Fundamentals of SO$_2$ depolarized water electrolysis and challenges of materials used

Anu Lokkiluoto
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Doctoral dissertation for the degree of Doctor of Science in Technology to be presented with due permission of the School of Chemical Technology for public examination and debate in Auditorium V1 at Department of Materials Science and Engineering (Espoo, Finland) on the 5th of April 2013 at 12:00 noon (at 12 o’clock).

Aalto University
School of Chemical Technology
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Abstract

Sulfur dioxide depolarized water electrolysis (SDE) produces sulfuric acid and hydrogen. Due to its lower cell voltage, the process requires far less electricity than traditional water electrolysis. When SO₂ is obtained from flash smelting, sulfides roasting, sulfur combustion, or any other similar operation, SDE is a part of the Outotec® open cycle process.

In the present work, materials to be used in SDE were studied together with the fundamentals of the process. Data on the co-production of concentrated acid and hydrogen are scarce in the earlier literature. Theoretical modeling work covering the entire concentration range was deemed necessary in addition to experimental testing to settle this issue. Based on the literature concerning PEM Fuel Cells, it was assumed that the water transport properties of the membrane used as a separator in the electrolysis have a significant effect on the water balance.

The activities of the electrolyte components were calculated for the whole concentration range of the ternary H₂O-H₂SO₄-SO₂ system relevant for the SDE process using a mathematical model elaborated during the present work. The calculated activities were combined with the model for water transport through a Nafion membrane, and an overall model for SDE was built. The reversible cell potential was calculated for the entire concentration range. The model was used to predict the overall water balance of the electrolysis process with changing electrolyte concentrations.

The stability of thin gold coatings and their activity towards electrochemical oxidation of SO₂ were studied first in autoclave tests and with linear sweep voltammetry, and the performance of the coatings was compared to that of gold. Next, the performance of the gold-coated electrodes was tested in bench-scale SDE. Even though the oxidation of SO₂ has previously been studied on gold, such experiments have seldom been carried out in as high concentrations of sulfuric acid as in this work, and the results obtained with gold coatings are believed to be original. The modeling results were compared with the actual performance of the electrolyzer.

Based on the combined results of the experimental and theoretical work, it was possible to explain and predict the remarkable changes in the SDE process that take place with changing electrolyte concentrations. A significant amount of water is transported from the anolyte to the catholyte through the membrane due to the electro-osmotic water drag effect. This phenomenon is beneficial for the production or concentration of sulfuric acid by SO₂ depolarized electrolysis. Thin gold coatings on stainless steel surface can be used to catalyze the anodic oxidation of SO₂, and similar electrodes can be used as cathodes.

Keywords  SO₂ depolarized electrolysis, sulfuric acid, hydrogen, Nafion membrane, water transport, gold
SO$_2$-depolarisoitu elektrolyysi tuottaa vetyä ja rikkihappoa. Käytettävä rikkiidioksidi voi olla peräisin erilaisista teollisuusprosesseista, kuten esimerkiksi sulfidisten mineraalien liikkisulatuksesta tai pasutuksesta, jolloin SDE on osa Outotec$^R$ open cycle-prosessia. SO$_2$-n kennonjännitetetä entävän eli depolarisoivan vaikutuksen vuoksi vetyä veden valmistus SDE:n avulla kuluttaa merkittävästi vähemmän sähköenergiaa kuin perinteisen elektrolyysiteknikat kuten alakalitelektrolyysi.

Tässä työssä tutkittiin SO$_2$-depolarisoituun elektrolyysiin sopivia materiaaleja sekä prosessin teoreettisia perusteita ja mahdollisuuksia. Aiemmista tutkimuksista on saatu ymmärrystä, että perinteisessä elektrolyysin menetelmissä saattaa käydä virtaa vähän sähköenergiaa, koska elektrolyyssisysteemissä on useita sähkötarvikkeita. Tutkimuksen tavoitteena oli löytää parempi materiaali ja prosessimääritysyöndyn kehittäminen.

Kulta-voidevoide restaaruuttiin esimerkiksi vesitasea ja Nafion-membraaniin, jotta katalyyseesi voitaisiin vahvistaa. Mallinnotuloksia verrattiin kokeellisesti vuoksi, että mallinnotulokset toivottivat, että mallinnotulokset voivat olla hyödyllisiä viitekeikkyyn, jotta perinteiseen elektrolyysinsäädön voidaan pystyä parempaan käyttöseen.
Preface

The research work presented in this dissertation was carried out at Aalto University and at one of its predecessors, Helsinki University of Technology, Research group of Materials Processing and Powder Metallurgy during the years 2008-2012. I am very grateful to my supervisor, Professor Michael Gasik. His vast knowledge and continuous flow of new ideas was very inspiring, and he encouraged me to truly question the known authorities and theories. Professor Pekka Taskinen has been my advisor since autumn 2008, and I wish to express my gratitude to him. He gave me a lot of practical advice during the course of this work, and I had the privilege to discuss with him the thermodynamics of real systems. After our discussions, I felt encouraged and better equipped to meet the challenges of this work.

I wish to thank the former and current staff of the Research group for Materials Processing and Powder Metallurgy and of the Department of Materials Science and Engineering, especially Mikael Friman, Markku Kaskiala, Tuomo Kuikka, Jorma Laine, Arttu Leinonen, Mira Meder and Miia Pesonen for their help in conducting the experimental work. I am also very grateful to the staff of the Mechanical workshop, who patiently built all kinds of weird stuff for my experimental setups based on very rudimentary blueprints.

I would like to thank Outotec and Metallinjalostajien rahasto for their financial support for this work. From Outotec, I would like to thank Heljä Peltola M. Sc. (Tech), whose goodwill and influence was crucial during the early stages of the experimental work, and I wish to thank Ilkka Kojo D. Sc. (Tech) for his valuable advice, which made this thesis much more readable. Our long discussions on environment and sustainability helped me to evaluate the larger societal impact of this work.

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I want to thank my friends and acquaintances, with whom I have shared many experiences and funny moments since my student days at Helsinki University of Technology. Some of you chose the academic path, some of you before me and some of you after me, and I want to thank you for the company. We had many discussions over lunch or coffee (or sometimes over a glass of wine) which happily mixed public and private life, scientific issues with the best techniques for curling lashes. I especially wish to thank my friend, Miia Kiviö, who was first my fellow student and then a colleague.

I want to thank my family-in-law for their support and encouragement during this work. My husband, Pekka Montola, has been the joy of my life, and I want to thank him for that, and for support and patience. I have spent my adult life seeking knowledge and beauty, but of the human love I have, you have gotten the most.

Helsinki, January 2013

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<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
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<tr>
<td>a</td>
<td>activity</td>
<td>-</td>
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<tr>
<td>c, C</td>
<td>concentration</td>
<td>mol/dm(^3), mol/m(^3)</td>
</tr>
<tr>
<td>D</td>
<td>diffusion coefficient</td>
<td>m(^2)/s</td>
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<tr>
<td>E</td>
<td>potential</td>
<td>V, mV</td>
</tr>
<tr>
<td>E(_0)</td>
<td>standard reversible potential</td>
<td>V, mV</td>
</tr>
<tr>
<td>F</td>
<td>formal concentration unit</td>
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<td>F</td>
<td>Faraday constant</td>
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<tr>
<td>G</td>
<td>Gibbs energy</td>
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</tr>
<tr>
<td>H</td>
<td>Henry’s law constant</td>
<td>-</td>
</tr>
<tr>
<td>J</td>
<td>flow, flux</td>
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<td>k</td>
<td>permeability</td>
<td>m(^2)</td>
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<tr>
<td>L</td>
<td>interaction parameter</td>
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<td>M</td>
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<tr>
<td>m</td>
<td>molality</td>
<td>mol/kg H(_2)O</td>
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<td>N</td>
<td>normality</td>
<td>mol H(^+)/dm(^3)</td>
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<td>S</td>
<td>entropy</td>
<td>J/mol K</td>
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<tr>
<td>V</td>
<td>specific flow rate</td>
<td>m(^3)/m(^2)·s or m/s</td>
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<td>x, X</td>
<td>molar fraction</td>
<td>-</td>
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<tr>
<td>z</td>
<td>number of electrons transferred in a reaction</td>
<td>-</td>
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### Greek symbols

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<tr>
<td>λ</td>
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<td>H₂O/ sulfonic acid group</td>
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<tr>
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<td>electro-osmotic water drag coefficient</td>
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<td>ρ</td>
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<td>w</td>
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<tr>
<td>xs</td>
<td>excess</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
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<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>HE</td>
<td>hydrogen electrode in the same solution as the electrode studied</td>
</tr>
<tr>
<td>HyS</td>
<td>Hybrid Sulfur Cycle</td>
</tr>
<tr>
<td>IEA HIA</td>
<td>International Energy Agency Hydrogen Implementing Agreement</td>
</tr>
<tr>
<td>ICP</td>
<td>Inductively coupled plasma mass spectrometry</td>
</tr>
<tr>
<td>LHV</td>
<td>lower heating value (for hydrogen 241 kJ/mol)</td>
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<td>LSV</td>
<td>linear sweep voltammetry</td>
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<tr>
<td>PEM</td>
<td>proton exchange OR polymer electrolyte membrane</td>
</tr>
<tr>
<td>PVD</td>
<td>physical vapor deposition</td>
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<tr>
<td>RHE</td>
<td>reversible hydrogen electrode</td>
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<tr>
<td>SCE</td>
<td>saturated calomel electrode</td>
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<td>SDE</td>
<td>SO₂ depolarized electrolysis</td>
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<td>SEM</td>
<td>scanning electron microscope</td>
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<td>SHE</td>
<td>standard hydrogen electrode</td>
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1 Introduction

1.1 Background

Renewable and cost-efficient production of hydrogen on a large scale is one of the key objectives of the “green economy”. Using hydrogen as an energy carrier, renewable energy produced at one location can be stored and transported for use at another time and place. Hydrogen-powered vehicles offer the chance to maintain or obtain the mobility now available in developed countries together with mitigation of CO₂ emissions and reduction of our dependence on fossil fuels. On the way to the hydrogen energy society, hydrogen can also be used to decarbonize energy from fossil sources, for example, in the production of syngas (Winter 2009). Over the years, there has been a tendency to move from solid fuels containing no hydrogen (coal) to fuels whose energy content is partially hydrogen (natural gas) (Züttel 2008).

Besides its use as an energy carrier, hydrogen is a commodity needed for many industrial processes. The major users of hydrogen are the electronics and electronic equipment industries, glass and food manufacturers, oil refineries and the chemical industry, as well as space mission programs. Hydrogen is also used as a reducing agent in many hydrometallurgical processes and it is the major energy carrier for fuel cells (Krüger 2008). In 2009, the amount of hydrogen produced for sale was about 50 Mt/a, with an annual increase of 10 % (Winter 2009). The replacement of fossil-fueled vehicles by hydrogen-fueled vehicles would require a substantial increase of hydrogen production (Winter 2009; Krüger 2008).

Today, steam methane reforming and alkaline electrolysis are the state-of-the-art processes for production of hydrogen on a large scale. Hydrogen production by the steam reforming of natural gas is not compatible with mitigation of CO₂ emissions, and for alkaline electrolysis, large amounts of electrical energy coming from renewable or other sources are needed. To find an alternative, different chemical and thermochemical routes have been investigated since the 1960s (e.g. Sattler 2010) and the best options have been indentified – for example, the Nuclear Hydrogen Initiative of the US Department of Energy identified the Hybrid Sulfur Cycle (HyS) together with the sulfur-iodine cycle as the first priority cycles for hydrogen production (Gorensek and Summers 2009). According to the analysis of these two
processes carried out within the IEA Hydrogen Implementing Agreement Task 25, HyS is the more favorable despite some challenges (Galzim, et al., 2011).

1.2 HyS cycle and the Outotec® open cycle process
The Hybrid Sulfur Cycle (HyS) or Westinghouse process (also known as Ispra Mark 11) was patented in 1975 (Brecher and Wu 1975), and described by Brecher, Spewock and Warde (1977). It is a two-step process, first a low-temperature electrochemical step and second a high-temperature, thermochemical step. The process flowsheet is shown in Fig 1.

![HyS flowsheet schematic](image)

Figure 1 HyS flowsheet schematic. Drawn after Brecher, Spewock and Warde (1977).

In the electrochemical step of the HyS cycle, sulfuric acid and hydrogen are produced by sulfur dioxide depolarized electrolysis (SDE). In the thermochemical part, the sulfuric acid formed in electrolysis is concentrated and decomposed thermally to SO₂ and O₂. The SO₂ is circulated back to the electrolysis step for hydrogen generation. The most energy-demanding part of the HyS cycle is the decomposition of sulfuric acid; a high temperature is
needed for fundamental thermodynamic reasons and the stabilities of sulfuric acid and sulfur trioxide.

To be feasible, the process was designed to be coupled with a very high temperature nuclear power plant, which would supply both the heat needed for the sulfuric acid concentration and decomposition steps and the electricity required for the electrochemical part (Brecher and Wu 1975; Brecher, Spewock and Warde 1977). A very high temperature reactor belongs to the group of “Generation IV” nuclear power plants, which have yet to be constructed (Kruger 2008; Charit and Murty 2010). One example of Generation IV is a pebble bed modular nuclear reactor, for which the outlet temperature of the cooling helium would be 950°C (McLaughlin, Paletta, Lahoda and Kriel 2006). The BWR (boiling water reactor) and PWR (pressurized water reactor) type reactors used nowadays produce steam, the temperature of which is less than 319°C and thus far below the feasible temperature range for decomposing sulfuric acid and sulfur trioxide further to sulfur dioxide (Forsberg 2009). The coupling of the HyS cycle with a solar heat source has also been studied in the attempt to achieve sufficiently high temperatures for sulfuric acid decomposition (Graf, et al., 2008; Corgnale and Summers 2011; Hinkley, O'Brien, Fell and Lindquist 2011).

For a short- to medium-term application, the new Outotec® open cycle process (OOC) is an attractive alternative for hydrogen production, as it involves only one stage (SDE) and does not require sulfuric acid decomposition (Lokkiluoto, et al., 2012). The SO₂ used in the process can be obtained from flash smelting, sulfides roasting, sulfur combustion or any other similar operation, and because sulfuric acid is commercial product, the cycle is left open (Rauser, Gasik, Peltola and Taskinen 2010; Gasik, Lokkiluoto, Peltola and Taskinen 2012). The process is shown in Fig 2.
Roughly one third of the world’s annual sulfuric acid is a by-product of metallurgical operations, while 60% of the sulfuric acid produced originates from the burning of elemental sulfur or from the roasting of pyrite carried out to produce feedstock for sulfuric acid manufacture (Lokkiluoto, et al., 2012). With the OOC process, hydrogen production could be coupled with metallurgical or other operations. With a worldwide production of sulfuric acid of 200-250 Mta, the by-product hydrogen opportunity with this process is 4-5 Mta (~35-45 PJ assuming hydrogen LHV energy value).

Sulfur dioxide depolarized electrolysis is a common step in both HyS and the new Outotec® open cycle process. For both processes, the sulfuric acid exiting electrolysis should be quite concentrated. For the HyS process, different estimates for the optimal sulfuric acid concentration have been presented: on the one hand, the less heat needed for the sulfuric acid concentration step (Fig 1), the more concentrated the acid. On the other hand, the increasing concentration increases electric energy consumption due to changes in the physical and chemical properties (density, viscosity, electric conductivity, chemical potential of the components etc.) thus rendering the process less effective compared to alkaline electrolysis (Appleby and Pinchon 1980). For example, while Lu, Garcia and Ammon (1981) concluded that the optimum acid concentration would be 30 wt % regarding the performance of SDE, Lu (1983) suggested that the best acid concentration for the overall performance of the HyS process would be 50-60 wt %. No such predetermined constraints exist for OOC: the more concentrated the sulfuric acid, the better.

Figure 2 Outotec® open cycle process schematic.
1.3 The principle of sulfur dioxide depolarized electrolysis

In standard water electrolysis the cathode reaction is hydrogen evolution, as shown in reaction (1a). The anode reaction is oxygen evolution (1b).

\[ 4H^+ + 4e^- \rightarrow 2H_2 (g) \quad (1a) \]
\[ 2H_2O (l) \rightarrow 4H^+ + 4e^- + O_2 (g) \quad (1b) \]

The overall reaction is

\[ 2H_2O (l) \rightarrow 2H_2 (g) + O_2 (g) \quad E_0 = +1.23 \text{ V} \quad (2) \]

The schematic of an SDE cell is shown in Fig 3.

\[ SO_2 (aq) + 2H_2O \rightarrow 4H^+ + 2e^- + SO_4^{2-} (aq) \quad (3) \]

The overall cell reaction in SDE is then (4):

\[ SO_2 (aq) + 2H_2O \rightarrow H_2SO_4 (aq) + H_2 (g) \quad E_0 = +0.158 \text{ V} \quad (4) \]
The clear advantage of the SDE process is that the standard reversible voltage $E_0$ of the net cell reaction (4) is only 0.158 V (Gorensek, Staser, Stanford and Weidner 2009), versus the $E_0 = 1.23$ V needed in conventional water electrolysis (2). In laboratory-scale tests, the realized cell voltage of SDE has been 0.5-1.2 V, depending on the current density and other operational parameters (O’Brien, Hinkley, Donne and Lindquist 2010; Staser and Weidner 2009; Steimke and Steeper 2006; Lu and Ammon 1982), compared with the 1.8-2.0 V of commercial alkaline water electrolysis (Stolten and Krieg 2010). Thus, SDE would require 25-60 % of the electrical energy required for direct water splitting by conventional electrolysis. Research groups at the Savannah River National Laboratory (SRNL), at the University of South Carolina (USC), at CEA, and at CSIRO have recently studied and modeled SDE (Steimke and Steeper 2006; Jomard, Feraud and Caire 2008; Staser and Weidner 2009; O’Brien, Hinkley, Donne and Lindquist 2010).

The anolyte and the catholyte are separated to prevent reduction of SO$_2$ on the cathode. In the cells used by Lu and Ammon (1982) and Junginger and Struck (1982), a diaphragm-type separator was used, but later diaphragms were replaced by membranes. Various advanced and experimental membranes developed for fuel cells have also been tested for SDE by Colon-Mercado and Hobbs (2007a), Staser, Ramasamy, Sivasubramanian and Weidner (2007), Staser and Weidner (2009) and Steimke, et al., (2009). The protons can pass through the membrane together with some water, but the membrane prevents passage of other molecules as well as that of electrons. Graphite has been the material used for the bipolar plates and platinum has been the catalyst used on both the anode and the cathode.

Models for the SDE and its key elements have been presented by Staser and Weidner (2009), Gorensek, Staser, Stanford and Weidner (2009) and Jomard, Feraud and Caire (2008). Staser and Weidner (2009) modelled a SDE cell with gaseous feed of SO$_2$ to the anode. With this construction, the reaction on the “dry” anodic side of the cell relies on the water supply from the cathodic compartment. Here water and proton fluxes inside the membrane are acting in opposite directions, which do not allow high current densities (Motupally, Becker and Weidner 2000). Many experimental SDE designs have liquid-fed catholyte and anolyte compartments (Lu and Ammon 1982; Gorensek, Staser, Stanford and Weidner 2009; Jomard, Feraud and Caire 2008; McLaughlin, Paletta, Lahoda and Kriel 2006;
Struck, Junginger and Boltersdorf 1980; Lokkiluoto, Gasik and Kuikka 2010). In this case, the SDE operation greatly depends on the concentration of the electrolytes and on the mass flow rates. The difficulty in modeling of the SDE performance arises partly from variation of water transport mechanisms through the membrane, some of which are not well known.

1.4 Objectives of the study

When this work was initiated, the aim was to find suitable materials for SO₂ depolarized electrolysis (electrodes and construction materials) and to define optimal process conditions for effective co-production of hydrogen and sulfuric acid. Metallic materials were preferred due to their superior mechanical properties compared to the carbon-based electrodes/bipolar plates traditionally used.

Nonetheless, it was realized quite early that better and deeper understanding of sulfur dioxide depolarized electrolysis (SDE) itself was needed in order to carry out the original tasks. SDE has been studied earlier as a part of the HyS Cycle, and thus there has been a predetermined goal for sulfuric acid concentration. No information was found in the literature on how concentrated the acid produced by this process could be. Theoretical modeling work covering the entire concentration range was deemed necessary as well as experimental testing to settle this issue. No thermodynamic model for the ternary system covering the whole concentration range was found in the literature, and thus a special description of the system was developed to calculate the activities of the components. The activities are needed as a function of concentration, temperature, and pressure to predict the solubility of SO₂ into sulfuric acid solutions, and to calculate the changes in the reversible cell voltage.

Based on the literature concerning PEM Fuel Cells, it was concluded that the water transport properties of the membrane used as a separator in the electrolysis may have a significant effect on the water balance, mostly due to the electro-osmotic water drag effect. While this phenomenon has been known to be detrimental to the behavior of fuel cells, the hypothesis was that this effect would be beneficial in SDE conditions by concentrating the product sulfuric acid. Since the membrane is in contact with sulfuric acid and sulfuric acid-SO₂ solutions in SDE instead of water, the changes in water activities with changing conditions are also needed for the water transport model.
Even though platinum has been the catalyst material most studied for SDE, gold has also been reported to show remarkable catalytic activity towards the electrochemical oxidation of SO$_2$. On this basis, the hypothesis was formed that metallic electrodes with a thin gold coating could be used. Because the anodic reaction is more difficult and less studied than the cathodic reaction (hydrogen evolution), the main emphasis was placed on anodic reaction.

