A Current-Voltage Model for Hydrogen Production by Electrolysis of Steam Using Solid Oxide Electrolysis Cell (SOEC)

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Abstract

A current-voltage model for solid oxide electrolysis cell (SOEC) was developed and validated. The cell voltage and overpotentials were simulated and compared to an existing model and a published experimental data. A good agreement was obtained between current model, the existing model and that of the experimental data with respect to cell voltage, cell overpotentials and individual overpotentials. Analysis on the current model generated values revealed a significant 71.37% contribution of ohmic overpotential to the cell overpotential over the combined electrode (concentration and activation) overpotentials of 28.65%. This means that the influence of the electrolyte in the cell overpotential is 2.5 times greater than the influence of the electrodes, as predicted by the current model, implying that the structure and characteristics of the electrolyte in solid oxide electrolysis cells (SOECs) has direct bearing on hydrogen generation. At 1273 K, the limiting density of the cathode was predicted by the current model at 100,000 Am^{-2} which was verified and supported by Ni *et al*. and the experimental data of Momma *et al*. The current model in general was found to be consistent in predicting parametric values for high temperature steam electrolysis using solid oxide electrolysis cells (SOECs).

Keywords: *hydrogen production, water electrolysis, HTE, solid oxide electrolysis cell, SOEC model*

1. Introduction

The search for a renewable and environmentally sustainable fuel which will eventually lessen or the most, eradicate the dependency to fossil fuels has been the challenge among scientists today. Hydrogen and its production for fuel and electricity is being developed for several decades due to the promising characteristics of hydrogen as fuel and its ability to be generated in an efficiently clean manner (Francis, 2002). Several processes and technologies were introduced since the 1970's to harness hydrogen gas from water, while the use of Solid Oxide Fuels Cells (SOFCs), and now the use of its reversed mode called Solid Oxide Electrolysis Cell (SOECs) gains popularity over the others due to its environmental sustainability and process efficiency, which exceeds the most efficient internal combustion engine (Tanaka *et al*., 2016) . Ni *et al*. (2007a) in their study mentioned that so far, water electrolysis is the most practical and promising technology for large-scale hydrogen production. Li *et al*. (2014) added that SOECs can utilize efficiently available heat at higher temperatures and can be coupled with nuclear or renewable energy sources. A solid oxide electrolysis cell (SOEC) is a device that utilizes and transforms electrical energy form passing electrons to chemical energy of the fuel (Stempien, 2013). In a typical SOEC, gas is fed to the porous cathode and when required electrical potential for water splitting is supplied to the SOEC electrodes, water molecules will dissociate to form hydrogen gas in the cathode and oxygen gas in the anode (see Figure 1).

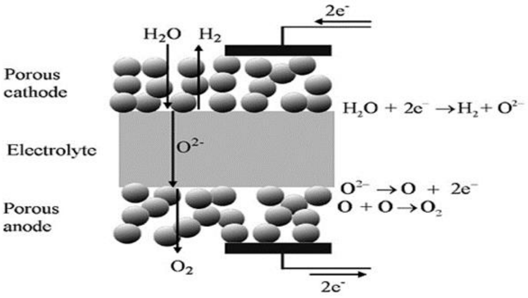

Figure 1. Hydrogen production by High Temperature Steam Electrolysis by Solid Oxide Electrolysis Cell (SOEC)

The electrochemical half-cell reactions in the SOEC are the steam electrochemical reduction,

$$H_2O + 2e^- \rightarrow H_2 + O^{2-} \qquad (1)$$

and the oxygen synthesis:

$$\tfrac{1}{2}\, O^{2-} \rightarrow 2e^- + \tfrac{1}{2}\, O_2 \qquad (2)$$

This is achieved by the flow of electrons from the anode to the cathode by means of an external power source. The ions liberate their electrons and recombine to form molecular O_2 on the anode side (Zoulaz *et al.*, 2013). High temperature steam electrolysis (HTE) on the other hand is an environmentally acceptable process for hydrogen production in the growing hydrogen markets (Argonne, 2013). Gas in the form of steam is fed in the SOEC at ideal temperatures of 800 - 1000˚C. The high temperature accelerates the reaction kinetics reducing energy losses (Ni *et al*., 2008a) . Water electrolysis has no side reactions that can yield undesired by products, therefore, the net balance is:

