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A Simulation Model for the Dynamic Analysis of a Stand-Alone PEM Fuel Cell

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ABSTRACT

The ever increasing demand for electrical energy and the rise in the electricity prices due to the recent instability of the oil prices in addition to the degrading of the air quality resulting from the emissions of the existing energy conversion devices has intensified research into alternative renewable sources of electrical energy.

In this paper a dynamic electrochemical model is developed to simulate a Polymer Electrolyte Membrane Fuel Cell (PEMFC) system to allow the development and improvement of electrical energy generation systems using this new promising technology. Although other models have been produced but most of these capture the fuel cell (FC) steady state behaviour by estimating its voltage for a particular set of operating conditions. The proposed model allows the incorporation of effects of different dynamic conditions in load current, pressure of input reactant gases, fuel cell operating temperature as well as the mass/heat transfer transient features in the fuel cell body. Its capability of predicting transient dynamics will also prove useful when attempting to develop a control strategy. The proposed model strength is modularizing the fundamental thermal-physical behaviour of a fuel cell and developing a modular block that can be used as a part of any other schematic solution required for fuel cells' study. The developed modular block (prototype) exhibits most of the basic fuel cell properties and incorporates essential physical and electrochemical processes that happen along its operation, allowing its easily moderation to model fuel cells with different cell parameters and allow investigation of their behaviour for any operating or design configuration. The prototype can be useful in future in studying the integration of fuel cells into distribution power systems. The proposed modular block is implemented in SIMULINK and is verified by generating model results and comparing this to benchmark results for a Ballard NEXA TM Power module. The proposed model was also compared to another simplified model; sample results for a Ballard V PEMFC were generated for both models indicating that the developed model is more accurate in simulating the fuel cell especially at high operating current densities.

KEYWORDS: Renewable Energy, Fuel cells, Mathematical modelling, Block Simulation.

1. INTRODUCTION

Most of the world's 115GW per annum power consumption is still generated from the combustion of fossil fuels. This technology, despite of its advanced development, is inefficient (max. efficiency about 50%), lead to a global warming (generate almost 35% of greenhouse emissions), as well as becoming expensive and insecure (recent instability of the oil

prices) [1]. Fuel cells [1, 2, and 3] are electrochemical devices that convert the chemical energy of a gaseous fuel directly into electricity, heat and water thereby eliminating pollution. They combine the best features of engines (can operate for as long as fuel is available) and batteries (produce electricity directly from fuel without combustion reducing emissions and noise and increasing efficiency). Two of their major advantages are their ability to provide power and heat at different scales and in location; and their ability to operate on fuels ranging from fossil fuels through biomass based fuels to renewable. PEMFC emerges as one of the most promising for both stationary and automotive applications [4]. They have more advantages like their high power densities, solid electrolyte-long stack life, low corrosion and higher efficiency n (average stack η is higher than that of Internal Combustion Engine). Different models of PEMFCs are available in literature [4-10] but these are either more suitable for electrochemical purposes rather than electrical engineering [4-7], or presented a very simplified electrical model [8-10] to be used in deriving a control system. Also most of the available models cannot be easily modified to allow investigation of alternative combinations of system design and operating parameters. Also, in power generation systems, the dynamic response is extremely important for the planner especially when there is injection of energy into the grid. Hence, this paper presents a modular design prototype that is easy to modify to allow simulation of different configurations of a PEMFC, reducing the time and cost associated with a parameter investigation and enable investigation of transients. The model can be used as an initial step to prescribe internal design modifications and/or external controller designs to improve its transient behaviour. The proposed model is implemented in MATLAB/SIMULINK [11, 12] and was verified by generating sample results for a Ballard NEXA TM Power module [13]. Results from the verification investigation were compared to benchmark/experimental data indicating that the developed prototype is accurate in simulating a PEM fuel cell and predicting its performance. The proposed model was also compared to a simplified model [8], results generated for a Ballard V PEMFC [14] were compared showing that the proposed model is more accurate in simulating the fuel cell, especially at operating current densities higher than 1 A/ cm^2 (1000mA/cm²).

