Electric Equivalent Circuit Model of an Alkaline Fuel Cell

MATTHIAS DŰRR, SINCLAIR GAIR*, ANDREW CRUDEN, JIM MC DONALD
Institute for Energy and Environment
University of Strathclyde
204 George Street, Glasgow G1XW
SCOTLAND, UK
http://www.instee.strath.ac.uk

Abstract: - The Centre of Economic Renewable Power Delivery (CERPD) at the University of Strathclyde has developed various fuel cell (FC) systems for stationary and vehicular applications. The aim of the research is to design and build reliable and cost efficient FC systems, which could replace existing conventional technology in the near future. To size each component of the system efficiently the behaviour of the alkaline fuel cell (AFC) stack has been modelled. The electric equivalent circuit model developed allows easy characterization of the fuel cell stack by electric parameters, such as internal resistance and stack capacitance.

The model is used to forecasts the behaviour of the fuel cell stack under various operating conditions. A mathematical analysis of the suggested equivalent circuit is presented in the paper. The so-called Nernst potential, which describes the open circuit voltage of the stack, is calculated using thermodynamic theory. Electrochemistry theory has been used to explain the causes of the different losses within the FC, such as activation, ohmic and concentration losses. In the model these losses are expressed using electric circuit elements. The circuit elements are derived from experimental tests, which are described in detail in the paper.

Key-Words: - fuel cells, modelling, equivalent circuit, alkaline, dynamic

1 Introduction

The Centre of Economic Renewable Power Delivery (CERPD) at the University of Strathclyde has developed various fuel cell (FC) systems for stationary and vehicular applications over the last 4 years. The aim of the research is the design and build of reliable and cost efficient hybrid FC/ battery systems, which could replace existing conventional technology in the near future. A domestic scale combined heat and power (CHP) alkaline fuel cell (AFC) system has been developed. A small AFC stack (1-3kW$_e$) is used to satisfy the average load demand of a domestic load profile for a stationary application. Whereas the load peaks are supplied by a battery system working in parallel with the AFC stack. Additionally, a part of the generated heat of the fuel cell can be easily extracted from the liquid electrolyte using a liquid/liquid heat exchanger [1] [2].The proposed circuit models the steady-state behaviour, as well as a dynamic behaviour of the alkaline fuel cell stack. Experimental tests and the circuit analysis are presented in detail in the paper.

2 The Alkaline Fuel Cell

A basic individual alkaline fuel cell (as shown in Figure 1) is composed of anode (negative electrode) and cathode with an electrolyte sandwiched in the middle. Gaseous hydrogen fuel is fed into the anode while an oxidant enters the cathode. The electrochemical reactions take place on the interface areas of anode and cathode where the dissolved gases and the electrolyte (KOH) come in contact in the presence of the catalyst.
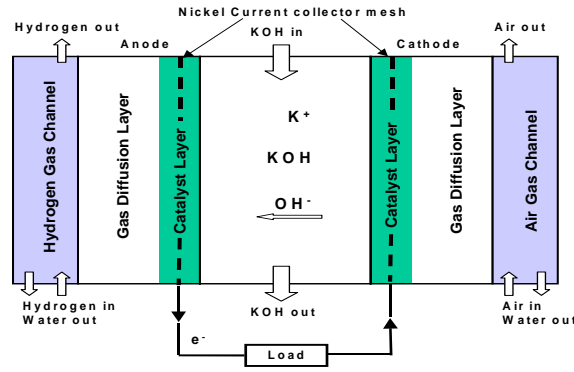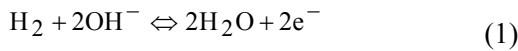
Fig. 1: Basic Alkaline Fuel Cell (AFC) module.