$$H_2O \rightarrow ½\,O_2 + H_2 \qquad (3)$$

However, real electrolysis of water in SOECs requires higher voltages for the reaction to take place - which is definitely higher than -1.23 V. This part is known as overpotentials or overvoltage (Argonne, 2013; Zoulas *et al*., 2013). Majority of the studies in SOECs today are based on the system level approach where electrochemistry of the process is assumed to be constant over the simulated range of current and power (Stempien *et al*., 2013). The vast available model on SOECs are focused either on predicting the electrical performance of the cell, fuel conversion and output system or process energy and exergy (Ni *et al*., 2007; Ni *et al*., 2008a; Stempien, 2013; Valerio, 2015). Several models for SOEC was generated since 1960s (Spacil, 1969; Shouler *et al*, 1981) which was associated with SOFC modeling. This paper attempts to develop a current-voltage model for the parametric study of hydrogen generation using high temperature electrolysis (HTE) of steam in SOEC. The model will primarily describe the influence of current density on individual and cell overpotentials as well as its influence on the performance of the of the SOEC stack and hydrogen generation at high temperature process was also included in the study.

2. Model Development

2.1 Fundamental Model Assumptions

The general equation for the required voltage in the SOEC [3, 6, 8, 9, 10] is contributed by the standard cell potential (E^0) and the sum of the overpotentials ($\eta_{a,c}$, η_{ohm}) as presented in equation (4).

$$E = E^0 + \eta_{conc,a} + \eta_{conc.c} + \eta_{act,a} + \eta_{act,c} + \eta_{ohmic} \qquad (4)$$

Where E is theoretical required voltage of the cell, $\eta_{conc,a}$ and $\eta_{conc.c}$ are electrode concentration overpotentials, $\eta_{act,a}$ and $\eta_{act,c}$ are electrode activation potentials and η_{ohmic} is the electrolyte overpotentials. The standard cell potential is computed based on the formula utilized by Ni *et al*. (2008a) on the dependency of cell potential to temperature:

$$E^0 = 1.253 - 2.4516x10^{-4}T \qquad (5)$$

For the steady state process, W is the minimum amount of work required by the process as stated by the First law of Thermodynamics and by enthalpy balance for a reversible process. Using the following series of equation, by inspection and simultaneous substitutions, a Nernst equation was derived for the theoretical required potential (E) in equation (11).

$$\Delta H = -Q + W \qquad (6)$$

$$\Delta G = \Delta H + T\Delta S \qquad (7)$$

$$\Delta G^0 = \Delta H^0 + T\Delta S^0 \qquad (8)$$

$$\Delta G = -RT \ln K_c \qquad (9)$$

$$-nEF = -nE^0F - RT \ln Kc \qquad (10)$$

$$E = E^0 + RT \ln K_c \qquad (11)$$

Utilizing the general equation for electrolysis if water in equation (3) and the relationship between concentration and partial pressures of the chemical species, equation (11) becomes equation (12) which is also the required voltage for SOEC at equilibrium.

$$E = E^0 - RT \ln \left[\frac{P_{H_2}(P_{O_2})^{\frac{1}{2}}}{P_{H_2O}} \right] \qquad (12)$$

where P_{H_2}, P_{H_2O} and P_{O_2} are partial pressures of hydrogen, water and oxygen.