The phenomena that needed to be studied in order to understand the SDE process include:

1. Electrochemical oxidation of SO$_2$ on the anode catalyzed by thin gold coatings
2. Competing anodic reactions to be avoided
3. Changes in activities of the electrolyte components with changing concentrations, T and p
4. Effect of the changing activities on the reversible cell voltage
5. Water transport through the Nafion membrane used to separate the anolyte and the catholyte
6. Summed effects of phenomena 1-5 on the overall performance of SDE

1.5 Structure of the thesis

Chapter 2 of this thesis is a literature review. Electrode materials and reactions together with behavior of materials relevant to this work in H$_2$O-H$_2$SO$_4$ and H$_2$O-H$_2$SO$_4$-SO$_2$ solutions are discussed in sections 2.1 and 2.2. The emphasis is on the anode, because the anode reaction is more complicated and less studied than the cathode reaction. In section 2.3, the literature review on the thermodynamics of electrolyte solutions is presented. This section covers both the available thermodynamic data and the earlier models used to calculate the activities of the components and to predict the solubility of SO$_2$. In section 2.4, properties of Nafion membranes are discussed.

The activities of the components of electrolyte solutions were calculated, and changes in the cell potential with changing electrolyte concentrations were calculated based on them. Water transport through the membrane and the membrane conductivity in contact with electrolyte solutions were modeled and calculated together with changes in the cell potential due to thermodynamic reasons. All this modeling work is presented in Chapter 3,
which is the theoretical section. This work is based on the literature presented in Chapter 2, but this division was made to emphasize the distinction between the author’s own work and the state of the art.

Chapter 4 of this thesis, Experimental work, reports the methods used to study electrode materials and reactions, and to validate the SDE model together with the results obtained. As in Chapter 2, the main emphasis of the studies of catalytic activity and material stability is on the anode side. The model for SDE presented in Chapter 3 is validated with data from bench-scale SDE experiments. Discussion is presented with the results both in the Theoretical and Experimental sections. The thesis ends with Chapter 5 Conclusions, which includes recommendations for future work.

The thesis includes two appendices, which report detailed results of the experimental work.
2 Materials and electrolytes of the SDE process – literature review

2.1 Stability of metallic materials and coatings in $H_2SO_4$-$SO_2$-$H_2O$ solutions

The electrodes/bipolar plates used in a fuel cell or in an electrolyzer should have good corrosion resistance, good surface conductivity and good heat transfer properties, in addition to which they should be easy to form and affordable. These properties are at least partially mutually exclusive.

Ferrous alloys and refractory or valve metals (Ti, Ta, etc.) may have good corrosion resistance due to passivation, but the passivation also causes high contact resistance. With coatings, enhancement in corrosion resistance and contact resistance can be attained simultaneously, and different coatings, including gold, have been tested and used for PEM fuel cells (Kumar, Ricketts and Hirano 2010). Because coatings may deteriorate, the base material should nevertheless have some reasonable corrosion resistance in itself. If the coating is nobler than the substrate, and has some porosity, the substrate, as less noble, may corrode beneath the coating and ultimately release the coating (Wiiala, et al., 1991).

The protective properties of the coating can be improved by decreasing the porosity and macroscopic defects. The porosity can be decreased by manufacturing homogenous crystals, and the best corrosion resistance can be achieved with amorphous coatings, which have no clear structure. By coating the substrate many times, the probability of defects occurring throughout the whole thickness of the coating is lowered and corrosion resistance is increased in this way, although porosity is not decreased (Elsener, Rota and Böhn 1989). To decrease macroscopic defects, the focus should be put on pretreatment of the substrate, and on the coating process, as macro defects are often caused by roughness of the surface (Jehn 2000).

Graphite has been the bipolar plate or electrode material normally used in $SO_2$ depolarized electrolysis. Due to superior mechanical properties, it was decided to use metallic materials for this study. Based on a preliminary literature search, both 316L stainless steel and titanium were found to have too little corrosion resistance in SDE conditions, and 904L stainless steel was selected as the electrode substrate. 904L is a stainless steel often used when handling sulfuric acid (Sedriks 1996, Outokumpu Stainless Cor-
rosion Handbook 2004). Some information was found about the behavior of 904L used as an electrode, but not for sulfuric acid solutions as concentrated as those used in SDE. At potentials exceeding the passive region, anodic dissolution of 904L may take place. On the other hand, even graphite dissolves when used as an anode, if the anodic potential is too high. Very little literature was found considering the effect of SO₂ on the stability of materials in sulfuric acid solutions.

2.2 Electrode materials and reactions

2.2.1 Anodic reactions

2.2.1.1 Oxidation of SO₂ on the anode
According to Staser, Gorensek and Weidner (2010), the anodic overpotential is the largest component of the actual SDE cell voltage and thus a more active catalyst could increase the overall efficiency of the SDE and HyS process. Platinum is a catalyst that has been widely used for this process both on the anode and on the cathode (Lu and Ammon 1982; Struck, Junginger, Boltersdorf and Gehrmann 1982; Colón-Mercado and Hobbs 2007b; O’Brien; Hinkley, Donne and Lindquist 2010; O’Brien, Hinkley and Donne 2010).

Oxidation of SO₂ has been studied on many materials. Materials that have been found to show catalytic activity towards the oxidation of SO₂ in aqueous sulfuric acid solutions include besides of platinum: palladium (Lu and Ammon 1980; 1982; Quijada and Vázquez 2000; Colón-Mercado and Hobbs 2007b), gold (Seo and Sawyer 1965; Samec and Weber 1975a, 1975b; Lu and Ammon 1980; 1982; Appleby and Pinchon 1980; Quijada, Morallón, Vázquez and Berlouis 2000; Quijada, et al., 2000), rhodium (Appleby and Pinchon 1980), ruthenium (Lu and Ammon 1982), lead dioxide (Scott and Taama 1999), glassy carbon (Scott and Taama 1999), graphite (Scott and Taama 1999; Koparal, Tezcan Ün and Öğütveren 2004), and mixed aluminum-vanadium oxides supported on carbon (Wiesener 1973).

Many different views on the mechanism of oxidation of SO₂ in acidic S(VI) solutions have been presented, and the mechanism most probably varies depending on the electrode material and on the concentration (pH) of the solution. In the present work, the emphasis is not on the mechanism, but on the overall behavior of the electrode/catalyst material, although some mechanisms suggested in the literature are briefly presented. A recent re-
view discussing the mechanism of the electrochemical oxidation of SO\(_2\) was written by O’Brien, Hinkley, Donne and Lindquist (2010).

Depending on the sulfuric acid concentration, electrode pre-treatment process and other experimental variables, platinum, palladium and gold have been considered to be the most active materials for anodic oxidation of SO\(_2\). Of all the materials studied by Appleby and Pinchon (1980), rhodium initially showed the most catalytic activity, but the activity decreased over time with the formation of a surface oxide. In the experiments of Appleby and Pinchon (1980), metallic gold was more active than platinum, but when supported on carbon/graphite, Pt was more active than Au, possibly due to differences in the actual surface area of the catalyst. Lu and Ammon (1980) found palladium to be superior to platinum, but later Colón-Mercado and Hobbs (2007b) concluded platinum to be better, partly because of the dissolution of palladium during the experiments. Lu and Ammon (1980) concluded that Pt and Pd showed more activity towards oxidation of SO\(_2\) than Au in 50 wt % sulfuric acid, but Quijada and Vázquez (2000) maintained that gold was inherently more active than platinum for the oxidation of SO\(_2\). From an engineering point of view, the cheaper price of gold compared to that of platinum would make it a more attractive option as a catalyst, even if the recent financial crisis has increased the gold price.

As stated in Appleby and Pichon (1979), the first oxidation peak of SO\(_2\) on platinum is situated at around 0.7 V vs. HE (hydrogen electrode at the same pH as the supporting electrolyte) and the second peak at around 1.2 V vs. HE. During the experiments of Scott and Taama (1999), the first oxidation peak of SO\(_2\) was reached on Pt surfaces at approx. 0.64 V vs. SCE (approx. 0.88 vs. SHE). According to Quijada, et al., (1995a, 1995b), SO\(_2\) is oxidized on Pt in the double layer region only if the surface is covered with sulfur, which means that the first peak mentioned above can be obtained only by suitable pretreatment of the electrode. They state that, during oxidation of bulk SO\(_2\) on Pt surfaces, previously adsorbed SO\(_2\) is desorbed oxidatively. The maximum oxidation maximum peak is reached at 1.2 V vs. RHE, and at higher potentials the formation of surface oxides starts to inhibit SO\(_2\) oxidation. The second oxidation peak is located in the oxygen adsorption region (Quijada, et al., 1995b).
Since the many authors cited below believe that adsorption of O or OH on a gold surface may have a strong effect on the anodic oxidation of SO$_2$, these processes are discussed briefly in the next two chapters.

The chemisorption of O on gold has been suggested as a precursor to oxide formation during the anodic polarization of gold, and the maximum coverage probably corresponds to one O per Au atom (Gmelin Handbook 1992). According to Nicol (1980), during the anodic oxidation of gold in non-complexing acids (like sulfuric acid), chemisorption of oxygen starts at potentials above 1.4 V vs. SHE and monolayer coverage is approached at 2 V vs. SHE. This electroadsorption of O has been reported to be inhibited by the adsorption of anions (Gmelin Handbook 1992).

Layers of electrosorbed OH have been reported to form on gold at the beginning of anodic oxidation in acid solutions. In 1 N H$_2$SO$_4$, the monolayer consists of one OH$^-$ species per gold atom. It has been suggested that adsorbed anions like SO$_4^{2-}$ stabilize the Au-OH species on the gold surface, and an increasing amount of SO$_4^{2-}$ ions would promote surface oxide formation (Gmelin Handbook 1992).

Samec and Weber (1975a) write that SO$_2$ is reduced on a gold surface at potentials $E<0.4$ V vs. HE (hydrogen electrode in 0.5 M sulfuric acid). According to Quijada, Morallón, Vázquez et al. (2000) and Quijada, et al., (2000), at 0.5 V vs. RHE no faradic processes occur on gold. They studied reduction reactions at potentials more negative and oxidation reactions at potentials more positive than that and report that SO$_2$ is oxidized at approx. 0.6 V (vs. RHE). This would thus be the minimum obtainable value for SDE cell voltage with gold anodes in the conditions corresponding to this experiment.

According to Quijada, Morallón, Vázquez et al. (2000) and Quijada, Huerta, Morallón and Berlouis (2000), SO$_2$ is not adsorbed strongly on a gold surface unlike on platinum, thus enabling effective oxidation of bulk SO$_2$. The oxidation process was concluded to be diffusion-limited. At a higher concentration of SO$_2$ (100 mM), they observed a sharp drop in the SO$_2$ oxidation current at 1.4 V vs. RHE, which they attributed to inhibition caused by adsorbed oxygen. At lower concentrations of SO$_2$, the oxygen adsorption current was superimposed onto the SO$_2$ diffusion tail, and they concluded that this might evidence the ability of SO$_2$ to oxidize electrochemically on the gold oxide layer. They thus concluded that gold was a better catalyst for
SO₂ oxidation than Pt. This difference between the activity of gold and platinum towards oxidation of SO₂ at lower potentials had already been noted by Seo and Sawyer (1965).

Samec and Weber (1975a, 1975b) concluded that SO₂ was adsorbed on a gold surface prior to its oxidation based on the sudden drop of the SO₂ oxidation rate at approx. 1.5 V vs. HE (hydrogen electrode in 0.5 M sulfuric acid), which they suggest to be caused by the fact that surface oxide formation hinders the adsorption. As the mechanism of SO₂ oxidation, they proposed a charge-transfer reaction followed by an irreversible chemical reaction, which leads to inactivation of the product of the charge-transfer reaction. The product of the charge-transfer reaction is hexavalent sulfur, S(VI). According to Lu and Ammon (1980), at potentials where adsorbed (oxygen) species are converted to metal oxides, inhibition of SO₂ oxidation frequently occurs.

Tolmachev and Scherson (2004) studied the oxidation of sulfite on gold electrodes in mildly acidic (pH 5.25) solutions. The Au electrode surface remained virtually free of oxide up to potentials positive enough for Au to be covered by about a monolayer of oxide, which they concluded to be due to the presence of sulfite. At more positive potentials (1.3-1.7 V vs. Ag/AgCl, 1.7-1.9 vs. SHE), a sudden drop in reactivity occurred, which they attributed to the formation of a place-exchanged gold oxide. They suggested a model that invokes competition between removal of adsorbed oxygen by sulfite to form sulfate via an oxygen-transfer reaction, and a structural transformation of absorbed oxygen into a much less reactive oxide. Their conclusion was that sulfite ions HSO₃⁻ and SO₃²⁻ are not absorbed on the Au electrode prior to its oxidation.

Burke and Nugent (1998b) found that when gold catalyzes the oxidation of a reductant, the oxidation of active gold atoms Au⁺ at active sites provides a mediator termed AuOₓ, and thus oxidation can take place only at potentials which are more positive than the potential needed for the transition Au⁺/AuOₓ to provide the mediator. For gold in acid media, this value was suggested to be 0.8 – 0.85 or 1.0 – 1.1 V vs. RHE depending on the type of the mediator and shifting with the pH. With decreasing pH, it was suggested the transition moved towards more negative potentials. Burke and Nugent note that this electrocatalytic behavior of gold is not relevant to all reactions taking place on gold, and if we compare the potential values they
give and the starting potentials of the first oxidation peak of SO₂ on gold, this seems to be true for this reaction. Nevertheless, participation of mediators in the oxidation of SO₂ on gold at higher potentials cannot be ruled out. According to Burke and Nugent (1998a), the onset of monolayer oxide formation frequently results in inhibition of the electrocatalytic activity of metals, which are active in their double-layer region. For gold, that commences at approx. 1.36 V vs. SHE in acid (Burke and Nugent 1998b). This agrees with the experimental evidence on the oxidation of SO₂ on gold cited above.

Seo and Sawyer (1965) reported that, with gold electrodes, the overpotentials measured relative to the observed rest potentials increased with increasing pH, and they thus concluded that the oxidation process involves molecular SO₂ rather than bisulfite ion, HSO₃⁻. They carried out their experiments in 0.1 F sulfuric acid. The increase in the anodic overpotential with increasing pH agrees with the increase in the potential of formation of the mediator needed for the oxidation reaction suggested by Burke and Nugent (1998a, 1998b). On the other hand, as discussed in Section 2.3.5 SO₂-H₂O-H₂SO₄ system, SO₂ exists mostly in molecular form at high concentrations of sulfuric acid.

Vitt, Larew and Johnson (1990) share the idea of a mediator needed for oxygen-transfer reactions on gold surfaces. They suggested the oxygen-transfer agent at gold electrodes to be adsorbed hydroxyl radical AuOH, even in acidic solutions. AuOH could enhance the adsorption of the oxidizing compounds by making the electrode surface more polar. The potential at which AuOH is formed would thus determine the lowest applied potential at which oxygen-transfer oxidation can occur. In 0.1 M H₂SO₄ (pH 1) at room temperature, they found the half-wave potential of sulfite ion, SO₃²⁻ oxidation to be 0.4 V vs. SCE (approx. 0.64 vs. SHE). Vitt, Larew and Johnson (1990) concluded that sulfite was adsorbed strongly on Au, because addition of sulfite prevented oxidation of some organic compounds on gold. This conclusion disagrees with the results of the spectroscopic studies obtained by Quijada, Morallón, Vázquez and Berlouis (2000), Quijada, et al., (2000) and by Tolmachev and Scherson (2004).

An increase in sulfuric acid concentration has been frequently observed to increase the anodic overpotential needed for oxidation of SO₂ and to decrease the rate of oxidation of SO₂ (the oxidation current in potential sweep experiments) (Koparal, Tezcan Ün and Ögütveren 2004; Colón-Mercado
and Hobbs 2007b). Whether this is caused purely by the thermodynamic reasons covered in Section 2.3.6 Change of cell potential with changing conditions, or whether this is partially caused by some other mechanism, e.g. blocking of active sites by adsorbed oxidized species on the anode surface, is unclear. According to Varga, Baradlai and Vértes (1997), unidentified complex adspecies formed by oxidation of aqueous SO\textsubscript{2} can adsorb on an oxide-free gold surface and inhibit the oxidation of bulk SO\textsubscript{2} but the adsorption strength of the bisulfate and sulfate ions HSO\textsubscript{4}\textsuperscript{-} and SO\textsubscript{4}\textsuperscript{2-} present in the supporting electrolyte is much lower. Gold is generally thought to be a very weak chemisorber (Burke and Nugent 1997a; 1997b; Varga, Baradlai and Vértes 1997; Quijada and Vázquez 2000).

### 2.2.1.2 Oxidation of SO\textsubscript{2} to dithionate

Based on the earlier work of Appleby and Pichon (1979), Lu and Ammon (1982) concluded that the poor performance of their experimental electrolyzer at a sulfuric acid concentration of 10 wt % was caused by the formation of dithionic acid H\textsubscript{2}S\textsubscript{2}O\textsubscript{6} rather than sulfuric acid in accordance with reaction (5)

\[
2 \text{H}_2\text{SO}_3 \rightarrow \text{H}_2\text{S}_2\text{O}_6 + 2 \text{H}^+ \tag{5}
\]

They concluded that at higher sulfuric acid concentrations this reaction should be suppressed, because SO\textsubscript{2} would then exist in molecular form due to the lower pH. Both of these studies were carried out with Pt electrodes/catalysts.

Varga, Baradlai and Vértes (1997) suspected the formation and adsorption of dithionate S\textsubscript{2}O\textsubscript{6}\textsuperscript{-} ion from the oxidation of SO\textsubscript{2} on gold surfaces besides sulfates, but they were not able to identify it unambiguously. Subsequently, based on in-situ vibrational techniques, Quijada, et al., (2000) concluded that formation of a short-lived dithionate-like S(V) species cannot be ruled out, but that an S(VI) species like sulfate ion or sulfuric acid is the final stable product of the electrochemical oxidation of SO\textsubscript{2} on gold.

### 2.2.1.3 Other anodic reactions of gold in H\textsubscript{2}SO\textsubscript{4}-H\textsubscript{2}O-SO\textsubscript{2} solutions

As discussed above, the oxidation of SO\textsubscript{2} to hexavalent sulfur species is inhibited at potentials where the gold surface becomes covered with adsorbed oxygen or oxides. By definition, SO\textsubscript{2} depolarized electrolysis ceases when oxygen evolution starts (i.e. the process taking place is then normal
electrolysis of water). Thus the oxidation of gold and oxygen evolution is touched on here only briefly.

The simplified E-pH diagram of gold shown in Figure 4 can be used to describe the behavior of gold in non-complexing acids (Nicol 1980). This means that in the thermodynamic sense, the nature of the anion formed by the dissociation of the acid is regarded irrelevant, and the concentration or activity of the H\(^+\) together with the potential (applied or redox-potential of the solution) dictates the stability domains. Within the domain of stability of water, gold is presumed to exist only as solid metal. Gold does not form thermodynamically stable oxides, but the predominant oxide is gold trioxide \(\text{Au}_2\text{O}_3\), corresponding to the trivalent oxidation state \(\text{Au}(\text{III})\). The other predominant oxidation state is \(\text{Au}(\text{I})\) (Gmelin Handbook 1992).

![Figure 4 Simplified E-pH diagram of gold. The concentration of all the soluble species is 10\(^{-4}\) M (Nicol 1980). Used with permission of Springer/Gold Bulletin.](image)

According to Nicol (1980), in non-complexing acids, the chemisorption of oxygen starts at potentials above 1.4 V vs. SHE, and monolayer coverage is approached at 2 V vs. SHE, which is followed by the growth of bulk oxide at higher potentials. This bulk oxide is \(\text{Au}_2\text{O}_3\) in acidic and gold trihydroxide
Au(OH)$_3$ in alkaline solutions. At higher potentials, the formation of Au$_2$O$_3$ is accompanied by O$_2$ evolution. The potential for oxidation of gold according to reaction (6) shifts cathodically by 60 mV per decade over a wide pH range (Nicol 1980).

$$2 \text{Au} + 3 \text{H}_2\text{O} \leftrightarrow \text{Au}_2\text{O}_3 + 6 \text{H}^+ + 6 \text{e}^- \quad (6)$$

Formation of Au$_2$O$_3$ films on gold anodes has been observed in sulfuric acid solutions ranging from 0.1-2 N at potentials around 1.3 V vs. NHE (Gmelin Handbook 1992). This layer is unstable in the presence of water, and decomposes with the evolution of oxygen if the current is stopped (Van Muylder and Pourbaix 1966). In complexing acids like aqua regia or in acidic solutions containing complexive agents, Figure 4 is not valid.

Because the pH scale cannot be used for meaningful descriptions of acids that are so concentrated that the molecular form of the acid is present, an E-pH diagram cannot be used to illustrate the behavior of gold over the whole concentration range of sulfuric acid relevant to SDE. The use of the Hammett function instead of pH may allow construction of more realistic potential-acidity diagrams at high concentration of acids than the traditional potential-pH-diagrams, as done by Kish and Ives (2011). The Hammett function is anyhow experimental (not thermodynamically derived) and a priori cannot be successfully extrapolated up to arbitrarily chosen concentrations (Michaelis and Granick 1942).

**2.2.1.4 Sulfates and sulftes of gold and complexive dissolution**

Senftle and Wright (1985) studied anodic dissolution of gold in concentrated sulfuric acid (96 – 98 %). At applied potentials ranging from 4 to 21 V, the anode was dissolved and auric sulfate Au$_2$(SO$_4$)$_3$ was formed. They suggested that during the electrolysis, the cause of the dissolution of gold was highly reactive free radicals formed in the concentrated sulfuric acid. Below a sulfuric acid concentration of 6.3 N, the gold electrodes were inert, and electrolysis was essentially that of water, despite the high applied potential. Au$_2$(SO$_4$)$_3$ seems to be stable only in concentrated sulfuric acid (Gmelin Handbook 1994).