The generated energy is in the form of electricity and heat with water produced as a by-product. In an oxidation process on the anode the hydroxide ions react with the supplied hydrogen and as a result water is generated and electrons are delivered to on external electric circuit:

$$H_2 + 2OH^- \Leftrightarrow 2H_2O + 2e^- \quad (1)$$

In a reduction process on the cathode the supplied oxygen reacts under participation of electrons from the external electric circuit with water to form hydroxide ions:

$$0.5O_2 + H_2O + 2e^- \Leftrightarrow 2OH^- \quad (2)$$
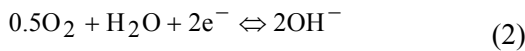
Hence the overall reaction of the hydrogen/oxygen AFC is defined as:

$$H_2 + 0.5O_2 \Leftrightarrow 2H_2O \quad (3)$$
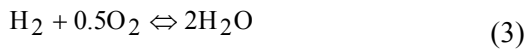
2.1 The equilibrium or reversible potential of an Alkaline Fuel Cell

In a fuel cell the chemical energy of the reactant species is directly transformed into electrical energy. However due to thermodynamic limitations only a part of the chemical energy can be transformed into electricity. This part is described by the Gibbs reaction enthalpy ΔG. The relationship between ΔG and the equilibrium or open circuit voltage (VOC) of a fuel cell is given by the following equation:

$$\Delta G = -nFE_{OCV} \quad (4)$$

where ΔG, n, F, E_{OCV} are the Gibbs enthalpy of reaction [J], number of electrons exchanged in reaction, Faradaic constant [96487 C mol^{-1}] and equilibrium potential or open circuit voltage [V], respectively.

When the reactants and products exist in the standard conditions, at ambient pressure (p_0=1.01325bar) and standard temperature (298.15K), the equilibrium potential is referred to as standard equilibrium potential and is related to the standard Gibbs enthalpy for the reaction as follows:

$$\Delta G^0 = -nFE^0_{OCV} \quad (5)$$

where ΔG^0, E^0_{OCV} are standard Gibbs enthalpy of reaction [J] and standard equilibrium potential [V], respectively. The related equivalent potential at non-standard conditions can be calculated using the so-called Nernst equation:

$$E_{OCV} = E^0_{OCV} + \frac{RT}{nF} \ln \frac{\prod \left[p_i^{zi} \right]_{prod}}{\prod \left[p_j^{zj} \right]_{react}} \quad (6)$$

where p_i, R, z_i, z_j, $\prod[\ldots]_{prod}$, $\prod[\ldots]_{react}$ are partial pressure of species i [bar], Universal gas constant [8.314 J mol^{-1} K^{-1}], number of moles of product species i, number of moles of reactant species j, product of parameter of product species and product of parameter of reactant species, respectively.

For a general hydrogen-oxygen reaction the Nernst equation is defined as:

$$E = E_0(T) - \frac{RT}{2F} \left[\ln \frac{p_{H_2O}}{p_{H_2} p_{O_2}^{0.5}} \right] \quad (7)$$

Equation 7 has been used in the model to calculate the open circuit voltage (OCV) for the modelled alkaline fuel cell stack [3].

2

2.2 Electrical Losses of the AFC

The theoretical EMF, which is achievable by a fuel cell, as determined by the Nernst Equation, is not achievable in reality. There are several sources of irreversible losses, which contribute to this, and they are commonly categorised as activation losses, ohmic losses and concentration losses. Additionally parasitic losses within the

- Ionic resistance of the electrolyte

- Ionic and electron resistance in the electrodes

- Resistance in the current collector and terminal connections
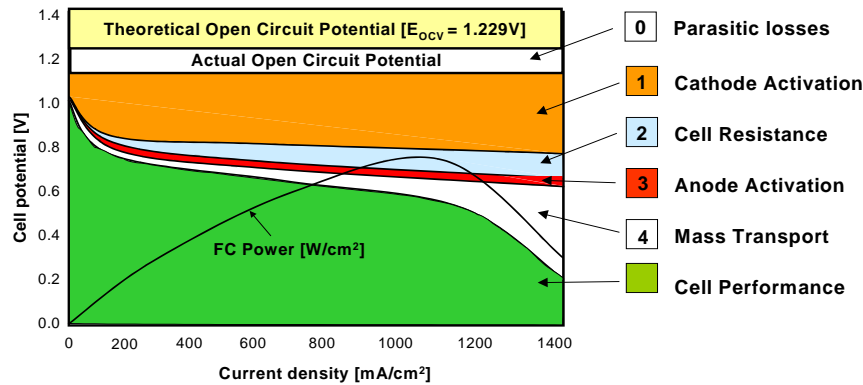

Fig. 2: Ideal and actual fuel cell voltage-current characteristics for a single cell

fuel cell, mainly caused by fuel crossover reduce the theoretical OCV further. Figure 2 illustrates the influence of the different anode and cathode losses over the current densities range.