2.2. Overpotentials

Overpotentials in an electrochemical cell is the excess or added voltage on top of the standard electrode potential needed for each half reaction to take place (Brisse *et al*., 2008). In SOECs, overpotentials are due to the presence of the electrodes and the dense electrolyte that takes part in the splitting of water. The theoretical framework of overpotentialas discussed by Smolinka *et al*. (2013) is the voltage drop due to the decrease of concentration in the cell as a function of concentration at any point in the stack ($C_{x=0}$) and the initial concentration (C^0), evaluated using the Nernst equation stated as equation (13) where $\emptyset = E$ and is treated as potentials.

$$\eta_{conc} = \Delta\emptyset - \Delta\emptyset_e = \frac{RT}{zF} \ln \frac{C_{x=0}}{C^0} \qquad (13)$$

2.2.1. Concentration Overpotentials

The water splitting which was assumed to be the only electrochemical reaction taking place in the electrode-electrolyte interphase. Using equation (13), and Figure 2, the cathode overpotential is written as equation (14):

$$\eta_{conc,c} = \frac{RT}{zF} ln \left[\frac{P^I_{H_2} P^0_{H_2O}}{P^0_{H_2} P^I_{H_2O}} \right] \qquad (14)$$

where the subscript c, corresponds to cathode, $P^I_{H_2}$ and $P^I_{H_2O}$ is the partial pressure of hydrogen and water on the electrode-electrolyte interface, and $P^0_{H_2}$ and $P^0_{H_2O}$ is the partial pressure of entering hydrogen and steam. From Figure 3, only one exit stream is involved (Oxygen gas), making the concentration potential in the anode be expressed simply as equation (15) (Stempien, 2013).

$$\eta_{conc,a} = \frac{RT}{zF} ln \left[\left(\frac{P^I_{O_2}}{P^0_{O_2}} \right)^{\frac{1}{2}} \right] \qquad (15)$$

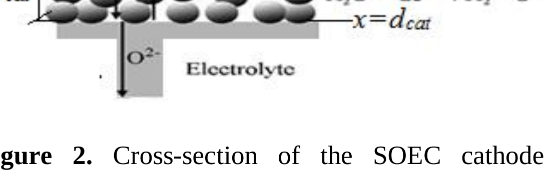

Figure 2. Cross-section of the SOEC cathode with boundary conditions.

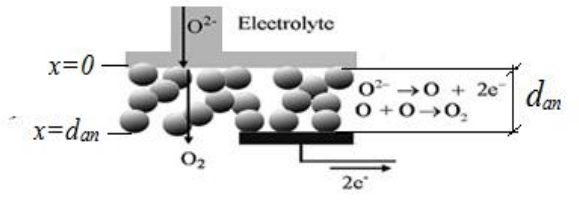

Figure 3. Cross-section of the SOEC anode with boundary conditions.

To simplify equations 14 and 15, analysis of the Triple Phase Boundary (TBP) is considered. The TBP is the region of contact between the electrodes, electrolyte and gaseous fuels (Ni *et al.*, 2007; Stempien, 2013; Ni *et al.*, 2008a). Using the Fick's Model on diffusion, pressure and molar flux (Chan *et al.*, 2002), and the theoretical boundary conditions considered to for the total and partial pressure of substances for each interphase in Figure 2 and 3, equation 14 is simplified equation (16) and equation (17) :

$$\eta_{conc,c} = \frac{RT}{2F}\ln\left[\frac{\left(1+\frac{JRTd_{cat}}{2FD_{H_2O}^{eff}P_{H_2}^0}\right)}{\left(1-\frac{JRTd_{cat}}{2FD_{H_2O}^{eff}P_{H_2O}^0}\right)}\right] \qquad (16)$$

$$\eta_{conc,a} = \frac{RT}{2F}ln\left[\left(1+\frac{RT}{D_{O_2}^{eff}P_{O_2}^0}\frac{J}{4F}d_{an}\right)^{\frac{1}{2}}\right] \qquad (17)$$

where J is the current density, T is the operating temperature, R is the Boltzman constant, F is the Faraday's constant, $D_{H_2O}^{eff}$ and $D_{O_2}^{eff}$ are effective diffusivities of water and oxygen determined using Bosanquet formula which is the combination of the Knudsen and the Chapman-Enskog theories on diffusion coefficients (Ni *et al.*, 2007; Ni *et al.*, 2008a).