To dissolve gold into solutions, complexing agents or ligands like cyanide CN$^-$ or chloride Cl$^-$, which form stable complexes with Au(I)- or Au(III)- ions, are needed. Sulfite ion is one possible complexing agent for gold, and alkaline solutions of gold sulfite complexes have been used since the 1840s
Solutions of gold are needed e.g. for electrodeposition processes (Hydes and Middleton 1979; Green and Roy 2006). The sulfites of gold include disulfitoaurate \([Au(SO_3)_2]^{3-}\) and tetrasulfitoaurate \([Au(SO_3)_4]^{5-}\) (Gmelin Handbook 1994). Nicol (1980) studied complex formation and the dissolution of gold. In Figure 5, potentials corresponding to the reduction of the oxidized forms of the ligands \(X_2\) are compared with those of the Au(I) complexes.

Nicol wrote: "On thermodynamic grounds, one would expect anodic oxidation of the ligand in preference to anodic dissolution of gold to occur only in those complexes positioned below the diagonal line." Figure 5 shows that the oxidation of SO\(_2\) on gold is more favorable than the complexive dissolution of gold. A more recent speciation study by Green and Roy (2006) confirms the instability of gold sulfites at pH<8.

### 2.2.2 Cathodic reactions

Platinum has been much studied as a catalyst for hydrogen production, and it is the material traditionally used in SDE (Colón-Mercado and Hobbs 2007b). According to Scott, Taama and Cheng (1999), in addition to plati-
num, nickel, stainless steel, glassy carbon, zirconium and Ebonex are all active for hydrogen production in sulfuric acid solutions.

According to Quijada, et al., (1995b), SO₂ is reduced to elemental sulfur S (not to hydrogen sulfide species H₂S or HS⁻) on Pt. Multilayer deposition of sulfur leads eventually to formation of an inhibiting film on the electrode surface. Quijada, et al., (1995b) reported that SO₂ is absorbed to the platinum surface at open-circuit potential. If the potential is subsequently changed in the negative direction, the adsorbed species is reduced to another adsorbed species with a lower oxidation state. This takes place at potentials related to hydrogen adsorption-desorption, which is thus strongly inhibited by adsorbed SO₂ and its reduced forms (Quijada, et al., 1995a). These adsorbates can be removed by oxidation, but several sweeps up to 1.5 V are needed. On platinum surfaces, adsorption of H precedes the generation of hydrogen.

Based on the amount of charge consumed, Samec and Weber (1975b) assumed SO₂ to be reduced to H₂S on a gold electrode. Quijada, Morallón, Vázquez and Berlouis (2000) and Quijada, et al., (2000) found that the first cathodic peak is between 0.2 and 0.1 V on gold and then there is another peak between -0.5 and -0.15 V. The first peak is related to the formation of adsorbed sulfur, and the latter was ascribed to the bulk reduction of SO₂ to H₂S.

Scott, Taama and Cheng (1999) studied zirconium and Ebonex as a cathode material in H₂SO₄-SO₂-H₂O solutions. These materials were active for hydrogen production, but not for reduction of SO₂ to elemental sulfur in an undivided cell. According to Scott, Taama and Cheng (1999), nickel, stainless steel, graphite and glassy carbon are active towards the reduction of sulfites in the same conditions. They assumed this takes place at approximately -0.25 V vs. SCE.

For the anodic and cathodic processes relevant to SDE conditions, one may conclude that:

- Oxidation of SO₂ is inhibited on gold at >1.4V SHE (~1.16 V vs. SCE) due to the formation of a layer of adsorbed oxygen or surface oxide.
- Dissolution of gold and formation of gold oxides takes place at potentials too high for oxidation of SO$_2$; in fact at potentials higher than the stability of water.
- The presence of SO$_2$ in sulfuric acid solution does not cause the complexing dissolution of gold anodes.
- Use of platinum as a cathodic catalyst should be avoided in SDE conditions if the crossover of SO$_2$ cannot be prevented because adsorption of SO$_2$ and its reduced forms inhibits adsorption of H, which precedes the generation of hydrogen. Gold would in that case be a better option, because SO$_2$ is not adsorbed on gold surfaces at open circuit potentials.
2.3 Thermodynamics of the \( \text{H}_2\text{SO}_4-\text{H}_2\text{O-SO}_2 \) system

2.3.1 Definitions

The systems discussed in the present work have several components and/or phases and they are non-ideal, and the concepts of chemical potential, activity and other measurable thermodynamic properties of components are frequently referred to. For clarity, the essential relationships and definitions are given below.

The integral Gibbs energy \( G \) for a multi-component solution (ideal or real) is:

\[
G = \sum x_i \mu_i
\]

This means that the chemical potential of component \( i \), \( \mu_i \), is the partial molar derivative of the Gibbs energy \( G \) according to equation (8):

\[
\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T,p,n_j}
\]

The behavior of components in solutions is bound together by the Gibbs-Duhem equation, the general form of which is:

\[
SdT - VdP + \sum x_i d\mu_i = 0
\]

When the pressure and temperature are constant, the Gibbs-Duhem equation (9) takes the form:

\[
\sum x_i d\mu_i = 0
\]

In ideal solutions, the chemical potential of \( i \) is given by equation (11):

\[
\mu_i = \mu^\circ + RT \ln x_i
\]

where \( x_i \) is the concentration of \( i \) in the solution given in the concentration scale selected. \( \mu^\circ \) is the chemical potential of component \( i \) in its standard state at the same temperature and pressure as the solution. In real solutions, the behavior of component \( i \) is compared with its behavior in ideal solutions by introducing the activity coefficient \( \gamma_i \):

\[
a_i = \gamma_i x_i
\]

and the chemical potential equation takes the form:

\[
\mu_i = \mu^\circ + RT \ln a_i
\]
There are various options for the selection of the standard state. If a pure component is selected, the selection is called Raoultian. Raoult’s law (14) gives the relationship between the partial pressure of \( i \), \( p_i \), the vapor pressure of pure liquid \( i \), \( p_i^o \), and the molar fraction of \( i \) in the liquid solution:

\[
p_i = x_i p_i^o
\]  
(14)

Raoult’s law is analogous to the definition of an ideal solution (11). When the molar fraction of component \( i \) approaches unity, its behavior approaches Raoultian behavior also in real solutions, and the activity coefficient approaches unity:

\[
\lim_{x_i \to 1} y_i = 1
\]  
(15)

If the solution is dilute in one component, for that component, the standard state can be selected to be an ideally dilute solution. This selection is called Henrian. The ideally dilute solution is a fictitious one, and the concentration of the solute is 1 m. Henry’s law is:

\[
p_i = H_i x_i
\]  
(16)

which gives a relationship between the partial pressure of \( i \) and its molar fraction in the liquid phase. The Henry’s law constant, \( H \), is determined experimentally.

For real solutions, the Gibbs energy can be divided into ideal (\( id \)) and excess (\( xs \)) terms:

\[
G = G^{id} + G^{xs}
\]  
(17)

which can be written as:

\[
G = \sum \mu_i^o x_i + RT \sum x_i \ln x_i + RT \sum x_i \ln y_i
\]  
(18)

To obtain the Gibbs mixing energy (\( mix \)) of the solution, the first term on the right-hand side in (18) is subtracted:

\[
G^{mix} = G - \sum \mu_i^o x_i
\]  
(19)

Following from the definition of Gibbs energy as the ability of the system to do external work, the relationship between the change of Gibbs energy \( \Delta G \) in an electrochemical reaction and the standard electromotive force (or the standard potential) \( E_0 \) of the cell is:
where \( z \) is the amount of electrons involved in the reaction. The standard state related to \( E_0 \) is by convention: \( T=25^\circ C, p=100 \) kPa (earlier 101.325 kPa) and the activities of all the components are unity. Following from the relationship of the Gibbs energy and the chemical potential, \( E_0 \) can be written as:

\[
E_0 = -\frac{\Delta G}{zF}
\]  

(20)

where \( \Delta G \) is the Gibbs energy. Following from the relationship of the Gibbs energy and the chemical potential, \( E_0 \) can be written as:

\[
E_0 = -\sum_i \frac{v_i \mu_i}{(zF)}
\]  

(21)

where \( v_i \) is the stoichiometric coefficient of component \( i \) in the reaction equation (negative for reactants and positive for products). If the \( \Delta G \) is negative, the reaction is spontaneous, and the \( E_0 \) is positive.

Whereas in melts, solid solutions or non-aqueous systems, the determination of partial thermodynamic quantities is usually not a problem, for aqueous systems this is not straightforward if charged species are in question. The major difficulty is the impossibility of defining the chemical potential according to equation (8), because it is not possible to increase the number of moles of any ion without simultaneously changing an equal amount of a counter-ion. Thus only the concentration of a pair of ions (cation – anion) of equal charges could be theoretically varied. If it is important to describe the speciation correctly, this problem is usually circumvented by one of two methods: either using theoretical models of the interaction of charged ions in the media (solvent), as e.g. in the classic Debye-Hückel electrostatic theory, or by defining hypothetical states and determining relative activities. As described above, the numerical activity values depend on the concentration scale and the standard state chosen.

Applications of derivatives of the Debye-Hückel theory and virial approximation are however only feasible for dilute solutions with low ionic strength. With use of additional coefficients, these models have been extended from the original concentration of 6 \( m \) to 40 \( m \) (Pitzer, Roy and Silvester 1977; Clegg, Rard and Pitzer 1994; Clegg and Brimblecombe 1995). The serious thermodynamic drawback of this approach is the difference in the treatment of the main component (solvent) vs. the others (solute), making the system non-symmetric. The use of the molality scale automatically excludes the whole composition range (for concentrated solutions molality approaches infinity), as pointed out by Hillert (1998) and by Kubaschewski and Al-
Formal substitution of these equations into the Gibbs-Duhem equation shows their limited validity. It is well known that in order to be used for the whole concentration range of the solution, the model has to be consistent with the Gibbs-Duhem equation (Gmitro and Vermeulen 1964).

### 2.3.2 Calculation of activities using the Gibbs-Duhem equation

If detailed knowledge of speciation is not needed, the treatment can be based on components instead of on charged species also in aqueous systems. Using experimental data of other known activities with the Gibbs-Duhem equation (10), one may write:

\[
\sum_{i=1}^{N} n_i d\mu_i = 0 \rightarrow \sum_{i=1}^{N} X_i d\ln \gamma_i = 0; \quad \sum_{i=1}^{N} X_i = 1
\]  

(22)

In a binary solution, the integral of equation (22) is traditionally expressed as

\[
\ln \gamma_2 = -\int_{\ln \gamma_1(0)}^{\ln \gamma_1} \frac{X_1}{1-X_1} d\ln \gamma_1
\]

(23)

where it is possible to determine the dependence of the activity coefficient of the second component if the first one is known. However, this integral might not converge when \(X_1 \rightarrow 1\) and to avoid this several approaches have been suggested. One of the most well known is the introduction of the Darken function (substituted activity coefficient) or Guggenheim’s polynomials for integral free energy (Kubaschewski and Alcock 1979, Lupis 1983). As shown by Hillert (1998), for binary systems it is very often easier to replace the integral with

\[
\ln \gamma_2 = -\int_{X_1(0)}^{X_1} \frac{X_1}{1-X_1} \left(\frac{\partial \ln \gamma_1}{\partial X_1}\right) dX_1
\]

(24)

which could be directly integrated if the derivative of the first component activity coefficient (or its functional dependence) is known. The lowest theoretical limit of this derivative is defined by equation (25):

\[
\left(\frac{\partial \ln \gamma_i}{\partial X_i}\right)_{T,P,x_j/k_i} > -\frac{1}{X_i}
\]

(25)
A similar concept might be applied for multi-component systems (Hillert 1998).

Various functions have been suggested for the composition dependence of the activity coefficient, and their usefulness has been discussed, for example by Redlich and Kister (1948). As noted by Bale and Pelton (1974), the functions used to express excess thermodynamic properties have to be “well-behaved,” i.e. they should be finite, follow dilute estimate limits (correct asymptotic behavior), and be differentiable within the existence of the solution. The selection of a polynomial form can be made such that some parts of the integral expression are cancelled out (Kubaschewski and Alcock 1979; Hillert 1998). For the binary system with full solubility limits (from 0 to 1), it might be taken as simply as a Redlich-Kister-type equation (26) (Ansara 1998):

\[ \ln \gamma_i = \sum_{i=1}^{N} a_i (1 - X_i)^i \]  

(26)

(this fulfils the requirement \( \ln \gamma_i = 0 \) when \( X_i \to 1 \), i.e. at the reference state of component 1). The type of the function (26) is only relevant when a direct analytical integration is being made; in other cases for numerical integration the specific type of the polynomial is not even required. A derivation of this expression by \( X_i \) and substitution into (24) will lead to an expression, which could be readily integrated.

2.3.3 \( \text{H}_2\text{SO}_4-\text{H}_2\text{O} \) system

The activity coefficients of water and sulfuric acid and the experimental data used to calculate them have been reported many times in literature. The publications cited in the present work are listed in Table 1.
## Table 1 Measurement type together with concentration range of the data used and cited in the present work.

<table>
<thead>
<tr>
<th>Author</th>
<th>Measurement type</th>
<th>Concentration range</th>
<th>Thermodynamic model</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clegg and Brimblecombe (1995)</td>
<td>review of isopiestic, vapor pressure, freezing point, emf, enthalpy and heat capacity data</td>
<td>0 – 40 m</td>
<td>Pitzer-type model</td>
<td>mole fractions instead of molality</td>
</tr>
<tr>
<td>Greenewalt (1925)</td>
<td>review of H$_2$O vapor pressure data</td>
<td>0 -95 wt %</td>
<td>none</td>
<td></td>
</tr>
<tr>
<td>Giauque, Hornung, Kunzlear and Robin (1960)</td>
<td>heat capacity, vapor pressure, freezing point and heat of dilution data</td>
<td>0 – 100 wt %</td>
<td>own model, activity = 0.13 at m = 1</td>
<td>NB! pure H$_2$SO$_4$ activity 3.41·10$^9$</td>
</tr>
<tr>
<td>Bolsaitis and Elliott (1990)</td>
<td>review of H$_2$O vapor pressure</td>
<td>0 – to azeotropic composition</td>
<td>mathematical function, Gibbs-Duhem integration</td>
<td></td>
</tr>
<tr>
<td>Massucci, Clegg and Brimblecombe (1996)</td>
<td>vapor pressure</td>
<td>5 – 26 m</td>
<td>none</td>
<td></td>
</tr>
<tr>
<td>Goronovsky et al. (1974)</td>
<td>Unknown</td>
<td></td>
<td>none</td>
<td>handbook; tabulated data</td>
</tr>
<tr>
<td>Rard, Habenschuss and Spedding (1976)</td>
<td>review of isopiestic, vapor pressure and emf data</td>
<td>0.1 – 27.7 m</td>
<td>own semi-empirical model</td>
<td></td>
</tr>
<tr>
<td>Staples (1981)</td>
<td>review of vapor pressure, isopiestic, freezing point and emf data</td>
<td>0.001 – 30 m</td>
<td>mathematical function</td>
<td></td>
</tr>
<tr>
<td>Bosen and Engels (1988)</td>
<td>review of total pressure, vapor pressure and enthalpy data</td>
<td>0 - 96 wt %</td>
<td>NTRL</td>
<td>Postulated complete 1 and 2 dissociations</td>
</tr>
<tr>
<td>Zeleznik (1991)</td>
<td>review of emf and freezing data</td>
<td>0.01 – 30 m</td>
<td>mathematical function</td>
<td></td>
</tr>
</tbody>
</table>

However, there are inconsistencies between the different measurements, which were carried out using various experimental techniques and different concentration ranges. One of the first reviews was made by Greenewalt in 1925, who assessed earlier measurements carried out by Burt, Briggs, Regnault, Sorel and Daudt, and considered Burt’s measurements (1904) to
be the most accurate. Although these measurements were made for a large concentration range, they were limited mainly to high temperatures, possibly due to the experimental difficulties of measuring very low water vapor pressures at room temperature. These data were later also assessed and tabulated into handbooks (Nikolsky et al. 1965; Green and Perry 2007). One of the most complete sets of measurements was performed by Giauque, Hornung, Kunzlelar and Robin (1960). They presented tabulated values of sulfuric acid activity coefficients, starting from 2 \( m \) concentration together with calculated activities of water. The data was extended up to the limits of pure acid and pure water.

The problem of acid vapor pressure data was discussed by Bolsaitis and Elliot (1990), who suggested that the \( \text{H}_2\text{SO}_4-\text{H}_2\text{O} \) system should be treated as a partial section of the more general \( \text{SO}_3-\text{H}_2\text{O} \) system, in which \( \text{H}_2\text{SO}_4 \) is an intermediate compound. They considered that discrepancies in vapor pressure measurements resulted from dissociation of gaseous sulfuric acid. More recent \( \text{H}_2\text{O} \) vapor pressure measurements were published by Massucci, Clegg and Brimblecombe (1996). They also reviewed earlier measurements and the different models used to correlate the data. Whereas data on sulfuric acid vapor pressures at room temperature have a substantial scatter, the results for water vapor pressures in a very wide range of compositions and temperatures were consistent.

Several different thermodynamic models for the water-sulfuric acid system have been published over the years. Some of them are based on component treatment while others have been elaborated to describe the speciation as accurately as possible.

Giauque, Hornung, Kunzlelar and Rubin (1960) adopted pure substances (water and acid) as the reference states, however for the water activity coefficient they fixed value of 0.13 at \( m = 1 \) (8.9 wt % \( \text{H}_2\text{SO}_4 \)). This resulted in an activity of pure acid equal to \( 3.41 \cdot 10^9 \). Rard, Habenschuss and Spedding (1976) used their own semi-empirical model to correlate the osmotic coefficient of sulfuric acid for the concentration range 0.1 – 27.7 \( m \). They warned that their model should be used with caution above 19 \( m \) due to the scarcity of experimental data. Staples (1981) calculated the activity and osmotic coefficients of the sulfuric acid-water system using his own model for the concentration range 0.001 – 30 \( m \). He evaluated all the vapor pressure, isopiestic, freezing point and emf data available in 1980.
Bosen and Engels (1988) modeled this system using the non-random two-liquid (NRTL) model. They postulated both the first and the second dissociations of sulfuric acid to be complete and independent of the concentration, which is clearly not correct. Bolsaitis and Elliot (1990) modeled the sulfuric acid - water system based on the Gibbs-Duhem equation, selecting the azeotropic composition as the reference state for sulfuric acid.

Zeleznik (1991) calculated activities and Gibbs energies using a mathematical function, but without vapor pressure measurements in favor of emf and freezing point data. The data agreed well with the models of Rard, Habenschuss and Spedding (1976) and Staples (1981) but only below 15 $m$ concentrations. In contrast, Massucci, Clegg and Brimblecombe (1996) claimed that the values obtained by Zeleznik (1991) were too high, deviating at $m > 10$. They stated that the values of Greenewalt (1925) and Giauque, Hornung, Kunzlear and Robin (1960) are higher than those obtained using Zeleznik’s (1991) correlation and supported the thermodynamic properties given in Giauque, Hornung, Kunzlear and Robin (1960). After careful consideration, the data in Zeleznik (1991) at high concentrations were rejected, because they appear to be strongly biased toward the emf data of Hamer (1935) and Hamed and Hamer (1935), which were later considered erroneous (Massucci, Clegg and Brimblecombe 1996). Rard and Clegg (1995) explicitly re-evaluated the emf measurements of Hamer (1935) and Hamed and Hamer (1935) and concluded that no consensus exists on the reliability of the original data.

Clegg and Brimblecombe (1995) tried to overcome molality-derived problems by using a mole fraction version of the Pitzer model. Massucci, Clegg and Brimblecombe (1996) did not recommend the model of Clegg and Brimblecombe (1995) to be used for concentrations over 40 $m$, and considered the correlations of Giauque, Hornung, Kunzlear and Rubin (1960) to be more suitable for that concentration range.

It is evident that calculated literature values can only be reliably compared when original measurement data (e.g. as for water vapor pressure) are available and their experimental error limits are validated. This gives the first-hand source for the direct determination of the water activity and the activity coefficient. Selection of pure substances as reference states in the water - sulfuric acid system is a suitable choice if temperatures are not too high, so that dissociation of sulfuric acid is still negligible.
2.3.4 \textbf{SO}_2-\text{H}_2\text{O} \textbf{system}

When \( \text{SO}_2 \) is dissolved in water, it may dissociate to some extent depending on its concentration, the presence of other ions and the pH of the solution (Rabe and Harris 1963; Siddiqi, et al., 1996; Pereda, Thomsen and Rasmussen 2000; Mondal 2007; Shaw, et al., 2011). Dissociation affects the solubility of \( \text{SO}_2 \) (Krissmann, Siddiqi and Lucas 1998; Maurer 2011). When the external pressure exceeds the vapor pressure of \( \text{SO}_2 \), a liquid \( \text{SO}_2 \) phase is formed due to the miscibility gap in the \( \text{SO}_2-\text{H}_2\text{O} \) system (Maass and Maass 1928; Shaw, et al., 2011). Increasing temperature decreases the solubility of \( \text{SO}_2 \) (Siddiqi, Krissmann and Lucas 1997a; Mondal 2007; Shaw, et al., 2011).

In earlier literature (e.g. Maass and Maass 1928) and as a consequence, in handbooks (e.g. Lyons and Nickless 1968; Müller 2008), sulfur dioxide dissolved in water is frequently referred to as sulfurous acid, \( \text{H}_2\text{SO}_3 \). According to more recent literature, the existence of sulfurous acid is very unlikely in aqueous solutions. However, Voegele, et al., (2002) managed to produce sulfurous acid. The molecule had a half-life of approximately 24 h in room temperature (300 K). They claim that water catalyzes the decomposition of \( \text{H}_2\text{SO}_3 \) into \( \text{SO}_2 \) and \( \text{H}_2\text{O} \), and when two water molecules are present, the half-life of \( \text{H}_2\text{SO}_3 \) is only 10 μs. Thus sulfurous acid is very short-lived in aqueous solutions. Hydrolysis or dissociation of \( \text{SO}_2 \) can be described with different reaction equations, which postulate different tetravalent sulfur species, e.g.: \((\text{SO}_2)_n(\text{n H}_2\text{O})\) (molecular \( \text{SO}_2 \) surrounded by \( \text{n} \) molecules of water), bisulfite \( \text{HSO}_3^- \) and sulfite \( \text{SO}_3^{2-} \).