The losses, often also called overpotential η are defined as the deviation of the open circuit voltage E_{OCV} and the actual cell potential E_{FC}:

$$\eta = E_{OCV} - E_{FC} \qquad (8)$$

with:

$$\eta = \eta_A + \eta_{iR} + \eta_C \qquad (9)$$

The fuel cell voltage therefore can be expressed in the form as following:

$$E_{FC} = E_{OCV} - \eta_A - \eta_{iR} - \eta_C \qquad (10)$$

where E_{FC}, E_{VOC}, η_A, η_{iR}, η_C are fuel cell potential [V], open circuit potential [V], activation losses [V], ohmic losses [V] and concentration losses [V], respectively.

Activation losses dominate at low current densities, caused by the kinetics of the charge transfer reaction across the electrode-electrolyte interface. Physically, part of the energy of the reaction is used to drive the electron transfer reaction and hence reduce the 'useful' work. The inherent electric resistance within the fuel cell causes ohmic losses, which occur from the:

$$\eta_{iR} = iAR \qquad (11)$$

where i, A, R are current density [A cm^{-2}], cell area [cm^2] and resistance [Ω], respectively.

The concentration losses are caused by the physical difficulties to transport reactant species to and product species away from the reaction area at higher current densities. As a consequence a concentration profile of the reaction and product species between the reaction interface and the bulk solution will develop which limits the FC performance and causes an irreversible loss [3].

2.3 Alkaline Fuel Cell Dynamics

The electrochemical process of a fuel cell is rather complex. In general the electrode reaction rate is governed by the rates of the dynamic processes listed below:

- Electrode kinetics

- The mass transport of reactants and products within the fuel cell

- Double layer capacity of the fuel cell

The effects of the above factors on the dynamic response of fuel cells are interactive and will depend on the current load applied to the cell, the rate of the load changes and the previous history of the load variations.

2.3.1 Double layer capacity

The double layer capacitance C_p expresses the true electric storage capability of the fuel cell. The overall capacitance of a cell is described as the sum of anode and cathode capacitance. The dielectric material in the case of an alkaline fuel cell is a potassium hydroxide solution. Figure 3 shows a schematic of the potential across the two electrodes and the electrolyte solution. The charge difference between electrode and electrolyte solution occurs within a very thin layer, which is called the Electrical Double Layer.
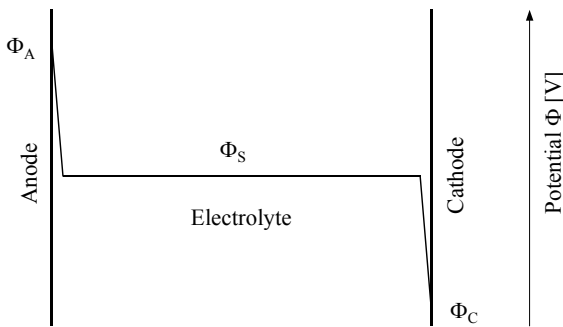

Fig. 3: Electrical potential within fuel cell

In the electric circuit model the double layer capacitance is represented with a capacitor Cd.

2.3.2 Faradaic process

The electrochemical reactions on the anode and cathode transfer charged particles (e.g. electrons, ions) across the electrode-electrolyte interface which causes oxidation or reduction of the species on the electrodes. Such charge transfer reactions are governed by the Faradaic law, i.e. the amount of chemical reaction caused by the flow of current is proportional to the amount of electricity passed. Knowing that the electron transfer process is by far faster than the mass transport process, the dynamics of the Faradaic process are mainly limited by the mass transport processes within the fuel cell.

