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A thermodynamic analysis of the SO$_2$/H$_2$SO$_4$ system in SO$_2$-depolarized electrolysis

Maximilian B. Gorenska,*, John A. Staserb, Thomas G. Stanfordb, and John W. Weidnerb

aComputational Sciences Directorate, Savannah River National Laboratory, Aiken, SC 29808  USA
bCenter for Electrochemical Engineering, Department of Chemical Engineering, University of South Carolina, Columbia, SC 29208  USA

Abstract

The hybrid sulfur thermochemical cycle has been proposed as a means to produce efficiently massive quantities of clean hydrogen using a high-temperature heat source like nuclear or solar. The cycle consists of two steps, one of which is electrolytic. The reversible cell potential for this step and, hence, the resulting operating potential will depend on the concentrations of dissolved SO$_2$ and sulfuric acid at the electrode. To understand better how these are related as functions of temperature and pressure, an Aspen Plus phase equilibrium model using the OLI Mixed Solvent Electrolyte physical properties method was employed to determine the activities of the species present in the system. These activities were used in conjunction with the Nernst equation to determine the reversible cell potential as a function of sulfuric acid concentration, temperature and pressure. A significant difference between the reversible and actual cell potentials was found, suggesting that there may be considerable room for reducing the operating potential.

Keywords: hybrid sulfur, hydrogen, SO$_2$-depolarized, electrolyzer, Aspen Plus, Aspen-OLI, Mixed Solvent Electrolyte model, reversible potential, SO$_2$ solubility, sulfuric acid

* Corresponding author. Tel.: (803) 725-1314; Fax: (803) 725-8829; E-mail address: maximilian.gorensk@srnl.doe.gov
1. Introduction

The hybrid sulfur (HyS) cycle has received much attention recently as a possible means for the efficient large-scale production of clean hydrogen [1,2,3,4,5,6,7]. Like other thermochemical cycles, it has the advantage over traditional methods of hydrogen production in that it does not consume fossil fuels or contribute to greenhouse gas emissions when coupled with advanced, high-temperature nuclear or high-temperature solar heat sources. Furthermore, the hydrogen product is highly pure.

HyS is one of the simplest thermochemical water-splitting cycles, comprising only two reaction steps and having only fluid reactants. The first reaction,

\[ \text{H}_2\text{SO}_4(aq) \rightarrow \text{H}_2\text{O}(g) + \text{SO}_2(g) + \frac{1}{2}\text{O}_2(g), \]  

common to all sulfur cycles, is thermochemical, since it entails heat transfer. It is endothermic and requires high temperatures (>800 °C) and a catalyst. The second reaction, the SO2-depolarized electrolysis of water,

\[ \text{SO}_2(aq) + 2\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{SO}_4(aq) + \text{H}_2(g), \]

is electrochemical, making the HyS a hybrid cycle. When reactions (1) and (2) are combined, the net result is the splitting of one mole of water into one mole of hydrogen and one-half mole of oxygen. This paper is concerned with the thermodynamics of the second reaction step.

Current HyS development efforts are focused on proton exchange membrane (PEM) electrolyzers to take advantage of their relatively compact size and short current path. The critical component of such an SO2-depolarized electrolyzer (SDE) is the membrane-electrode assembly (MEA), which consists of a PEM such as Nafion® sandwiched between two
electrocatalyst layers. Aqueous SO\textsubscript{2} reacts at the MEA anode with water to form H\textsubscript{2}SO\textsubscript{4} (here considered to be fully dissociated), protons, and electrons [1,5],

$$\text{SO}_2(aq) + 2\text{H}_2\text{O}(l) \rightarrow \text{SO}_4^{2-} + 4\text{H}^+ + 2e^- \quad (3)$$

An externally applied potential difference between the electrodes causes the protons to migrate through the membrane and the electrons to flow through an external circuit to the cathode, where they recombine to form hydrogen,

$$2\text{H}^+ + 2e^- \rightarrow \text{H}_2(g) \quad (4)$$

The sum of the anode and cathode potentials, −0.158 V, is the net potential difference of the SDE at standard conditions, which compares very favorably with that for water electrolysis at −1.229 V.

