

Thermodynamic behaviour of proton exchange membrane fuel cell under different thermal treatment regimes

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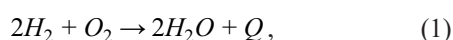
Abstract. Thermodynamic behaviour of the low-temperature proton exchange membrane fuel cell (PEM FC) was under investigation. Different types of behaviour were observed depending on the thermal treatment of the FC. In the case of the relatively slow heating of reactant gases, the thermodynamic behaviour of the FC resembles the behaviour of the reversible FC, with an inverse proportionality between the open-circuit voltage and temperature during the heating-cooling cycle. In contrast, heating of the whole FC frame leads to predominantly direct proportionality during the heating-cooling cycle and, in addition, to hysteresis.

Keywords: proton exchange membrane, fuel cell, thermodynamics, temperature.

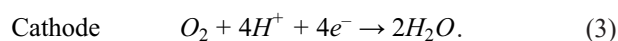
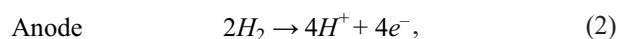
INTRODUCTION

There is a growing interest towards sustainable low-carbon sources of energy, including hydrogen energy [1,2]. A key element of the advanced hydrogen-based energetics is a fuel cell (FC). There are different types of FCs operating with various half-reactions taking place on electrodes, at different temperature ranges, etc. [2,3]. Proton exchange membrane fuel cell (PEM FC) attracts attention due to high energy efficiency, compact design, low operating temperature and relatively fast start-up.

The PEM FC overall reaction is



where Q is heat [3]. Half-reactions on anode and cathode are:



Equilibrium (reversible) thermodynamics of gases, which is the base of the thermodynamics of any type of FCs, shows that the output voltage of the reversible FC is related to Gibbs free energy change (ΔG) in the electrochemical reaction between hydrogen and oxygen gases [4–7]. The maximum efficiency of the reversible FC, also known as the standard potential, equals to 1.23 V for liquid water as a reaction product between oxygen and hydrogen occurring under standard conditions (room temperature of 25 °C and pressure of 1013 mbar) [8].

The dependence of the reversible FC on temperature at constant pressure can be estimated using the Gibbs–Helmholtz equation and the relation between thermodynamic potentials, i.e. enthalpy (H) and Gibbs free energy [9,10]:

$$\Delta H = \Delta G - T \left(\frac{\partial \Delta G}{\partial T} \right)_p, \quad (4)$$

$$\Delta G = \Delta H - T\Delta S, \quad (5)$$

where T and p are the temperature and pressure, respectively. Gibbs free energy is the energy available to

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produce useful work. The relation between G and open-circuit voltage E_{cell} on FC is given by

$$\Delta G = -nFE_{cell}, \quad (6)$$

where $n = 2$ and $F = 96\,485 \text{ C/mol}$ is the Faraday constant [6,8,10]. The next equity can be found combining (4), (5) and (6):

$$\left(\frac{\delta E_{cell}}{\delta T}\right)_P = \frac{\Delta S}{nF}. \quad (7)$$

It follows that

$$\Delta S = nF \left(\frac{\delta E_{cell}}{\delta T}\right)_P \quad (8)$$

and

$$E_{cell} = E_{cell}^0 + \frac{\Delta S}{nF} (T - T^0), \quad (9)$$

i.e., assuming that ΔS is independent of temperature, it is a straight line with the slope equal to $\Delta S/nF$ [6,8,10,11]. This equation shows the variation of the reversible FC voltage E_{cell} with the temperature at constant pressure.

The aim of this study was to identify experimental conditions for observing real FC behaviour similar to that of an ideal reversible FC.

MATERIALS AND METHODS

The PEM FC from H-TEC Education (USA) with a Nafion 212 membrane was used [12]. The anode and cathode of the FC have the same catalyst loading, i.e. $0.5 \text{ mg/cm}^2 \text{ Pt/C } 60\%$ and $0.25 \text{ mg/cm}^2 \text{ PtB mix}$. The electrode area is 16 mm^2 .

The reactant gases (H_2 and O_2) were produced using the PEM electrolyser (EL) from H-TEC Education (USA).