Rabe and Harris (1963) studied the vapor pressures of \( \text{SO}_2-\text{H}_2\text{O} \) solutions at temperatures ranging from 30 to 80 °C. For the Henry’s law H constant they suggested equation (27):

\[
H = \exp\left(\frac{2851.1}{T} - 9.3795\right) \quad (27)
\]

Siddiqi, Krissmann, et al., (1996) and Siddiqi, Krissmann and Lucas (1997a, 1997b) studied the solubility of \( \text{SO}_2 \) in water. The amount of S(IV) present both in the liquid and the vapor phase was determined in situ using spectrophotometric methods (Siddiqi, Krissmann and Lucas (1997a, 1997b). The partial pressures of \( \text{SO}_2 \) ranged up to approx. 0.7 kPa. Siddiqi, et al., (1996) modeled the solubility of \( \text{SO}_2 \) using the Debye-Hückel theory to calculate the activities of ionic species formed by the dissociation...
tion/hydrolysis reactions of SO$_2$. The calculated and measured values agreed well at 293.15 K. Siddiqi, et al., (1996) compared the values predicted by their model with the experimental values given in Perry's Chemical Engineers' Handbook (Perry and Green 1984), and with the earlier experimental data of Rabe and Harris (1963). They concluded that the values quoted in Perry's are too high, while the modeling results agreed well with the results of Rabe and Harris (1963). They suggested that this model could be extended up to concentrations of 1 m and at least up to temperatures of 313.15 K. Regarding concentration, this is quite a peculiar suggestion, because usually the Debye-Hückel theory is considered to be reasonably accurate at ionic strengths of ≤ 0.1 m or even less (Levine 1978; Glueckauf 1959). Siddiqi, Krissmann and Lucas (1997a) extended the measurements up to 333 K. Their measured values agreed well with their model and the earlier experimental data from the literature.

To predict the solubility of SO$_2$ in water and to be able to extend the treatment to multi-component systems, Siddiqi, Krissmann and Lucas (1997b), used the Pitzer's model modified by Edwards to model the activities of ionic and molecular species. They fitted the model parameters with their own experimental data and then tested the parameters with earlier data reported in the literature. They found that the model was able to reproduce the literature values well with their parameters.

Pereda, Thomsen and Rasmussen (2000) used the extended UNIQUAC model for the binary H$_2$O-SO$_2$ system as part of a model for a multi-component system. They pointed out that if typical errors in vapor pressure measurement range from 5 to 10 %, deviations less than that are not likely to be obtained when the measured values are reproduced by calculations. The relative deviations are then highest at the lowest partial pressures of SO$_2$.

Mondal (2007) studied the absorption of SO$_2$ into distilled water. The temperatures at which the experiments were carried out ranged from 293 to 333 K, and the SO$_2$ pressures from 0.447 to 0.963 kPa. For the Henry's law constant, Mondal proposed equation (28):

$$lnH = -\frac{37.15.2}{T} + 16.765$$  \hspace{1cm} (28)
Mondal (2007) compared values calculated by equation (28) with his own experiments and earlier values from the literature up to 1 kPa, and found good agreement.

Shaw, et al., (2011) studied and modeled the solubility of SO\textsubscript{2} in water. The experiments were carried out at 25 and 40 °C and the pressures of SO\textsubscript{2} ranged from 0.2 to 3.6 atm. They used a model like Henry’s law for solubility and compared their modeling results with their own experiments and earlier experimental work. The model agreed well with experimental results at 40 °C, especially at pressures <3 atm, but at 25 °C, the model started to deviate from experimental results at 1.5 atm. At both temperatures, the model predicted higher solubility than that experimentally observed. Shaw, et al., (2011) suggested that the deviation at 25 °C could be caused by the formation of a second liquid phase not predicted by the model or that the model was unable to estimate the molecular interactions correctly at higher pressures. At pressures higher than 1-1.5 atm, the experimental data preceding the work of Shaw, et al., (2011) were quite sparse, especially at 25 °C.

From the work of Rabe and Harris (1963), Mondal (2007), and Shaw, et al., (2011) it can be concluded that a Henry’s law-like formulation predicts the solubility of SO\textsubscript{2} in water well at pressures less than 1-1.5 atm. This approach is much simpler than the Pitzer-type models.

2.3.5 \textbf{SO}_{2}-\textbf{H}_{2}\textbf{O}-\textbf{H}_{2}\textbf{SO}_{4} system

The solubility of SO\textsubscript{2} is lower in low concentrations of sulfuric acid than in pure water (Hayduk, Asatani and Lu 1988; Govindarao and Gopalakrishna 1993). This is explained by the effect of H\textsuperscript{+} ions on the dissociation or hydrolysis of sulfur dioxide. When the concentration of sulfuric acid is increased, the solubility behavior of SO\textsubscript{2} can be described as physical solubility, while in less acidic (or alkaline) solutions the solubility is enhanced by the “chemical solubility” caused by hydrolysis reactions or chemical reactions with other possible species present in the solution (Maurer 2011; Zhang, Wang, Dalla Lana and Chuang 1998).

Hayduk, Asatani and Lu (1988) reported SO\textsubscript{2} solubility data in 97 wt % sulfuric acid in the temperature range 298.2-323.2 K. Their experiments covered partial pressures of SO\textsubscript{2} ranging from 10 to 25 kPa and 101.3-405.2 kPa for pure SO\textsubscript{2}. They also evaluated earlier measurements in their paper. In their words, “a good deal of inconsistency is evident even in the regions
where overlapping of the earlier measurements occur." They concluded that Henry’s law could be used to predict the solubility at 293 and at 298 K, but that deviations occur at higher temperatures. To extrapolate solubilities, they suggested a Henry’s law-like, log scale formula, which defines the linear relationship between the molar fraction of the dissolved gas $x_p$ and the partial pressure of the gas even if Henry’s law is not obeyed:

$$p = hx_p$$  \hspace{1cm} (29)$$

$$\log p = \log h + \log x_p$$  \hspace{1cm} (30)$$

$$P = H + X$$  \hspace{1cm} (31)$$

The results of Hayduk, Asatani and Lu (1988) confirmed earlier observations that SO$_2$ has the minimum solubility in 85 wt % sulfuric acid, which corresponds to the equimolar concentration of sulfuric acid and water.

Hunger, Lapicque and Storck (1990) studied the solubility of SO$_2$ in sulfuric acid solutions at concentrations < 17 wt %. Temperatures were 25 and 50 °C and p(SO$_2$) ranged from $10^{-4}$ to 0.1 atm. They found that Henry’s law was valid for total pressures of less than 1 bar.

Besides carrying out solubility measurements, they also evaluated different methods used for the estimation of activity coefficients. They calculated the activity coefficients using two different methods. The first was the Bromley method. According to Hunger, Lapicque and Storck (1990), this model generally gives good results up to 6 m, but dissociation can affect the results. When using this model, they assumed the activity of water, and the activity coefficients of sulfuric acid and SO$_2$, to be unity. The second model that Hunger, Lapicque and Storck (1990) considered useful was Pitzer’s model modified by Beutier and Renon, but they tested it only for the SO$_2$-Na$_2$SO$_4$-H$_2$O system. Their main conclusion was that the influence of SO$_2$ on the thermodynamics of the H$_2$O-H$_2$SO$_4$ system could be ignored. They also concluded that dissociation of SO$_2$ happens to an appreciable extent only at sulfuric acid concentrations < 0.05 m, and that the pH of the solution reaches negative values at sulfuric acid concentrations > 1.8 m.

Govindarao and Gopalakrishna (1993) studied the H$_2$O-H$_2$SO$_4$-SO$_2$ system at low sulfuric acid concentrations <2.815 m and low partial pressures of SO$_2$ (190-1575 Pa) at 30-80 °C. They concluded that when the sulfuric acid concentration exceeds 0.37 m, Henry’s law is followed because the SO$_2$
exists in that case mostly in the molecular form. At lower concentrations, the dissociation or hydrolysis reactions of SO$_2$ affect solubility, which is not a linear function of the (partial) pressure of SO$_2$. For the temperature dependence of Henry’s law constant they gave the following equation:

$$lnH = 27.92 - \frac{3785.9}{T}$$  \hspace{1cm} (32)

Govindarao and Gopalakrishna (1993) suggested that this Henry’s law-type formulation of the solubility of SO$_2$ could be extended up to sulfuric acid concentrations <37 m (78.5 wt %). At higher concentrations sulfuric acid starts to dissolve SO$_2$, and another expression, which takes into account both the acid concentration and temperature should be used.

Krissmann, Siddiqi and Lucas (1997; 1998) studied the adsorption of SO$_2$ into sulfuric acid solutions. Krissmann, Siddiqi and Lucas (1997) carried out experiments at 298 K where the p(SO$_2$) was approx. 1 kPa. To model the solubility, they used Pitzer’s model modified by Edwards et al. They presented results for a sulfuric acid concentration ranging from 0 to 0.5 M, and stated that the experimental and calculated values agreed well. The calculated values also agreed with the measurements of Hunger, Lapicque and Storck (1990).

Zhang, Wang, Dalla Lana and Chuang (1998) studied the solubility of SO$_2$ in sulfuric acid solutions with concentrations of 60-96 wt % at temperatures ranging from 298 to 393 K. The partial pressures of SO$_2$ ranged from 96 to 258 kPa. They found that a function modified from Henry’s law could be used to predict the solubility in this concentration range. The Henry’s law constant depended strongly on temperature, and reached its maximum value at a sulfuric acid concentration of approx. 79 wt %. They suggested that ideal gas assumption is valid under these temperature and partial pressure ranges.

Gorensek and Summers (2009) and Gorensek, Staser, Stanford and Weidner (2009) modeled the H$_2$O-H$_2$SO$_4$-SO$_2$ system with an OLI Mixed solvent electrolyte package. Their aim was to model and optimize SDE as part of a model for the HyS process. The concentration range was from 0.1 – 70 wt % for H$_2$SO$_4$, and from 15.5 to 9.1 wt % for SO$_2$ (saturation or miscibility limit of SO$_2$). They claimed that the fit of the model could have been much better if the ternary system were in question, especially concerning the solubility of SO$_2$. The model used by Gorensek and Summers (2009)
and Gorensek, Staser, Stanford and Weidner (2009) dictated the assump-
tions that sulfuric acid is fully dissociated, and as a consequence, both sul-
fate and bisulfate are present in significant quantities over the entire con-
centration range. These assumptions were clearly not correct for the entire
concentration range of their work.

Based on the literature cited above, it can be concluded that Henry’s law-
like formulations can be used to predict the solubility of SO₂ in sulfuric acid
solutions ranging from 22 to 79 wt % provided that the external pressure
does not exceed the vapor pressure of SO₂. At lower concentrations, the
dissociation of SO₂ enhances solubility (“chemical solubility”). At higher
concentrations, the minimum solubility is reached, and the solubility is re-
ported to increase as a function of the sulfuric acid (or SO₃) concentration.

2.3.6 Change of cell potential with changing conditions

The effects of the concentration or activity of the components, and the
change in temperature and pressure on the cell potential (or emf) are given
by the Nernst equation (33), which defines the reversible cell potential E as
a sum of the standard potential E₀ and these additional factors:

\[ E = E₀ + \frac{RT}{zF} \ln \prod_j (a_j)^{v_j} \]  (33)

For SDE, the Nernst equation can be written slightly differently, depending
on the reaction scheme (and species) assumed. One example is equation
(34) (Appleby and Pinchon 1980):

\[ E = E₀ + \frac{RT}{zF} \ln \left( \frac{pH_2}{pSO₂} \left( \frac{(aHSO₄⁻)(aH⁺)}{(aH₂O)^2} \right) \right) \]  (34)

According to Appleby and Pinchon (1980), the reversible cell potential cal-
culated from the Nernst equation (34) is 0.22 V vs. HE in 44 wt %, but
approx. 0.4 V in 85 wt % at 60 °C. They found that the effect of temperature
on the cell voltage is small up to a concentration of 50 wt %. Lu and Am-
mon (1982) calculated the reversible cell potentials using the mean activity
coefficient for the sulfuric acid. At 50 °C and 1 atm, their calculated values
for 10, 30, and 50 wt % sulfuric acid were 0.13, 0.22 and 0.3 V, respective-
ly. The value obtained for 10 wt % sulfuric acid is lower than the standard
reversible potential for the oxidation of SO₂, and thus the activity values
used (but not cited) by Lu and Ammon (1982) seem to be inaccurate.
Gorensek, Staser, Stanford and Weidner (2009) calculated the reversible cell potential from the Nernst equation. To model the activities, they used the OLI MSE model together with Aspen Plus. In addition to the effect of concentrations, they studied the effects of temperature and pressure. At 80 °C, the calculated cell voltage was 0.45 V at a sulfuric acid concentration of 70 wt % (anode at 1 bar and cathode at 7 bar).

O’Brian, Hinkley, Donne and Lindquist (2010) used the method of Hunger, Lapicque and Storck (1990) to calculate the activity coefficients for sulfite, bisulfate and sulfate ions. They calculated the reversible cell potential as a function of pH, but assumed the concentrations of both H₂SO₄ and SO₂ to be constant (1 M). Even though such calculations have been presented in the literature (also for other systems), it is quite difficult to understand how the pH can change from one end of the scale to the other so that the concentrations of the components postulated are simultaneously constant. A solution containing 1 M H₂SO₄ and 1 M SO₂ with pH 14 is surely not a ternary solution of sulfuric acid, SO₂ and water.

The reversible cell potential of SDE is known to increase with increasing sulfuric acid concentration, but due to the restrictions of the models used to calculate activities or predetermined goals for the sulfuric acid concentration related to the HyS process, no calculations have been carried out for ranges up to concentrated (96 wt %) sulfuric acid.
2.4 Properties of Nafion membranes

A membrane used in a divided electrochemical process should combine relatively high proton conductivity with low electronic conductivity and act as a physical barrier to possible gas flows. Some gas, however, can cross the membrane through its pores with water (Barbir 2005). For the present work, Nafion 117 membrane was selected and used later in the experimental validation, although data for other Nafion materials were also used for comparison. Nafion 117 was reported to have the least SO₂ transfer capability from anolyte to catholyte (carry-over), which has to be avoided as it decreases SDE performance by forming elemental sulfur at the cathode (Steimke and Steeper 2006; Colon-Mercado and Hobbs 2007a; Staser and Weidner 2009).

Nafion is a cation-selective perfluorocarbon-sulfonic acid ionomer (PSA) (Barbir 2005). A PSA has a Teflon-like, hydrophobic PTFE backbone, whereas the hydrophilic ends of the side-chains of the membrane consist of SO₃⁻ and H⁺ ions. The microstructure of Nafion 117 is not exactly known and may depend on the manufacturing technology and on the thermal and chemical pretreatment processes (Mauritz and Moore 2004). The average equivalent weight (EW) of Nafion 117 is 1100 g/eq, i.e. 1100 g of polymer chain fraction per one sulfonic group -HSO₃ (Mauritz and Moore 2004; Barbir 2005).

Properties of Nafion-type membranes have been extensively studied, but almost exclusively for PEM fuel cell conditions (Mauritz and Moore 2004; Yan, Toghiani and Wu 2006; Himanen 2008; Gasik 2008; Myles, et al., 2011). For this application, various models, covering critical properties like membrane protonic conductivity and water transport, exist in the literature. However, these models are not readily applicable to SDE, because the conditions are rather different. The main differences of Nafion membrane in SDE and in the PEM fuel cell are a) presence of high concentration of SO₂ and its possible carry-over into catholyte space, b) the direction of protonic and water flux, and c) higher concentration of sulfuric acid and lower hydration levels of the membranes.

Verbrugge and Hill (1988; 1990a; 1990b; 1990c) studied and modeled the transport of water, bisulfate ions and protons in Nafion 117 equilibrated with sulfuric acid together with the pore structure of the membrane. According to
them, due to the high sulfonate ion concentration inside the pores of Nafion 117 membrane, HSO\textsubscript{4}\textsuperscript{−} (not SO\textsubscript{4}\textsuperscript{2−}) is the dominant ion when the membrane is immersed in sulfuric acid solutions. They suggested that the diffusion coefficients of protons and bisulfate ions could be correlated to their free-solution values (Verbrugge and Hill 1990c). The proton diffusion coefficient was reported to be the largest when the concentration of the sulfuric acid was 1 M (≈9.6 wt %), which coincides with the highest membrane conductivity. The measured water diffusion coefficient was then 5.3·10\textsuperscript{−6} cm\textsuperscript{2}/s (Verbrugge and Hill 1990a; 1990b; 1990c). The diffusion coefficient of HSO\textsubscript{4}\textsuperscript{−} was estimated to drop significantly at acid concentrations exceeding 3 M (≈25 wt %) (Verbrugge and Hill 1988). This is believed to be caused by the electrostatic repulsion of the fixed sulfonate ions, although specific adsorption of counter-ions would allow higher co-ion concentration inside the membrane (Verbrugge and Hill 1988). This transport model (Verbrugge and Hill 1990b) was based on the dilute solution theory, and is suitable for systems, which can be regarded as dilute in the transporting ion, and therefore not suitable for the whole concentration range relevant for SDE.

2.4.1 Membrane hydration and water activity

Membrane hydration (usually defined as the amount of water molecules per one sulfonic group, λ) is one of the key parameters determining the properties of the membrane. Eikerling, Kharkats, Kornyshev and Volkovich (1998) described the water content of a membrane (in contact with vapor) in a different way - as the ratio of the volume occupied by water to the volume of the full water-filled membrane, instead of using λ values. Maximal water content for the membrane equilibrated with liquid water at ambient conditions was reported to be λ\textsubscript{max} = 25 (Barbir 2005; Zawodzinski, et al. 1993a). This specifies the equivalent water molar fraction inside the membrane as X\textsubscript{w} = λ/(1 + λ). The water molar concentration (mol/m\textsuperscript{3}) is correspondingly

\[ C_w = \frac{\rho_w}{M_{EW}}, \]

(35)

with membrane density (for dry membrane ≈2000 kg/m\textsuperscript{3}) and molecular equivalent weight (1.1 kg/mol for Nafion 117). The density of the membrane depends on the water content (the membrane undergoes some swelling when the water fraction increases). At ambient conditions, the linear expansion was measured by Springer, Zawodzinski and Gottesfeld (1991) as 1+0.0126λ.
Parameter $\lambda$ is directly linked with the activity of water ($a_w$) inside the membrane. For example when the membrane is equilibrated with liquid water (activity $a_{w,l} = 1$), $\lambda = 22$ at 30°C and $\lambda = 17$ at 80°C (Motypally, Becker and Weidner 2000). For equilibration with saturated water vapor ($a_{w,v} = 1$), $\lambda = 14$ at 30°C. The presence of water is a prerequisite for the dissociation of the sulfonic acid groups to $\text{SO}_3^{-}$ and $\text{H}^+$ and for the mobility of hydrated protons (Motypally, Becker and Weidner 2000; Eikerling, Kharkats, Kornyshev and Volfkovich 1998). Springer, Zawodzinski and Gottesfeld (1991) made a cubic polynomial fit of the hydration ($\lambda$) to water activity in water-saturated vapor as:

$$\lambda_{v}(30^\circ \text{C}) = 0.043 + 17.81a_{w,v} - 39.85a_{w,v}^2 + 36a_{w,v}^3. \quad (36)$$

It is seen that this equation (36) assumes a small yet non-zero hydration level (~0.043) when water vapor activity (i.e. also water partial pressure) approaches zero. This means some water is formally supposed to be retained inside the membrane even when it is completely “dry.” The measurement of very low hydration values is difficult and it might be speculated that the equilibrium thermodynamic hydration degree of dry membrane should approach zero. For a higher water content (high $\lambda$) of the membrane, the water activity is normally assumed to be unity (Zhou, et al., 2007), but Meier and Eigenberger (2004) concluded based on their results that the non-ideality of water inside the membrane has to be taken into account. When a Nafion-type membrane is in contact with sulfuric acid solutions, the water activity definitely cannot be assumed to be unity – it strongly depends on the acid concentration and temperature. If dissolved $\text{SO}_2$ is present, ternary interactions should also be considered, especially because a miscibility gap is formed at elevated pressures in the (liquid) $\text{H}_2\text{O}$-$\text{H}_2\text{SO}_4$-$\text{SO}_2$ system.

### 2.4.2 Water transport through the membrane

The water flux across a Nafion-type membrane depends on several factors, the major ones being current density, electrolyte composition, temperature, and pressure. The net flux is composed of several partial contributions, which may act in opposite ways. The first, associated with electro-osmotic water drag, strongly depends on membrane hydration degree $\lambda$ and on current density. The second, water diffusion, is essentially non-linear and depends on temperature, $\lambda$ gradient and membrane type. The third is caused by the osmotic pressure gradient and is complemented by the hydraulic
part (D'Arcy flow), which depends on pressure gradient, temperature, membrane permeability, and $\lambda$ gradient.