2. THE FUEL CELL SYSTEM

A fuel cell stack is formed of a number of cells referred as MEA (Membrane-electrode assembly) composed of a membrane (electrolyte) sandwiched between two porous electrodes. The stack' voltage is determined by the number of cells. Current is determined by the active area of the cells. Other parts of a fuel cell system include: pumps, blowers, compressors, cooling system, a power conditioning (voltage regulator to make the cell DC output suitable for connection to an electrical load) and sometimes a DC/AC inverter. A fuel processing system is needed if the fuel cell does not use pure hydrogen. A controller is needed to coordinate the parts of the system. The fuel cell system consists in general of four sections as shown in Fig.1: fuel processing, power generation in the fuel cell stacks, power conditioning and heat

recovery and/or power generation in integrated gas and steam turbines driven by the exhaust gases of the fuel cell and the fuel processing sections.

To utilize this system a mathematical model, that simulates it, is necessary in order to analyze the system behaviour in different operating conditions.

3. PEMFC BASIC PRINCIPLES AND MODELLING

A PEMFC depends primarily on a modified polymer membrane (Nafion: as it is mechanically strong, can absorb large quantities of water and is a good proton conductor), coated with highly dispersed catalyst particles (best is platinum although it is the major factor in the cost of PEMFC). The electrodes are usually flat and porous to allow the electrolyte from one side and the gas from the other side to penetrate it. It has a low operating temperature between 50 and 90 °C. The electrochemical equations are given by:

At Anode: $H_2 \rightarrow 2 H^+ + 2e^-$

At Cathode: $2 H^+ + 2e^- + \frac{1}{2} O_2 \rightarrow H_2 O + heat$

Overall reaction: H_2 + $\frac{1}{2} O_2 \rightarrow H_2 O$ + heat

Where: first equation determines the amount of hydrogen needed to be fed to the anode to meet a load, second equation determines amount of oxygen needed to be fed to cathode to maintain reaction, while the third equation determines water produced. The energy released is given by ΔG_f , which is the difference between the Gibbs free energy of products and that of reactants. It is more convenient to consider these quantities in their per mole form (g_f).

 $\Delta G_{\rm f}$: change in the Gibbs free energy of formation.

: $\Delta g_f = g_f$ of products - g_f of reactants

$$\therefore \Delta g_{f} = (g_{f})_{H,O} - (g_{f})_{H,} - \frac{1}{2} (g_{f})_{O}$$

Gibbs free energy of formation is not a constant; it changes with temperature and state (liquid or gas) as in table 1.

Modelling of a PEMFC:

3.1 Anode and Cathode (Reactants) flow Models:

In these models the dynamically varying pressure of the reactant gas flows (hydrogen and air) are calculated.

To calculate the O₂ usage rate:

We know from the basic reaction of fuel cell that 4 electrons are transferred for each mole of oxygen,

- \therefore Charge = 4F × amount of oxygen
- \therefore Oxygen usage (rate) = I/4F moles/s
- Oxygen usage = IN/4F moles/s; where:

F: Faraday constant or the charge on one mole of electrons = 96.485 C

N: number of cells in a stack.

I: rate of flow of charge (current) in a single cell.

Or, since $P = V_{FC} \times I \times N$, then $I = P/NV_{FC}$

 \therefore Oxygen usage = P/4F V_{FC} moles/s

Where: P: power of fuel cell stack, and V_{FC}: voltage of each cell.

From the molar mass of O₂

: Oxygen usage = $8.29 \times 10^{-8} \times (P/V_{FC}) \text{ Kg/s}$

However the molar proportion of oxygen in air is 0.21 then; Air usage = $3.57 \times 10^{-7} \times (P/V_{FC})$ Kg/s

To calculate the H₂ usage rate:

Similarly, from the basic reaction of fuel cell 2 electrons are transferred for each mole of hydrogen, so:

Charge=2F× amount of hydrogen, then

Hydrogen usage = I/2F moles/s, or

Hydrogen usage = $P/2F V_{FC}$ moles/s

The molar mass of H₂ is 2.02×10^{-3} kg/mol, that:

The Hydrogen usage = $1.05 \times 10^{\text{-8}} \times (P/V_{FC}) \; Kg/s$

The H_2 usage rate is useful to know the electrical energy that could be produced from a given mass or volume of hydrogen [Specific enthalpy (HHV) = 39.7 kWh/kg].

