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Calculation of reversible electrode heats in the proton exchange membrane fuel cell from calorimetric measurements

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ABSTRACT

A calorimeter was used to measure the heat production in polymer electrolyte membrane (PEM) fuel cells operated on hydrogen and oxygen at 50 °C and 1 bar. Two cells were examined, one using a 35 μm thick Nafion membrane and a catalyst loading of 0.6/0.4 mg Pt cm^{-2}, for the cathode and anode layer, respectively, the other using a 180 μm thick Nafion membrane and loading of 0.4/0.4 mg Pt cm^{-2}. The cells investigated thus had different membranes and catalyst layers, but identical porous transport layers and micro-porous layers. The calorimeter is unique in that it provides the heat fluxes out of the cell, separately for the anode and the cathode sides. The corresponding cell potential differences, ohmic cell resistance and current densities are also reported. The heat fluxes through the current collector plates were decomposed by a thermal model to give the contributions from the ohmic and the Tafel heats to the total heat fluxes. Thus, the contributions from the reversible heat (the Peltier heats) to the current collectors were determined. The analysis suggests that the Peltier heat of the anode of these fuel cell materials is small, and that it is the cathode reaction which generates the main fraction of the total heat in a PEM fuel cell. The entropy change of the anode reaction appears to be close to zero, while the corresponding value for the cathode is near $-80\,\mathrm{J\,K^{-1}\,mol^{-1}}$.

1. Introduction

The energy that is dissipated as heat in fuel cells is interesting for several reasons. It provides key information for design of auxiliary system components; in particular the cooling system. Increased knowledge about the dissipated energy can also help explain its origin [1], thereby enabling efforts to mitigate and minimize these losses. These issues are now receiving increased attention [2,3], and motivated the construction of calorimeters and the measurements of the thermal signature of low temperature proton exchange membrane (PEM) fuel cells [4,5]. In the present work the aim is to use the calorimeter to determine the asymmetry in the heat production, and the origins of the reversible heat contributions. The total reversible heat production corresponds to the reaction entropy. The local contributions are known as the Peltier heats of the electrodes, as described by non-equilibrium thermodynamics [6,7].

The long term motivation of this work is to facilitate the calculation of not only the temperature profile across the cell, but also the electric potential profile. This requires information about mass diffusivities of reactants and products, thermal conductivities and ohmic resistances of the various materials, interfacial resistances between cell layers and, finally, the Peltier heats of the individual electrodes. This work should be seen as an effort to obtain some of the required data and thereby enhance the understanding of the processes taking place in the PEM fuel cell.

The origin of the single electrode reaction entropy for PEM fuel cells is discussed in several studies [8–15] but no direct measurements are reported for a PEM fuel cell. The first analysis of this thermodynamic entity in fuel cells was made by Jacobsen et al. [16] studying molten carbonate cell electrodes and later by Kjelstrup et al. [17], studying the oxygen electrode with solid oxide electrolyte. The magnitude of the total reaction entropy for a hydrogen/oxygen fuel cell producing liquid water is well known ($-82\,\mathrm{J\,K^{-1}\,mol^{-1}}$ at standard conditions). The single electrode reversible heat is given by the electrode temperature multiplied by the difference in the entropy entering and leaving the electrode; see [6] for a derivation. The Peltier heats can give rise to a local increase or decrease in the anode and cathode electrode temperatures and contribute to thermal gradients [1], see [6,7] and references therein for more examples. In this paper we report measurements that give further insight into the local entropy changes in PEM fuel cells.

The outline of the paper is as follows. We present the thermodynamic basis for the energy dissipation assessment in Section 2. The apparatus description and the procedures to measure the heat fluxes and to deconvolute the experiments are provided in Section 3. The results are presented and discussed in Section 4.

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2. Thermodynamic basis

The efficient energy conversion taking place in fuel cells is to a substantial degree dictated by the thermodynamics. The conventional modelling approach taken in the literature is to consider only the work from a fuel cell, while ignoring, or treating the energy dissipated as heat in an ad hoc manner. In some situations, empirical relationships are used, rather than fundamental equations based on thermodynamic properties. This limits the possibility to assess the sources of dissipation and the ability to further improve efficiency and system performance. In this section the PEM fuel cell reactions are initially revisited, followed by a recapitulation of the thermodynamic relationships of the cell. Finally, the reversible heat contributions, and in particular the Peltier heats of the individual electrodes and how these may be determined, are described.

2.1. The fuel cell reaction

The electrochemical reaction in the PEM fuel cell is well known (Eqs. (1)–(3)). At the operating conditions in question (50 °C and reacting gases saturated with water vapour at 1 bar) hydrogen and oxygen is consumed and liquid water is formed. In addition, there is electro-osmotic transport of water from the anode to the cathode side corresponding to the transference number (electro-osmotic drag coefficient) t_w, leading to an additional term in Eqs. (1)–(3). This is related to the hydrated protons transported across the membrane. While this term is less important for the electric work, it may be significant for the local heat production. The cathode reaction reads:

$$\frac{1}{4}\mathrm{O}_{2(g)} + \mathrm{H}^+ + \mathrm{e} + t_w\mathrm{H_2O}_{(l)} \rightleftarrows \left(\frac{1}{2} + t_w\right)\ \mathrm{H_2O}_{(l)} \tag{1}$$