2.2.2. Activation Overpotential

The relationship between overpotentials and current density is expressed using the Butler-Volmer Equation (Argonne, 2013):

$$J = J_{0,i}\left[\exp\left(\frac{\alpha zF\eta_{act,i}}{RT}\right) - \exp\left(\frac{(1-\alpha)zF\eta_{act,i}}{RT}\right)\right] \qquad (18)$$

where *i* corresponds to either the anode or the cathode*;* J_0 is the exchange current density; α is the symmetrical factor or charge transfer coefficient and z is the number of electrons transferred. For water electrolysis, α and *z* are found to be 0.5 and 2, respectively (Choi, *et al*, 2004). Inserting this values and the values of *Jo* from Table 1 to equation (18) gives the generalized form for the activation over potential for the cathode and the anode as:

$$\eta_{act,i} = \frac{RT}{F}ln\left[\frac{J}{2J_{0,i}} + \sqrt{\left(\frac{J}{2J_{0,i}}\right)^2+1}\right] \qquad (19)$$

3.2.3. Ohmic Overpotential

The ohmic overpotential in a SOEC, according to Ferguson *et al.* (1996) as cited by Ni *et al.* [9], obeys the Ohm's law where, it becomes a function of electrolyte thickness (L) and temperature (T).

$$\eta_{ohmic} = 2.99\,x\,10^{-5}\,JL\,e^{\left(\frac{10300}{T}\right)} \qquad (20)$$

3. Model Validation

The validation was performed using Ni *et al.*'s (2008a) model and Momma *et al.*'s (1997) experimental data on current-density and overpotentials. Table 1 lists the parameters used in the HTE SOEC electrochemistry modeling analysis (Momma *et al*, 1997). In this analysis, the current-voltage characteristics of hydrogen production was analyzed using a SOEC with cathode, anode and electrolyte made up of Ni-YSZ, LSM-YSZ and YSZ, respectively in the anode supported mode. Steam molar ration was found to be 60% at operating pressure of 1 bar. Statistical test was performed using MINITAB Statistical Software v. 17.

3.3 Cell Voltage

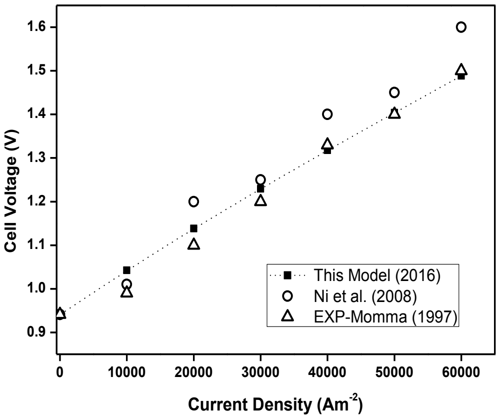

Figure 4. Comparison between model simulation results versus theoretical results of Ni *et al.* (2008a) and experimental results of Momma *et al.* (1997).

A good agreement between Ni *et al.*'s (2008a) model and the experimental model was achieved by the current model as shown in Figure 4. It was found that at 1273 K, the relationship between current density and cell potential obeys the same trend with that of the existing model and that of experimental results.The model developed in this paper was found to be of closer association to the experimental data obtained by Momma *et al*. (1997). This indicate that the values generated by the current model is comparable and can be considered to be almost the same as that of the existing model of Ni *et al.* [9] in 2008 and the experimental values obtained by Momma *et al.* (1997). While similar to the published literature and studies on SOECs, an equilibrium voltage of 0.941 is obtained for this model.

