THERMAL MODELLING OF A DIRECT METHANOL FUEL CELL STACK

ARGYROPOULOS P. SCOTT K. TAAMA W.M.
Chemical and Process Engineering Department, University of Newcastle, NE1 7RU.

A model is presented for the Direct Methanol Fuel Cell (DMFC), based on the differential thermal energy conservation equation, which describes the thermal behaviour of the cell stack. In the model the material and energy balances are posed initially in one dimension, along the length of the stack. This enables estimations of the temperature profile along the stack and the interactions between the various components in the cell stack. The model enables an assessment of the effect of the fuel condition (liquid or vapour), operating conditions and of the cell component physical properties.

Keywords: Fuel cell, Direct methanol, Modelling, Thermal energy balance.

NOMENCLATURE

A	Area (m^2)
c_p	Specific heat (J/kgr K)
F	Faraday constant (A sec/mol)
h	Convective heat transfer (W/m^2K)
i	Current (A)
K	Thermal conductivity (W/mK)
l	Length (m)
$\dot{m}$	Mass flowrate (kgr/sec)
n	Number of electrons transferred through the cell
q	Heat (W)
T	Temperature (K)

Subscripts

agdl	Anode gas diffusion layer
a	Anode
acl	Anode catalyst layer
bp	Bipolar plate
c	Cathode
cc	Carbon cloth
ccl	Cathode catalyst layer
cgdl	Cathode gas diffusion layer
mea	Membrane electrode assembly
mem	Membrane

Greek Letters

ΔH	Reaction Enthalpy (J/kg mol)
η	Overpotential (V)
ρ	Resistivity (1/Ohm m)
σ	Stefan Boltzmann constant (W/m^2K^4)

INTRODUCTION

A fuel cell stack consists of a number of single cells connected in electrical series. Each cell is connected to the adjacent one through bipolar plates which have flow channels, for the flow of fuel and oxidant, machined on their both side surfaces and are in electrical contact with the carbon backing layer, on the membrane electrode assembly (MEA). Thus, the bipolar plates serve both as gas or liquid flow channels, and current collectors, as well as providing separation between the fuel and the oxidant flows in adjacent cells. At the ends of the stack, are blocks consisting of the following parts: two stainless steel end plates, which are used for aligning and compressing the stack body, two Teflon made sheets which isolate the end plates from the copper made current collector plate. The carbon-backing layer serves as support for the un-catalysed gas diffusion layer and for the catalyst layer, made from Pt-Ru dispersed on

carbon and bonded with a Nafion/Teflon mixture, which is in contact with the Nafion membrane, which serves both as cell separator as well as the electrolyte. At the other side of the membrane there is the cathode with is similar to the anode except that the electrocatalyst used in the cathode is Pt supported on carbon. This repeated section: bipolar plate-flow channels-carbon backing layer-uncatalysed layer-anode catalyst layer-membrane-cathode catalyst layer-uncatalysed layer- carbon backing layer- constitutes the fuel cell stack which is shown schematically in Fig. 1

THERMAL MODEL

To describe the distribution of temperature in a DMFC stack through a simulation model a series of assumptions are made to simplify the mathematical treatment:

- Catalysts layers are thin compared to the membrane, and act as either heat source or heat sink.
- The catalyst layer is extremely thin so that no concentration gradient exists.
- The membrane has a high thermal resistance and Joule heat is liberated into both fluids.
- Heat is transferred by electro-osmotic flow of water and methanol across the membrane

cathode Cathode and anode side outlet temperatures are the same for all the cells (we assume that the outlet of each cell is well mixed in the manifold and has a uniform temperature).

- The surface of the graphite plate is in direct contact with the carbon cloth so we assume that they are at the same temperature.
- The channels are shallow and thus there is no temperature gradient between the top and the bottom.
- Anode and cathode streams are acting as coolants, in such a way that they control the amount of heat carried away from the cell.

The model of the various regions in the fuel cell stack is developed below.

GAS DIFFUSION LAYERS

This layer is made from ‘A’ type carbon cloth manufactured by E-TEK. This is a plain weave cloth. It has a weight of 116g/m2 and thickness of 0.35mm. The cloth has good mechanical strength and longer durability than the carbon paper, which is also in use for DMFC. On the one side of the cloth a paste like material is spread out evenly. This is an extremely thin layer of uncatalysed Vulcan XC72-R carbon black sintered with 10%wt teflon. Essentially the only net heat production in this layer is that due to Ohmic heating of the carbon-based material of the backing layer. The electrical conductivity of this material is relatively high and thus the potential dropthrough the structure will be small.