We assume that this half reaction dominates at the chosen experimental conditions. The anode half cell reaction is:

$$\frac{1}{2}\mathrm{H}_{2(g)} + t_w H_2O_{(l)} \rightleftarrows \mathrm{H}^+ + \mathrm{e} + t_w H_2O_{(l)} \tag{2}$$

The overall cell reaction is thus

$$\frac{1}{2}\mathrm{H}_2 + \frac{1}{4}\mathrm{O}_2 + t_w\mathrm{H_2O}_{(l)} \rightleftarrows \left(\frac{1}{2} + t_w\right)\mathrm{H_2O}_{(l)} \tag{3}$$

2.2. Overall analysis of work and heat in the fuel cell

The fuel cell is an open system, which exchanges heat, mass and work with the surroundings. The first law of thermodynamics under reversible conditions reads:

$$\Delta U = T\Delta S - p\Delta V - nFE_{\mathrm{rev}} \tag{4}$$

and for a given pressure, p, and temperature, T, we have

$$\Delta G = \Delta H - T\Delta S = -nFE_{\mathrm{rev}} \tag{5}$$

where ΔU, ΔS, ΔV, ΔG and ΔH are the changes in internal energy, entropy, volume, Gibbs energy and enthalpy, respectively. The gas pressure, p, and the temperature of the fuel cell, T, are those of the fuel cell surroundings, i.e. gas channel and the current collector plates. The electric potential measured under reversible conditions is E_{rev}, F is Faraday's constant and n is the number of moles of electrons transferred in the cell reaction (Eq. (3)), here $n = 1$. The ratio $\Delta H/F = -E_{tn}$ is called the thermo-neutral potential.

Under reversible conditions, heat added to the cell defines its entropy change. In this fuel cell, ΔS is negative and relatively large (water is formed in the liquid state and gas molecules are consumed, cf. Eq. (3)). Therefore, a large positive heat is delivered to the surroundings, in this study constituted by the calorimeter. The theoretical value of E_{rev} is 1.23 V at $T = 298$ K when water is in the liquid state and the reactant gases are at 1 bar [18]. The negative reaction entropy contributes −0.25 V and $E_{\mathrm{tn}} = -\Delta H/nF = 1.48$ V at $T = 298$ K (see Eq. (9)). Accordingly, even at low current densities the relative heat production in the cell is substantial.

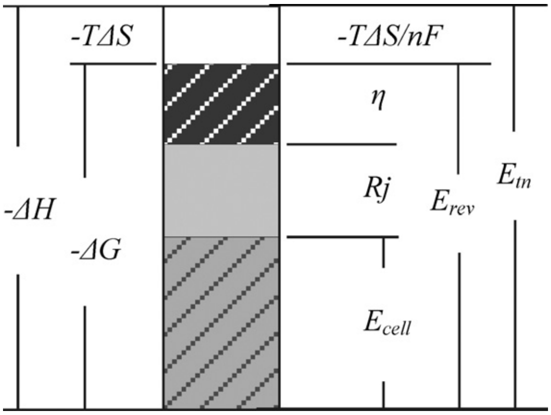

Fig. 1. Thermodynamic properties (to the left) and the corresponding cell potentials and potential losses occurring in the fuel cell (to the right). The thermo-neutral potential (right), E_{tn}, is represented by the negative reaction enthalpy (left), $-\Delta H$. Part of this energy is needed to compensate for the entropy change at a given temperature, $-T\Delta S$, leaving us with the maximum available work, $-\Delta G$ (left), represented by the reversible potential, E_{rev}. At non-reversible conditions, the cell potential, E_{cell}, is equal to the reversible potential minus the ohmic potential losses, Rj, and the Tafel potential losses, η.

At non-reversible conditions, when there is a net electric current flowing through the cell, the entropy production of the system plus near surroundings is no longer zero. There is now more heat delivered to the calorimeter than that equivalent to $-T\Delta S$. This is reflected in the polarization curve of the cell, where the cell potential E_{cell} is plotted as a function of current density j. The cell potential is

$$E_{\mathrm{cell}} = E_{\mathrm{rev}} - \eta - Rj \tag{6}$$

The two last terms on the right hand side give the part of the potential electrical work, E_{rev}, that is now dissipated as heat. The symbol η represents the sum of the electrode overpotentials which is dominated by the cathode [19]. The overpotential can be described by the Butler–Volmer or Tafel equation. The last term is the ohmic potential loss, with R as the total resistance, and j as the current density, measured here per geometric cross-sectional cell area. In this study, experimental conditions are used that minimize mass transfer-limitations in the electrodes, meaning that η to a good approximation is equal to the reaction overpotential of the cathode

The relations between these well known thermodynamic properties and the electrochemical entities are illustrated in Fig. 1.

By multiplying Eq. (6) by the current density and introducing Eq. (5) solved for E_{rev}, the specific cell power is obtained:

$$P = E_{cell}j = \frac{T\Delta S - \Delta H}{nF}j - \eta j - Rj^2 \tag{7}$$

We can now identify the heat delivered to the calorimeter per unit of time and area;

$$Q_{FC} = -\frac{T\Delta S}{nF}j + \eta j + Rj^2 \tag{8}$$

The first term represents the reversible contribution and the two last terms are irreversible energy dissipation terms.

$$P_{FC} + Q_{FC} = -\frac{\Delta H}{nF}j = E_{tn}j \tag{9}$$

The thermoneutral power of the cell is the hypothetical power corresponding to the reaction enthalpy.