3.2. Cell Overpotentials

Figure 5 presents the good agreement in the cathode overpotential between the current model, the existing model and that of the experimental data. This trend of cathode overpotentials can be due to very thin nature of the cathode as compared to the electrolyte. The complexity of

Table 1. Parameters used in the HTE SOEC model analysis

Parameter	**Value**
Operating temperature, T (K)	1273
Operating pressure, P (bar)	1.0
Pre-exponential factor for Anode exchange current density,γ_a (Am^{-2})	2.051 x 10^{9}
Pre-exponential factor for Cathode exchange current density, γ_c(Am^{-2})	1.344 x 10^{10}
Activation Energy for anode, $E_{act,a}$ (Jmol^{-1})	1..2 x 10^{5}
Activation Energy for cathode, $E_{act,c}$ (Jmol^{-1})	1.0 x 10^{5}
Electrode porosity, n	0.48
Electrode tortuosity, ε	5.4
Average pore radius, r (μm)	1.07
Anode Supported Electrolyzer	
Electrolyte thickness, L (μm)	50
Cathode thickness, d_{cat} (μm)	50
Anode thickness, d_{an} (μm)	100

the electrochemical reaction taking place in the interphase allots for the smooth surface of the graph (Brisse *et al.*, 2008). The microstructures also constributes of the cathode is most likely to influence its voltage consumption. Figure 6 also suggests that both models and experimental values all agree that the cathode current density coincides at the same value which is at 100,000 Am^{-2}, which can be considered as the limiting density of the cathode in an the HTE SOEC at 1273 K.

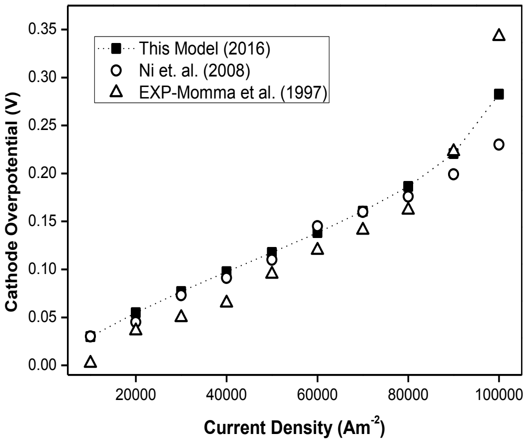

Figure 5. Comparison of the two (2) Model and Experimental current-voltage characteristics of the cathode concentration overpotential.

The anode concentration overpotential and the ohmic overpotential model generated values and experimental values were presented in Figure 6 and Figure 7. Contrary to the values of the cathode overpotential, the anode concentration overpotential as relatively small. This is phenomenon is attributed to the efficient transport of reactants that occur in the anode-electrolyte interface (Ni *et al.*, 2008a). The ohmic overpotential, on the other hand, is relatively large as compared to the other two overpotentials. This supports the initial findings that ohmic overpotentials contributed most to the cell overpotentials at different values of current density. The very small activation overpotentials in a SOEC is mainly contributed by the operating temperature that decreases ionic conductivity and increasing electrode reactivity, allowing increased ion mobility (Choi *et al.*, 2004).

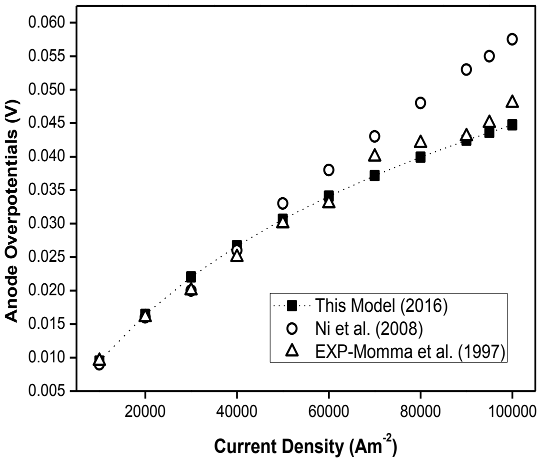

Figure 6. Comparison of the current, Ni *et al.* (2008a) model and Momma *et al.* (1997) experimental current-voltage characteristics of the anode concentration overpotential.