Overall the carbon backing layers can be initially modelled as regions with a uniform effective conductivity in which linear conduction takes place and convective heat transfer, in which the dominant factor is that associated with the electro-osmotic flow of water and methanol:

$$K_{agdl}\frac{d^2T}{dx^2}+\sum_i \dot{m}_{i,cc}\bar{c}_{p,i}\frac{dT}{dy}=-i^2\frac{l_{agdl}}{\rho_{agdl}A_{mea}} \qquad (1)$$

where l_{cc} is the thickness of the carbon backing layer, i is the local current density and ρ_{cc} is the resistivity of the carbon porous structure.

The cathode layer is similarly modelled

$$k_{cgdl}\frac{d^2T}{dx^2}+\sum_i \dot{m}_{i,cgdl}\bar{c}_{p,i}\frac{dT}{dy}=-i^2\frac{l_{cc}}{\rho_{cc}A_{mea}} \qquad (2)$$

The above are valid under the assumption that heat losses to the surrounding environment can be considered as small due to the negligible thickness of that layer.

ANODE CATALYST LAYER

The catalyst layers are considered as composites of Pt/Ru-C powder and ionomer. The enthalpy changes associated with the electrocatalytic reactions mean that temperature changes will occur in the catalyst layer. These temperature changes are different in both layers and are dependent upon the rates of heat conduction and heat convection associated with water and methanol electro-osmotic transport. The differential equation that gives the temperature profile in this section is:

$$K_{acl}\frac{d^2T}{dy^2}+\left(\dot{m}_{H_2O,crossover}\bar{c}_{p,H_2O}+\dot{m}_{MeOH,crossover}\bar{c}_{p,MeOH}+\sum_{\mathrm{i}}\dot{m}_{\mathrm{i}}\bar{c}_{p,m,i}\right)\frac{\mathrm{dT}}{\mathrm{dy}}+$$

$$l_{acl}\left(i_c\eta_a-\frac{i^2}{\rho_{acl}A_{mea}}+\frac{i\times\Delta H_a}{nF}\right) \quad (3)$$

MEMBRANE

The membrane in use is Nafion 117 from DuPont. Modelling of the Nafion type membrane of thickness lm is based on the following assumptions:

- A fully hydrated continuum with effective ionic and electronic conductivities
- Heat conduction defined by effective thermal conductivity $K_{eff,mem}$
- Heat transfer by the bulk flow of solvent (water and methanol)
- The heat losses to the surrounding environment can be considered as small due to the negligible thickness of the membrane.

The amount of heat produced in the membrane can be attributed to the following two sources:
The differential equation that gives the temperature profile in this section is:

$$k_{mem}\frac{d^2T}{dy^2}+\left(m_{H_2O,drag}c_{pH_2O,m}+m_{MeOH,drag}c_{pMeOH,m}\right)\frac{dT}{dy}=-i^2\frac{l_{mem}}{\rho_{mem}A_{mea}} \quad (4)$$

CATHODE CATALYST.

If we consider the cathode catalyst layer, proton transfer across the polymer electrolyte to this region will carry with it water and methanol. As, in the steady state, the water transferred from the anode must equal that discharged into the cathode vapour phase (that produced by reaction), there will be a relatively large variation in water “concentration” in this layer. This is because at the vapour side of the catalyst layer (y=0) there is zero current flowing from the electrolyte to the catalyst and thus zero ionic (proton) flow and consequently zero electro-osmotic flow. Water is removed at this point by its effective diffusion rate. In principle, this situation requires a model for water transfer and the associated reactions. However, if we assume that the local rate of water is essentially constant and proportional to the overall current density I_T then we can ignore the complication of a water balance.
The differential equation that gives the temperature profile in this section is:

$$K_{ccl}\frac{d^2T}{dy^2}+\left(\dot{m}_{H_2O,crossover}\bar{c}_{p,H_2O}+\dot{m}_{MeOH,crossover}\bar{c}_{p,MeOH}+\sum_{\mathrm{i}}\dot{m}_{\mathrm{i}}\bar{c}_{p,m,i}\right)\frac{\mathrm{dT}}{\mathrm{dy}}+$$
$$l_c\left(i_c\eta_c-\frac{i^2}{\rho_{ccl}A_{mea}}+\frac{i\times\Delta H_c}{nF}\right)\quad(5)$$

BIPOLAR PLATES

The bipolar plates interconnect each cellproviding an electrical connection between the cells and also the main heat transfer area between the cells. Each MEA is compressed between two bipolar plates. This means that the carbon cloth is in direct contact with the surface of the plate, and ideally with negligible contact resistance and as a first approximation we can consider that the surface temperature of the bipolar plate and the carbon cloth is the same. We assume that heat is being transferred from the surface of the bipolar plate and from the surface of the carbon cloth, defined by the same heat transfer coefficient.

