



The Seebeck coefficient and the Peltier effect in a polymer electrolyte membrane cell with two hydrogen electrodes



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ABSTRACT

We report that the Seebeck coefficient of a Nafion membrane cell with hydrogen electrodes saturated with water vapour, at 1 bar hydrogen pressure and 340 K, is equal to $670 \pm 50 \mu\text{V/K}$, meaning that the entropy change of the anode reaction at reversible conditions ($67 \text{ J}/(\text{K mol})$) corresponds to a reversible heat release of 22 kJ/mol. The transported entropy of protons across the membrane at Soret equilibrium was estimated from this value to $1 \pm 5 \text{ J}/(\text{K mol})$. The results were supported by the expected variation in the Seebeck coefficient with the hydrogen pressure. We report also the temperature difference of the electrodes, when passing electric current through the cell, and find that the anode is heated (a Peltier heat effect), giving qualitative support to the result for the Seebeck coefficient. The Seebeck and Peltier effects are related by non-equilibrium thermodynamics theory, and the Peltier heat of the cathode in the fuel cell is calculated for steady state conditions to $6 \pm 2 \text{ kJ/mol}$ at 340 K. The division of the reversible heat release between the anode and the cathode, can be expected to vary with the current density, as the magnitude of the current density can have a big impact on water transport and water concentration profile.

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1. Introduction

The heat production in fuel cells consists of a reversible part (the cell's entropy change times the temperature) and an irreversible part (the energy dissipated as heat). The sum provides information that is important for design of auxiliary systems; in particular cooling systems. Knowledge of the dissipated energy can help locate causes of power losses in the cell [1]. This may give us a possibility to mitigate or reduce them. It is therefore important to understand both parts.

The heat production in the polymer electrolyte fuel cell (PEMFC) has received increased attention among modellers the last ten years. This is well summarized by Bapat and Thynell [2], Ramousse

et al. [3], Das and Bansode [4] and Zhang and Kandlikar [5]. The single electrode reaction entropy, that is relevant for the reversible heat production at electrodes, is discussed [3,6–13]. We are not aware of any experimental results with hydrogen electrodes and the Nafion membrane as electrolyte, but values for the standard electrode where hydrogen is consumed has been reported [6,14]. The values differ widely, from $-66.6 \text{ J}/(\text{K mol})$ (obtained from half cell potentials and assumptions of the single entropies) for a 1 molal acid solution [6], to $-87.6 \text{ J}/(\text{K mol})$ from calorimetry at varying current densities at standard conditions [14]. For the alkaline fuel cell, a value near zero was obtained [7].

Using calorimetry on a disc-shaped fuel cell, we measured the heat flux out of the anode current collector separate from the flux out of the cathode current collector [15,16]. The heat flux on the anode side differed significantly from the heat flux on the cathode side in these experiments. It was concluded, that a small part of the reversible heat in the cell evolved at the anode at current densities of 0.2–0.8 A/cm². The aim of this work is to shed further light on these results, contributing to the understanding of thermal management in the PEM fuel cell.

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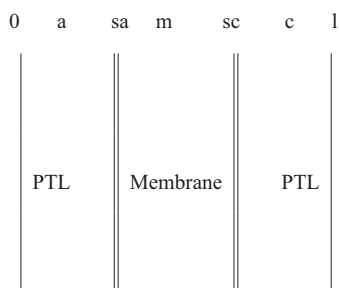


Fig. 1. A cross section of a the cell is illustrated, showing the five characteristic layers and the notation used throughout the paper.

We shall use a cell with two hydrogen electrodes and a polymer electrolyte membrane, the Nafion membrane. The hydrogen–hydrogen cell was used by Meland et al. [17,18] and Malevich et al. [19–21] for impedance studies. The hydrogen–hydrogen cell has also been used to elucidate proton transport [22] and water transport in the anode of the fuel cell [23]. The use of this cell, gives the best opportunity to study the reversible electrode heats in the anode of the PEMFC without disturbances from irreversible effects (i.e. oxygen reduction reaction kinetics). The advantage is that one can obtain directly the reversible hydrogen electrode heat effect from the experiments. The effect at the oxygen electrode can then be computed from knowledge of the hydrogen electrode and the overall entropy change in the cell. This shall be done here.

The reversible heat produced by the hydrogen electrode, can be obtained from electromotive force (emf) measurements when the $\text{H}_2(\text{g})|\text{H}_2(\text{g})$ polymer electrolyte cell is exposed to a temperature gradient (a Seebeck coefficient measurement), or by finding the local heat effect by applying an electric current (a Peltier experiment). We shall report theoretical and experimental studies of the Seebeck and Peltier coefficients. Such studies are documented in the literature of non-equilibrium thermodynamics, for an overview see e.g. [24]. Early theoretical and experimental analyses of these properties for fuel cells were carried out by Jacobsen et al. [25] for carbonate reversible electrodes and molten carbonate electrolyte, and by Kjelstrup et al. [26] for oxygen electrodes and yttrium stabilized zirconia electrolyte.

