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Three steps in the anode reaction of the polymer electrolyte membrane fuel cell. Effect of CO

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Abstract

We studied the influence of CO poisoning of the anode in the polymer electrolyte membrane fuel cell (PEMFC) using electrochemical impedance spectroscopy (EIS). The anode impedance was found by first feeding neat hydrogen gas and next hydrogen with CO into one of the electrodes, keeping neat hydrogen gas on the other electrode as a reference. The electrodes were E-TEK Elat gas-diffusion electrodes with 0.5 mg Pt/cm^2, and the membrane was Nafion® 117. The CO concentration was 103 ppm, and the total pressures were 1, 2.5 and 4 bar. Operating temperatures were kept constant, 30.0 °C or 50.0 ± 0.1 °C. Bias voltages of 0 and 0.05 V were used. Three steps were revealed in the reaction mechanism, the slow adsorption/diffusion step, the charge transfer step and the proton hydration step, confirming earlier results. Carbon monoxide affects the charge transfer step by blocking active sites and by affecting the surface polarisation. We further conclude that CO adsorbs to the porous carbon matrix, and reduces significantly the rate of surface diffusion of hydrogen to the surface.

Keywords: PEMFC; Anode; CO poisoning; Impedance; Electrode reaction mechanism

1. Introduction

In the polymer electrolyte membrane fuel cell (PEMFC), the largest overpotential is encountered at the oxygen electrode, the cathode, but this is only when the feed to the anode is neat hydrogen. When hydrogen contains small amounts of CO (around 100 ppm), as is the case when it is produced by reformer technology, the anode will be poisoned, and the anode overpotential becomes larger [1,2]. It is believed that CO occupies the Pt sites and affects hydrogen adsorption by lowering the accessible surface [3,4]. In addition, CO lowers the reactivity of the uncovered sites by dipole interaction and electron capture [5]. It is thus important to understand the anode under normal conditions and when it is poisoned with CO. Our aim here is to study the dynamic response of the anode for these conditions. A theoretical model that describe the rate-limiting processes at the anode was thus developed earlier [14,15], distinguishing between the transport up to the catalyst, at the catalytic site and from this site into the membrane.

Various porous gas-diffusion electrode models that also have been used for the PEMFC, have developed since the late 1960's [6–8]. Most of these models have treated the electrodes in their steady state [9–11]. The dynamic response of the system, the topic of this investigation, was also studied [12,13]. Most of the focus has been on the oxygen electrode since this contributes most to the losses in the PEMFC in normal operation.

In two previous articles [14,15], we investigated the anode reaction with electrochemical impedance spectroscopy (EIS) and found three steps in the reaction mechanism. The anode reaction was investigated in a cell with two hydrogen electrodes. The cell temperature, applied potential and hydrogen gas pressure were varied. Three steps were revealed, most importantly because we used temperatures below 50 °C. The steps are discussed in detail

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in the section that follows below. This work gives a good basis for investigations of the CO effect.

EIS provides a simple way to separate the contribution of CO poisoning from the behaviour without CO, and evaluate the influence of other parameters [16,17]. We shall use this technique here.

The purpose of this paper is to find how the three postulated steps [14,15] in the PEMFC anode reaction are affected by the presence of CO. In order to again see all three steps, we shall continue to use (mainly) the lowest temperature that was used before (30 °C). We shall again be able to document that three steps are present. Using the three steps as a premise, we shall see that presence of CO changes only one of the three relaxation times, and that the observed changes in relaxation time, resistances and other parameters, can all be explained by a large surface coverage of CO on Pt (near 0.9), by changes in the polarisation of the catalyst, and by CO adsorption onto the porous carbon. In this manner we shall therefore also present a model for the CO effect on the anode, that is consistent with our previous model, and with other documented effects of CO in the literature [17].

The article is organised as follows. We repeat first (Section 2) the essentials of our previously published model for hydrogen oxidation in the porous anode of the PEMFC. The expressions derived for the impedance of the surface are also repeated. Experimental conditions and results are given in Section 3. In order to confirm our experimental methods, we also report results for the complete fuel cell poisoned with CO. Similar results were obtained by others [17]. The CO concentration used here (103 ppm) was one that is normally present in the reformer gases after purification [1].