Two types of thermal treatment set-ups were used in the experiments. Firstly, only reactant gases generated by the PEM EL were heated (Fig. 1) and, secondly, the

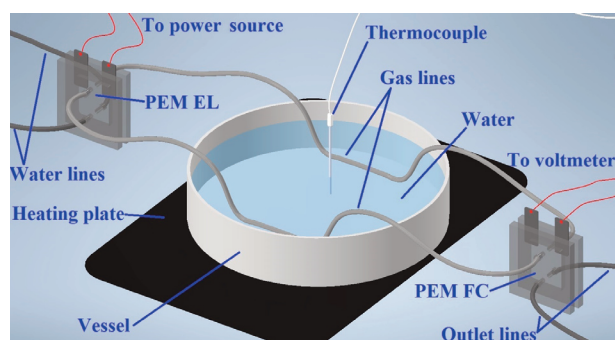


Fig. 1. Set-up for heating of reactant gases.

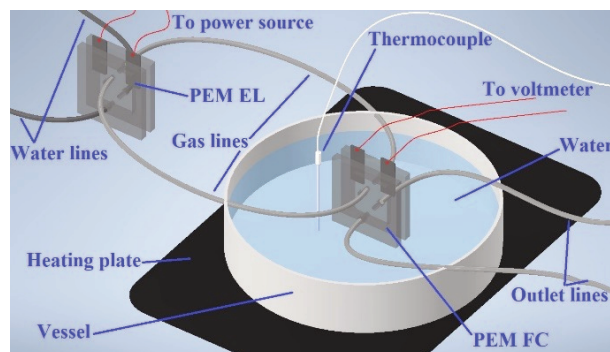


Fig. 2. Set-up for heating of the FC frame.

FC was immersed in the water tank and heated up (Fig. 2). Natural cooling was applied during all experiments. The FC-generated voltage was measured in open-circuit conditions using a voltmeter. The present type of FC is designed to operate at approximately atmospheric pressure for the reactant gases, which means that the FC operates at or just slightly above atmospheric pressure. Temperature of the water was measured using a K-type thermocouple.

RESULTS AND DISCUSSION

Figure 3 shows the behaviour of the FC at room temperature. After a stabilisation period, a stable voltage value was established. The results of the tests for two types of thermal treatments are shown in Figs 4 and 5, respectively. Two types of behaviour were found. The curves with behaviour I can be seen in Fig. 4a and b, which were observed in the case of heating of gases (Fig. 1). The main trend is an inverse dependence between the voltage and temperature, i.e. with the increase of temperature the

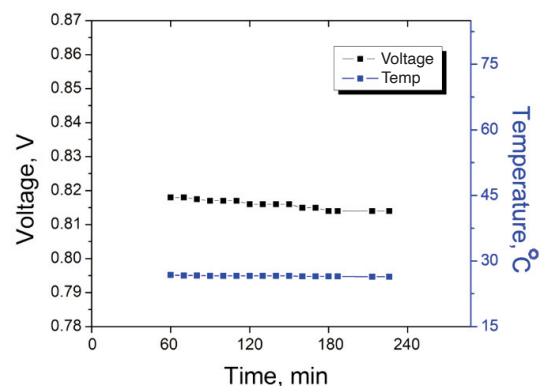


Fig. 3. Relation between the voltage and temperature at room temperature for the PEM FC.

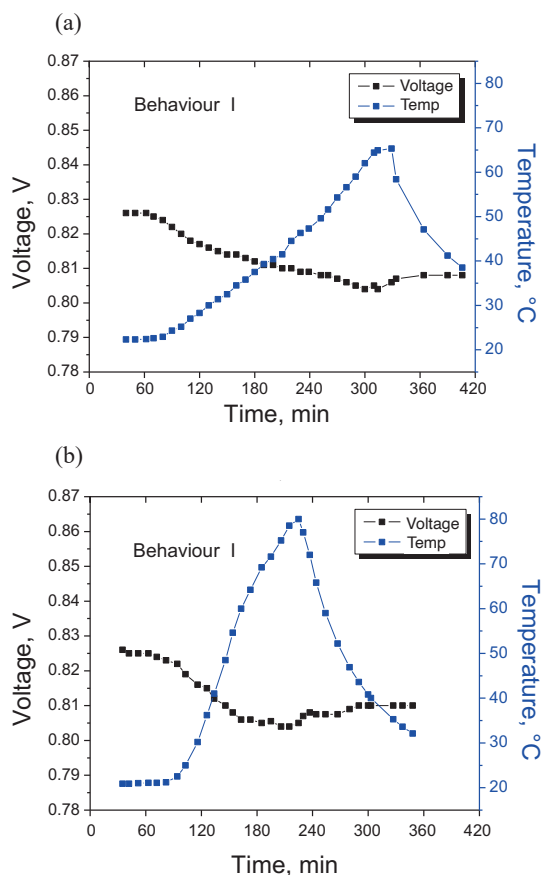


Fig. 4. Results of experiments leading to behaviour I between the voltage and temperature.

voltage decreases and vice versa. In contrast, in the case of behaviour II (Fig. 5a and b, and set-up of the experiment in Fig. 2), the voltage increases with the temperature increase after a short period of inverse dependence – again, direct dependence appears between the voltage and temperature.

