Study on in-situ electrochemical impedance spectroscopy measurement of anodic reaction in SO2 depolarized electrolysis process

XUE Lulu, ZHANG Ping*, CHEN Songzhe, WANG Laijun
(Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing, 100084, China)

* Corresponding author. Tel.: +86 10 89796065; fax: +86 10 62771740.
E-mail addresses: zhangping77@mail.tsinghua.edu.cn

Abstract

SO2 depolarized electrolysis (SDE) is the pivotal reaction in hybrid sulfur process, one of the most promising approaches for mass hydrogen production without CO2 emission. The net result of hybrid sulfur process is to split water into hydrogen and oxygen at a relatively low voltage, which will dramatically decrease the energy consumption for the production of hydrogen. The potential loss of SDE process could be separated into four components, i.e. reversible cell potential, anode overpotential, cathode overpotential and ohmic loss. So far, it has been identified that the total cell potential for the SO2 depolarized electrolyzer is dominantly controlled by sulfuric acid concentration of the anolyte and electrolysis temperature of the electrolysis process. In this work, an in-situ Electrochemical Impedance Spectroscopy (EIS) measurement of the anodic SDE reaction was conducted. Results show that anodic overpotential is mainly resulted from the SO2 oxidation reaction other than ohmic resistance or mass transfer limitation. This study extends the understanding to SDE process and gives suggestions for the further improvement of the SDE performance.

Key words: hybrid sulfur cycle; SO2 depolarized electrolyze; in-situ electrochemical impedance spectroscopy.

1. Introduction

The hybrid sulfur process (HyS), which is also known as the ‘Westinghouse process’, is first put forward by the Westinghouse Electric Corp. [1]. HyS process is one of the simplest thermochemical processes for hydrogen production, and involves only two steps, i.e. an electrochemical reaction substep and a thermochemical reaction substep. The reactions are as follows.

\[ \text{SO}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2 \] (Electrochemical) \hspace{1cm} (1)

\[ \text{H}_2\text{SO}_4 \rightarrow \text{SO}_2 + \text{H}_2\text{O} + 1/2 \text{O}_2 \] (Thermochemical) \hspace{1cm} (2)

The electrochemical substep, i.e. the SO2 depolarized electrolysis (SDE) process, is the key issue in hydrogen production. Half-cell reactions of the electrochemical reaction are shown below.

Anode: \[ \text{SO}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + 2\text{H}^+ + 2\text{e}^- \] \hspace{1cm} (3)

Cathode: \[ 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \] \hspace{1cm} (4)

There are two types of design for the SDE substep: the liquid-fed system and the gas-fed system. For both designs, water is fed on the cathode side. Although sulfuric acid at the cathode side could
provide more proton for the reduction reaction for hydrogen production, it could be reduced to elemental sulfur or hydrogen sulfide. The side reaction on the cathode side would decrease the reaction efficiency and may poison the catalyst on cathode side. Besides, water in the cathode side could help the membrane hydrated and could wash away the hydrogen bubbles and side reaction productions. Gaseous SO$_2$ is fed into the anode side of the gas-fed electrolyzer while liquid sulfuric acid saturated with SO$_2$ is employed as the anolyte in the liquid-fed system.

The liquid-fed system configuration was used by Savannah River National Laboratory (SRNL) [2-13]. The anolyte is liquid sulfuric acid saturated with dissolved SO$_2$. At the anode side, SO$_2$ reacts with water to produce sulfuric acid, protons and electrons according to reaction 3. The protons will pass through the membrane under an applied potential and react with the electrons at the cathode side to produce hydrogen according to reaction 4. In the SRNL SDE configuration, it is of great importance for recirculation of the anolyte and catholyte. The circulation of the anolyte could enhance the mass transfer, i.e. the transport of dissolved SO$_2$ to the anode surface and the removal of sulfuric acid from the anode surface. Moreover, due to the limitations of SO$_2$ solubility and its conversion rate, circulation of the anolyte could improve the efficiency of electrochemical substep. The flow of the catholyte (water) could sweep hydrogen product and element sulfur from the cathode surface, and to keep the proton exchange membrane (PEM) hydrated. Besides, the recirculation of the anolyte and catholyte in SRNL’s test [10] could help control cell temperatures by flowing through heat exchangers and recover waste energy from overpotentials in the form of heat[14].

