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Electrochimica Acta 51 (2006) 1622–1628

ELECTROCHIMICA Acta

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Electrochemical impedance spectroscopy applied to polymer electrolyte fuel cells with a pseudo reference electrode arrangement

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Received 23 June 2004; received in revised form 18 October 2004; accepted 8 February 2005

Abstract

The nature of the solid electrolyte and the low electrode–electrode gap in polymer electrolyte fuel cells (PEFCs) makes it difficult to introduce a reference electrode into the fuel cell in order to separate anodic and cathodic overpotential contributions. A suitable experimental setup should not disturb the current distribution in the fuel cell. In order to satisfy the boundary conditions, we introduced a pseudo reference electrode into the fuel cell. With this setup, we have measured the impedance of both electrodes separately with respect to the pseudo reference electrode at different current densities. A state-space model was used to study the hydrogen oxidation reaction in order to identify kinetic parameters.

Keywords: Electrochemical impedance spectroscopy; Polymer electrolyte fuel cells; Hydrogen oxidation reaction; State-space model; Pseudo reference electrode

1. Introduction

The availability of in situ diagnostic tools to identify the rate limiting processes in hydrogen/oxygen polymer electrolyte fuel cells (PEFC) is of utmost importance for the further development of this technology. A powerful method to perform such measurements is the electrochemical impedance spectroscopy (EIS). Compared to other in situ methods, EIS usually yields a better discrimination of the different fundamental processes occurring in PEFCs, such as the charge transfer kinetics or double layer charging. Usually, the EIS measurements are carried out on the whole cell, and the anode contributions of the hydrogen oxidation reaction (HOR) to the total cell impedance are neglected, the measured impedance being completely attributed to the oxygen reduction reaction (ORR) and to the electrolyte. However, it was shown that the anode might contribute substantially to the cell voltage loss, especially at high current densities [1,2]. Yet, under typical fuel cell conditions, such integral impedance spectra cannot distinguish anode and cathode contributions. The most common way to separate anode and cathode contributions to the cell voltage loss is to use a reference electrode (RE). Due to the nature of the solid polymer electrolyte membrane one cannot easily introduce a reference electrode into the fuel cell, as it is done in electrochemical cells containing a liquid electrolyte, and therefore determine single electrode behaviour. In PEFCs, several problems occur with the incorporation of a reference electrode due to the thin solid electrolyte [3,4] so that the use of conventional electrolyte bridges and Luggin-capillaries lead to erroneous results. Nevertheless, for a better understanding of fuel cells a more detailed investigation of the reactions occurring at the electrodes is necessary.

For the present study, we have introduced a micrometer size pseudo reference electrode into the solid electrolyte of a PEFC adapted to the particular constraints of this cell, in order to separate the integral impedance of the cell into anode and cathode contributions. In particular, the impedance measurements of the anode allows identifying different HOR process steps, which we attribute to the hydrogen adsorption, proton generation, and proton diffusion process at high current densities; the latter includes water transport in the aqueous phase within the polymer structure. These different

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doi:10.1016/j.electacta.2005.02.108

processes are investigated in dependence of the operating current density. We used a state-space approach to calculate the impedance response based on a kinetic model of the basic reaction pathway for the hydrogen oxidation reaction. Hence, it is possible to obtain kinetic parameters for the specific reaction at different current densities for an operating fuel cell that are not accessible in a two-electrode EIS measurement.