Two different PEM SDE configurations are being developed under United States (US) Department of Energy, Office of Nuclear Energy (DOE-NE) sponsorship. Researchers at the Savannah River National Laboratory (SRNL) are working on an SDE for DOE-NE’s Nuclear Hydrogen Initiative (NHI), in which SO\textsubscript{2} dissolved in sulfuric acid is continually fed to the anode, where it reacts with the solvent (water) to form H\textsubscript{2}SO\textsubscript{4} product [1]. Water is also supplied to the cathode to help keep the PEM hydrated. Researchers at the University of South Carolina (USC) are testing an alternative design under DOE-NE’s Nuclear Energy Research Initiative (NERI) in which gaseous SO\textsubscript{2} is fed to the anode, while liquid water is fed to the cathode [2,3]. Water diffuses across the PEM to the anode, driven by the difference in its activity on either side. The SO\textsubscript{2} dissolves in the liquid at the anode and reacts with water to form H\textsubscript{2}SO\textsubscript{4}. Under steady-state conditions, the porous anode becomes saturated with an aqueous solution of H\textsubscript{2}SO\textsubscript{4} and SO\textsubscript{2} that is continually withdrawn as product. Both SDE configurations have been demonstrated over
a range of operating (temperature, pressure, and current density) and design (MEA composition and thickness) conditions.

To maximize SDE efficiency, the actual cell potential should be as close to the reversible cell potential (0.158 V at 25°C and standard conditions) as possible. Any overpotential requires increased energy input, which will ultimately be dissipated as heat instead of being converted into useful chemical energy (i.e., hydrogen). In addition to membrane thickness, membrane and electrocatalyst composition, temperature, pressure, and current density, the cell potential also depends on H₂SO₄ concentration. A higher H₂SO₄ concentration leads to a higher reversible cell potential and lower SDE electric-to-chemical energy conversion efficiency due to an increase in the activity of the H₂SO₄ product. However, higher H₂SO₄ concentration is desirable for maximizing the thermal-to-chemical energy conversion efficiency of the high-temperature decomposition of H₂SO₄ to SO₂, water, and oxygen that makes up the other half of the HyS cycle [1]. Optimization of the cycle, therefore, will require trade-offs between the two steps in determining the value of H₂SO₄ concentration that will give the best overall process efficiency.

A thorough understanding of the thermodynamic properties of the aqueous SO₂/H₂SO₄ system is necessary to understand fully the limiting HyS SDE electric power requirements. To this end, we have employed Aspen Plus equipped with the Aspen-OLI interface and OLI Systems, Inc.’s Mixed Solvent Electrolyte (MSE) model to calculate species activities for this system over a wide range of conditions and used these values with the Nernst equation to predict reversible potentials. The results of these calculations should help guide future SDE development efforts and provide some bounds on HyS cycle performance.
2. Model development

The currently accepted value of the standard reduction potential for the sulfate-sulfite couple (the half-cell reaction is usually reported as a reduction by convention) may be found in Bard, Parsons and Jordan’s 1985 compilation [8],

\[ \text{SO}_4^{2-} + 2e^- + 4H^+ \rightarrow \text{H}_2\text{SO}_3(aq) + \text{H}_2\text{O}(l), \quad E^\circ = 0.158 \text{ V}, \quad (5) \]

where \( E^\circ \) is the standard reduction potential versus the standard hydrogen electrode (SHE). It can also be written in a slightly different form, as in Bratsch’s 1989 paper [9],

\[ \text{SO}_4^{2-} + 2e^- + 4H^+ \rightarrow \text{SO}_2(aq) + 2\text{H}_2\text{O}(l), \quad E^\circ = 0.158 \text{ V,} \quad (dE^\circ/dT = 0.784 \text{ mV/K}). \quad (6) \]

Many papers incorrectly report the standard reduction potential for the sulfite-sulfate couple to be 0.17 V vs. SHE [3,4,10,11,12]. It is likely that this value was obtained from the original proposal of the HyS cycle, in which the inventors used the well-known relationship between the Gibbs free energy and the equilibrium cell potential to calculate \( E^\circ \) [13]. The reason for the discrepancy is that Brecher and Wu only had access to older thermodynamic data [14], which have since been rendered obsolete [15]. Continuing use of the outdated value of the standard reduction potential is further propagated by its appearance in a widely used contemporary reference [16].

If the standard reduction potential for reaction (3) is recalculated using currently accepted standard Gibbs free energies of formation for the species involved [15], a value of \( E^\circ = -0.158 \text{ V} \) vs SHE is obtained. This, then, is the value of the standard reduction potential for reaction (3) that will be used henceforth.