The gas-fed system was developed and tested at University of South Carolina (USC) [15-21]. The cathode side of the SDE cell is maintained at a higher pressure than the anode side, to drive a net water flux across the membrane and remains it hydrated. Water flows through the PEM form cathode to anode side will reacts with the gaseous SO$_2$ to produce sulfuric acid through reaction 3. The sulfuric acid product will be accumulated and removed. The circulation rate of the catholyte in gas-fed cell should be much higher than that of the liquid-fed system for controlling the SDE cell temperature[14]. Furthermore, the product of downstream sulfuric acid decomposition substep need to be gaseous SO$_2$ to feed in the anode side. However, to output pure SO$_2$, SO$_2$ and O$_2$ that are the product of reaction 2 should be separated. It is more convenient to separate them by solubility difference, therefore, the flow sheet of the gas-fed SDE based HyS process will be more complex.

The total voltage of SDE process could be separated into four components as shown in equation 5.

\[ V = U_{eq} + \eta_a + \eta_c + iR_a \]  

(5)

$U_{eq}$ is the reversible cell potential, which is a function of temperature and sulfuric acid concentration in anolyte, and it goes up with the increase of acid concentration. $\eta_a$ is the anode overpotential, which is under the influence of catalyst surface area, current density and SO$_2$ concentration in anolyte. The anode overpotential rises up with the current density’s increase and SO$_2$ concentration’s decline. Meanwhile, the SO$_2$ concentration in anolyte is limited by the saturation concentration of SO$_2$, which depends on temperature, pressure and sulfuric acid concentration of anolyte. $\eta_c$, the cathode overpotential, is generally lower than the anode overpotential. It is influenced by the current density and catalyst surface area. $iR_a$ is the ohmic loss.
in total cell voltage, which is caused by the resistance between electrolyte and membrane electrode assembly (MEA). The ohmic loss is proportional to current density, and could be reduced through placing anode and cathode close together. In our previous work[22], the influences of electrolyte temperature and sulfuric acid concentration on total cell voltages were studied. Results show that under the process conditions of 80°C and 30wt% sulfuric acid, the SDE cell could reach the best electrolysis performance.

Staser et.al[15] studied the components of the total cell potential in gas-fed SDE cells. A model based on the thermodynamics theory and experimental parameters was established. Results indicated that the total cell potential for SDE process is mainly controlled by water transport. Furthermore, the water transport from the cathode to the anode side influences the concentration of sulfuric acid product. Plus, the concentration of sulfuric acid product on the anode side has strong influence on the performance of hybrid sulfur process, including the equilibrium potential of and the reaction kinetics for SDE’s anode side reaction, and the resistance of PEM. On the other hand, the liquid-fed SDE cell system is mainly infected by the mass transfer of dissolved SO₂ from the bulk sulfuric acid solution to the surface of the anode electrode, so the components in cell potential for liquid-fed SDE system should be investigated. Due to the differences between the determinants for liquid-fed and gas-fed SDE cell, the research method for gas-fed cell could not be imitated to liquid-fed system.

Furthermore, the anode overpotential of liquid-fed system is thought to be the main contributor to the total cell potential. Therefore, the accurate measurement of the anode overpotential is quite important for further understanding and improving of the cell performance for liquid-fed process.

Electrochemical impedance spectroscopy (EIS) is a non-destructive technique and could provide time dependent information about the properties about ongoing processes. It is a diagnose tool that has been used for unraveling complex non-linear processes, i.e. the electrochemical systems such as electrolytic cells and battery. The frequency dependence of impedance of an electrochemical process is measured through EIS by applying a sinusoidal AC potential (or current) to the cell and analyzing the current (or potential) response[23]. EIS has already become a primary tool for researches of PEM fuel cell, including analyzing performance losses in various processes in fuel cell. The applications of EIS in PEM fuel cell are mainly focused on modeling of the electrochemical process with equivalent circuit (EC) [24] and identifying the contributes of various processes to total resistance such as charge transfer and mass transport[25, 26].