In the equivalent circuit model these losses are represented by a variable resistor Ro in parallel with a capacitor C_d. The resistor Ro is dependant on the fuel cell current.

3 The Equivalent Fuel Cell Model

The alkaline fuel cell stack has been modelled using electric circuit theory, Figure 4. The Nernst voltage is represented by a controlled voltage source and has been calculated using equation 7. The internal resistance Ri of the fuel cell

symbolises the ohmic resistance of both electrodes and the electric resistance caused by the liquid electrolyte. Parasitic losses reduce the actual cell potential and are represented in the model by a resistor Rp in parallel with the Nernst voltage source. The dynamic behaviour of the AFC is modelled with a parallel resistor-capacitor branch. The double layer capacitance represented by a capacitor C_d, has a constant value and depends on the physical design of the fuel cell stack. The electrode kinetics and mass transport effects are represented by a variable resistor Ro, which depends on the current load applied to the cell and the rate of change of the load.
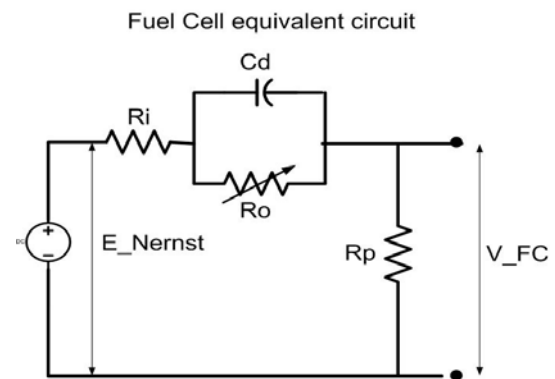

Fig. 4: Fuel cell equivalent circuit model

All model parameters have been determined through experimental tests in the laboratory.

3.1 Theoretical analysis of the equivalent circuit

The proposed equivalent circuit has been used to simulate various conditions, which can arise in practice, especially in regard to transient behaviour. The theoretical results have been compared to laboratory test results. The suggested FC circuit has been transformed into an equivalent Thevenin circuit using electric circuit theory and the capacitor voltage and current have been calculated. Figure 5 shows the series RC circuit.
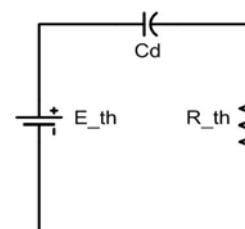

Fig. 5: Equivalent Thevenin circuit

The voltage within the series RC circuit is:

$$R_{th}i(t) + v(t) = R_{th}C_d \frac{dV}{dt} + v(t) = E_{th} \tag{12}$$

with:

$$i(t) = C_d \frac{dv(t)}{dt} \tag{13}$$

The overall response to the load switch is the sum of the natural and forced response:

$$v(t) = Ke^{-t/\tau} + E_{th2} \tag{14}$$

The initial conditions will allow us to determine the factor K:

$$v(0) = E_{th1} = Ke^0 + E_{th2} \tag{15}$$

It follows:

$$K = E_{th1} - E_{th2} \tag{16}$$

Inserting equation 16 in equation 14 leads to the voltage response of the capacitor to load switching:

$$E_{Cd} = (E_{th2} - E_{th1}) * (1 - e^{-t/\tau}) + E_{th1} \tag{17}$$

with:

$$\tau = C_d * R_{th2} \tag{18}$$

The current through the capacitor has been described as:

$$I_{Cd} = ((E_{th2} - E_{th1})/R_{th2}) * e^{-t/\tau} \tag{19}$$

The current through the resistor Ro follows using Ohm's law:

$$I_{Ro} = ((E_{th2} - E_{th1}) * (1 - e^{-t/\tau}) + E_{th1})/Ro \tag{20}$$

Consequently the current through the load resistor is determined using Kirchhoffs current law:

$$I_L = I_{Cd} + I_o = ((E_{th2} - E_{th1})/R_{th2}) * e^{-t/\tau} + ((E_{th2} - E_{th1}) * (1 - e^{-t/\tau}) + E_{th1})/Ro \tag{21}$$