The overall SDE reaction (2) needs to be modified before applying the OLI MSE model to calculate reversible cell potentials at nonstandard conditions. To be consistent with reactions
(5) and (6), sulfuric acid is assumed to be fully dissociated into sulfate anions and protons, and the reaction rewritten as a reduction,

$$2\text{H}^+ + \text{SO}_4^{2-} + \text{H}_2(\text{g}) \rightarrow \text{SO}_2(\text{aq}) + 2\text{H}_2\text{O}(\text{l}). \quad (7)$$

This electrochemical system was analyzed using Aspen Plus equipped with the Aspen-OLI interface to obtain the activities of each component at varying solution compositions. These values were then used with the Nernst equation,

$$E_T = E_T^o - \frac{RT}{nF} \ln Q_T,$$

where

$$Q_T = \frac{(a_{\text{SO}_2}) \cdot (a_{\text{H}_2\text{O}})^2}{(a_{\text{SO}_4}) \cdot (a_{\text{H}_2}) \cdot 10^{-p\text{H}}} \quad (9)$$

and

$$E_T^o = E^o + (T - 298.15) \cdot \left(\frac{dE^o}{dT}\right), \quad (10)$$
to obtain the reversible cell potential as a function of species concentration, temperature, and pressure. Note that the activities of the solutes (SO$_2$, SO$_4^{2-}$, and H$^+$) are calculated on a molal basis, since their standard states are at unit molal concentration.

Reaction (7) could have been rewritten using bisulfate anion, HSO$_4^-$, instead of sulfate, SO$_4^{2-}$,

$$\text{H}^+ + \text{HSO}_4^- + \text{H}_2(\text{g}) \rightarrow \text{SO}_2(\text{aq}) + 2\text{H}_2\text{O}(\text{l}), \quad (11)$$
in which case the standard potential would have to have been recalculated ($E^o = 0.0986$ V) and the activity quotient, $Q_T$, modified to match the change in reaction stoichiometry. However, as shown by Wang et al. [17], the OLI MSE model predict both sulfate and bisulfate are present in
significant quantities over the entire range of sulfuric acid concentrations considered here, matching the available data. Thus, there is no reason to change reaction (7), since either approach will result in the same value of $E_T$, using the appropriate activity quotient and standard potential in the Nernst equation.

The OLI MSE model speciation assumes protons do not remain free in solution as $H^+$, but are solvated to form $H_3O^+$ instead. Since $H^+$ is not actually present, the activity of $H^+$, and, therefore, the value of pH in equation (9) can not be directly determined from the model. However, it is easy to show that $a_{H_{3O}} = (a_{H^+})(a_{H_2O})$, leading to the result,

$$pH = \log_{10} a_{H_{3O}} - \log_{10} a_{H_{2O}} \quad [18].$$

A simple Aspen Plus flowsheet model was prepared in which the environments at the anode and cathode were simulated using Flash3 and Flash2 blocks, respectively. Since SO$_2$ and water can form two, separate, immiscible liquid phases under certain conditions, a three-phase flash separator was used to represent the anolyte.

Before adding flowsheet components, the Aspen-OLI interface was used to set up the OLI MSE model properties method. An excellent description of this properties model and its ability to represent the sulfuric acid system is available elsewhere [17]. Confirmation of the model’s capacity for characterizing the solubility of SO$_2$ in water and sulfuric acid has also been previously documented [1].

Sensitivity analyses were used to determine the solubility of SO$_2$ in 30, 40, 50, and 60 wt% H$_2$SO$_4$ at several different temperatures between 20°C and 100°C over the 0- to 20-bar pressure range in a Flash3 block. At lower pressures, the quantity of SO$_2$ admitted was adjusted (using a Design Spec) to achieve the vapor-liquid saturation (bubble) point. This is representative of the USC SDE in which the aqueous solution of H$_2$SO$_4$ and SO$_2$ in the porous
anode exists in equilibrium with a (primarily) SO₂ vapor phase. It also represents the limiting case for the SRNL SDE where the liquid sulfuric acid feed is pre-saturated with dissolved SO₂. For higher pressures, the limiting factor was miscibility; thus, the quantity of SO₂ was adjusted to achieve an incipient SO₂ liquid phase [2,3,6]. This is clearly applicable to the SRNL SDE operating at pressures in excess of the vapor pressure of SO₂. In each case, the liquid phase activities of water, SO₂, and sulfate anion and the solution pH were then calculated by Aspen Plus from the OLI MSE model. A separate Flash2 simulation was performed for the catholyte, assuming it consisted of pure water and hydrogen in equilibrium at the same temperature and pressure as the anolyte. This is representative of conditions at the cathode for both the SRNL and USC SDEs, which produce hydrogen saturated with the water used to keep the PEM hydrated. The vapor phase activity of hydrogen was calculated from the results (hydrogen partial pressure and fugacity coefficient) by Aspen Plus. These results were used in conjunction with equations (8), (9), and (10) to calculate the reversible cell potential for every case.