The EIS technique can be implemented in two ways, the in-situ and ex-situ technique. The in-situ test is often used for a single fuel cell or a fuel cell stack. Due to the complexity of the in-situ test system, there are not many integrated systems that are adapted to the in-situ measurement. Therefore, ex-situ test is preferred by many fuel cell researchers. Ex-situ measurement is usually carried out in a three-electrode system, which is composed of a working electrode, a reference electrode and a counter electrode, placed in a conventional three compartment cell[27, 28]. If the working electrode in the three compartment system is a catalyst coated electrode, a gas diffusion electrode (GDE) is desired. Therefore, a special design of the cell is required. Due to the complex design of the reaction cell and the non-stability and poor repeatability of the measurement results, the ex-situ with GDE is not the best choice. Furthermore, it is hard to apply a controlled activation process for ex-situ cells, and the activation process is quite important for the subsequent process even the electrolysis performance. Initially, we’ve tried to apply the ex-situ EIS measurement for the liquid-fed SDE system in the form of three-compartment design. However, the ex-situ
measurement is not able reveal the actual mechanism of the liquid-fed SDE process, and the non-repeatable results may lead to completely different explanations. The study carried out by USC[15] has shown that the anode overpotential contributes the most to the total cell potential of gas-fed SDE cell. Because the anode feed and mass transfer are the most complicated difference between liquid-fed and gas-fed SDE process, which should be first studied in liquid-fed SDE cell. Therefore, the anode overpotential in liquid-fed SDE cell is analyzed by in-situ EIS measurement.

2. Experimental

Figure 1 is the structure diagram of the customized liquid-fed SDE cell we used for this work. The cell has a symmetrical structure design. The flow fields are solid graphite blocks with 35mm×35mm× 2mm flow channels on each side. Inside the flow fields are a piece of carbon paper on each side, which serves as the gas diffusion layer on both sides of the MEA. The innermost layer and the “heart” of the electrolysis cell is the MEA, with active area of 9.69cm². The MEA was prepared under the optimized preparation conditions that we concluded from our previous work[22]. Nafion® N115 is chosen to be the membrane in the MEA, loaded with carbon-supported platinum as electrode and electrocatalyst on both sides. The catalyst loading amount on both cathode and anode sides are 1.0mg-Pt cm⁻².

The in-situ EIS measurement is carried out in the configuration that is exactly the same electrolysis that we used in our previous work[22]. In order to focus on the anodic overpotential in SDE process, and to eliminate the influence brought by the cathode side, half-cell design is used with hydrogen passing through the cathode side, instead of water, which serves as both the counter and the reference electrode. The anolyte is the concentrated sulfuric acid saturated with dissolved SO₂. Inserting a three-electrode connection for the electrolysis cell is difficult, because it is impossible to insert the conventional reference electrode like Ag/AgCl into the thin PEM. Furthermore, the cathode polarization is negligible against to anode polarization, which means that this two electrode measurement system has little effect when the cathode is a pure hydrogen electrode[29]. And the two electrode set-up will allow the measurement to obtain specific electrochemical information of different components and process by fitting the impedance spectra to an equivalent circuit. The experimental set-up is a once-through design. The facility is located in a chemical hood. In electrolysis process, the anode tank serves as an absorber in which sulfur dioxide gas is dissolved into the sulfuric acid solution to form anolyte. The flow rate of sulfuric acid and hydrogen is 500ml min⁻¹ and 30ml min⁻¹, respectively. All tubing and valve connectors’ materials
on the anode side are fluorocarbon polymer (PTFE or PFA). All the electrochemical experiments are conducted using an electrochemical workstation (Zahner Electrochemical Workstation Zennium).