### 2.4.2.1 Electro-osmotic water drag

The electro-osmotic water drag coefficient ($\xi$) is defined as the number of water molecules dragged per proton across the membrane (Springer, Zawodzinski and Gottesfeld 1991; Zawodzinski, et al., 1993a; Meier and Eigenberger 2004; Barbir 2005). This is based on the fact that a single proton cannot exist in aqueous media but immediately becomes solvated, forming $\text{H(H}_2\text{O)}_n^+$ cations. The molar flux of water (mol/m$^2$s) caused by this drag across the membrane is:

\[
J_{w,\text{drag}} = 2J_{H^+} \xi(\lambda) = \frac{i}{F} \xi(\lambda)
\]  \hspace{1cm} (37)

where $J_{H^+}$ is the protonic flux, $i$ is the current density and $F$ is the Faraday number (Sivasubramanian, et al., 2007; Yan, Toghiani and Wu 2006). The thermodynamic boundary values dictate that the drag coefficient would theoretically approach zero in a dry membrane. At maximal (saturated) hydration, the drag coefficient should reach maximum values, unless polarization effects are considered (at large current densities the water drag mechanism would be different from the pure electro-osmotic drag). In the literature, several equations and assumptions have been made of the value of the drag coefficient (LaConti, Fragala and Boyack 1977; Fuller and Newman 1992; Zawodzinski; Davey, Valerio and Gottesfeld 1995; Staser and Weidner 2009), which are not very consistent with each other.

### 2.4.2.2 Water diffusion in the membrane

Production or consummation of water on one side of the membrane together with water drag phenomenon can cause large concentration gradients across the membrane. Water diffusion, sometimes referred to as back diffusion, is caused by the water concentration gradient (Springer, Zawodzinski and Gottesfeld 1991; Zawodzinski, et al., 1993b; Barbir 2005; Yan, Toghiani and Wu 2006). There are various opinions about this water diffusion mechanism, but also a general consensus that the mechanism(s) depends on membrane hydration ($\lambda$) as well as external conditions (it might be different if the membrane is in contact with gas or liquid). Recently Myles, et al., (2011) compared different experimental methods to obtain water diffusion coefficient in membranes together with the assumptions related to these methods and their drawbacks, but it became evident from
their work that some evaluations of water diffusion are inconsistent and probably erroneous.

If only the water concentration gradient is present across the membrane (no electrical current and no pressure differential), water might be assumed to be the only diffusing component. Springer, Zawodzinski and Gottesfeld (1991) and Zawodzinski, et al., (1993a, 1993b) suggested that even if intradiffusion (intrinsic self-diffusion) takes place in the absence of (or with very low) concentration gradients, the immobility of the membrane allows the interdiffusion coefficient to be approximated using measured intra- or self-diffusion coefficients provided that these values are corrected regarding the variation of activity with the water content. Springer, Zawodzinski and Gottesfeld (1991) used both intradiffusion and interdiffusion coefficients, pointing out that they may not have the same values. They also correctly presented the thermodynamic driving force for water diffusion as a gradient of chemical potential (or activity) across the thickness of the membrane:

\[ J_{w,D} = -\frac{D_{id,w}}{RT} \nabla \mu_w = -D_{id,w} \nabla \ln a_w \]

and then substituted variables to express this activity \(a_w\) as a function of the gradient of \(\lambda\). Later Meier and Eigenberger (2004) mentioned that water transport due to the concentration or chemical potential gradient of water should not be described as simple diffusion. Therefore, the self-diffusion coefficient (as in the tracer diffusion concept) might not be applicable to this case, unlike in homogeneous liquid solutions. Xie and Okada (1995) suggested that the self-diffusion coefficient of water in a Nafion membrane is two or three times lower than the same in liquid water, additionally depending on the water content of the membrane.

However, when calculating the formal Fickian diffusion coefficient, a possible error appeared in the Springer, Zawodzinski and Gottesfeld (1991) paper using \(D\lambda\) (i.e. the product \(D\cdot\lambda\)) in the text instead of \(\lambda\) being just the index, \(D\lambda\) (as later in their text). This has led to one extra \(\lambda\) in their equation (20). Furthermore, their fitted hydration and activity equation as above leads to singularity at low \(\lambda\) values due to the singularity when differentiating the original equation (2) at low \(\lambda\) values. Later, Motupally, Becker and Weidner (2000) and a number of other authors, including recent publica-
tions (Myles, et al., 2011), have erroneously assigned the use of the Darken (thermodynamic) factor for the correction of diffusion coefficients as

\[ D_{w,Fick} = D_{w,id} \left( \frac{\partial \ln a_w}{\partial \ln \lambda} \right). \]  

(39)

The derivative (39) is however not the true Darken factor, because the latter is deduced from the second derivative of Gibbs energy by the molar concentration, not from the derivation by \( \lambda \) (Hillert 1998):

\[ D_{w,Fick} = D_{w,id} \left( \frac{\partial \ln a_w}{\partial \ln X_w} \right). \]  

(40)

The Darken factor is used in diffusion theory to express the interdiffusion and tracer diffusion coefficients (e.g. Weppner and Huggins 1977) only when the gradient of concentration is used instead of the gradient of chemical potential, since the latter already incorporates the necessary activity dependence, as noted by Springer, Zawodzinski and Gottesfeld (1991). Therefore when the gradient of water activity (not concentration) is used, no additional Darken correction factor is required.

To obtain the true Darken factor, the equation (39) commonly used in literature has to be additionally multiplied by \((1+\lambda)\) due to the relation \(X_w = \lambda/(1+\lambda)\). This gives a deviation by order of magnitude in the diffusion correction factor at high \(\lambda\) values, which is shown in Figure 6.

Figure 6 Comparison between “Darken factor” (39) by Motupally, Becker and Weidner (2000), and the true thermodynamic Darken factor (40).

For numerical evaluation, Motupally, Becker and Weidner (2000) made a numerical fit of \(D_{w,id}(\lambda)\), but unfortunately their polynomial leads to negative
values of the diffusion coefficient for $\lambda < 0.5$. This does not usually pose a problem for PEM conditions (high $\lambda$ values) but it might be critical for SDE conditions when the acid concentration becomes higher and the hydration becomes lower.

### 2.4.2.3 Water transport due to external and osmotic pressure

The third important component of water flux is a combination of hydraulic permeability flux and osmotic flux. Unfortunately, there is some confusion in the literature when dealing with the terms permeability, permittivity, and osmotic flow. For the purpose of clarity, the definitions used in the present work are given below:

**Permeability** ($k$) is the measure of the porous media topology and structure (depending on pore radii, porosity, tortuosity, etc.) which links the specific flow rate ($m^3/m^2\cdot s$ or $m/s$) with driving pressure gradient (Pa/m) and fluid viscosity $\eta$ (Pa·s) in the D'Arcy or Brinkman laws:

$$\dot{V} = \dot{u} = -\frac{k}{\eta} \nabla P$$ (41)

Permeability is a function of the porous media only and does not depend on the fluid properties, and its unit is surface area ($m^2$). However, if properties of the media are sensitive to the applied pressure, permeability may depend on the applied pressure gradient, and in that case a poroelastic-like model has to be employed.

**Osmotic permeability** ($k_{os}$) is the measure of the permeability of a porous material to conduct fluid flow under a purely osmotic pressure $\Pi$ gradient (in the absence of hydraulic pressure differential). It is similar to the D'Arcy formula; the difference being in the driving force and in the different sign (fluid moves against the hydraulic pressure gradient but forward to the osmotic pressure gradient):

$$\dot{V}_{os} = \frac{k_{os}}{\eta} \nabla \Pi, \quad \Pi = \frac{RT}{V_m} \ln a_w$$ (42)

The $k_{os}$ is often concentration-dependent. These definitions usually hold for saturated flow (no other fluids or gas bubbles in pores), ignoring extra gravity forces and other factors (such as applied electric or magnetic field).
Meier and Eigenberger (2004) defined hydraulic permeability and the water flux via the D’Arcy equation (41). They determined permeability for a single hydraulic pressure differential (yet uncorrected for membrane swelling due to \( \lambda \) variation). However, they applied the differences in the chemical potential of water on either side of the membrane (thus assuming a zero hydraulic pressure gradient) and normalized permeability using the internal water volume fraction. In their approach, the water concentration gradient causes the osmotic pressure gradient, which in turn causes a convective flux of water through the membrane opposing the electro-osmotic water drag.

They based their work on that of Eikerling, Kharkats, Kornyshev and Volkovitch (1998), who noted that if a membrane is saturated with water, the driving force of the water flow (opposing the electro-osmotic drag) is the gradient of hydraulic pressure (simple D’Arcy equation), while the situation is different if the membrane is not fully saturated. Meier and Eigenberger (2004) also assumed equality of water activities inside the Nafion membrane and in the gas phase in contact with the membrane, which is certainly not true – even if the water vapor and liquid water inside the Nafion membrane are in equilibrium, they definitely have different reference states of chemical potentials, so:

\[
\mu_{w,\text{mem}}^0 + RT \ln \alpha_{w}^{\text{mem}} = \mu_{w,\text{gas}}^0 + RT \ln \alpha_{w}^{\text{gas}} \quad \text{but} \quad \alpha_{w}^{\text{mem}} \neq \alpha_{w}^{\text{gas}}.
\]  

Permeability \((\text{m}^2)\) for \( \lambda < 30 \) was approximated by Meier and Eigenberger (2004) as

\[
k_p = (0.38 + 0.04\lambda + 0.014\lambda^2) \cdot 10^{-20}.
\]  

For equation (44), Meier and Eigenberger (2004) used data concerning the permeability of \( \text{O}_2 \) through a dry membrane. Adding an incorrect equation for electro-osmotic flow (where their estimated water drag approaches unity for a dry membrane instead of zero) but omitting the diffusion in the final equation has led to confusion in the numerical results in their paper when simulating different combinations of parameters.

In the paper of Staser and Weidner (2009), the Nafion permeability \( P_M \) was defined as the slope of the molar flux vs. applied pressure differential and expressed in \( \text{mol/cm}^2\cdot\text{s}\cdot\text{kPa} \). This is not the true permeability definition (which must be in units of surface area). Furthermore, when calculating water flux, Staser and Weidner (2009) additionally divided \( P_M \) by the mem-
brane thickness (i.e. to express the pressure gradient instead of the pressure differential), leading to incorrect water flux units in mol/m$^3$·s instead of mol/m$^2$·s. The expression of the hydration of the membrane given in Staser and Weidner (2009) also leads to negative water intake values if the water fraction drops below some finite limit.

2.4.3 Protonic conductivity

The protonic conductivity ($\kappa$, Sm/m) of a membrane is one of the most important properties to determine the limiting current density and ultimately the performance of an electrolyzer or a fuel cell. The conductivity of the membrane depends on its water content and on the temperature, and if in an application under current, on the current density. For example, in a fuel cell with a low hydration, the resistance of a membrane in a fuel cell at zero current is 15...35 % higher than the specific resistance of a Nafion membrane in contact with liquid water (Büchi and Scherer 1996). For $\lambda > 5$, the relationship between $\lambda$ and proton conductivity was reported to be almost linear (Barbir 2005). The protonic conductivity of a membrane increases strongly with temperature (Zawodzinski, et al., 1993a; Springer, Zawodzinski and Gottesfeld 1991).

Normally in liquid water-acid solutions, the contribution of the vehicular diffusion of protons (protons moving when carried by water molecules) increases with decreasing water concentration while the structural diffusion of protons dominates at higher water concentrations (Zhou, et al., 2007; Zawodzinski, et al., 1993b). Structural diffusion (also known as the Grotthus mechanism (Mauritz and Moore 2004)) was however reported by Zhou, et al., (2007) to contribute only to about a half of the total diffusivity of protons in Nafion 117 membranes at $\lambda = 22$ (full hydration).

Based on the literature reviewed above, it can be concluded that water transport through a Nafion-like membrane is a complicated phenomenon, and that the models presented in the literature cannot be used for an SDE process with liquid electrolytes without modification.
3 Theoretical work

3.1 Thermodynamic assessment of the $\text{H}_2\text{SO}_4$-$\text{H}_2\text{O}$-$\text{SO}_2$ system

In the present work the goal was to find the activity or activity coefficient of a component as a function of the concentration to be used for modeling SDE. No model able to cover all the concentration range was found from the literature, and thus a new model was elaborated. Component-based mathematical treatment was selected in order to be able to extend the model for the whole concentration range relevant for SDE. This approach is an expansion of the calculation of the activities of the pseudobinary sulfuric acid/water system (Lokkiluoto and Gasik 2012). Another option would have been a treatment based on speciation. As a result of this selection, speciation of sulfuric acid and aqueous solutions of $\text{SO}_2$ are not further discussed.

The dissociation of sulfuric acid has been studied for example by Young, Maranville and Smith (1959), Chen and Irish (1971), Bolsaitis and Elliot (1990), Hunger, Lapicque and Storck (1990) and Sippola (2012). Bollas, Chen and Barton (2008) evaluated the predictive quality of various models regarding the correct description of speciation. The dissociation or hydrolysis reactions of dissolved $\text{SO}_2$ have been discussed for example by Lyons and Nickless (1968), Hunger, Lapicque and Storck (1990), Siddiqi, et al., (1996), Siddiqi, Krissmann and Lucas (1997a, 1997b), Mondal (2007), and O’Brien, Hinkley, Donne and Lindquist (2010).

3.1.1 $\text{H}_2\text{SO}_4$-$\text{H}_2\text{O}$ pseudobinary

The molar fraction was taken as the concentration scale and pure components (sulfuric acid and water) at constant temperature (298.15 K) and total pressure (1 bar) were selected as reference states. A straightforward derivation of (26) by $X_1$ and substitution into (24) leads to an expression, which could be readily integrated:

$$\ln \gamma_2 = \sum_{i=3}^{N} a_i (1 - X_i)^{i-2} \left( \frac{i-1}{i-2} \right) - \ln \frac{1}{1+X_1} + C,$$

where integration constant $C$ is defined from the boundary conditions – the reference state of component 2. If this is a pure component, $\ln \gamma_2 = 0$ when $X_2 \to 1$, then $C$ is:
\[ C = \sum_{i=3}^{8} a_i \left( \frac{i-1}{i-2} - 1 \right) . \] (46)

Its physical meaning is \( C = \ln \gamma_2^\infty \), i.e. it is the logarithm of the activity coefficient of component 2 at infinite dilution. Because \( C \) is always real (46), the activity coefficient of any substance at infinite dilution will always be a positive definite (the relation (25) holds). The coefficients of the polynomial for the \( \text{H}_2\text{O}-\text{H}_2\text{SO}_4 \) system are shown in Table 2 and the calculated activity coefficients in Fig. 7. The experimental data used for the fitting are listed in Table 1.

**Table 2 Polynomial coefficients for equations (45) and (46).**

<table>
<thead>
<tr>
<th>Polynomial coefficient power ( (i) )</th>
<th>Coefficient value ( (a_i) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>-43.7257</td>
</tr>
<tr>
<td>4</td>
<td>+57.17556</td>
</tr>
<tr>
<td>5</td>
<td>-44.1760</td>
</tr>
<tr>
<td>6</td>
<td>+30.96849</td>
</tr>
<tr>
<td>7</td>
<td>+5.237048</td>
</tr>
<tr>
<td>8</td>
<td>-2.06512</td>
</tr>
<tr>
<td>9</td>
<td>-30.5754</td>
</tr>
<tr>
<td>10</td>
<td>+15.58557</td>
</tr>
</tbody>
</table>

\[ C = \ln(\gamma_{\text{H}_2\text{SO}_4}) \] -23.8376
Figure 7 Water activity coefficient vs. acid molar fraction. Error limits of ±5% are for the data of Giauque, Hornung, Kunzlear and Rubin (1960).

The polynomial coefficients in the equations above do not have any direct physical meaning and they are generally not the same as Wagner’s interaction parameters, defined by partial derivation for dilute estimates during the Taylor’s series expansion (Hillert 1998; Kubaschewski and Alcock 1979). The calculated activity coefficients of water (26) and sulfuric acid (45) are shown in Fig. 8.
Figure 8 Calculated $\ln \gamma$ for water and sulfuric acid vs. acid molar fraction at 25°C.

It is noteworthy that for this high concentration range, there are very few reliable data available and in many cases it has been extrapolated to 25°C either from high (boiling point) or low (freezing point) temperature measurements (Greenewalt 1925; Massucci, Clegg and Brimblecombe 1996; Zeleznik 1991). Thus comparison of previously published data on activities in this system makes sense only for water, because there are good correlated data on water vapor measured by different methods. Fig. 9 shows the calculated activities of water and sulfuric acid at 25°C, where the water activities were directly assessed from the water vapor pressure and the acid activities were calculated with (45) using the Gibbs-Duhem equation integration.
Figure 9 Calculated activities of water and sulfuric acid at 25°C (pure components as reference states).

Fig. 9 shows that the system is essentially non-ideal and for acid molar fractions <0.2 (~59 wt %), the activity of sulfuric acid is low.

The change in the Gibbs energy of the mixing of sulfuric acid and water is shown in Fig. 10.

Figure 10 Gibbs free energy of mixing in the H$_2$O-H$_2$SO$_4$ system.

It can be seen that the minima of the excess and the total mixing Gibbs energies are around 78 wt % acid (molar fraction ~0.4 or ~36 $m$). This
might be one of the reasons for the disagreement of different results for molalities \( m > 40 \) because in that case the solvent becomes essentially acid-rich and not water-rich, so the assumption of water as the main solvent component is no longer valid.

### 3.1.2 \( \text{SO}_2-\text{H}_2\text{O} \) and \( \text{SO}_2-\text{H}_2\text{SO}_4 \) binaries

Tabulated water activity data based on water vapor pressure measurements together with the amount of dissolved \( \text{SO}_2 \) (in the concentration scale) from literature data at 20-30°C were used to derive a polynomial fit of the activity and the free energy of solvation at 25°C and 1 atm. The sources of experimental data used are listed in Table 3.

**Table 3 Sources of data used for calculations.**

<table>
<thead>
<tr>
<th>Author</th>
<th>( \text{SO}_2 )</th>
<th>( T )</th>
<th>( \text{H}_2\text{SO}_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hayduk, Asatani and Lu, 1988</td>
<td>10-405.2 kPa</td>
<td>298.2, 323.2 K</td>
<td>97 wt %</td>
</tr>
<tr>
<td>Zhang, Wang, Dalla Lana and Chuang, 1998</td>
<td>96-258 kPa</td>
<td>298, 383, 393 K</td>
<td>60–96 wt %</td>
</tr>
<tr>
<td>Hunger, Lapicque and Storck, 1990</td>
<td>10^-0.1 atm</td>
<td>25 and 50 °C</td>
<td>&lt; 2 M (17 wt %)</td>
</tr>
<tr>
<td>Govindarao and Gopalakrishna, 1993</td>
<td>190-1575 Pa</td>
<td>30-80 °C</td>
<td>0-2.815 ( \text{m} )</td>
</tr>
<tr>
<td>Siddiqi, et al., 1996</td>
<td>&lt; 0.534 kPa</td>
<td>298.15 K</td>
<td>0</td>
</tr>
<tr>
<td>Krissmann, Siddiqi and Lucas, 1997</td>
<td>~1 kPa</td>
<td>298</td>
<td>0-0.5 M</td>
</tr>
<tr>
<td>Mondal, 2007</td>
<td>0.447-0.963 kPa</td>
<td>293-333 K</td>
<td>0</td>
</tr>
<tr>
<td>Siddiqi, Krissmann and Lucas, 1997a; 1997b</td>
<td>0.01-0.7 kPa</td>
<td>298-333 K</td>
<td>0</td>
</tr>
<tr>
<td>Nikolsky et al., 1965 (handbook)</td>
<td>0-1032 mmHg</td>
<td>10-110 °C</td>
<td>0</td>
</tr>
</tbody>
</table>

An example of activities in the \( \text{H}_2\text{O}-\text{SO}_2 \) system for 20 and 30°C is shown in Fig. 11.
Figure 11 Activity of SO₂ by direct measurements of both water and SO₂ pressures (Nikolsky et al. 1965) as a function of $X_{SO₂}$ dissolved up to saturation (the activity reference state).

Numerical fitting of the activity or activity coefficient is prone to larger errors due to the scatter of experimental points. Therefore, experimental data like that presented in Fig. 11 were first converted into the free energy of the solution. This free energy was fit using a standard polynomial model:

\[
G_{mix}(x) = G_{id}(x) + G_{ad}(x); \quad G_{id}(x) = RT \left( x \ln(x) + (1-x) \ln(1-x) \right); \\
G_{ad}(x) = x (1-x) \left( L_{00} + (1-x)L_{10} + xL_{01} + (1-x)^2L_{20} + x^2L_{02} \right)
\]

(47)

where $L_{ij}$ are the unknown interaction parameters to be found and $x$ is the molar fraction of SO₂ in the binary system. An example of fitting for 20°C is shown in Fig. 12 and the estimated free energies at different temperatures in Fig. 13. For example, data for 25°C and 1 bar might be well described by the set of parameters: $L_{00} = 11689.02$, $L_{10} = 4524.8913$, $L_{01} = 10666.98$, $L_{20} = -8499.6776$, $L_{02} = 2957.9001$ (all in J/mol).
Figure 12 Integral Gibbs energy of H$_2$O-SO$_2$ solutions at 20°C. Experimental points come from different sources listed in Table 3, and the line presents polynomial fitting by Eq. 47.

Figure 13 Calculated integral Gibbs energies of H$_2$O-SO$_2$ solutions at different temperatures and 1 atm total pressure.

In the same way as for the SO$_2$-H$_2$O system, data for solubility of SO$_2$ in concentrated sulfuric acid were used (Zhang, Wang, Dalla Lana and Chuang 1998; Nikolsky et al. 1965). There is much less reliable data published for pure sulfuric acid so in uncertain cases the SO$_2$ solubility curves in diluted and concentrated (97-99 wt % H$_2$SO$_4$) were used to extrapolate solubility towards pure acid. The same fitting model as above (47) was
used and this binary system was found to be adequately described by $L_{00} = 5636.322$, $L_{10} = 22160.926$ and $L_{20} = -2390.474$, setting $L_{01}$ and $L_{02}$ to zero. Although a better fit might be obtained with more parameters, it was considered unreasonable due to the scarcity of experimental data.