In the case of the experiments leading to the results of behaviour I, only reactant gases were heated up. Due to geometry, gases travelled a distance of 15–20 cm from the water tank through tubes surrounded by air at room temperature to the FC (Fig. 1), i.e. the heating of gases was likely not intensive. On the other hand, in the experiments leading to the results of behaviour II, the whole FC frame and gases were more intensively heated.

In conclusion, it is assumed that heating or cooling water leads to the corresponding heating or cooling of gases, and the actual gas temperature might be lower than the measured water temperature.

Both types of experiments can be compared with theoretically predicted behaviour for the reversible FC. It should be stressed that the theory of the reversible FC

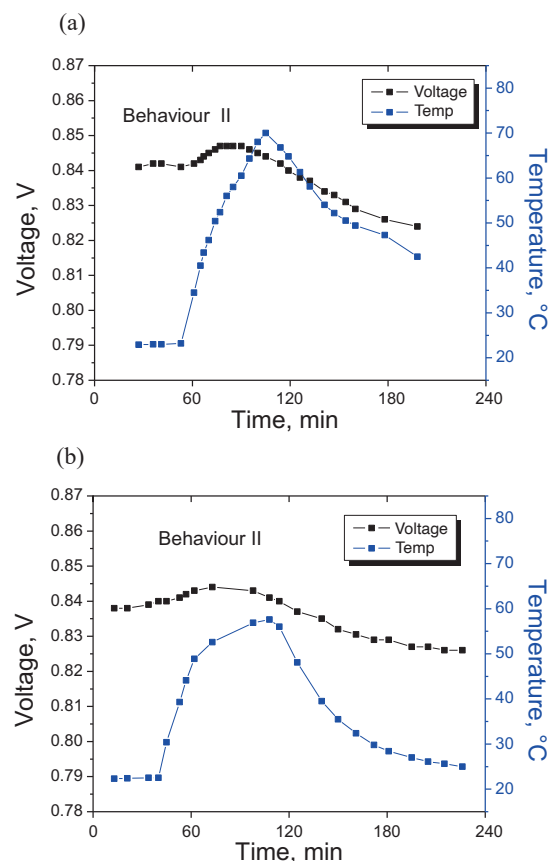


Fig. 5. Results of experiments leading to behaviour II between the voltage and temperature.

is based on the equilibrium thermodynamics of gases, assuming the temperature increase or decrease is slow enough to finish the relaxation process after each step of the temperature increase or decrease. In the case of the reversible FC, the dependence of the voltage on temperature is a straight line with an inverse dependence between the voltage and temperature (see Introduction). Assuming that ΔS is independent of temperature and equal to -0.163 kJ/mol for the higher heating value (HHV) [10,13,14], the slope for the reversible FC is equal to -0.00085 (Fig. 6). The straight line passes the reference point 1.23 V at 25 °C.

The results of both types of experiments on the PEM FC (Figs 4 and 5) are also shown in Fig. 6 for comparison with the behaviour of the reversible FC.

It can be stated that the results corresponding to behaviour I look very similar to the ones for the reversible FC. The slopes of the curves observed in the experiments with behaviour I and II were evaluated and shown in Fig. 7 as well. A good agreement between the results of the experiments with behaviour I and those of the re-

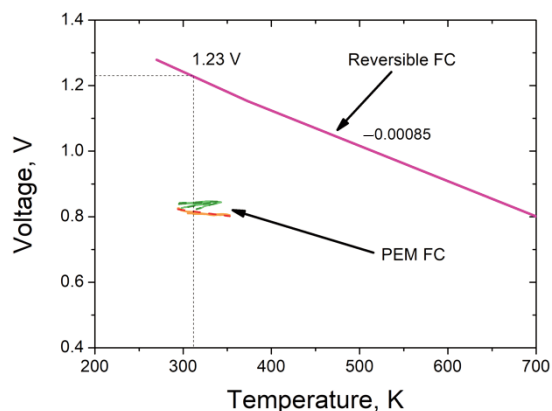


Fig. 6. Relation between the voltage and temperature for the reversible FC and PEM FC.