During cell operation a fraction of the inlet stream is consumed as reactants. Since we are using both fuel and oxidant in excess, a portion of the remaining inlet stream, is heated and leave the cell in an elevated temperature. In addition CO_2 or water which are the by-products of the half cell reactions are also flowing out of the gas diffusion layer and thus, are transferring some heat with them. The energy flow in and out the cell can be defined as:

$$q_a=\dot{m}_{MeOH,excess,a}\bar{c}_{p,_{MeOH}}\left(T_{a,out}-T_{a,in}\right)+\dot{m}_{H_2O,excess,a}\bar{c}_{p,_{H_2O}}\left(T_{a,out}-T_{a,in}\right)+$$
$$\dot{m}_{CO_2,total,a}\bar{c}_{p,_{CO_2}}\left(T_{agdl,in}-T_{a,out}\right)\quad(6)$$

$$q_c=\dot{m}_{MeOH,crossover,c}\bar{c}_{p,_{MeOH}}\left(T_{cgdl,out}-T_{c,out}\right)+\left[\dot{m}_{H_2O,crossover,c}+\dot{m}_{H_2O,produced,c}\right]\bar{c}_{p,_{H_2O}}\left(T_{cgdl,out}-T_{c,out}\right)+$$
$$\dot{m}_{H_2O,humidity,c,in}\bar{c}_{p,_{H_2O}}\left(\mathrm{T_{c,out}}-\mathrm{T_{c,in}}\right)+\dot{m}_{O_2,excess,c}\bar{c}_{p,_{O_2}}\left(\mathrm{T_{c,out}}-\mathrm{T_{c,in}}\right)+\dot{m}_{N_2,total,c}\bar{c}_{p,_{N_2}}\left(\mathrm{T_{c,out}}-\mathrm{T_{c,in}}\right)\quad(7)$$

The change in the sensible heat of the excess feed/oxidant is attributed to the convection heat transfer mechanism from the bipolar plate and the gas diffusion layer. In addition we assume that energy flows from the anode to the cathode. This is expected since the anode stream should be always heated to provide enough heat for the endothermic anodic reaction, when in the cathode side the exothermic reaction produces heat which is being removed from the oxidant and possibly from the next anode inlet stream. We believe that with the low flow rates in use with the system, and since it is expected that the heat transfer coefficient of the gas side is considerably lower than the the anode side, that the cathode stream is not sufficient to remove all the heat from there. Thus, we are expecting heat to be transferred to the next cell through the bipolar plate. The differential equation, which governs the heat flow, is:

$$K_{bp}\frac{d^2T}{dx^2}=\left(h_{air}A_{\exp}\left(T_{plate,ext}-T_{env}\right)+\sigma\mathrm{T}^4_{\mathrm{plate,exp}}-i^2\frac{l_m}{\rho_{bp}A_{bp}}\right)\quad(8)$$

where K_{bp} is the thermal conductivity of the plate, i is the current density based on the cross sectional area of the electrode A_{mea}.

MODEL RESULTS

The aforementioned equations are solved with an iterative procedure until a specific convergence criterion is satisfied. This criterion is the difference between two successive iterations of the calculated anode side mean outlet temperature not to exceed .0001K. C++ is used for programming and solving the algorithm.

Figure 2 presents the typical temperature profile for a three-cell stack, which is fed with liquid water-methanol solution at 80°C. The first case is for an active area of 207cm^2 and the other one for 272cm^2, but with all the other parameters kept constant. It should be noted that the nodes present result for the inlet and the outlet of each layer the profile is not a function of stack length. The cells are operated at a constant uniform current density of 100mA/cm^2, with a flow rate of 3×10^{-6}kgr/sec.
Some important preliminary observations can be drawn:

1. The model predicts that the heat produced from the stack in the first case is not sufficient to maintain the stack in a temperature higher than 50°C when in the second case is sufficient to keep it in 75°C. This means that there is a need for supplying heat from an external source but this demand is significantly lowered if in the same system we increase the active area. It should pointed out that the results concern a small stack of 3 cells, which is not thermally insulated.
2. The temperature gradient between the two end graphite blocks is smaller than 1°C.
3. The heat transfer coefficients are extremely small (15 and 2 W/mK for the anode and cathode side respectively).
4. Increasing the fuel flow rate results in increasing heat removal from the stack and hence it is cooling down the stack.
5. The extremely low flow rates in use are result in very low Reynolds number and hence conduction is the prevailing heat transfer mechanism.