3.1.3 $\text{H}_2\text{SO}_4$-$\text{H}_2\text{O}$-$\text{SO}_2$

For the ternary system, data and evaluations of the respective binaries were employed. In the liquid phase, the solubility of $\text{SO}_2$ is now a function of the acid concentration and this means that the reference state (saturation of $\text{SO}_2$ in the liquid) is a dynamic one. Using the experimental data listed in Table 3, a numerical fitting for the saturated $\text{SO}_2$ concentration (molar fraction) was made (25°C):

$$X^*_\text{SO}_2(Y) = 0.0358 \ Y^4 - 0.0389 \ Y^3 + 0.0845 \ Y^2 - 0.0441 \ Y + 0.0277$$

(48)

where $Y$ is the molar fraction ratio of acid in the $\text{SO}_2$-free solution ($Y = X_{\text{H}_2\text{SO}_4} / (X_{\text{H}_2\text{O}} + X_{\text{H}_2\text{SO}_4})$). As in the thermodynamic reference state, this composition will have unity $\text{SO}_2$ activity and the reverse of $X^*_{\text{SO}_2}$ is equal to the coefficient of activity in the saturated state. As can be seen from Fig. 14, these calculated $\text{SO}_2$ concentrations correspond very well to the experimental data.

![Figure 14 Calculated (48) vs. measured (references in Table 3) $\text{SO}_2$ solubilities in different sulfuric acid solutions at 25°C.](image)

The free energy of the ternary mixture is described by (49), where $G^\text{los}$ is the ternary excess term:
\[ G^{\text{id}} = RT \left( X_{\text{H}_2\text{O}} \ln(X_{\text{H}_2\text{O}}) + X_{\text{H}_2\text{SO}_4} \ln(X_{\text{H}_2\text{SO}_4}) + X_{\text{SO}_2} \ln(X_{\text{SO}_2}) \right), \]
\[ G^{\text{mix}} = X_{\text{H}_2\text{O}}X_{\text{H}_2\text{SO}_4}X_{\text{SO}_2}(L_{111} + X_{\text{H}_2\text{O}}L_{211} + X_{\text{H}_2\text{SO}_4}L_{121}) \]  

(49)

The form of the excess mixing contribution depends on the method used for mixing the binary system data into the ternary triangle (Lupis 1983; Hillert 1998). In the present work the symmetric method of Muggianu (Muggianu, Gambino and Bros 1975) has been used. If the three components (water, acid and SO\(_2\)) are marked with \( i, j \) and \( k \) indices, then the equations could be written as:

\[ G^{\text{mix}}_{ij} = \frac{4X_iX_j}{(2X_i + X_k)(2X_j + X_k)} G^{\text{str}}_{ij}(Y_i, Y_j); \quad Y_{ij} = X_i + \frac{X_k}{2} \]
\[ G^{\text{mix}} = G^{\text{mix}}_{ij} + G^{\text{mix}}_{ik} + G^{\text{mix}}_{jk} \]  

(50)

where all the combinations of the mixing energy are calculated by changing the respective indices. Other methods for calculating ternary Gibbs energy exist, which usually result in ±10-15% differences. As this is close to the uncertainty of the experimental data, the Muggianu’s approximation was considered to be quite sufficient. The experimental data fit to the whole ternary system energy (49) and (50) led to the values of the ternary parameters as \( L_{111} = -60000 \), \( L_{211} = -3000 \) and \( L_{121} = -35000 \) J/mol. As in the binary cases, a better fit might be obtained with more parameters but it is not justified if no reliable experimental data are available.

The calculated Gibbs energies for this ternary system (the sum of \( G^{\text{id}} \), \( G^{\text{mix}} \) and \( G^{\text{bs}} \)) are shown in Fig 15. As follows from this contour plot, additions of sulfuric acid give the main contribution to the free energy variations. Highly positive values in the SO\(_2\)-rich corner correspond to the two-phase area of saturated liquid and SO\(_2\)-rich gas (i.e. the area where the liquid composition no longer changes with increasing of SO\(_2\) concentration in the system; only changes related to sulfuric acid affect free energies and the saturation limits).
Figure 15 The free Gibbs energy in the ternary SO$_2$-H$_2$SO$_4$-H$_2$O system at 25°C.

The calculated activity coefficients for water and sulfuric acid are shown in Figures 16 and 17.

Figure 16 Activity coefficient of water in the H$_2$SO$_4$-H$_2$O-SO$_2$ system in the area of the only liquid phase equilibrium up to SO$_2$ saturation at 25°C and 1 atm.
Based on thermodynamic analysis it can be concluded that SO2 has a minor effect on the liquid phase thermodynamic functions at ambient conditions; acid concentration is the most critical variable. This agrees with earlier predictions known in the literature, however here the consistent vapor-liquid equilibria was numerically described and fitted to the experimental data, which now provides the opportunity to apply these thermodynamic values for SDE conditions.

3.1.4 Change of equilibrium cell potential for thermodynamic reasons

The driving force for the overall electrochemical reaction in SDE can be written as

\[ 2H_2O + SO_2(aq) = H_2SO_4(aq) + H_2(g), \]

\[ \Delta G = \Delta G^\circ + RT \ln \left( \frac{P_{H_2} a_{H_2SO_4}}{a_{SO_2} a_{H_2O}^2} \right). \]  

(51)

As seen in (51), an increase in acid activity and decrease in the activities of SO2 and water increase the free energy and decrease the driving force. The reaction would theoretically proceed until the \( \Delta G \) value became zero. The last term in (51) can be converted to a thermodynamic overpotential component, which might be considered an extra term required to perform the reaction. In Figure 18, the change of this component of the cell voltage.
for SDE is shown with changing concentrations (activities) of H₂O, H₂SO₄, and SO₂.

Figure 18 Calculated H₂SO₄-H₂O-SO₂ equilibrium overpotential additionally required to perform the SDE reaction. The dark top line depicts the SO₂ saturation limit.

It is seen that dissolved SO₂ has a minor effect on the thermodynamic overpotential. When the sulfuric acid concentration increases, the required potential also rises almost linearly until the acid concentration reaches ~0.5 (~80-85 wt. %). After that the voltage changes much more slowly. This trend agrees with earlier predictions from the literature, although the numerical values are different as most of the experimental data for SDE were obtained at higher temperatures (60-85°C) and hydrogen pressures.

3.2 Properties of a Nafion-type membrane in SDE conditions

3.2.1 Membrane hydration and water activity

To model the water transport through a Nafion membrane used in SDE conditions, several new correlations were found necessary (Lokkiluoto and Gasik, 2013). For atmospheric pressure and the assumption of zero SO₂
presence in the membrane, a new fit of water activity and hydration was made for the equilibrium with liquid electrolytes:

$$\lambda_v(30^\circ C) = 27.944a_w - 65.55a_w^2 + 59.033a_w^3$$

(52)

Although the differences with the equation of Springer, Zawodzinski and Gottesfeld (1991) (36) are minor, with (52), the thermodynamic dilution limit is correctly implemented: zero water activity should theoretically correspond to a zero water fraction, otherwise the definition of the chemical potential is violated.

### 3.2.2 Water transport through the membrane

#### 3.2.2.1 Electro-osmotic water drag coefficient $\xi$

In the present work an approximation for the water drag coefficient $\xi$ was made in the form of a simple equation, which reflects the boundary conditions and reproduces most of the experimental results within the practically relevant accuracy:

$$\xi_v = \frac{\sqrt{\lambda_v}}{3}, \quad \xi = \frac{\sqrt{\lambda}}{2}$$

(53)

for equilibrium with saturated water vapor (index $v$) and liquid water, respectively. Fig. 19 shows calculated values in comparison with other published data. It can be seen that the equation (53) slightly underestimates drag coefficient values at saturation, but passes through most of the experimental values at lower water hydration, which is exactly the region of interest of SDE.
3.2.2.2 Water diffusion in the membrane

By substituting variables and making rearrangements, as done by Springer, Zawodzinski and Gottesfeld (1991), a new expression for the Fickian diffusion coefficient might be written as (54):

$$D_{w,\text{Fick}} = D_{w,\text{id}} D_{\text{corr}}(\lambda) = \frac{D_{w,\text{id}} \lambda}{(1 + 0.0126 \lambda)^2} \frac{\partial \ln a_w}{\partial \lambda}$$

(54)

The difference in the correction factor used in equation (54) obtained with the true thermodynamic Darken factor (40) instead of equation (39) is shown in Fig. 20.
Equation 54 has no numerical singularities within the whole relevant range of $\lambda$ and provides a consistent thermodynamic description of the diffusion flow as:

$$J_{w,D} = -\frac{D_{w,Fick}(\lambda) \rho_{dry}}{M_{EW}} \nabla \lambda = -D_{w,eq} \nabla \lambda,$$  

(55)

where the equivalent diffusion coefficient is used to mimic Fick law behavior. The original numerical data of Springer, Zawodzinski and Gottesfeld (1991) have been re-fitted using a non-linear procedure (coefficient expressed in m$^2$/s):

$$D_{w,eq}(\lambda) \cdot 10^{10} = \frac{4.403106}{1 + \exp \left( -\frac{\lambda - 5.2833}{1.68443662} \right)} (0.44145 + 0.04037 \lambda).$$  

(56)

with a high correlation (DOF adjusted $r^2 = 0.99957651$). This fit (56) does not lead to negative diffusion coefficient values even at zero hydration. Simplifying the numerical expressions, for Nafion 117 at 25-30°C the water equivalent flux coefficient (mol/m·s) is obtained as:

$$D_{w,eq}(\lambda) = \frac{(17670.4 + 1615.9262 \lambda)(340632 + 10973575 \exp(8.8355 - 4.349\sqrt{\lambda})) \sqrt{\lambda}}{(5000 + 63 \lambda)^2 (1 + \exp(3.313654 - 0.5937 \lambda))(1 + \exp(8.8355 - 4.349\sqrt{\lambda}))} \cdot 10^{-10}$$  

(57)
This equation (57) incorporates all values for membrane density, swelling effect, water activity derivative, equivalent weight, etc. (even if the mechanism of the diffusion is not constant, and may not even be true diffusion). The dependence of this coefficient is shown in Fig. 21, together with the diffusion coefficient as fitted by Motupally, Becker and Weidner (2000). This correlation should not be considered as an indication of any particular diffusion mechanism — it is an engineering formula aiming at the correct description of the water diffusion process.

![Figure 21 Equivalent flux coefficient (mol/m·s) at 30°C in Nafion 117: solid line – present work (57), dotted line – calculated from Motupally, Becker and Weidner (2000) (including density and molar weight). Note for the latter singularity at λ ~ 0.043 and negative values for λ < 0.51.](image)

### 3.2.2.3 Water transport due to external and osmotic pressure

Xie and Okada (1995) assumed the interstitial viscosity of water in a membrane to be triple of that of pure water, while Eikerling, Kharkats, Kornyshev and Volfkovich (1998) assumed the viscosity of water inside the membrane to be the same as that of water. In the present work, the latter assumption was used since there is not yet enough experimental evidence to select other water viscosity values.

The complete equation for the porous saturated flow driven by pressure gradients should be expressed as

\[
J_{w,\text{pres}} = \frac{\lambda \rho_{\text{mem}}}{M_{\text{EW}}} \left( -\frac{k}{\eta} \nabla P + \frac{k_{\text{os}}}{\eta} \nabla \Pi \right),
\]

(58)
Taking into account variable substitution, this may be rewritten in terms of the gradient of $\lambda$. For example, in the case of a zero porous flow (i.e. only osmotic flux):

$$J_{w, osm} = - \left( k_{osm}(\lambda) \frac{\lambda \rho_{mem} RT}{M_{EW} \eta V_M} \frac{\partial \ln a_{w}^{mem}}{\partial \lambda} \right) \nabla \lambda = -K'_{osm}(\lambda) \nabla \lambda$$

which has the same form as the diffusion flux equation (55) and must be added to the total water flux sum. The contributions of (55) and (59) are shown in Fig. 22 as a function of the membrane hydration.

![Figure 22](image)

**Figure 22** Equivalent flux coefficient and osmotic flux coefficient contributions (mol/m·s) as a function of membrane hydration (note log X scale).

As these coefficients are multiplied by the same gradient of $\lambda$, it is seen that the contribution of the diffusion part is in this case marginal, having its maximum at $\lambda \sim 4.5$, which is nevertheless by order of magnitude smaller than the osmotic coefficient contribution. This effect of the diffusive contribution has been studied in many experiments and might be one of the reasons why even an incorrect diffusion coefficient expression as shown in Figures 20 and 21 did not lead to significant variations in fitting the experimental data.

### 3.2.2.4 Net water flux in the membrane

The total water flux additionally has an electro-osmotic contribution (or more correctly, a protonic drag effect). According to Yan, Toghiani and Wu (2006), water transport through a membrane due to external pressure gradients alone is usually negligible compared to the electro-osmotic drag and
back diffusion, because typical membranes have very low hydraulic permittivity and this might be ignored in most operating conditions. Thus the final equation for the net water flux (ignoring purely hydrodynamic permeation) will take the form:

\[
J_{w,net} = \left( -D_{w,eq}(\lambda) + K_{w,eq}^+(\lambda) \right) \nabla \lambda + \frac{i}{F} \xi(\lambda).
\] (60)

This flux will be constant in the case of steady state operation of SDE. In such a case, the hydration distribution inside the membrane (along the relative coordinate \(x\)) could be found from the equation (60), solved for unknown \(\lambda(x)\). Fig. 23 demonstrates the solution of this differential equation for 20 wt % acid in the anolyte and 1000 A/m² current density – here the net flux was specified and the hydration distribution inside the membrane was numerically solved.

![Figure 23](image)

**Figure 23** Calculated distribution of hydration in the Nafion 117 membrane for 1000 A/m² current density and 20 wt % sulfuric acid in the anolyte for three different net flux values (60).

Equation (60) is applicable for both PEM fuel cells and SDE, as the only difference is in the boundary conditions (current direction, water activities on both sides and net water generation rates being positive for the fuel cell (oxidation of hydrogen) and negative for SDE (oxidation of \(SO_2\)).
3.2.3 Protonic conductivity

Another fit of experimental data was used taking into account a slight non-linearity in the dependence of conductivity with hydration, and an example of the calculated conductivity values for 30°C data with equation (61) is shown in Fig. 24.

$$\kappa = \frac{\lambda (1 + 0.07335\lambda)}{2.060411 + 0.167712\lambda} \exp\left(4.088 - \frac{1229}{T}\right). \quad (61)$$

![Figure 24 Protonic conductivity of Nafion 117 membrane at 30°C with literature data and the fit using equation (61).](image)

3.3 The model for SDE

Catholyte and anolyte acid concentrations were calculated using the above equation (60), complemented by the water consumption according to the reaction $\text{SO}_2(\text{aq}) + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4(\text{aq}) + \text{H}_2(\text{g})$ (4). The water activity needed for the calculation of the fluxes was evaluated using the model described above. The model calculations were executed as a MathCAD 13.0 worksheet and the output values of acid concentrations in the anolyte and catholyte were calculated at a fixed current density of 910 A/m$^2$ and a temperature of 25°C. The net water flux was included taking the finite difference between the hydration values from the anolyte and catholyte sides of the membrane into (60) instead of explicit gradients. The possible evaporation of water with vented hydrogen was ignored.
The model includes water transport and changes in the cell voltage due to changes in electrolyte compositions (both thermodynamic and those caused by changes in the conductivity of electrolytes and the membrane). The changes in the conductivity of the electrolytes with changing concentration were fitted numerically from tabulated data given in Lobo (1989).

The results of the calculation are compared with experimental data in the next section.
4 Experimental work

4.1 Materials and chemicals

The materials studied included 904L steel, gold, and gold coatings. Performance of gold coatings was compared with pure gold and with commercial platinum-coated titanium electrodes. The performance of 904L steel was studied to evaluate the stability of the coatings on that substrate.

The specification of 904L steel is C max 0.020, Si max 0.70, Mn max 2.00, P max 0.030, S max 0.010, Cr 19.0-21.0, Mo 4.00-5.00, Ni 24.0-26.0, N max 0.15 and Cu 1.20-2.00 (Wegst 2001). The EN/DIN code of 904L steel is 1.4539, while the code 904L is according to ASTM/UNS.

For autoclave corrosion and linear sweep voltammetry tests, 904L was used in a disc shape. Samples were sawn and rotary-cut from a 904L steel bar. The bar was supplied by Harald Pihl Oy. The thickness of the discs was approx. 2 mm and their diameter was 15.5 mm. Subsequently, the sample preparation before coating varied.

For the SDE tests, electrodes prepared from a 904L sheet were used. The material was supplied either by ElectroCell or by Outokumpu.

All the gold coatings were manufactured by Diarc-Technology Oy using their own low-temperature PVD method.

Two disc-shaped samples with the same dimensions as the 904L samples were prepared from a gold sheet. The gold sheet was supplied by Kultakeskus Oy, and was of K999 purity.

The reagents used were 95-97 wt. % sulfuric acid, distilled water, anhydrous Na$_2$SO$_3$ and gaseous SO$_2$. The Na$_2$SO$_3$ was from Merck, and was of analysis grade. The sulfuric acid came from Merck, J.T. Baker, or Sigma Aldrich, and was of analysis or reagent grade. The compressed gaseous SO$_2$ was scientific gas from AGA/The Linde Group.

4.2 Methods

4.2.1 Autoclave experiments

Autoclave experiments were carried out to study the effect of the temperature, sulfuric acid concentration and presence of SO$_2$ on the stability of thin
gold coatings and on the corrosion performance of 904L stainless steel. The autoclave equipment concept is shown in Figure 25.

![Figure 25 Autoclave system set-up.](image)

The samples were fastened into sample holders, which were fastened to the stirrer rod. The autoclave was filled with sulfuric acid so that the test samples together with the sample holder were covered. After that the autoclave was purged with nitrogen for 2-3 hours. The purging time was selected so that the gas space would be changed twice during the purging with a gas flow of 1L/min. Some of the experiments were carried out in a nitrogen atmosphere, and part in an SO\textsubscript{2} atmosphere. Pure gaseous SO\textsubscript{2} was fed to the autoclave after nitrogen purging.

The first series of autoclave tests was performed as the experimental part of T. Kuikka's diploma work (Kuikka 2010). The test matrix can be seen in Table 4. Here the stirring was continuous. The materials tested included bare 904L steel, and 904L coated with Au. Before coating, the samples were polished first with SiC paper, grades 240, 400 and 1200, and after that with 6, 3 and 1 μm diamond pastes. The target thickness of the gold coating was 100 nm. Duplicate samples were tested.
Table 4 Autoclave test matrix of the first test series.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>H$_2$SO$_4$ [wt %]</th>
<th>Gas</th>
<th>T [°C]</th>
<th>Duration [d]</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>N$_2$</td>
<td>30</td>
<td>15</td>
</tr>
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<tr>
<td>6</td>
<td>80</td>
<td>N$_2$</td>
<td>50</td>
<td>14</td>
</tr>
<tr>
<td>7</td>
<td>80</td>
<td>SO$_2$</td>
<td>30</td>
<td>14</td>
</tr>
<tr>
<td>8</td>
<td>80</td>
<td>SO$_2$</td>
<td>50</td>
<td>14</td>
</tr>
</tbody>
</table>

When the test was finished, the samples were rinsed with distilled water and dried, and analyzed by optical microscopy. Some selected samples were also analyzed by SEM. Additionally, untested reference samples were analyzed with a microscope. All specimens were weighed before and after the experiments to ensure the identification of the samples. No mass losses that were significant enough for any conclusions to be made were observed.

The test matrix of the second test series is shown in Table 5. The aim of the second test series was to study the stability of gold coatings over a longer time scale, and to study the effect of the substrate roughness on the stability. All the experiments were carried out at 30 °C and the duration of the tests was 2 months. The stirring was intermittent (1 h on, 5 h off) during experiments 2 and 3. Otherwise the test procedure was the same as during the first test series. Only the samples with gold coating were tested with one bulk gold sample. Two different substrate surface qualities, Ra1 and Ra2, were prepared. Ra1 samples were prepared manually. They were first polished with SiC paper, grades 240, 400 and 1200, and polished after that with 6, 3 and 1 μm diamond pastes, similarly to the first test series. Ra2 samples were prepared using a machine. The samples were first ground by MD-Piano and then polished with MD-Allegro using a 9-μm DiaPro diamond suspension. The gold coating thickness target was 200 nm. The bulk gold sample used in autoclave experiments was ground with 1200 grade SiC paper, and polished with diamond pastes grades 6, 3, and 1 μm.
Table 5 Autoclave test matrix for the second test series. The temperature was 30 °C.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>H$_2$SO$_4$ [wt %]</th>
<th>Gas</th>
<th>Duration [d]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
<td>N$_2$</td>
<td>61</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>SO$_2$</td>
<td>61</td>
</tr>
<tr>
<td>3</td>
<td>85</td>
<td>SO$_2$</td>
<td>62</td>
</tr>
</tbody>
</table>

Optical microscope, SEM and XPS were used for characterizing the samples tested in the autoclave. The optical microscope used was a Leica DS150 equipped with a digital camera. The SEM-EDS used was a LEO 1450. XPS analyses were carried out at Jozef Stefan Institute, Ljubljana, and the analysis procedure is described in detail in Appendix 1.

### 4.2.2 Linear sweep voltammetry experiments

Linear sweep voltammetry is an electrochemical method, which enables the study of the effects of applied potential on the current whilst varying solution composition and temperature. Linear sweep voltammetry was selected as the test method to study the behavior of different materials planned to be used as electrodes in the SDE process under applied potential. The test samples were studied at both oxidizing (anodic) and reducing (cathodic) potentials at room temperature in sulfuric acid solutions with and without 0.1 M Na$_2$SO$_3$. The cathodic scans without sulfite/SO$_2$ correspond to the cathode side of SO$_2$ depolarized electrolysis, and the anodic scans with sulfite/SO$_2$ correspond to the anode.