versible FC points to the fact that the conditions during the measurements resembled the conditions of the equilibrium thermodynamics mentioned above. The reversible-like behaviour of the FC, with inverse proportionality between the voltage and temperature and almost no hysteresis can be seen in Fig. 7 (see two curves corresponding to behaviour Ia and Ib). The heating rate for the results shown in Fig. 4a was approximately two times slower than the heating rate for the results shown in Fig. 4b. The maximum heating temperature was also different, i.e. 65 °C and 80 °C, respectively. However, the reversible-like behaviour was still observed with the line slope of about -0.00037 for both experiments.

In the experiments where the FC was immersed in a water tank (behaviour II), hysteresis was observed (Fig. 7). Although the slope of both lines (behaviour IIa and IIb) during the heating up period was about 0.0001, the line slopes were different during cooling. The line slope was steeper when the maximum heating temperature was higher, i.e. 70 °C compared to 55 °C.

The study indicates that the line slope of the PEM FC differs from that of the ideal reversible FC, depending on the extent of divergence of the experimental conditions from ideal equilibrium conditions. The slope changes from -0.00085 to a more positive value. In other words, the relation between the voltage and temperature changes from inverse to direct proportionality.

It should be stressed that the reversible (ideal) FC voltage dependence on temperature shown in Fig. 6 is a calculation using the equilibrium thermodynamics approach for gases. The behaviour of real FCs, such as PEM FC, alkaline FC, solid oxide FC, etc. under different conditions can strongly differ from theoretical predictions and depends on the type of FC, current density, gas pressure, FC materials and other factors [6,14–16].

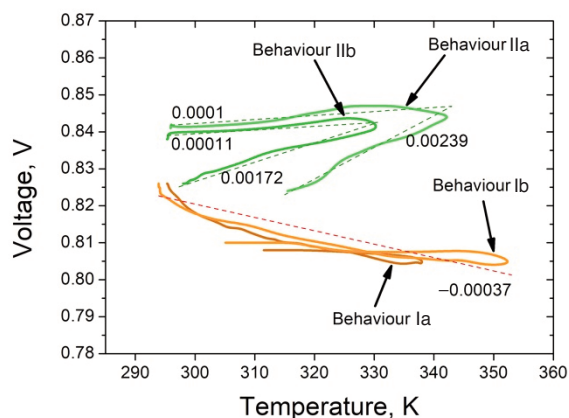


Fig. 7. Relation between the voltage and temperature for the PEM FC.

CONCLUSIONS

The dependence of the output voltage of the FC on temperature can be described by equilibrium thermodynamics. Two different thermodynamic behaviours of the PEM FC were found depending on thermal treatment. The less intensive thermal treatment of reactant gases results in reversible-like behaviour of the PEM FC, similar to the behaviour of the reversible (ideal) FC, with corresponding inverse proportionality between the open-circuit voltage and temperature during the heating-cooling cycle. In the case of more intensive heating of the FC, the dependence changes to predominantly direct proportionality with hysteresis.

ACKNOWLEDGEMENTS

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Prootonivahetusmembraaniga kütuselemendi termodünaamiline käitumine erinevatel termilise töötlemise režiimidel

Konon Kesküll ja Vitali Podgursky

Artiklis uuritakse madaltemperatuurse prootonvahetusmembraaniga kütuselemendi (PEM FC) omadusi. PEM-kütuselemendi termodünaamika viitab sellele, et täielikult pööratava kütuselemendi maksimaalne teoreetiline väljundpinge on seotud vaba energia muutusega vesiniku ja hapnikugaaside vahelises elektrokeemilises reaktsioonis. See pinge, tuntud ka kui standardpotentsiaal, võrdub 1,23 V. Sõltuvalt kütuselemendi termilisest töötlemisest täheldatakse kahte erinevat termodünaamilist käitumist. Reaktiivgaaside suhteliselt aeglase kuumutamise korral sarnaneb kütuselemendi termodünaamiline käitumine pöörduva kütuselemendi käitumisega, kusjuures avatud vooluahela pinge ja temperatuuri vaheline pöördvõrdelisus ilmneb kütte-jahutustsükli ajal. Seevastu kütuselemendi raami kuumutamine toob kaasa peamiselt otsese proportsionaalsuse kütetsükli ajal ja lisaks hüstereesi.