3.2 Membrane Hydration Model:

This represents the process of water transfer across the membrane. Dry membranes reduce proton conductivity and flooded ones block the pores in the electrodes leading to high voltage losses. Ideally, air (oxygen) blown over the cathode diffuse water from the cathode to the anode and throughout electrolyte and dry out any excess water providing a suitable state of hydration, but perturbations can happen. Thus an adjustable parameter ψ [3] that is influenced by membrane preparation procedure and relative humidity will be included in the proposed model.

 $\psi = 14$ under ideal condition of 100% relative humidity.

 $\psi = 22$ or 23 under oversaturated conditions.

3.3 Stack Voltage Model:

The typical electrical characteristic of a fuel cell is normally given in the form of a polarization curve, which is a plot of the cell voltage versus cell current density (current/unit cell active area). The difference between actual voltage V $_{F,C}$ and

ideal voltage of a fuel cell E_{Nernst} represents the losses in the cell. As more current is drawn the voltage decreases (due to the FC electrical resistance, inefficient reactant gas transport and slow reaction). As low voltage indicates low efficiency of the FC, then low load operation is preferred. Notice that since Gibbs free energy of formation changes with temperature and state, thus the polarization curve varies with different operating conditions as different temperatures, reactant partial pressures and membrane humidity. Therefore, the voltage model should calculate the stack voltage as a function of stack current, reactant partial pressures, cell temperature, and membrane humidity using a combination of physical and empirical relationships. The output voltage for a PEMFC is basically defined by [3]:

$$V_{F.C} = N [E_{Nernst} - L]$$

VFC: Stack Voltage.

E_{Nernst} = Cell potential obtained in an open-circuit thermodynamic balance (no load).

(1)

$$L = Voltage \ losses = \Delta V_{activation} + \Delta V_{ohmic} + \Delta V_{conc}$$

 $\Delta V_{activation}$: activation losses.

 ΔV_{ohmic} : ohmic losses.

 ΔV_{conc} : concentration losses.

• To find E_{Nernst}:

As it was shown before for each mole of hydrogen 2 electrons flow, thus the flowing charge is:

Charge = - 2F coulombs

Electrical done work = charge ×voltage

Then, $\Delta g_f = -2FE$ joules

That: $E = -\Delta g_f / 2F$

(2)

E: maximum electromotive force or reversible produced open circuit voltage of fuel cell at standard temperature 25 °C.

 Δg_{f} : per mole change in Gibbs free energy of formation (J/mol), which is the available energy to do external work.

To obtain E_{Nernst} [7] an extra term is added to take into account changes in temperature with respect to standard reference temperature 25 °C.

 $\therefore E_{\text{Nernst}} = -\Delta g_f / 2F + \Delta S / 2F (T - T_{\text{ref}})$ (3)

 ΔS : Change of the entropy (J/mol).

T: Fuel cell operation temperature in K; and T_{ref}: the reference temperature.

As the Gibbs free energy changes with reactant pressure and concentration; Thus:

$$\Delta g_{f} = \Delta g_{f_{o}} + RT \ln [P_{H_{2}} \times (P_{O_{2}})^{\frac{1}{2}}] / P_{H_{2}O}$$

:
$$E = E_o/2F + RT \ln [P_{H_2} \times (P_{O_2})^{\frac{1}{2}}] / P_{H_2O}$$
 (4)

Where: E_o is the cell EMF at standard pressure.

R: universal gas constant = 8.3145 J / K. mol.

P_{H2}, P_{O2}, P_{H2O}: Partial pressures of hydrogen, oxygen and water atmosphere.

From equations (3), (4) and by substituting with the known values of the (F and R) constants and the reference temperature, we obtain the final equation:

$$E_{\text{Nernst}} = 1.229 - 0.85 \times 10^{-3} \times (T - 298.15) + 4.3085 \times 10^{-5} \times T \times [\ln(P_{\text{H2}}) + \frac{1}{2} \ln(P_{\text{O2}})]$$
(5)

• To find the losses L:

This is divided to activation losses, crossover losses, ohmic losses and concentration losses.