The test apparatus used in the present work can be seen in Figure 26. The counter electrode was a platinum flag. The reference electrode was an SCE protected with a special glass jacket in a separated compartment connected to the main cell by a salt bridge and a Haben-Luggin capillary. The 1000 ml cell was made of glass, and it had a gas-tight Teflon lid.
The test specimen to be studied was fastened in a sample holder made of Teflon. Each test specimen was tested only once, with the exception of the bulk Au electrode. Immediately before the experiments, the specimens were cleaned in an ultrasonic bath.

The sweep rate \( v \) was 20 mV/s. The potential ranges of the experiments were -300...+1900 mV (anodic scans without sulfite), +200...+1900 mV (anodic scans with sulfite), and -800...0 or -800...+200 mV vs. SCE (cathodic scans). The anodic scan with sulfite was started at 0.2 V vs. SCE to avoid reduction of \( \text{SO}_2 \). The open circuit potential (OCP) was measured at the beginning of each experiment. The potentiostat used was an ACM Instruments Auto Tafel.

The solution was de-aerated prior to the experiments with instrument grade \( \text{N}_2 \) for at least 30 min. If \( \text{Na}_2\text{SO}_3 \) was used, it was dissolved in distilled water, and 50 ml of this solution was injected into the cell after de-aerating. The solution was stirred for approx. 1 min, after which a sample was taken with a pipette. The experiment was started immediately after that. Another sample was taken after the experiment. The amount of SO\(_2\)/HSO\(_3\)^{−} was analyzed by iodometric back-titration. The sulfuric acid concentrations were 15, 40, and 60 wt %. 

Figure 26 The three-electrode cell used in the LSV test.
Au coated samples and uncoated 904L steel samples were tested and compared with a bulk Au-electrode. The samples were polished first with SiC paper, grades 240, 400, and 1200, and subsequently with 6, 3, and 1 μm diamond pastes. The target thickness of the gold coating was 100 nm. The gold sample used in the LSV experiments was ground with 1200 grade SiC paper, and polished with diamond paste grades 6, 3, and 1 μm. Thus the samples were prepared identically to the samples tested in the autoclave tests.

Additionally, some samples were prepared after cutting and before coating as follows: The samples were ground in a Buehler Phoenix 4000 using SiC paper grade 1200. Atantalum interlayer was added to improve the coating adhesion and thus corrosion resistance. The tantalum-gold (Ta-Au) coating was a gradient coating, the inner part of which was Ta rich and dense. The outer part of the coating was Au rich and porous so that the surface area was enhanced. Total target thickness of the gradient coating was 100 nm. These samples were studied only in anodic conditions, and testing was carried out in 40 and 60 wt % sulfuric acid with and without 0.1 M Na₂SO₃.

4.2.3 Analytical methods

An online method able to determine SO₂ and sulfuric acid concentrations was sought, but no suitable way to distinguish between S(IV) (SO₂ and sulfites) and S(VI) (SO₃, sulfuric acid and sulfates) species was found. Instrumental methods based on conductivity or pH cannot distinguish between these species, and spectroscopic methods were neither available nor a viable option due to the high price of such equipment. Thus traditional titrimetric methods were chosen, even though they are time-consuming and cannot be carried out online. These methods were used for analysis of the LSV electrolytes and in the bench-scale SDE experiments.

In the iodimetric method for determining S(IV) in acid solutions, an excess amount of iodine is added to the solution. Iodine oxidizes tetravalent sulfur to hexavalent, and the iodine that is not consumed is titrated with sodium thiosulfate (Vogel 1989). Immediately a sample was taken, it was added to the iodine solution. Two samples were analyzed in parallel. The samples were analyzed as soon as possible to avoid the escape of SO₂ from the sample.

The concentration of sulfuric acid was determined by titration with NaOH. After taking the sample, it was diluted and allowed to stand for several
hours to let the $\text{SO}_2$ that was present escape. Three samples were analyzed in parallel. It was initially suspected that the presence of sulfite/$\text{SO}_2$ could cause slight errors in the determination of $\text{H}_2\text{SO}_4$ concentration by acid-base titration, but that the changes in acid concentration would nevertheless be seen. The comparison of the sulfuric acid concentrations predicted by the model with the measured concentrations does not show any significant systematic errors.

### 4.2.4 Experiments in bench-scale SDE

An experimental SDE test facility able to carry out tests of several weeks in length was designed and constructed. It allows experiments with sulfuric acid concentrations varying from up to 80 wt % saturated with $\text{SO}_2$, at temperatures of 20-60°C with varying flow rates. The test facility is shown in Fig 27.

![Figure 27 View of the experimental SDE test system.](image)

The flow system consists of separate anolyte and catholyte circuits where $\text{SO}_2$ is fed directly to the anolyte tank. The material of the anolyte and catholyte circulation tubes and all the valves and joints is PVDF. The anolyte and catholyte tanks are made of Teflon-lined stainless steel, heated with embedded resistance heaters. The volume of both the anolyte and catholyte circuits is 22 liters. The data acquisition system was supplied by Nokeval (Finland), and the core electrolysis cell by ElectroCell (Denmark), with an active cell area of 0.1 $\text{m}^2$. The data acquisition system was used to record the temperatures of the electrolytes in the electrolyte tanks, before the cell and after the cell and the pressures of the electrolytes after the cell.
The cell voltage was measured with a Hewlett Packard 34401A multimeter and recorded.

The results of the electrolysis test series were used to validate the SDE model, and to evaluate the behavior of gold-coated electrodes.

The anodes used in all the experiments were various types of gold coated 904L steel plate (coated by a proprietary DIARC method by Diarc-Technology Oy). The cathode materials were varied to study their effect on the cell voltage and included Pt coated titanium (by ElectroCell), bare 904L steel (Outokumpu), and 904L steel with gold coating similar to the anodes. Nafion 117 membranes were used.

4.3 Results and discussion

4.3.1 Autoclave tests

4.3.1.1 First test series

The analysis of the corrosion resistance and coating stability of the samples was performed based on optical microscopy and on the results of SEM analysis of selected samples. The actual microscope pictures are shown in Appendix 1.

In the first four (1-4) tests in 50 wt % sulfuric acid, no visible changes in 904L were observed with an optical microscope. With SEM microscopy, there were no visible changes in the tests carried out at the lower temperature (30 °C, 1 and 3). In 80 wt % sulfuric acid, corrosion could be spotted at 50 °C even with an optical microscope as shown in Figure 28. The magnification of the samples is 20-fold.
The gold coating showed no signs of corrosion when studied by optical microscopy. Some traces of precipitates were seen on the surfaces, but it was concluded that they originated from washing and drying, because these stains were not seen when the samples were taken out of the autoclave, but only after washing and drying. SEM analysis showed that the gold coatings resisted the test series without fatal failures. In the nitrogen atmosphere (50 wt %, N₂, 30 °C), little pitting was detected. Figure 29 shows Au-coated samples in nitrogen (A) and sulfur dioxide (B) atmospheres with 50 wt % sulfuric acid, and Figure 30 shows Au-coated samples in nitrogen (A) and sulfur dioxide (B) atmospheres with 80 wt % sulfuric acid.
Figure 29 Au coatings in 50 wt % sulfuric acid, T=30 ºC: (A) Test 1, N2, (B) Test 3, SO₂.

Figure 30 Au coatings in 80 wt % sulfuric acid, T=30 ºC: (A) Test 5, N2, (B) Test 7, SO₂.
Based on the SEM micrographs, it was concluded that the corrosion resistance of 904L and the stability of gold coating increased in the presence of SO₂ at both acid concentrations. Generally, 80 wt % acid was more corrosive for 904L than 50 wt % acid, and the higher temperature accelerated corrosion.

4.3.1.2 Second test series

The immediate observation after the two-month tests was that all the coatings seemed undamaged. The coating of both samples with the smooth substrate Ra1 and of one sample with the rough substrate Ra2 had changed color during experiment 3 (85 wt % acid). After washing with distilled water, the coating was partially lost from both samples with the "smooth" substrate surface in experiment 1 and from one sample with a smooth substrate in experiment 3. The coating of the samples with the rougher substrate surface Ra2 did not fail. In experiment 1 with 15 wt % sulfuric acid there was no visible destruction of the coating nor of the stainless steel under the removed coating. A sample with a "smooth" substrate surface as observed by SEM is shown in Figure 31.

![Figure 31 Smooth surface, Au coating, 15 wt % H₂SO₄.](image)

The SEM images of the coated samples tested in 30 and 85 wt % sulfuric acid are shown in Appendix 1 together with SEM images of the pure gold sample after test 3. In the SEM images, the appearance of the coatings on
the smooth surface tested in 30 wt % sulfuric acid (Figure 32) was similar to that of coatings tested during the first test series, see Figures 29 and 30. During the first test series, the sulfuric acid concentrations were 50 and 80 wt %, but the test period was much shorter (2 weeks vs. 2 months).

Figure 32 Smooth substrate, Au coating in 30% sulfuric acid with \( \text{SO}_2 \).

The appearance of the samples with a coating on a smooth surface tested in 85 wt % is clearly different; it could be described as sponge-like or roughened, as shown in Figure 33.
The appearance of the coatings on a rough substrate is fairly similar to samples tested in both 30 and 85 wt % acid as shown in Figures 34 and 35. The appearance of the samples with a rough substrate cannot be compared directly to samples from the first test series as no coatings were added on a rougher surface in that series.
In order to obtain more insight into the surface composition, for some samples XPS analyses were carried out.
• Sample **K15**: Au coatings, rough & smooth, 15% H₂SO₄
• Sample **K30**: Au coating rough, 30%H₂SO₄ + SO₂ saturated
• Sample **K85**: Au coating rough, 85%H₂SO₄ + SO₂ saturated

All the results from the XPS analyses together with the details of the analysis procedure are given in Appendix 1. According to the depth profile analysis, the average coating thickness was approx. 50 nm, as shown in Figure 36. S and C (from organic contamination) were present only on the surface, in the first 3-5 nm.

![Figure 36 XPS depth profile obtained for sample K15 (smooth substrate surface).](image)

The XPS depth profile of sample K85 is shown in Figure 37. Sample K85 was one with no change in color during the autoclave testing.
On the basis of the depth profiles, there was no detectable acid/SO₂ penetration towards the substrate after 2 months of exposure at any concentration, but there were differences in the surface chemistry. Of all the samples there was most sulfur present on the surface of sample K85; the majority of the bound S atoms were in the 0/2 (elemental S or Au-S sulfide) state. According to the XPS analysis, both samples (rough & smooth substrates) tested in 15 wt % sulfuric acid had similar XPS spectra.

Based on the results of the autoclave experiments, it was concluded that the smooth substrate surface had too little coating adhesion. The gold coating had not withstood 2 months in 85 wt % sulfuric acid + SO₂ intact, even though the solution had not penetrated the coating. A change in the sample color and roughening of the surface were observed.

The corrosion performance of 904L and the stability of the gold coatings were better in sulfuric acid + SO₂ than in sulfuric acid alone. This may be caused by the reducing nature of SO₂. SO₂ is known to be a fairly strong reductant, and its salts, the sulfites, are also reductants (Maass and Maass 1928).

4.3.2 Linear sweep voltammetry

4.3.2.1 First test series

More detailed information concerning the experiments made by linear sweep voltammetry is gathered in Tables 1 and 2 in Appendix 2 including...
temperature, potential range, amount of SO$_2$/HSO$_3^-$, and open circuit potential (OCP).

The overall anodic and cathodic behavior of all the materials is shown in Figures 38-43. The separate voltammograms for different materials are shown in Appendix 2. All the experiments were carried out at room temperature.

**Figure 38** Anodic scan, all materials. 15 wt % sulfuric acid, $v=20$ mV/s. Dashed lines (---) with 0.1 M sulfite/SO$_2$.

**Figure 39** Anodic scan, all materials. 15 wt % sulfuric acid, $v=20$ mV/s. Dashed lines (---) with 0.1 M sulfite/SO$_2$. Detail of the previous figure.
In anodic experiments with sulfite (dashed lines), there is a peak located between 0.35 V and 1.1 V vs. SCE both on the gold and gold-coated electrodes. This peak may be related to the oxidation of sulfite/\text{SO}_2. With increasing sulfuric acid concentration, this peak shifted towards more positive potentials, and the current density decreased. On the gold electrodes, the current dropped between \(-1.1\) V and \(1.3\) V, which agrees with literature results concerning the inhibition of oxidation of \text{SO}_2 on gold at high potentials.
On 904L steel, a plateau of low current density was observed between -0.1 V and 1.1 V, Figs. 38–41. With increasing sulfuric acid concentration the current density increased and the anodic peak around 1 V moved towards more positive potentials. With the addition of sulfite, the current density of the plateau decreased. Such a plateau is typical for stainless steels in passive state. Subsequently, the current increased very sharply between 1 V and 1.1 V, and a yellow color was observed in the solution during this peak. The sharp rise in current and the yellow color detected in the solution may be related to the dissolution of Cr(VI) from 904L steel in the transpassive state. In this region, the gold-coated electrodes behaved similarly to 904L, which can be seen especially well in the voltammograms without sulfite. The yellow color was also observed in the solution in these experiments. As a result, it was concluded that the protective properties of the gold coatings tested were not sufficient at this high potential region. In this region, oxidation of SO$_2$ is nevertheless inhibited on gold.

Figure 42 Cathodic scan, all materials. 15 wt % sulfuric acid, $v = 20$ mV/s. Dashed lines (---) with 0.1 M sulfite/SO$_2$. 
In cathodic experiments (Figs 42–43) without sulfite (solid lines), the current started to increase between -0.35 V and -0.6 V. Bubble formation was observed, and this behavior may be related to hydrogen evolution. There was no significant difference between gold, gold coating, and 904 L. In the experiments with sulfite (dashed lines), the current started to increase the first time between -0.09 V and -0.17 V, and the increase was steepest with gold and gold coating. For gold-coated electrodes, there was a current peak between approx. -0.34 V and -0.5 V. These values agree quite well with the formation of an adsorbed sulfur layer at 0.14 vs. RHE and with the reduction of bulk SO$_2$ to soluble S(-II) species at -0.075 V vs. RHE mentioned by Quijada, Morallón, Vázquez and Berlouis (2000) and Quijada, et al., (2000). At more negative potentials, the current started to increase again. The behavior of 904L electrodes in a solution containing sulfite agrees with the observation of Scott, Taama and Cheng (1999): SO$_2$/sulfite can also be reduced on stainless steel.

In Figure 44, the behavior of gold-coated electrodes is shown on the hydrogen scale. The cathodic side (without sulfite) corresponds to the cathode of SO$_2$ depolarized electrolysis, and the anode side (with sulfite) corresponds to the anode. Because the current density is shown in logarithmic scale, absolute values of the cathodic current density are used. In a process corresponding to Figure 44, the cell voltage would be approx. 0.8 V.
4.3.2.2 Samples with Ta-interlayer

More detailed information is gathered in Table 3 in Appendix 2 including temperature, potential range, amount of SO₂/HSO₃⁻, and open circuit potential (OCP).

In Figures 45 and 46, the behavior of the Ta/Au coating in 40 wt % sulfuric acid is compared to the earlier Au coating and bulk gold. In experiments with sulfite/SO₂, SO₂ was oxidized on the Ta/Au coating, but the oxidation current was lower and the peak was shifted to somewhat more positive potentials. On the other hand, when the potential exceeded 1.1 V (vs. SCE), there was no similar observed dissolution of the electrode as with the earlier gold coating. The current increased, but to a much lesser extent. Thus it is suggested that the Ta/Au coating was less active but more resistant to corrosion.
In Figure 47, the anodic behavior of the Ta/Au coating in 60 wt % sulfuric acid is shown compared to that of gold. Since the earlier Au coatings were not tested in 60 wt % sulfuric acid, no comparison could be made with them. SO$_2$ was oxidized on Ta/Au starting from approximately the same potential as on gold (approx. 0.5 V vs. SCE). The oxidation current was
much smaller than in 40 wt % sulfuric acid (Fig. 46) and in 15 wt % (Fig. 39). The oxidation currents obtained in 40 wt % sulfuric acid both with the gold and the gold-coated electrodes agree with the work of Lu and Ammon (1982). Whereas the 0.1M aim for S(IV) concentration was achieved with 40 wt % acid, with 60 wt % acid the real measured concentration of S(IV) was ~0.06 – 0.08 M, and thus it is suggested that the lower current density is caused partially by this factor. Even though the solubility limit of SO₂ was not exceeded, it is suggested that the dissolution kinetics were slower at this concentration, because the analyzed amount of SO₂ was repeatedly smaller at the beginning of the experiment than at the end.

![Graph](image)

**Figure 47 Anodic scan. 60 wt % sulfuric acid, v=20 mV/s. Dashed lines (---) with sulfite/SO₂.**

The conclusions drawn from all the LSV experiments are:

- Thin gold coatings on a 904 L stainless steel surface can be used as an anode to oxidize SO₂/sulfite in sulfuric acid solutions.
- Thin gold coatings on stainless steel or 904 L stainless steel can be used as a cathode for hydrogen evolution.
- Oxidation of SO₂ is more difficult with increasing H₂SO₄ concentration as predicted by thermodynamics. This result also agrees with the literature.
- Corrosion resistance or the stability of a gold-coated anode at high potentials can be improved with a tantalum interlayer, but the catalytic activity of the gold coating towards oxidation of SO₂ at lower potentials may be diminished.
Although the oxidation of SO\textsubscript{2} has been studied on gold, experiments have seldom been carried out in as high concentrations of sulfuric acid as in the present work, the notable exceptions being the works of Appleby and Pinchon (1980) and Lu and Ammon (1982). The results obtained with gold coatings are believed to be original.

### 4.3.3 Validation of the SDE model with experimental data

#### 4.3.3.1 Initial tests

Testing was started first with water electrolysis (15 wt % H\textsubscript{2}SO\textsubscript{4}), and H\textsubscript{2} and O\textsubscript{2} were produced. SO\textsubscript{2} was then added to the anolyte, and the cell was depolarized with H\textsubscript{2} generation and no O\textsubscript{2} generation. Figure 48 shows a current/voltage plot of three test runs. The depolarization effect of SO\textsubscript{2} was approx. 0.65 V with gold-coated electrodes. The current-voltage plot was achieved by decreasing the voltage stepwise by 0.05 – 0.1 V. When the current stabilized after 10-30 s., the value was recorded.

![Figure 48 The depolarization effect of SO\textsubscript{2}. Bench-scale electrolyzer, 15 wt % sulfuric acid, room temperature, flow rate 80 L/h.](image)

#### 4.3.3.2 Electrolysis test series for the validation of the SDE model

All tests were performed at a constant current density of 910 A/m\textsuperscript{2} and at ambient temperatures (22-26°C). Samples (~100 mL) were taken regularly from both the anolyte and catholyte side for analysis of SO\textsubscript{2} and sulfuric acid concentration. The feed rate of the SO\textsubscript{2} fed into the anolyte was regulated by the feeding pressure (<3 bar) and the amount was measured with scales and compared with the values obtained by off-line iodometric titra-
The concentration of sulfuric acid was determined by titration with the NaOH.

The summary of the test conditions is shown in Table 6. The numbering of the anode-cathode pairs is as follows: 1 is Ti/Pt, 2 is uncoated 904L, 3 is gold-coated electropolished 904L, 4 is gold-coated 904L and 5 is gold-coated 904L with a Ta interlayer.

Table 6 Summary of the SDE experiments. Different anode and cathode materials are marked 1...5 as explained in the text.

<table>
<thead>
<tr>
<th>Exp</th>
<th>Anode-Cathode types used</th>
<th>Anolyte start, wt % acid</th>
<th>Catholyte start, wt % acid</th>
<th>SO2 g/kg start anolyte</th>
<th>duration, h</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3-3</td>
<td>0.50</td>
<td>33.01</td>
<td>73.19</td>
<td>165</td>
</tr>
<tr>
<td>2</td>
<td>3-3</td>
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<td>72</td>
</tr>
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<td>40.30</td>
<td>18.50</td>
<td>37.09</td>
<td>141</td>
</tr>
</tbody>
</table>

The initial anolyte concentration was 0.5 wt % and increased progressively to 35-40%. At the same time, the catholyte was diluted due to the net water flux as predicted by equation (60) and the catholyte acid concentration was dropped from 33% to 18-20%.

With increasing H2SO4 concentration, the anode performance was found to be sensitive to SO2 concentration. When the amount of SO2 in the anolyte dropped too low, the anode substrate material (904L) was found to dissolve. During one experiment, the Au coating was observed to be delaminating from the steel substrate, but the electrolysis continued on the delaminated gold foil (the concentration of sulfuric acid increased). It was concluded that adhesion of Au to the steel needed to be improved and the number of defects to be diminished. When the anolyte was analyzed with an ICP after the experiment, no gold was detected. It was thus concluded that the gold had not dissolved, but only mechanically delaminated.

It is suggested that the anodic dissolution of 904L took place as a competing reaction because it was easier than oxygen evolution. Even though the anode material was the same as in the initial water electrolysis experi-
ments, the activity of water was lower due to the higher concentration of sulfuric acid, as calculated by the thermodynamic model.

During some experiments carried out in a bench-scale SDE with commercial Pt-coated cathodes, the observed cell voltages were higher than with Au-coated electrodes, and after the experiments, peeling of the catalyst layer coated with elemental sulfur was observed. According to the literature, in cathodic conditions Pt is poisoned by SO$_2$, and thus Pt should not be used as a catalyst on the cathode side unless carry-over of SO$_2$ can be prevented.

In Fig. 49, concentrations of the anolyte and catholyte from the experiments are compared with the results of the MathCAD model. In the experiments, different cathode materials, flow rates, SO$_2$ concentrations, pressures and feed methods were used, but current density and temperature were the same. The correlation between these data is remarkable – the largest deviations start to appear only at extreme concentrations (e.g. for cases with very low or very high SO$_2$), when titration analysis data scatter becomes significant.