The voltage is therefore:

$$E_L = I_L * R_L \tag{22}$$

Using the switching test techniques the time constant τ has been determined for the equivalent circuit. Having calculated the Thevenin resistance after switching R_{th2} allows the calculation of the fuel cell stack capacitance C_d.

$$C_d = \frac{\tau}{R_{th2}} \tag{23}$$

The internal resistance has been calculated as:

$$R_i = \frac{E_{VOC}}{E_{L1}} R_L \tag{24}$$

where E_{VOC}, E_{L1} are open circuit voltage [V] and initial load voltage after switching [V], respectively.

The value of Ro has been calculated at different load levels and depends on the fuel cell load level. Equation 25 is used to calculate Ro:

$$R_o = \left(\frac{E_{VOC}}{E_L} - 1\right)R_L - R_i \tag{25}$$

4. Parameter Validation

The model parameters have been validated through experimental tests on the fuel cell stack using the theoretical considerations of section 3.1. The Nernst or open circuit voltage has been calculated using equation 7. The parasitic losses, expressed with Rp, were determined through comparison between the theoretical and actual measured VOC of the fuel cell stack. The laboratory fuel cell system used for the experiments is shown in Figure 6.

Fig. 6: The AFC laboratory test system

Load switching tests have been used to determine the internal resistance Ri, the reaction resistance Ro and the double layer capacitance Cd of the fuel cell stack. The parameters used in the model are summarised in Table 1.

Parameter	Symbol	Unit	Value
Cells connected in series	n	-	12
Cells connected in parallel	s	-	4
E_Nernst @65°C and 40mbar gas pressure	E_Nernst	V	1.17
Double layer capacitance	Cd	F	2.85
Internal resistance	Ri	Ω	0.04
Faradaic resistance	Ro	Ω	$= f(I_{FC})$
Parasitic loss resistance	Rp	Ω	320

Table 1: Alkaline fuel cell stack model parameter [4]

5 Simulation Results

The model has been used to forecast the behaviour of the alkaline fuel cell stack at different load levels. The dynamic responses of the simulation and the actual fuel cell during load switching tests have been compared. Figure 7 shows the voltage response of the simulation and the actual fuel cell for a load switch from open circuit to a resistive load of 0.5Ohm.
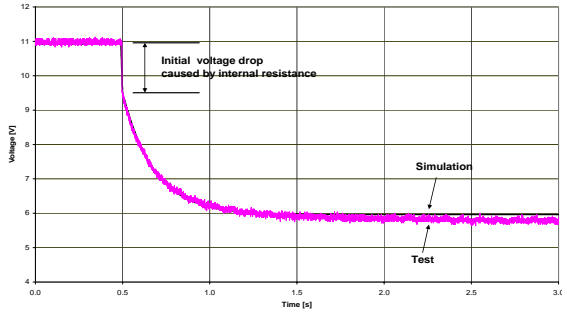

Fig. 7: Voltage response during switching test

Figure 8 shows for the same test the current response of the model and the actual AFC stack.

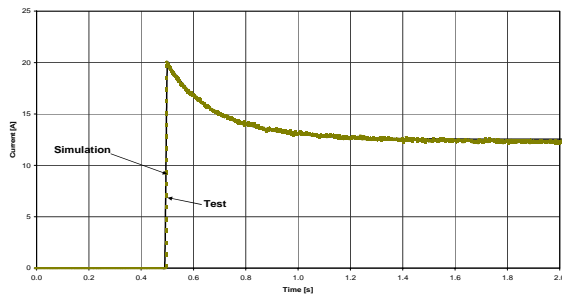Fig. 8: Current response during switching test

6 Discussion and Conclusions

The equivalent circuit model presented describes the fuel cell behaviour accurately within the modelled range (1A-70A fuel cell current). The dynamic behaviour has been analysed theoretically and has been confirmed through experimental tests. New work has started to replace Ro with an impedance element to make the model applicable for frequency analysis of the fuel cell stack. The model can be used for all types of fuel cells.

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