2. Experimental

The experiments were carried out in circular stainless steel fuel cells without a flow field to keep the gas humidification and therefore the current distribution over the entire active cell area as homogeneous as possible. Furthermore, the active cell area of 28.3 cm^2 is large enough to exclude edge effects. This cell design can only be used with pure gases and cannot be operated with air due to the oxygen depletion at the electrode–electrolyte interface, hence a one-dimensional cell is realised. The cell was operated with hydrogen and oxygen at 75 °C at ambient pressure and with a stoichiometric factor for the feed gases of $\lambda = 1.5$. Hydrogen was humidified at a dew point of 75 °C, whereas oxygen was fed dry. E-TEK electrodes with a catalyst loading of 20 wt% Pt/C (0.6 mg/cm^2 platinum), impregnated with 0.6 mg/cm^2 Nafion solution, were employed for both anode and cathode. Nafion 115 from DuPont served as electrolyte. The EIS measurements were carried out using a Zahner IM6 workstation (Kronach, Germany) in galvanostatic mode with an ac current amplitude of 0.2 A and frequency ranges of 5 mHz–25 kHz (100 and 400 mA/cm^2), in two cases up to 80 kHz (200 and 500 mA/cm^2) and 5 mHz–100 kHz (300 mA/cm^2). The potentials between anode and cathode, anode/cathode and pseudo reference electrode were measured to ensure the stability of the pseudo reference electrode potential during an EIS measurement. The pseudo reference electrode, a carbon filament insulated except for the tip of the filament, with a diameter of ∼25 μm, was placed between two polymer electrolyte membranes. This ensures the position of the pseudo reference electrode in the centre of the electrolyte. The experimental setup is schematically depicted in Fig. 1. Pseudo reference electrodes are often used in electrochemistry when the implementation of standard reference electrodes (e.g. calomel, Ag/AgCl, Hg/Hg$_2$SO$_4$) into a cell is difficult. The advantages of pseudo reference electrodes are the easy implementation and their stable potential depending on the concentration of dissolved ions in the electrolyte. Pseudo reference electrodes are used to bypass a Luggin capillary or other standard reference electrodes in liquid electrolytes when measuring EIS at high frequencies. One disadvantage is the unknown dc potential of the pseudo reference electrode, however this fact is negligible in EIS measurements, when the dc potential is not of importance, as only the amplitude is used for the calculation of the impedance. Whereas in a liquid electrolyte the contact between the reference electrode and the electrolyte is of a minor difficulty, this is not the case for a PEFC when a solid electrolyte is used. Problems may appear at the interface, due to a bad and insufficient contact between the electrolyte and the pseudo reference electrode, hence no stable potential maybe established and no kind of reliable measurement may be possible. We did not encounter this problem in this experiments described.

3. Model and simulation

In the present work, we concentrate on the hydrogen oxidation reaction. Nevertheless, the model can be extended by a separate module to include the oxygen reduction reaction as well. Quantitative assessment of the kinetic parameters for the HOR is of great importance, e.g. in conjunction with the assessment of the electrocatalytic activity of the anode catalyst and its CO-tolerance. Based on the theoretically derived equations for the electrochemical reaction of hydrogen, the model yields the kinetic parameters for the HOR. No assumption is needed to analyse the impedance response by an equivalent circuit and to identify parameters of the electrode kinetics by circuit elements like capacitors or resistances [5–7].

For the hydrogen oxidation reaction we consider the following steps:

- Mass transport limitations of the reactants, H_2 and H_2O, from the bulk towards the reaction zone and mass transport of the product, H_3O^+, off the reaction zone. (The H_2O molecule is formally considered to be a reactant, see below.)
- Adsorption and desorption of H_2 at the interface.
- Charge transfer reaction of the adsorbed species H_{ad}.

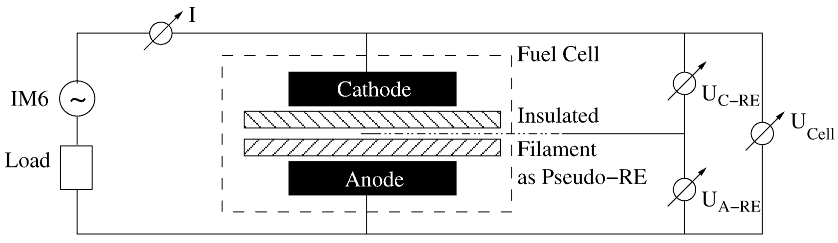

Fig. 1. Experimental setup used for the impedance measurements.