![Figure 49 Comparison of the acid concentration in SDE catholyte and anolyte (Table 6) with the values predicted with the equation (60).](image-url)
5 Conclusions

In the present work, the materials to be used in sulfur dioxide-depolarized water electrolysis (SDE) were studied together with the fundamentals of the process. In order to gain a better understanding of the process, the activities and other thermodynamic properties of the electrolyte components were calculated using a mathematical model elaborated during the present work. The whole concentration range of the ternary H$_2$O-H$_2$SO$_4$-SO$_2$ system relevant for SDE was assessed. On this basis, the reversible cell potential was calculated for the whole concentration range.

A new model for water transport through a Nafion-like membrane was developed, and the calculated thermodynamic properties of the electrolytes were combined with the transport equations. This model for SDE was used to predict the overall water balance of the electrolysis process with changing electrolyte concentrations, mass flows, current densities, temperatures, and pressures. The modeling results were then compared with the actual performance of a bench-scale electrolyzer.

In the present work, the possibility to use thin gold coatings as catalyst material instead of platinum was studied. The stability of thin gold coatings and their activity towards electrochemical oxidation of SO$_2$ were studied first with autoclave tests and linear sweep voltammetry, and the performance of the coatings was compared to that of gold. SEM and XPS techniques were used to characterize the stability of the coatings. The performance of electrodes with thin gold coatings was then tested in bench-scale SDE. Even though the oxidation of SO$_2$ has previously been studied on gold, experiments have seldom been carried out in such high concentrations of sulfuric acid as in this work, and the results obtained with gold coatings are believed to be original.

No consensus exists on the mechanism of electrochemical oxidation of SO$_2$ on gold surface. By varying the scan rate during voltammetrical experiments (linear or cyclic), and by carrying out Tafel analyses, more information could be obtained, especially if these techniques were combined with in situ spectroscopical methods. As a recommendation for the future work, that kind of experiments should be carried out at relevant concentrations of sulfuric acid and dissolved SO$_2$. 
Based on the combination of the results from the experimental and theoretical work, it was possible to explain and predict the changes taking place in the SDE process with changing electrolyte concentrations and other process parameters.

A significant amount of water is being transported from the anolyte to the catholyte through the membrane due to the electro-osmotic water drag effect. This phenomenon is beneficial for production or for concentration of sulfuric acid by SO$_2$ depolarized electrolysis. The contribution of this effect decreases with increasing anolyte concentration, especially if the catholyte concentration is decreased simultaneously because of the combined effects of other water transport mechanisms.

It was confirmed, that thin gold coatings on a stainless steel surface can be used to catalyze the anodic oxidation of SO$_2$ and to protect the electrodes. In addition, similar electrodes can be used as cathodes.

As a recommendation for the future work, testing of gold nanoparticles as a catalyst in a membrane-electrode assembly (MEA) would be a logical continuation.

For the practical performance of the SDE process, the optimal combination of the acid concentrations in electrolytes, electric energy consumption and stability of the anodes should be determined on a case-by-case basis. The models developed during this work could be used for such optimization.

Another recommendation for the future work is related to the potential-pH-diagrams and the relationship between the concentration of an acid (or a base) and the pH. Instead of pH, e.g. the Hammett function can be used to construct more realistic potential-acidity diagrams at high concentration of acids. However, because these functions do not have a rigorous thermodynamic derivation, the question arises: what should be used instead of them to describe concentrated solutions correctly. These issues should be a subject of a separate theoretical study.
References


Clegg, S.L., Brimblecombe, P., 1995. Application of a Multi-component Thermodynamic Model to Activities and Thermal Properties of 0 – 40 mol kg$^{-1}$ Aqueous Sulfuric Acid from ~200 to 328 K. *Journal of Chemical and Engineering Data*, 40, pp. 43-64.


Rard, J.A., Clegg S.L., 1995. A review of some aspects of electromotive-force measurements for the cells: Pt[H$_2$(g, p$^o$)]H$_2$SO$_4$(aq)|PbO$_2$(s)|PbSO$_4$(s)|Pt, and Pt[H$_2$(g, p$^o$)]H$_2$SO$_4$(aq)|Hg$_2$SO$_4$(s)|Hg(l)|Pt, with p$^o$ = 0.1 MPa. *The Journal of Chemical Thermodynamics*, 27, pp. 69-98.


Appendix 1
Autoclave experiments

First test series
The test matrix of test series 1 is shown in Table 1.

Table 1 Autoclave test matrix for the first test series.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>H$_2$SO$_4$ (% wt)</th>
<th>Gas</th>
<th>T [°C]</th>
<th>Duration [d]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>N$_2$</td>
<td>30</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>N$_2$</td>
<td>50</td>
<td>15</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>SO$_2$</td>
<td>30</td>
<td>14</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>SO$_2$</td>
<td>50</td>
<td>14</td>
</tr>
<tr>
<td>5</td>
<td>80</td>
<td>N$_2$</td>
<td>30</td>
<td>14</td>
</tr>
<tr>
<td>6</td>
<td>80</td>
<td>N$_2$</td>
<td>50</td>
<td>14</td>
</tr>
<tr>
<td>7</td>
<td>80</td>
<td>SO$_2$</td>
<td>30</td>
<td>14</td>
</tr>
<tr>
<td>8</td>
<td>80</td>
<td>SO$_2$</td>
<td>50</td>
<td>14</td>
</tr>
</tbody>
</table>

Optical microscopy results for the first test series
Untested reference samples are shown in Figure 1. The curved scratches seen in the figures originate from the sample preparation process. The magnification of the samples in the figures is ~20 x, and it is the same in all the optical microscope figures presented below.

Figure 1 Untested reference samples: left 904L and right Au coating.

904 L steel
904 L samples from tests 1-4 are shown in Figure 2.
Figure 2 Pictures from tests 1 – 4, non-coated 904 L in 50 wt % sulfuric acid. A=30 °C, N₂; B=30 °C, SO₂; C=50 °C, N₂ and D=50 °C, SO₂. The scale is same for all the samples.

**Gold-coated samples**

Figures 3 and 4 show the gold-coated samples tested in 50 wt % and 80 wt % sulfuric acid solutions. Some traces of precipitates can be seen on the surfaces, but it is proposed here that they originate from washing and drying, as these stains were not seen when the samples were taken out of the autoclave, but only after washing and drying.
Figure 3 Pictures from tests 1 – 4, Au-coated 904 L in 50 wt % sulfuric acid. The scale is same for all the samples.

Figure 4 Pictures from tests 5 – 8, Au-coated 904 L in 80 wt % sulfuric acid. The scale is same for all the samples.
Scanning electron microscopy (SEM) results for the first test series

Selected samples taken from the 30 °C tests were studied by SEM. The scale of the defects detected in SEM analysis was 1 μm.

904 L steel

Figures 5A and 5B show a comparison between the behavior of 904 L in 50 wt % sulfuric acid (A) and in 50 wt % sulfuric acid containing SO$_2$ (B) at 30 °C. Figures 6A and 6B show a similar comparison between the behavior of 904 L in 80 wt % sulfuric acid.

Figure 5 904 L after two weeks in 50 wt % sulfuric acid, T=30 °C: (A) Test 1, N$_2$, (B) Test 3, SO$_2$. 
Figure 6 904 L after two weeks in 80 wt % sulfuric acid, T=30 °C: (A) Test 5, N₂, (B) Test 7, SO₂.
Second test series

The test matrix of test series 2 is shown in Table 2.

Table 2 Autoclave test matrix for the second test series. Temperature was 30 °C during all the experiments.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>H₂SO₄ [% wt]</th>
<th>Gas</th>
<th>Duration [d]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
<td>N₂</td>
<td>61</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>SO₂</td>
<td>61</td>
</tr>
<tr>
<td>3</td>
<td>85</td>
<td>SO₂</td>
<td>62</td>
</tr>
</tbody>
</table>

SEM results for the second test series

Experiment 1

The peeling gold coating on the smooth 904 L substrate surface after the experiment is shown in Figure 7.

Figure 7 Smooth substrate surface, Au coating, 15 wt % H₂SO₄.

The coating on a smooth substrate surface is shown in Figure 8 and the coating on a rough substrate surface in Figure 9.
Figure 8 Smooth substrate surface, Au coating, 15 wt % H$_2$SO$_4$.

Figure 9 Rough substrate surface, Au coating, 15 wt % H$_2$SO$_4$.

Experiment 3
The appearance of a pure gold sample after experiment 3 is shown in Fig. 10.
Figure 10 Pure gold in 85% sulfuric acid with SO$_2$. 
XPS analysis results for the samples of the second test series

XPS analyses were carried out at Jozef Stefan Institute, Ljubljana, and the XPS parameters were:

- XPS spectrometer: PHI TFA-XPS
- X-ray source: Al-monochromator, 1486.6 eV
- Analysis spot: 0.4 mm in diameter, depth ~6 nm
- Energy resolution: ~ 0.65 eV
- Etching rate 4.4…4.6 nm/min

The XPS surface spectra for both samples tested in 15 wt % sulfuric acid are shown in Figure 11. Both samples (rough & smooth substrate surface) have similar XPS spectra.

![Figure 11 XPS surface spectra: K15. Sample 1: rough substrate surface (Ra2); Sample 2: smooth substrate surface (Ra1).](image)

The XPS surface spectra of samples K30 and K85 are shown in Figures 12 and 13.
Figure 12 XPS spectrum from the surface of sample K30 (Ra2).

In Figure 12, C and O come from organic contamination and are not relevant to the analysis.

Figure 13 XPS spectrum from the surface of sample K85 (Ra2).

In Figure 13, C and O come from organic contamination. The origin of Cu is unclear. More sulfur is observed at the surface compared to Figure 12; see relative intensities of S 2p ~ Au 4f peak.

The sulfur spectra for all the samples are shown in Figures 14, 15, and 16.
Figure 14 XPS sulfur spectrum: sample K15.

The chemical information obtainable from the sulfur spectra shown in Figure 14 is:

- ~ 2/3 of surface S is bound in sulfide-like bonds (valence 2\(^-\)), probably Au-thiol
- ~ 1/3 of surface S is bound in the S(4\(^+\)/6\(^+\)) valence states

Figure 15 XPS spectrum of S 2p from the surface of sample K30 (Ra2). NB! Label Au 4f is erroneous.
The chemical information obtainable from the sulfur spectra shown in Figure 15 is:

- \(~1/5\) of surface S is bound in sulfide-like bonds (valence 2\(^-\)) or neutral (0)
- \(~4/5\) of surface S is bound in the S(4\(^{+/6+}\)) valence states

The chemical information obtainable from the sulfur spectra shown in Figure 16 is:

- \(~1/5\) of surface S is bound in sulfide-like bonds (valence 2\(^-\))
- \(~2/3\) of surface S is bound in 2\(^-\) or neutral (0)
- \(~1/8\) of surface S only is bound in the S(4\(^{+/6+}\)) valence states

The gold spectra for samples K30 and K85 are shown in Figures 17 and 18.
Figure 17 XPS spectrum of Au 4f from the surface of sample K30 (Ra2).

Figure 18 XPS spectrum of Au 4f from the surface of sample K85 (Ra2).

The depth profile of sample K30 is shown in Figure 19, and a close-up of the depth profile for sample K85 is shown in Figure 20.
Figure 19 XPS depth profile on sample K30 (Ra2).

Figure 20 XPS depth profile obtained on sample K85 (Ra2).
Appendix 2
Linear sweep voltammetry

Test series 1

Information concerning the linear sweep voltammetry test series 1 given in Tables 1 and 2 includes: the temperature, the potential range, the amount of $\text{SO}_2^-/\text{HSO}_3^-$ and the open circuit potential (OCP). In Table 1, the sulfuric acid concentration is 15 wt %, and in Table 2, 40 wt %. More experiments were performed, but only the most representative results are reported here.

Table 1 Experiments carried out in 15 wt % $\text{H}_2\text{SO}_4$. The potential range [V] and OCP [mV] are vs. SCE.

<table>
<thead>
<tr>
<th>experiment</th>
<th>sample</th>
<th>potential range [V]</th>
<th>S(IV) [mol]</th>
<th>OCP [mV]</th>
<th>T [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>22_6_09_A</td>
<td>gold</td>
<td>-0.3....+1.9</td>
<td>-</td>
<td>219.1</td>
<td>25</td>
</tr>
<tr>
<td>15_6_09A</td>
<td>904 L</td>
<td>-0.3....+1.9</td>
<td>-</td>
<td>-84.9</td>
<td>25</td>
</tr>
<tr>
<td>17_6_09A</td>
<td>Au coat.</td>
<td>-0.3....+1.9</td>
<td>-</td>
<td>-371.8</td>
<td>24</td>
</tr>
<tr>
<td>23_6_09A</td>
<td>gold</td>
<td>+0.2....-0.8</td>
<td>-</td>
<td>294.1</td>
<td>25.5</td>
</tr>
<tr>
<td>15_6_09C</td>
<td>904 L</td>
<td>+0.2....-0.8</td>
<td>-</td>
<td>-221.6</td>
<td>25</td>
</tr>
<tr>
<td>17_6_09B</td>
<td>Au coat.</td>
<td>+0.2....-0.8</td>
<td>-</td>
<td>-317.7</td>
<td>24.5</td>
</tr>
<tr>
<td>29_6_09B</td>
<td>gold</td>
<td>+0.2....+1.9</td>
<td>0.098</td>
<td>141.3</td>
<td>28</td>
</tr>
<tr>
<td>2_7_09B</td>
<td>904 L</td>
<td>+0.2....+1.9</td>
<td>0.096</td>
<td>-105.0</td>
<td>31</td>
</tr>
<tr>
<td>1_7_09A</td>
<td>Au coat.</td>
<td>+0.2....+1.9</td>
<td>0.094</td>
<td>-146.7</td>
<td>28</td>
</tr>
<tr>
<td>30_6_09B</td>
<td>gold</td>
<td>+0.2....-0.8</td>
<td>0.093</td>
<td>186.8</td>
<td>27.5</td>
</tr>
<tr>
<td>3_7_09A</td>
<td>904 L</td>
<td>+0.2....-0.8</td>
<td>0.1</td>
<td>-96.3</td>
<td>27</td>
</tr>
<tr>
<td>2_7_09A</td>
<td>Au coat.</td>
<td>+0.2....-0.8</td>
<td>0.1</td>
<td>74.3</td>
<td>28</td>
</tr>
</tbody>
</table>
Table 2 Experiments carried out in 40 wt % H₂SO₄. The potential range [V] and OCP [mV] are vs. SCE.

<table>
<thead>
<tr>
<th>experiment</th>
<th>sample</th>
<th>potential range [V]</th>
<th>S(IV) [mol]</th>
<th>OCP [mV]</th>
<th>T [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>7_7_09A</td>
<td>gold</td>
<td>-0.3...+1.9</td>
<td>-</td>
<td>286.9</td>
<td>25.5</td>
</tr>
<tr>
<td>13_7_09A</td>
<td>904 L</td>
<td>-0.3...+1.9</td>
<td>-</td>
<td>-355.8</td>
<td>25</td>
</tr>
<tr>
<td>21_7_09A</td>
<td>Au coat.</td>
<td>-0.3...+1.9</td>
<td>-</td>
<td>-200.3</td>
<td>26</td>
</tr>
<tr>
<td>7_7_09B</td>
<td>gold</td>
<td>0...-0.8</td>
<td>-</td>
<td>71.8</td>
<td>27</td>
</tr>
<tr>
<td>20_7_09A</td>
<td>904 L</td>
<td>0...-0.8</td>
<td>-</td>
<td>-385.5</td>
<td>26</td>
</tr>
<tr>
<td>8_7_09C</td>
<td>Au coat.</td>
<td>0...-0.8</td>
<td>-</td>
<td>-305.7</td>
<td>26</td>
</tr>
<tr>
<td>26_8_09A</td>
<td>gold</td>
<td>+0.2...+1.9</td>
<td>0.095</td>
<td>32.2</td>
<td>26</td>
</tr>
<tr>
<td>16_7_09B</td>
<td>904 L</td>
<td>+0.2...+1.9</td>
<td>0.098</td>
<td>-42.1</td>
<td>26</td>
</tr>
<tr>
<td>16_7_09A</td>
<td>Au coat.</td>
<td>+0.2...+1.9</td>
<td>0.093</td>
<td>-19.8</td>
<td>27</td>
</tr>
<tr>
<td>17_7_09B</td>
<td>904 L</td>
<td>+0.2...-0.8</td>
<td>0.094</td>
<td>-57.1</td>
<td>27</td>
</tr>
<tr>
<td>17_7_09A</td>
<td>Au coat.</td>
<td>+0.2...-0.8</td>
<td>0.092</td>
<td>-163.0</td>
<td>27</td>
</tr>
</tbody>
</table>

The overall behavior of 904 L is shown in Figures 1 and 2. Figure 1 shows the voltammograms for 15 wt % sulfuric acid and Figure 2 those for 40 wt %. A plateau of low current density was observed between -0.1 V and 1.1 V. With the addition of sulfite, the current density of the plateau decreased. The plateau is suggested to correspond to the passivation of 904 L. With increasing sulfuric acid concentration the current density increased and the sharp increase in current around 1 V moved towards more positive potentials.
Figure 1 Steel 904L. 15 wt % sulfuric acid, \( v=20 \text{ mV/s} \). Dashed lines (---) with 0.1 M sulfite/SO\(_2\). Note the logarithmic scale of the current density.

Figure 2 Steel 904 L. 40 wt % sulfuric acid, \( v=20 \text{ mV/s} \). Dashed lines (---) with 0.1 M sulfite/SO\(_2\). Note the logarithmic scale of the current density.

The overall behavior of the gold-coated electrodes is shown in Figures 3 and 4. Without SO\(_2\)/sulfite, there was a low current plateau located between -0.1 V and 1.1 V. The current density of the plateau decreased with increasing sulfuric acid concentration. At higher potentials, the current increased sharply, corresponding to the dissolution of the 904 L substrate. In the solutions with sulfite/SO\(_2\), there was a plateau of sulfite oxidation between 0.3 V and 1.15 V. With increasing sulfuric acid concentration, this plateau shifted towards more positive potentials, and the current density decreased. On the cathodic side, in solutions containing sulfite, the current
started to rise sharply at -0.1 V, which is suggested to correspond to the formation of adsorbed sulfur layers. Similar behavior is also observed for 904L (Figures 1 and 2), but the currents involved are smaller.

![Graph showing current density vs. voltage for Au-coated 904L with 15 wt% sulfuric acid.](image)

**Figure 3** Au-coated 904 L. 15 wt % sulfuric acid, v=20 mV/s. Dashed lines (---) with 0.1 M sulfite/SO$_2$. Note the logarithmic scale of the current density.

![Graph showing current density vs. voltage for Au-coated 904L with 40 wt% sulfuric acid.](image)

**Figure 4** Au-coated 904 L. 40 wt % sulfuric acid, v=20 mV/s. Dashed lines (---) with 0.1 M sulfite/SO$_2$. Note the logarithmic scale of the current density.

In Figures 5 and 6, the behavior of a gold coating is compared with the behavior of a bulk gold electrode. It can be seen that the peak corresponding to sulfite oxidation was located at the same potential range on gold and on the gold coating, even though the current was lower on the gold coating. It can also be seen that the steep increase in the current, suggested to corre-
spond to the dissolution of the 904L substrate, occurred at more anodic potentials than the oxidation of sulfite.

Figure 5 Gold and Au-coated 904 L. Anodic scan, 15 wt % sulfuric acid with 0.1 M sulfite/\nSO_2, v=20 mV/s. Detail of the complete voltammogram.

Figure 6 Gold and Au-coated 904 L. Anodic scan, 40 wt % sulfuric acid with 0.1 M sulfite/\nSO_2, v=20 mV/s. Detail of the complete voltammogram.

Samples with Ta-interlayer

Information concerning the linear sweep voltammetry testing of samples with Ta-interlayer given in Table 3 includes: the temperature, the potential range, the sulfuric acid concentration, the amount of SO_2/\nHSO_3^- and the
open circuit potential (OCP). More experiments were performed, but only the most representative results are reported here.

Table 3 Linear sweep voltammetry tests of samples with Ta-interlayer. The potential range [V] and OCP [mV] are vs. SCE.

<table>
<thead>
<tr>
<th>exp.</th>
<th>sample</th>
<th>potential range [V]</th>
<th>S(IV) [mol]</th>
<th>OCP [mV]</th>
<th>T [°C]</th>
<th>H₂SO₄ [% wt]</th>
</tr>
</thead>
<tbody>
<tr>
<td>26_10_11C</td>
<td>Ta/Au</td>
<td>-0.3....+1.9</td>
<td>-</td>
<td>228.9</td>
<td>23</td>
<td>40</td>
</tr>
<tr>
<td>31_10_1B1A</td>
<td>Ta/Au</td>
<td>-0.3....+1.9</td>
<td>-</td>
<td>136.0</td>
<td>27</td>
<td>60</td>
</tr>
<tr>
<td>07_11_11E</td>
<td>Ta/Au</td>
<td>+0.2....+1.9</td>
<td>0.097</td>
<td>181.0</td>
<td>24.5</td>
<td>40</td>
</tr>
<tr>
<td>17_11_11A</td>
<td>Ta/Au</td>
<td>+0.2....+1.9</td>
<td>0.071</td>
<td>98.9</td>
<td>29</td>
<td>60</td>
</tr>
<tr>
<td>21_11_11</td>
<td>gold</td>
<td>+0.2....+1.9</td>
<td>0.057</td>
<td>180.3</td>
<td>27</td>
<td>60</td>
</tr>
</tbody>
</table>
Anu Lokkiluoto

Fundamentals of SO₂ depolarized water electrolysis and challenges of materials used