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A physical model of Direct Methanol Fuel Cell anode impedance

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HIGHLIGHTS

- We developed and validated a physically based impedance model of DMFC anode.
- Liquid convection through gas diffusion layer is an intermittent phenomenon.
- Mass transport losses through gas diffusion layer are relevant even at low current densities.
- Oscillation of membrane cross-over fluxes influences low-medium frequency region.

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ABSTRACT

In the present work a physically based model of direct methanol fuel cell anode impedance has been developed and validated at different operating current densities. The proposed model includes the two-phase mass transport of both methanol and water through diffusion and catalyst layers and the methanol oxidation reaction involving CO adsorbed intermediate. Model simulations are in good quantitative agreement with experimental observations and permit to evaluate the origin of anode impedance features. Model results confirm that the high frequency 45° linear branch is caused by proton transport limitations within the catalyst layer and that the low frequency inductive behavior is due to surface coverage by CO reaction intermediate. Moreover model predictions elucidate the contribution to the impedance of mass transport phenomena through diffusion layer, that is relevant even at low current density and increases along the channel length. In particular liquid convective fluxes are considered as a process of pressure buildup and breakthrough at diffusion layer intersecting fibers, resulting in a discontinuous phenomenon. By means of this intermittent description it is possible to correctly reproduce mass transport limitations through diffusion layers, that manifest themselves as a second arch superimposed to the first one, peculiar of kinetic losses.

1. Introduction

The Electrochemical Impedance Spectroscopy (EIS) is a powerful in-situ measurement technique that permits to evaluate the kinetic and transport phenomena of an electrochemical system [1,2]. It consists in perturbing the fuel cell operation with a small AC current signal over a wide range of frequencies and in measuring the voltage response. The module and the phase shift between voltage response and current perturbation are due to the electrical impedance of the fuel cell and provide useful information on the entity of internal fuel cell losses.

Despite the potentialities of this measurement technique the interpretation of experimental observations is very complicated and modeling plays a fundamental role in the analysis of experimental data. Until now the interpretation has mostly been carried out by means of equivalent circuit method (ECM) [3–6]. Even though simple and fast, this method is not reliable, since the equivalent circuit is not unique; moreover ECM provides only few useful qualitative information.

M. Orazem [7] proposed an innovative approach for a quantitative interpretation of EIS measurements: the developed methodology consists in expressing the equivalent circuit element as a function of the physical parameters of the system. In Ref. [8] this method was used for the interpretation of cathode impedance of a polymer electrolyte membrane fuel cell (PEMFC), but in principle it could be applied to any electrochemical system, including direct methanol fuel cell (DMFC). However the results still depend on the considered equivalent electric circuit. A similar methodology has been adopted by T.S. Zhao et al. [9] to investigate the simultaneous oxygen reduction and methanol oxidation at the cathode of a DMFC.

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An alternative approach is represented by physically based EIS models, that in the last years attracted increasing scientific interest [10–19]. The development and experimental validation of this type of models are very complicated, but the results are not related to the choice of a suitable equivalent electric circuit and model predictions permit to investigate the origin of different impedance features.

In the literature many works regarding both solid oxide fuel cells (SOFCs) [10–12] and PEMFCs [13,14] technology can be found. Bessler et al. carried out an extensive physically based model activity on SOFC [15–17]: the flexibility and modularity of the developed models, including detailed elementary kinetic electrochemistry and diffusion processes, allowed the assignment of the origin of SOFC impedance features with high accuracy. Springer et al. [18] developed one of the first numerical models for PEMFC cathode impedance: the first impedance loop was attributed to the effective charge-transfer resistance and double-layer charging, while the second one was related to the mass-transport limitation in the gas phase. Guo and White [19] presented a PEMFC cathode impedance model consisting of many flooded spherical agglomerate particles, permitting a more detailed comprehension on impedance behavior.

In DMFCs the anode catalyst layer (CL) internal losses are not negligible, as in PEMFC technology; moreover the mass transport phenomena at anode side are very complex, due to the two-phase and multi-component nature of the flows. Thus the interpretation of impedance behavior is even more complicated than in PEFC and SOFC technology, in fact in the literature only few modeling analyses can be found [20–24], generally concerning the cathode.

Kulikovsky reported a clear and detailed explanation of the mathematical development of DMFC cathode impedance model [20,21], analyzing the effects of physical phenomena on the shape of cathode impedance spectrum. However the models are not integrated along channel length and no attempts to fit experimental data have been done. Sundmacher et al. presented a detailed analysis of the methanol oxidation kinetics on a DMFC anode in a cyclone flow cell [23], but the homogeneous concentration distribution over the membrane electrode assemblies (MEA) does not permit to investigate mass transport limitations. Therefore in the literature limited effort has been dedicated to develop a whole DMFC anode impedance model and a detailed comprehension of the physicochemical phenomena regulating anode operation is required to further optimize components, operation strategies and lifetime.