3.3.1 Activation losses:

This is due to slowness of reactions taking place in the cell. A proportion of the generated voltage is lost in driving the chemical reaction that transfers electrons to or from the electrode.

$$\therefore \Delta V_{act} = A \ln (i/b)$$
(6)

 $A = A_a + A_c$; and $b = i_{oa}^{(Aa/A)} + i_{oc}^{(Ac/A)}$

Where A: slope of Tafel line, it is a constant in volts and is higher for a slow reaction.

b: is a constant in amperes.

3.3.2 Fuel crossover and internal currents:

This energy loss results from the waste of fuel passing through the electrolyte (*fuel crossover*), as well as some electron conduction through the electrolyte (electrolyte should only transport ions), resulting in a noticeable voltage drop (added to the activation losses). Thus the final Cell activation losses become:

$$\Delta V_{act} = A \ln \left[(i + i_n) / i_o \right]$$
(7)

Where, in: is the internal and fuel crossover equivalent current density.

io: exchange current density, it's higher for fast reaction reducing the activation losses and improving cell performance.

3.3.3 Ohmic losses or resistive losses:

This is due to either internal current losses caused by the leakage of some electrons passing through the membrane instead of being utilized, or due to resistive losses caused by electrons flow through the resistance of the whole electric circuit (hydrated membrane reduces ohmic losses). It is proportional to current density.

$$\Delta V_{\rm ohm} = ir \tag{8}$$

Where, r: is the area-specific resistance.

3.3.4 Mass transport or Concentration losses:

This is due to the change in concentration of reactants at the surface of the electrodes as the fuel is used causing reduction in the partial pressure of reactants, resulting in a reduction in voltage given by: $\Delta V_{\text{trans}} = -RT/n'F \times \ln(1 - i/i_1)$ (9)

Where, n': differs for different reactants (it is 2 for hydrogen and 4 for Oxygen).

Or ΔV_{trans} can be also found by using another approach [3] that is entirely empirical and has become more favoured lately,

because it gives same results, provided constants m and n are chosen properly:

$$\Delta V_{\text{trans}} = -m \exp(ni) \tag{10}$$

The value of m will typically be about 3 x 10^{-5} V, and n about 8 x 10^{-3} cm²/mA.

Combining all losses, the cell voltage becomes:

$$V = E - \Delta V_{ohm} - \Delta V_{act} - \Delta V_{trans}$$

$$\therefore V = E - i \times r - A \times \ln \left[(i + i_n) / i_o \right] + m \times \exp(ni)$$
(11)

Equation (11) is often simplified in a practical way as the crossover current in is usually very small.

$$\therefore V = E - ir - A \times \ln(i/i_o) + m \times \exp(ni)$$
(12)

 $V=E-ir-(A \ln(i) - A \ln(i_0)) + m \times exp(ni)$ (13)

Put constants together, so: $E_{oc} = E + A \ln(i_o)$

$$\therefore V = E_{oc} - i \times r - A \times \ln(i) + m \times \exp(ni)$$
(14)

This simplified emperical model was checked here by developing a SIMULINK [10] modular block for it. Example values of the used constants are given by table 2. Results obtained for a Ballard V fuel cell [12] is given in figure 2 showing that this model is only accurate in simulating the fuel cell at operating current densities less than 1 A/cm².

3.4 Proposed Model:

A more exact (non-simplified) model is proposed here, in which equation (5) is used to obtain the Cell Reversible Voltage E_{Nernst} taking into account changes in temperature with respect to the standard reference temperature [3]. Then all the voltage losses are considered using the following equations:

1. Activation Losses:

The activation voltage drop, including both anode and cathode, can be calculated using [3, 5, 7, and 9]:

$$\Delta V_{act} = -[\xi_1 + \xi_2 \times T + \xi_3 \times T \times \ln(C_{O_2}) + \xi_4 \times T \times \ln(i_{FC})] \quad (15)$$

$$C_{O_2} = P_{O_2} / (5.08 \times 10^6 \times e^{(-498/T)}).$$

Where, T: cell operating temperature in Kelvin (K).

ξ: parametric coefficients for each cell, whose values are defined based on theoretical equations with kinetic, thermodynamic, and electrochemical foundations.

 C_{O_2} : is the concentration of oxygen in the catalytic interface of the cathode (mol/cm³).

i_{FC}: is the cell operating current in (A).