A second series of simulations was also run in which the temperature and pressure were held constant (80°C, 1 bar at the anode, 7 bar at the cathode), and the acid concentration varied from 0.1 to 70 wt%. The solubility of SO₂ in the acid was determined as in the earlier bubble point simulations, and reversible cell potentials calculated in identical fashion.

3. Results and discussion

Figures 1 through 4 show the OLI MSE model-predicted solubility of SO₂ as a function of system pressure in sulfuric acid at concentrations of 30, 40, 50, and 60 wt%, respectively. For any given temperature and sulfuric acid concentration, it is clear that as the system pressure increases from 1 bar, so does the quantity of SO₂ that can be dissolved in the acid, at least until
the miscibility limit is reached. Beyond that point, any additional SO$_2$ will form a separate, SO$_2$-rich liquid phase that is in equilibrium with the aqueous, sulfuric acid phase. For example, at 80°C and in 30 wt% sulfuric acid, the solubility of SO$_2$ reaches a limit of 28.0 g per 100 g of sulfuric acid at 14.76 bar; above this value, the increase in SO$_2$ solubility with pressure is negligible.

These figures (1 through 4) also show that SO$_2$ solubility decreases with increasing temperature, as one would expect. In 40-wt% sulfuric acid, for instance, the solubility of SO$_2$ at a 4.00-bar system pressure is predicted to drop from 21.1 to 2.59 g per 100 g of sulfuric acid as the temperature rises from 40 to 100°C. More importantly for this discussion, the OLI MSE model predicts that SO$_2$ solubility decreases as the sulfuric acid concentration is increased. For example, the solubility of SO$_2$ decreases from 7.54 to 5.49 g per 100 g of sulfuric acid at 80°C and 6.00-bar system pressure when the acid concentration is raised from 30 to 60 wt%. This behavior is more clearly shown in Figure 5, which plots the predicted solubility of SO$_2$ at 80°C and 1-bar pressure as a function of sulfuric acid concentration.

Figures 6 through 9 show the reversible potential of the sulfate-sulfite couple as a function of pressure at sulfuric acid concentrations of 30, 40, 50, and 60 wt%, respectively, calculated from the Nernst equation using OLI MSE-generated species activities. The reversible potential as a function of sulfuric acid concentration at a fixed temperature of 80°C, and anode and cathode pressures of 1 and 7 bar, respectively, is shown in Figure 10. (The USC SDE is operated with a pressure differential across the PEM; its anode is at atmospheric pressure, while a backpressure regulator maintains its cathode at 7 bar.) It is clear that $E_T$ increases with sulfuric acid concentration. For example, at 80°C and 6.00 bar, the reversible potential grows from 0.206
V at a sulfuric acid concentration of 30 wt% (Figure 6) to 0.347 V at a sulfuric acid concentration of 60 wt% (Figure 9).

This result indicates that sulfuric acid concentration has a major impact on electrolyzer operation. Not only does increasing the sulfuric acid concentration decrease the solubility of SO$_2$, which may lead to mass transport limitations at the anode, but it also increases the operating cell potential. The net result is higher energy consumption by the SDE at higher acid concentrations. Clearly, less concentrated sulfuric acid is desirable for efficient SDE operation. However, more concentrated sulfuric acid is better for the high-temperature decomposition reaction that regenerates SO$_2$ [1]. Therefore, optimizing the efficiency of the HyS cycle requires a trade-off between the electrolyzer and the decomposition reactor energy requirements.