Section 4 contains spectra and spectra details, mostly for the main temperature investigated, 30 °C. In the tabulation of fitted parameters, we compare the values of the poisoned electrode with the unpoisoned, before conclusions are drawn.

2. The three steps of the anode reaction

As mentioned above, we are testing a model reported earlier [14,15], consisting of three rate-limiting steps for the oxidation of hydrogen in the PEMFC anode. The model assumes that hydrogen gas is first adsorbed at any position x along the pores in the carbon matrix leading up to the Pt catalyst:

$$\frac{1}{2}H_2(g) \rightarrow \frac{1}{2}H_2(a) \tag{1}$$

The reaction is reversible giving

$$r(x,t) = k^{a}_{H_2} c^{g}_{H_2} - k^{d}_{H_2} c^{a}_{H_2}(x,t) \tag{2}$$

where $k^{a}_{H_2}$ and $k^{d}_{H_2}$ are reaction rate constants for adsorption and desorption, respectively, while $c^{g}_{H_2}$ and $c^{a}_{H_2}$ are concentrations in the gas phase, and at the surface, respectively. Once adsorbed, hydrogen diffuses along the carbon surface to the platinum (to position $x = 0$) where it reacts according to the familiar Tafel–Volmer mechanism:

$$H_2(a) \rightarrow 2H_{ads} \tag{3}$$

$$H_{ads} \rightarrow H^{+}(s) + e^{-}(a) \tag{4}$$

where (a) denotes the anode and (s) the platinum surface. The molecule dissociates into protons and electrons at active sites in the electrode surface of the platinum particles. Electrons are eventually transported into the carbon phase.

The protons bind on the average to one water molecule before they leave the surface [18,19]. In the third rate-limiting step net charge moves into the cation exchange membrane (m) as hydronium ions:

$$H^{+}(s) + H_2O(m) \rightarrow H^{+}H_2O(m) \tag{5}$$

2.1. The equivalent circuit

For the first of these three steps we derived a Gerischer impedance, using non-equilibrium thermodynamics. The fit of the experimental data to this impedance was always better than a fit to the finite length Warburg impedance, the most likely alternative. The impedance of Step 1, the step for adsorption and surface diffusion was given by [14]

$$Z_{ad} = \frac{RT}{2F^2 c^{a}_{H_2,eq}\sqrt{2Dk^{d}_{H_2}(1 + i\omega\tau_{ad})}} \tag{6}$$

where the relaxation time in the absorption process due to the chemical reaction (2):

$$\tau_{ad} = \frac{1}{k^{d}_{H_2}} = \frac{c^{a}_{H_2,eq}}{c^{g}_{H_2} k^{a}_{H_2}} \tag{7}$$

The hydrogen concentration in the pores, $c^{g}_{H_2}$, was constant in the experiment, giving also a constant value for the concentration of absorbed gas at equilibrium, $c^{a}_{H_2,eq}$.

The fit of the experimental results to the theoretical expressions gave furthermore Y_0 and τ_{ad} in the following expression for Z_{ad}:

$$Z_{ad} = \frac{1}{Y_0\sqrt{\tau^{-1}_{ad} + i\omega}} \tag{8}$$

The expression for the relaxation time, $\tau^{-1}_{ad} = k^{d}_{H_2}$, is given in Eq. (7). The other variable, the admittance, is

$$Y_0 = \frac{2F^2}{RT} c^{a}_{H_2,eq}\sqrt{2Dk^{d}_{H_2}\tau_{ad}} = \frac{2F^2}{RT} c^{a}_{H_2,eq}\sqrt{2D} \tag{9}$$

This admittance Y_0 is proportional to the hydrogen concentration in the adsorbed phase. This concentration is, at equilibrium, proportional to the gas concentration of hydrogen, and such a proportionality was found [15]. The slope of Y_0 versus the concentration was used to estimate a diffusion constant for hydrogen along the surface, using the assumption $c^{a}_{H_2,eq} = c^{g}_{H_2,eq}$, or $k^{a}_{H_2} = k^{d}_{H_2}$. This admittance did not depend on the applied bias potential.

The theoretical expression for the impedance of the whole surface was found as