CONCLUSIONS

We have developed a model of the thermal behaviour of the DMFC cell stack, which will enable to study the variation of the temperature of the various components in the cell. The model will also allow us to assess the thermal requirements for the fuel cell stack operation under practical conditions. The influence of the current and power generated, in relation to the supply and utilisation of the fuel and oxidant, on the operating temperature for maximum power output can be evaluated.

REFERENCES

1. Borroni-Bird, C.E., 1996, Fuel cell commercialization issues for light duty vehicle applications, *Journal of Power Sources*, 61: 33-48.
2. Maggio, G. Recupero, V. Mantegazza, C., 1996, Modelling of temperature distribution in a solid polymer electrolyte fuel cell stack, *Journal of Power Sources*, 62: 167-174.
3. McCabe, W. L. Smith, J. C. Harriott, P., 1995, *Unit operations of Chemical Engineering*, 5th International ed., McGraw-Hill Chemical Engineering Series, Singapore: McGraw Hill.

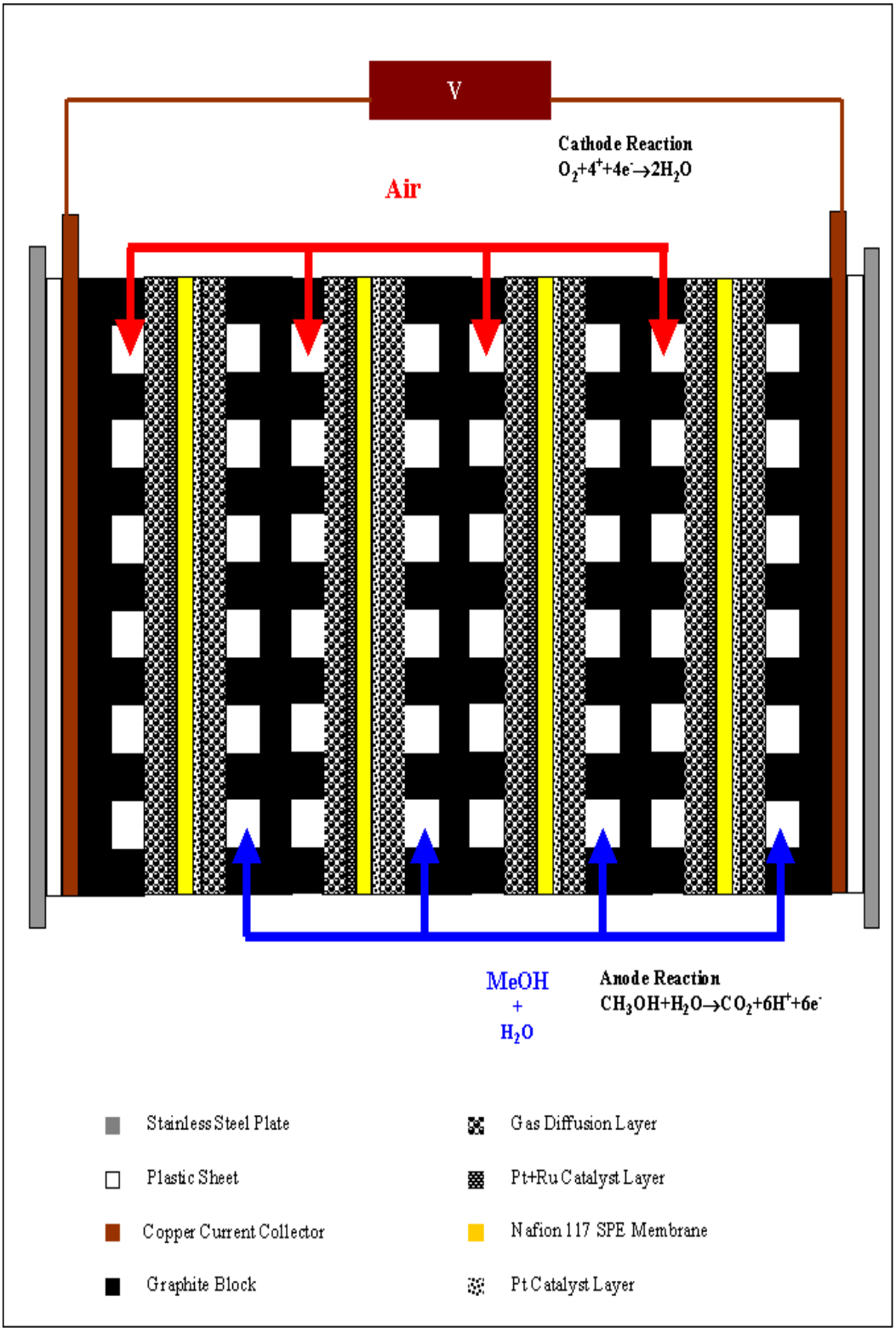

Figure 1: Schematic diagram of the fuel cell stack

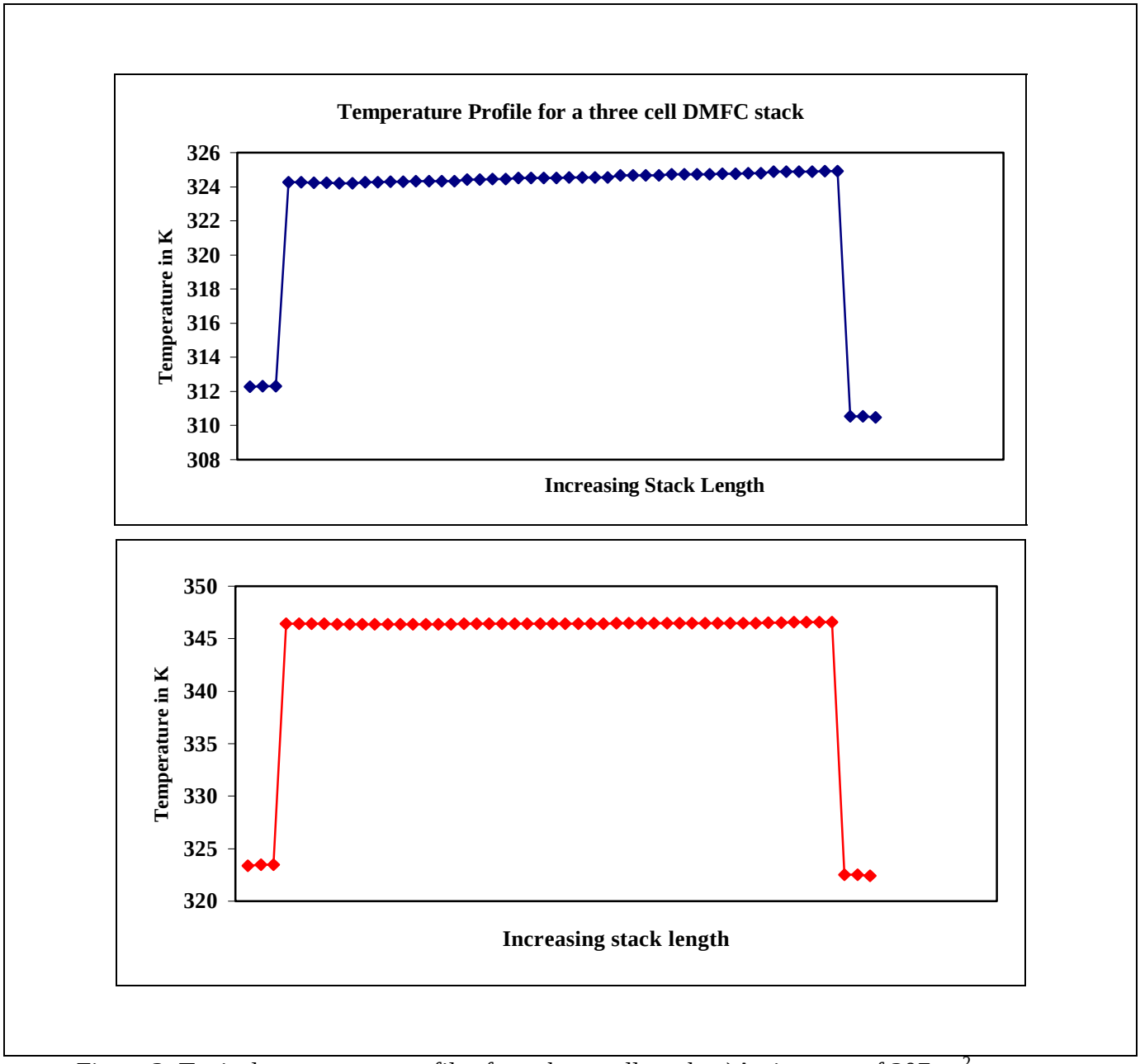

Figure 2: Typical temperature profiles for a three-cell stack: a)Active area of 207cm^2 b)Active area of 272cm^2.