2. Ohmic Losses:

It will be obtained using the general expression for resistance including all membrane parameters.

 $R_M\!=\!\rho_M\times L \; / \; A$

 $\rho_{M} = (181.6 \times [1 + 0.03 \times (i_{FC} / A) + 0.062 \times (T/303)^{2} \times (i_{FC} / A)^{2.5}]) / ([\psi - 0.634 - 3 \times (i_{FC} / A)] \times exp [4.18 \times ((T - 303)/T)])$

Where, the exponential term is the temperature correction if the cell is not operating at 30°C (303K).

 Ψ : a parameter functions of relative humidity; Ψ = 14 (ideal condition), 23 (oversaturated).

L: thickness of the membrane in cm, where L= 178µm for Nafion 117:7mil, L= 127µm for Nafion 115:5 mil, and L=

51µm for Nafion 112:2mil.

A: cell active area in cm².

 ρ_{M} : is the specific resistivity of the membrane to the electron flow (Ω .cm).

Then the ohmic voltage drop is determined by:

 $\Delta V_{ohm} = i_{FC} \times (R_M + R_C) \tag{16}$

R_c: is resistance to protons transfer through the membrane, and usually considered constant.

3. Concentration Losses:

This will be determined by:

$$\Delta V_{con} = -B \times \ln(1 - j/j_{max})$$
(17)

Where; B: is a parametric coefficient in volts, which depends on the cell and its operation state.

j: actual current density of the cell (A/cm²); $j = i_{FC}/A$

 j_{max} : is the maximum current density at which the fuel is used at same rate of the maximum supply speed, it is in range of (500–1500 mA/ cm²).

The above proposed mathematical model equations were all implemented in MATLAB/Simulink [11, 12] software to develop a modular block (prototype) for simulating the fuel cell.

The proposed MATLAB/SIMULINK Modular Block (prototype) for simulating the PEMFC:



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Constituents of the proposed prototype:
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4. VERIFICATION INVESTIGATION

For the validation of the proposed model prototype and checking its ability to be used as a tool for simulating a fuel cell stack, a single cell model Ballard Mark V (Nafion 117) was used for the investigation. The FC parameters used for this simulation is given in table 3. Results obtained for the proposed model was then compared to those obtained using the simplified model and are both given in figure 2. Results confirm that the proposed model prototype is more accurate in simulating the fuel cell especially at higher current densities above 1A/cm².

The FC operating temperature and the fuel/air flow are the two important dynamic properties of a fuel cell. It has to be noted that membrane temperature and gases partial pressures change with cell current, with increasing current partial pressure of hydrogen or oxygen decreases, whereas temperature increases. The proposed prototype allows the investigation of these dynamic properties, it will be demonstrated here how they will affect the fuel cell voltage. The effect of the change of cell temperature on output voltage is shown in fig. 3, a rise of only 20°C results in a voltage rise. The effect of the fuel/air (hydrogen & oxygen) input pressures was also demonstrated, an increase in fuel/air input pressure from the atmospheric pressure was found to raise the exchange current density, which has an apparent effect of raising the open circuit voltage as can be seen in fig. 4.

The total number of cells in a stack affects the resulting stack voltage as can be seen in Fig. 5. On using 1000 cells the stack voltage is raised to about 800 V at normal atmospheric pressure and low current density.

Correlation of the proposed model with experimental investigation for the lab Ballard NEXA TM Power module [13] given by Fig.6 is also performed. Comparisons between the proposed model predicted results and the benchmark/experimental results [13] are given in Figures 7 & 8 consequently confirming the validation of the proposed prototype.

5. STACK EFFICIENCY

 η = electrical energy produced per mole of fuel/- Δ h f

Where: $\Delta h_{f_{r}} = -241.83 \text{ kJ/mol}$ if product is steam (HHV) and is -285.84 kJ/mol if product water (LHV). The maximum possible efficiency (thermodynamic efficiency) is when the electrical energy is equal to change in Gibbs free energy. Where; η : fuel cell efficiency.

HHV: higher heating value.

LHV: lower heating value (probably used in calculating efficiency since it gives the higher figure).