This work proposes a complete and validated physical model of DMFC anode impedance, increasing the understanding of anode operation and providing a quantitative interpretation of the experimental measurements. The work is organized as follows. In Section 2 the experimental measurement of DMFC anode impedance is reported, subsequently, in Section 3, the model development is described. Then, in Section 4, the model results and the origin of different impedance features are illustrated and finally some conclusions are given in Section 5.

2. Experimental

2.1. Cell hardware

The experimental measurements were conducted using the same fuel cell, as well as equipment, which has already been characterized in terms of anode polarization, performance, methanol cross-over and water transport in previous publications by the authors [25–27].

The MEA was purchased already assembled by balticFuelCells GmbH with an active area of 22.1 cm^{-2}, consisting of Pt–Ru anode (4 mg cm^{-2}, Pt:Ru = 2), a Nafion® 117 membrane and Pt cathode (4 mg cm^{-2}). Anode diffusion layer presents gas diffusion layer (GDL) without micro porous layer (MPL), while the cathode one has got MPL: for this reason this MEA is named MEA GM, as in previous publication [27]. The fuel cell is thermostated at 333 K, the anode is supplied with a 3.25wt.% aqueous solution of methanol at 1 g min^{-1} flow rate, while the cathode operates with a hydrogen flow rate (see paragraph 2.2) of $2.14 \cdot 10^{-4}$ g min^{-1}.

2.2. Electrochemical measurements

In hydrogen–air fuel cells contributions of the anode are usually negligible due to fast kinetics of hydrogen oxidation reaction and a standard practice consists in neglecting anode impedance [18]. In DMFC the slow methanol electro-oxidation does not permit to clearly distinguish anode and cathode contributions by measuring the full fuel cell impedances. However it is possible to eliminate contributions of the cathode in a half-cell DMFC by feeding the cathode with hydrogen, so that protons are reduced and hydrogen is evolved [28–31]. In this configuration the cathode works as a dynamic hydrogen electrode (DHE) and it is suitable as a reference and counter electrode for DMFC anode impedance measurements.

The anode spectra were recorded with an Autolab PGSTAT 30® provided with a frequency response analysis module. The impedances are measured under galvanostatic control and the amplitude of the sinusoidal current signal is adjusted so that the potential amplitude does not exceed 10 mV. The frequency is included between 10 kHz and 50 mHz with a logarithmic distribution. The obtained experimental values are processed by a retrospective use of Kramers–Kronig transforms [1,32] in order to verify the validity of the measurements. The impedance values that do not satisfy such relations are not considered meaningful. Fig. 1 reports two

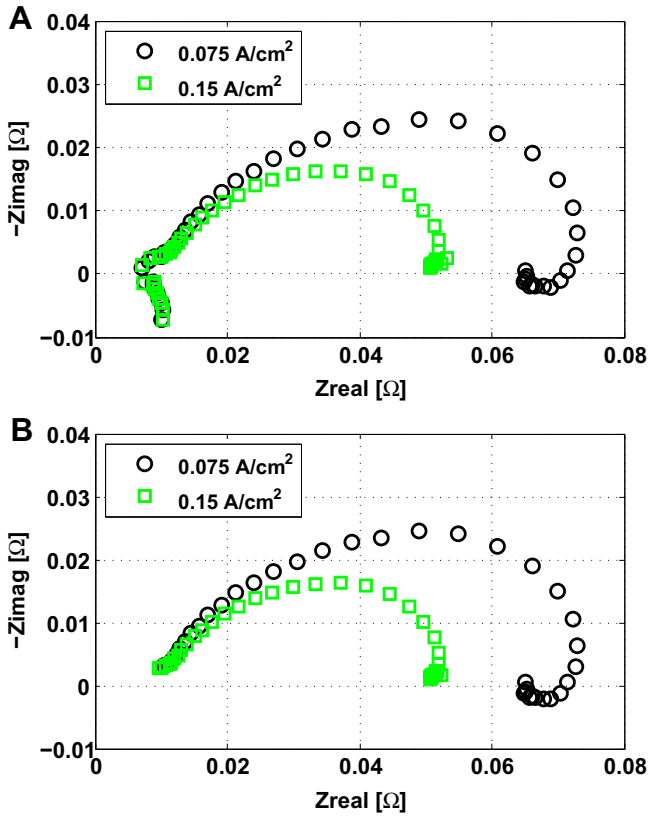

Fig. 1. Anode Nyquist plots at different current densities: a) raw data; b) after the use of Kramers–Kronig relations.