EIS experiments were conducted in the frequency range from 100 kHz to 0.1 Hz, with AC signal amplitude of 10 mV. The EIS experiment needs to be carried out under a constant voltage or current density condition. Based on the study of polarization curves under various reaction conditions in our previous work[22], U-I curves could be divided into three sections. Firstly, when current density is lower than 150mA/cm², cell voltage increases from the reversible voltage U eq to about 800mV. This increase is probably caused by the kinetic overpotential term and the ohmic overpotential. After that, cell voltage increases rapidly to about 1.2 to 1.8V, when the mass transfer resistance begins to appear. And the last section is a gentle linear region, due to the re-equilibrium of SDE reaction. Therefore, the EIS experiments are carried out under 0.5V, 1.0V and 1.6V, in order to reveal the reaction mechanism of anode overpotentials in different reaction regions. And the electrochemical process is carried out under controlled conditions, with the temperature of 25, 40 and 80°C and sulfuric acid concentration of 20-60wt%.

3. Results and discussion

3.1 Typical EIS impedance spectrum analysis

In potentiostatic mode of EIS measurement, an AC potential perturbation (which is 10mV in this work) is applied to the electrolysis cell and to measure the current response for calculating of the AC impedance of the cell. The measurement results are usually presented in a Nyquist plot, which is of the imaginary impedance against the real impedance. Analysis of the measurement data could be applied by establishing an equivalent circuit to represent the dynamic characteristics of the process. The reaction information could be determined by fitting the impedance data with the equivalent circuit equation using a non-linear least square procedure. Depending on the reaction mechanism of the EIS measurement, different patterns of Nyquist curves could be observed.

The typical spectra for anode reaction in SDE process under different potentials are shown in Figure 2. All spectrums under different cell potentials contain an impedance arc in the Nyquist plot. And the spectrum for 1.6V contains a straight line in low-frequency region. The single impedance arc that is a semicircle loop, is often called the “kinetic loop”, which occurs when the electrochemical process is dominated only by the interfacial kinetics of the reaction. The high-frequency intercept of the arc on the real axis stands for the total ohmic resistance of the reaction. The ohmic resistances vary depending on the cell temperatures and concentrations of sulfuric acid on the anode side. Radius of the impedance arc represents the charge transfer resistance, which declines with increasing cell voltages. Moreover, there is a straight line in the Nyquist curves at 1.6V under all experimental temperatures and sulfuric acid conditions. The straight line in the relatively low-frequency region appears could be identified as the mass transport limitation of reactant species. The mass transport impedance line becomes progressively more dominant under high cell voltage, with the charge transfer resistance’s decrease. Because the current density rises up with increase cell potentials, which also represents the rate of reaction. So reactants are consumed at a significantly higher rate under high cell voltages. On the other hand, the platinum in the anode electrode forms to an oxide passivation layer, when cell potential is higher than 1.0 V[30]. Therefore, the mass transfer of SO₂ as reactant to the surface of platinum is limited under high cell voltages.
3.2 Anodic resistance under various conditions

The equivalent circuits for anode reaction of the SDE process are shown in Figure 3. $R_1$ is the high frequency intercept of the impedance arc with the Zreal axis, which represents the total ohmic resistance of the anode reaction in SDE cell. The ohmic resistance of anodic SDE cell is composed of the contact resistances between components and ohmic resistances of components, like the PEM, catalyst, gas diffusion layer and bipolar plates. $R_2$ is the electrochemical reaction resistance, or the charge transfer resistance that is represented indicated by the impedance arc. CPE$_1$ is not a conventional double-layer capacitance, but is a constant phase element (CPE). The use of CPE is because that the capacitance caused by the double-layer charging is distributed along the length of the pores in the porous electrode of MEA[31]. $R_3$ is the mass transfer resistance that only occurs under high cell voltage (1.6V). The total resistance of the cell could be expressed as blow,

$$\begin{align*}
R &= R_1 + \frac{1}{Z_{CPE1}} & \text{(Low cell voltage: 0.5V, 1.0V)} \\
R &= R_1 + \frac{1}{Z_{CPE1}} + \frac{1}{Z_{CPE2}} + \frac{1}{R_3} & \text{(High cell voltage: 1.6V)}
\end{align*}$$

Since the CPE appears only at high frequencies, the resistance of which could be ignored [24]. The total resistance of the cell could be simplified as follows:

$$\begin{align*}
R &= R_1 + R_2 & \text{(Low cell voltage: 0.5V, 1.0V)} \\
R &= R_1 + R_2 + R_3 & \text{(High cell voltage: 1.6V)}
\end{align*}$$