: Maximum efficiency possible= $\Delta g_f / \Delta h_f \times 100 \%$

The output voltage of a fuel cell V_c is then related to efficiency by adapting equation (2). If all the energy from the hydrogen fuel is transformed to electrical energy, then: $E = -\Delta h_f / 2F = (1.48)$ at HHV and (1.25) at LHV.

Therefore actual efficiency (output/input) is then:

 $\eta = (V_c/1.48) \times 100\%$ (with reference to HHV)

 $\eta = (V_c/1.25) \times 100\%$ (with reference to LHV)

However, in practice not all the fed fuel is used. Thus a fuel utilization coefficient can be defined as:

 μ_f = mass of cell's reacted fuel/mass of input fuel to cell

 $\eta = \mu_f V_c / 1.48 \ 100\%$ (with reference to HHV)

 $\eta = \mu_f V_c / 1.25 \ 100\%$ (with reference to LHV)

This equation (HHV) is implemented in both the simplified and proposed models' prototypes to obtain the efficiency curves. The resulting efficiency curves from both models for the used Ballard V PEMFC are compared in figure 9.

6. CONCLUSION

Two prototypes for modelling the fuel cell, by using both the simplified and the proposed mathematical models respectively, were developed tested and compared. Although the prototype produced using the simplified model gave reasonable results, the proposed model prototype was found to give better results especially at current densities greater than 1A/cm². A further advantage of the proposed prototype is that it can be changed easily because it is built out of different autonomous operating blocks. The proposed prototype can be useful in many applications in future such as:

- 1. Estimate the performance of a specific fuel cell system and investigate its behaviour as an initial step toward investigating internal design modifications and/or external controller designs to improve its transient response.
- 2. Estimate the performance of a specific application that uses a fuel cell system, for example the integration of a fuel cell into a power system.

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8. FIGURES



Fig. 1 Block Diagram of a Fuel cell Power Plant





Fig. 2: Resulting Polarization Curve for a fuel cell on using the proposed fuel cell model, compared to that obtained on using simplified model (current density up to 1500 mA/cm² or 1.5 A/ cm²)



Fig. 3 Effect of temperature change on the output fuel cell voltage



Fig. 4: Polarization Curves shows the resulting boost in fuel cell voltage when operating at a higher hydrogen and oxygen pressures.



Fig. 5 The resulting polarization curve (using proposed model) for a stack PEMFC system made of 1000 cells



Fig. 6 Lab Ballard NEXA TM Power module



Fig. 7 Proposed Model resulting Polarization and Power Curves for the lab Ballard NEXA TM Power module



Fig. 8 Benchmark/experimental Polarization and Power Curves for the lab Ballard NEXA TM Power module



Fig. 9 Efficiency Curve using both proposed and simplified empirical models prototype (reference to HHV)

9. TABLES

Table 1 Δg_f for the reaction (H₂+ $\frac{1}{2}$ O₂ \rightarrow H₂ O) at various temperatures; -ve sign means that energy is released:

Form of water product	Temperature (°C)	Δg_{f} (kJmol ⁻¹)
Liquid	25	-237.2
Liquid	80	-228.2
Gas	80	-226.1
Gas	100	-225.2
Gas	200	-220.4
Gas	400	-210.3
Gas	600	-199.6
Gas	800	-188.6
Gas	1000	-177.4

Table (2) Example constants for equation 14:

Constant	Ballard Mark V PEMFC at 70°C	
$E_{oc}(V)$	1.031	
$r (k\Omega cm^2)$	2.45 x 10 ⁻⁴	
A (V)	0.03	
m (V)	2.11 x 10 ⁻⁵	
$n (cm^2/mA)$	8 x 10 ⁻³	

Table (3) Parameters of the used Ballard Mark V Fuel Cell

Parameter	Value	Parameter	Value
Т	70 °C (343 K)	ξ1	-0.948
А	50.6 cm^2	ξ2	0.00286+0.0002*
			$\ln(A) + (4.3 \times 10^{-5}) \times$
			ln C _{H2}
L	178 * 10 ⁻⁴ cm	ξ3	7.6 * 10 ⁻⁵
P _{H2}	1 atm.	ξ4	- 1.93 * 10 ⁻⁴
P _{O2}	1 atm.	Ψ	23
В	0.016 V	jmax	1.5 A/cm^2
R _C	0.0003 Ω	jn	0.0012 A/cm^2