that the molybdenum rod was covered by a thin sulfide layer. Because of the very low dissolution constant of MoS_2, once formed, the MoS_2 would not tend to dissolve. Because of the hydrolysis of Na_2S, the saturated Na_2S solution is also a strong hydroxide solution. Therefore, the formation of molybdenum hydroxide within the surface layer is probable during the specimen immersion.

During ESCA analyses, sputtering was performed with 500 V argon beam. The removal of deposited material depends on the density of the material and the amount of time used for sputtering. The sputtering area is usually approximately a few square millimeters, which in case of deposited materials, gives a good average removal of surface contaminations for the analysis. Lack of calibration curves for a specific sputtering process and nonhomogeneous concentration profile of multisubstance samples make the estimation of depth profiling difficult. The depth of material removal is a few nanometers, depending on the sputtering time and material density. Sputtering does not remove material evenly across the analyzed surface. Heavier materials, such as molybdenum-containing species, are removed more slowly than sodium-containing substances. Thus, molybdenum and its compounds are preferentially revealed for the analysis. In this study, during sputtering of samples after removal of the carbon-containing top layer, possibly 100 nm of mixed substance layer was removed before the metal surface was reached.

We stored the molybdenum rods in an air atmosphere after immersion in saturated Na_2S solution; the surface therefore might be covered by thin adsorbed air contamination layers. Interpretation of ESCA-spectra is dependent on line position libraries and on thermodynamic calculations of possible and probable substances in the environment of the experiment. In this study, the possible existence of MoS_2 was based on molybdenum 3d and sulfur 2p peak indications, indicating MoS_2. Probably also MoS_3 is present in the deposit layer near the molybdenum surface. Indications of hydroxide substances near the metal surface also are possible. Sodium seems to be present through the deposit layer and oxygen as sodium oxide with increasing hydroxide component toward the metal surface.

Noble metals (platinum and iridium) have a very low overpotential for hydrogen evolution in 2.5M NaOH. Thus, they can be used to detect the H_2/H^+-equilibrium potential with reasonable accuracy. In pure 2.5M NaOH, the H_2/H^+-equilibrium potential was measured to be at potential -0.075 ±0.02 V versus the MSRE. Increasing sulfide concentration decreased the potential difference between the MSRE and H_2/H^+-equilibrium potential on pure molybdenum, with a slope of 12 mV/dec of sulfide.

The MoS_2/MoS_3 electrode reaction can be written with respect to S^{2-} species via Eq. 1, with the corresponding Nerst equation for the half-cell electrode potential (E_o), given in Eq. 2.

$$MoS_2 + S^{2-} \leftrightarrow MoS_3 + 2e^- \quad (1)$$

$$E_o = E_o^{\ o} + \frac{2.303 \cdot RT}{2F} \cdot \log\left(\frac{[MoS_3]}{[MoS_2] \cdot [S^{2-}]}\right) \quad (2)$$

where $E_o^{\ o} = -0.748\ V_{SHE}$ [5], T is temperature (K), F is Faraday's constant, and R is the gas constant. Assuming that the activity of MoS_2 and MoS_3 are equal to unity, the equation reduces to

$$E_o = -0.748 - 0.044 \cdot \log[S^{2-}] \quad (3)$$

The equilibrium potential for reaction 3 is about 0.15 V higher than that estimated based on the potential for start of hydrogen evolution on platinum and iridium in pure NaOH solution. Moreover, the effect of sulfide concentration, as predicted based on Eq. 3, would be 44 mV/dec sulfide, whereas the experimentally determined value is 12 mV/dec sulfide. One reason for such a high deviation of the slope could be that the activity coefficient of sulfide might deviate from 1. Some dissolution of MoS_3 probably takes place at this high pH, thus effectively forming a mixed potential electrode, although a rather stable one.

ESCA results support the existence of MoS_2 and MoS_3 in the surface film on MSRE. Based on this and the above calculations, the half cell reaction of the MSRE is probably that shown in reaction 1. However, some uncertainty remains as the predicted dependence on sulfide concentration is clearly different from that determined experimentally.

The MSRE we evaluated is a practical reference electrode, while its half cell potential depended slightly on sulfide concentration. The sulfide concentration dependence might be attributable to the fact that the MSRE stability area is on the metastable extension of the MoS_2 and MoS_3. The potential error is about ±50 mV. Even so, the MSRE can be used as a practical reference electrode in anodic protection of digesters and in other applications where knowledge of the potential of the digester walls is needed.

CONCLUSIONS

The results of the experiments and thermodynamic studies support the following conclusions:

The method of preparation of the MSRE (i.e., soaking in saturated Na_2S solution at room temperature) resulted in a stable electrode. Total thickness of the resulting layer was estimated to be 100 nm. According to the ESCA studies, the thin film on molybdenum contained a layer of mixed $Mo(OH)_4/MoS_2$, MoS_2, MoS_3, and partly oxidized NaS_2 with some oxidized sodium molybdate.

The MSRE was successfully calibrated during simulated cooking at 170°C. The experimentally determined half cell

potential of the MSRE was -0.91 ± 0.02 V_{SHE}. The half cell potential of the MSRE depended on the sulfide concentration of the solution, with a slope of 12 mV/dec sulfide. Eq. 1 use should be consistent. **TJ**

ACKNOWLEDGEMENTS

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ABOUT THE AUTHORS

This study is important as an application of electrochemistry to the operation of digester houses. It complements previous studies of where I have applied electrochemistry and monitoring in bleach plants.

The most difficult aspect of this study was to determine the right half cell reaction for molybdenum sulfide. I tried to calculate the Nernst equation for the half cell reaction and then discussed the results.

From this study, I discovered a way to scale the reference electrode during operation. That was the most exciting result. Finally, mills have a good study of the reference electrode used in the digesting house.

The next step is to find new applications, where a reliable reference electrode is needed in the digesting house.

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