Figure 4 is a typical fitting result of the EIS measurement with the sulfuric acid concentration of 30wt%. Fitting results at other sulfuric acid concentrations are in the same trend. As we discussed above, the ohmic resistance ($R_1$) is determined by the electrolysis temperature and sulfuric acid concentration, the value of which remains the same under various cell voltages. The ohmic resistance increases with the concentration of sulfuric acid in the anolyte, which could be attributed to the decline of the activity of the active species in the electrolyte. It could be indicated from Figure 4 that under all the reaction conditions mentioned above the SO$_2$ oxidation reaction resistance or the charge transfer resistance ($R_2$), takes the biggest part in the total anodic reaction resistance. The
reaction resistance decreased with rising cell voltage, which may attributed to the improved kinetic of SO₂ oxidation reaction. The reaction kinetics is influenced not only by the SO₂ solubility in various concentration of sulfuric acid, but also by the pH value of the reaction system[32]. That is, the components of active species varies with the concentration of sulfuric acid, and the reversible potential of the SO₂ oxidation reaction and the Nafion membrane conductivity change as well. Under all the reaction conditions, the lowest SO₂ oxidation reaction resistance appears at the 30wt% sulfuric acid and 80°C, which is consistent with the experimental results that we got in our previous work about the SDE performance[22]. The mass transfer resistance (R₃) appears only at high cell voltages (≥1.6V), which was generated by the high current density. Higher current density means higher consumption rate of SO₂, which will leads to limited concentration of reactant at the surface of anode electrode. Meanwhile, the oxidation passivation layer of the catalyst may be generated at high cell voltage.

Fig. 4 Typical fitting results for anodic EIS analysis as a function of cell voltage and temperature.

The sulfuric acid concentration is 30wt%.

Figure 5 is a summary of SO₂ reaction resistance under all reaction conditions. It is obvious that under the same reaction condition, the reaction resistance under higher cell voltages (0.02–0.16 ohm at 1.6V) is much lower than that of the lower cell voltages (0.16–2.48 ohm at 1.0V and 0.66–7.65 ohm at 0.5V), the reason of this phenomenon is stated above. Figure 5 also reveals that the reaction resistance reaches its lowest level under high temperatures and diluted sulfuric acid solution in anolyte, which is consistent with its reaction kinetic. That is, the SO₂ is an endothermic reaction that high temperature would benefit to the performance. However, the solubility of SO₂ served as a reactant in sulfuric acid will drop dramatically under increase temperature, which will have negative impact on the electrochemical reaction kinetic. On the other hand, sulfuric acid is served as product in the SO₂ oxidation reaction that the concentration of which would also have influence on the reaction kinetic. The reaction resistance goes higher under increase sulfuric acid concentration. Meanwhile, the concentration of sulfuric acid would also have impact on the efficient of sulfuric acid decomposition process that comes after the SDE process. With higher sulfuric acid concentration, there will be less input energy needed for the concentrate process of the sulfuric acid solution. Thus, there must be tradeoff between the efficiencies of sulfuric acid decomposition process and the SDE process. Moreover, the maximum temperature for the Nafion membrane served in SDE cell is 100°C, which is not the best choice for the SDE process. The PEM should be improved or replaced by some other PEM that has higher tolerance of temperature.
4. Conclusions

In-situ EIS method was developed and conducted to measure the resistance contributions of the anode reaction.
1. The mass transfer resistance of the anodic reactants appeared only at high cell voltages (1.6V), which may be attributed to the high consumption rate of reactant and the oxide layer of catalyst.
2. Results showed that under all the reaction conditions, the SO₂ oxidation reaction resistance takes the biggest part in the total anodic reaction resistance.
3. The reaction resistance reaches its lowest level under high reaction temperature, low sulfuric acid solution concentration and high cell voltage, which is determined by the reaction kinetic. Membranes that could resist higher temperatures (>100°C) should be used for improving of the SDE performance.

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6. References