One should keep in mind that the Nernst equation (8) is a thermodynamic model that does not account for kinetics or mass transport limitations. It is used strictly to determine the equilibrium potential at zero current (i.e. zero reaction rate), so kinetics do not come into consideration. Furthermore, since the reaction rate is zero, there is negligible demand for SO$_2$ or other reactants at the electrodes so mass transport limitations are not in effect. It also does not account for the relationship between sulfuric acid concentration and PEM conductivity. The resistivity of Nafion membranes increases with acid concentration [19], which can significantly elevate the operating potential at high current densities.

It is clear from Figure 10 that the reversible cell potential calculated by the Nernst equation is significantly lower than that reported for an operating electrolyzer [3,6]. In some cases, the difference is as high as 0.5 V. For example, at 0.20 A/cm$^2$, the sulfuric acid concentration for Nafion® 115 is 2.8 $M$, (22.6 wt%), corresponding to a Nernst equation reversible cell potential of 0.216 V. The operating potential is 0.639 V [6]. At 0.50 A/cm$^2$, the
sulfuric acid concentration is 5.88 \textit{M}, corresponding to a reversible cell potential of 0.309 V. The operating potential was measured to be 0.801 V [6].

The large difference between the actual operating and the ideal reversible cell potentials indicates cell potential dependencies beyond sulfuric acid concentration, and could be due to complex and irreversible mechanisms for SO$_2$ oxidation [20,21,22]. It may also be due to increased membrane resistance in the presence of concentrated sulfuric acid [19].

The differences between the observed potential and that calculated by the Nernst equation indicate that improvement of the electrolyzer may be possible. For example, the membrane resistance could possibly be reduced with the use of novel polymer electrolytes and by operation at elevated temperatures. Sulfuric acid concentration at the anode could be decreased as well by increasing water transport to the anode. While this would result in a lower reversible cell potential (Figure 10) and a higher SO$_2$ solubility (Figure 5) at all current densities, less concentrated sulfuric acid would be detrimental to the efficiency of the downstream decomposition step. Clearly, a trade-off exists between sulfuric acid concentration and electrolyzer performance.

Results of current interrupt and hydrogen pump experiments at USC suggest that the two main contributions to the overpotential are kinetic losses at the anode and the ohmic resistance of the membrane in the presence of concentrated sulfuric acid [23]. Therefore, it should be possible to lower the operating cell potential (i.e. decrease the gap between the operating and reversible potentials) by developing catalysts that are more active with respect to the oxidation reaction and membranes that are more conductive in the presence of concentrated sulfuric acid.
4. Conclusions

The OLI Systems MSE model has been used in conjunction with Aspen Plus to determine the thermodynamic properties of the aqueous SO$_2$/H$_2$SO$_4$ system. This system is used in the HyS thermochemical cycle. The model provides an understanding of the effect of sulfuric acid concentration on the solubility of SO$_2$, which can lead to mass transport limitations, and allows us to calculate the reversible cell potential via the Nernst equation. The reversible cell potential allows us to determine the operating overpotential as a function of sulfuric acid concentration, which has implications on the energy requirements of the electrolyzer and indicates possible room for improvement of electrolyzer performance by optimizing operating and design parameters.

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References


Figure 1. SO$_2$ solubility in sulfuric acid as a function of system pressure. The concentration of sulfuric acid is 30 wt%.
Figure 2. SO₂ solubility in sulfuric acid as a function of system pressure. The concentration of sulfuric acid is 40 wt%.
Figure 3. $\text{SO}_2$ solubility in sulfuric acid as a function of system pressure. The concentration of sulfuric acid is 50 wt%.
Figure 4. SO$_2$ solubility in sulfuric acid as a function of system pressure. The concentration of sulfuric acid is 60 wt%.
Figure 5. SO₂ solubility in sulfuric acid as a function of acid concentration. The system temperature is 80°C and the pressure is 1 bar.
Figure 6. Reversible potential as a function of system pressure (anode and cathode). The concentration of sulfuric acid is 30 wt%.
Figure 7. Reversible potential as a function of system pressure (anode and cathiode). The concentration of sulfuric acid is 40 wt%.
Figure 8. Reversible potential as a function of system pressure (anode and cathiode). The concentration of sulfuric acid is 50 wt%.
Figure 9. Reversible potential as a function of system pressure (anode and cathode). The concentration of sulfuric acid is 60 wt%.
Figure 10. Reversible potential as a function of sulfuric acid concentration. The system is at 80°C, with the anode at 1 bar and the cathode at 7 bar.