The current model generated values of cell overpotentials was presented in Figure 8. The obviously very large magnitude of ohmic overpotentials indicates that the current model was able to predict the great influence of the electrolyte in the cell overpotential of a high temperature steam electrolysis using SOECs. Figure 9 on the other hand supports these findings. The percent contributions of each overpotentials were statistically determined with respect to the cell overpotentials. As indicated, the influence ohmic overpotentials (71.37%)

was 2.5 times as that of the combined influence (28.63%) of the anode and the cathode concentration (18.77%) and activation overpotentials (9.86%). The model also agrees that the least contributing factor to cell overpotential is the activation overpotential.

4. Conclusion

The current model allowed prediction of the cell voltage and cell overpotentials based on a given current density by combining thermodynamic, mass and molecular transport models. Trends in properties and model generated values were found consistent with the existing published models and experimental data on SOECs. The predicted equilibrium voltage of 0.941V and a limiting current density of 100,000 Am^{-2} was obtained, which was strongly supported by several existing models and past experimental data. The Ohmic overpotential as found to be the primary contributor to the cell overpotential. This indicates the direct effect or bearing of electrolyte structure and characteristics on hydrogen generation in SOECs at 1273K. The very small contribution of activation overpotential at 1273 causes molecules to be driven farther apart increasing ion mobility. The cathodic overpotential illustrates the complexity of the electrochemical reaction reaction taking place in the cathode-electrolyte interface and serves as the basis of predicting the limiting current density of the system

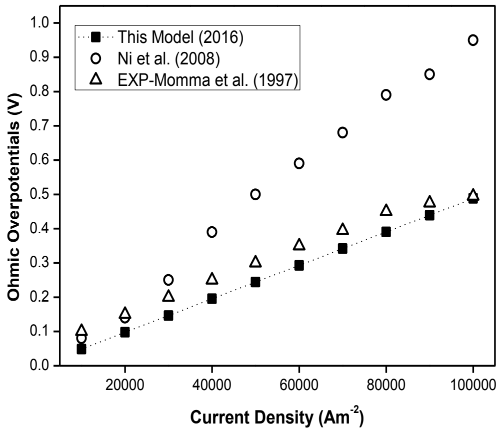

Figure 7. Comparison of the current model, Ni *et al.* (2008a) and Momma *et al.* (1997) Experimental current-voltage characteristics of the ohmic overpotential.

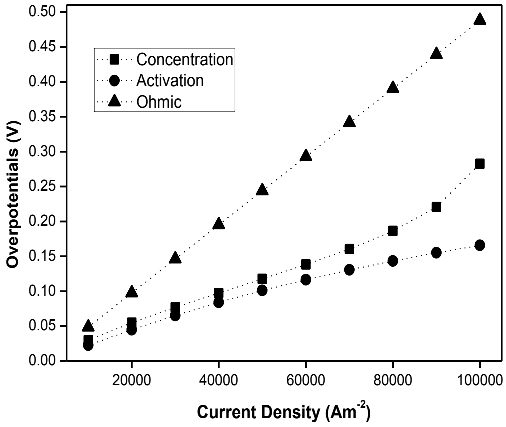

Figure 8. Current Model predicted overpotentials at 1273 K.

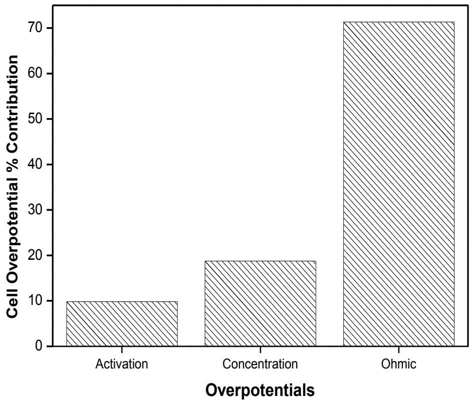

Figure 9. Predicted %contribution of the individual overpotentials to the cell overpotentials at 1273 K. (% contributions obtained from the ANOVA performed on the model predicted values at α=0.05; R^2=0.913; p-value=0.002 using Tukey's Test as post hoc analysis)

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