The single electrode reversible heat, or the Peltier heat, is given by the electrode temperature multiplied by the difference in the entropy entering and leaving the electrode [27]. The Peltier heat can give rise to a local increase or decrease in the electrode temperature [28–31], and contributes therefore to thermal gradients, see [1,27,24,29] and references therein.

The outline of the paper is as follows. We describe the system in Section 2, give the thermodynamic basis and the theory for the Seebeck and the Peltier effects in Section 3. The two experimental set-ups and the procedures are described in Section 4. The Seebeck coefficient measurements are first presented. We next report on the temperature profile between the electrodes when an electric current is passing the cell. The results are presented and discussed in Section 5.

2. The polymer electrolyte cell with hydrogen electrodes

For the analysis of the experiments to be reported, we consider a cylindrical cell, with half cells mirror symmetric around the centre plane given by the polymer electrolyte membrane. There are five subsystems; the anode backing (*a*), the two catalyst layers (*sa* and *sc*), the membrane (*m*), and the cathode backing (*c*), but the two backings and the catalyst layers are identical. An illustration of the cell is given in Fig. 1. The figure labels the left and right electrode backings by (*a*) and (*c*). These backings consist of a Porous Transport

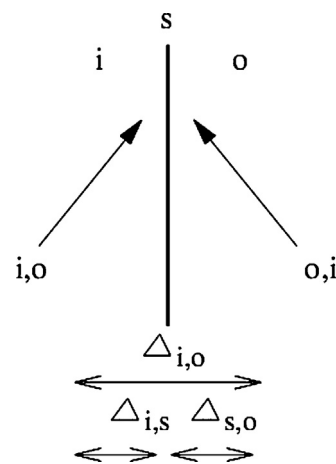
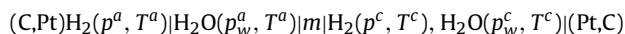


Fig. 2. Notation used for transport across interfaces. A position is indicated by two superscripts, say *i, o*, where the first symbol (*i*) denotes the layer (or phase) and the second denoted the nearest layer (*o*). A difference between two positions is indicated by two subscripts, say *i, o*, for Δ , meaning that the difference should be taken between states *o* and *i*.

Layer (PTL) coated with a micro porous layer (MPL) of carbon (not indicated in the figure). The membrane (*m*) that separates the electrode compartments, is a Nafion membrane for transport of protons and water. The electrode regions are denoted *sa* and *sc*, respectively. Platinum wires are connected to the catalytic layers, and we measure the emf between two Cu-wires, attached to the Pt wires. The Pt–Cu contacts are at the temperature of the room. The positions of the current collector plates on the two sides are at positions 0 and 1 at the beginning and end of the graphite backings. We shall apply a potential difference between the current collectors and measure the corresponding electric current.

With standard electrochemical notation, the cell is:



When current is passing the cell, water is carried along with the charge carriers, the protons. This is called electro-osmosis. When the sides of the membrane are kept at different temperatures, water can also be transported by thermal osmosis [32]. The water phase is continuous through the system. Both transport phenomena give contributions to the electric potential, as we shall see. These contributions to the cell potential are normally small, but thermal osmosis can give a significant contribution to the heat flux, as we shall see. We are therefore in need of a systematic description of these interacting phenomena. The theory connecting these effects is non-equilibrium thermodynamics. By using this systematic theory, one obeys the proper symmetry of effects and as well as criteria given by the second law. The expressions show how that the nature of the electrolyte has an impact on the single electrode heat.

The analysis using non-equilibrium thermodynamics for heterogeneous systems was explained in detail, see Chapter 19 of Kjelstrup and Bedeaux [24], and we follow their procedure and notation. Symbols are further explained in Fig. 2. In this figure *i* and *o* denote separate phases, meaning *a, m* or *c*, while *s* is the electrode (catalyst) region (*sa* or *sc*), cf. Fig. 1. A position in the *o*-phase next to the *i*-phase is given by superscript *o, i*. The difference between the value on the *i*-side and the *o*-side is given by $\Delta_{i,o}$, etc. The membrane is a homogeneous phase, thanks to the presence of water. The backings *a* and *c* contain a porous graphite phase (for electron conduction), which we deal with separate from the gas filled, homogeneous pores.

The electrode regions are coarse grained in this analysis, where they are considered as two-dimensional subsystems. This simplifies matter. The finer structure of these regions will be integrated

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