



Advanced impedance study of polymer electrolyte membrane single cells by means of distribution of relaxation times



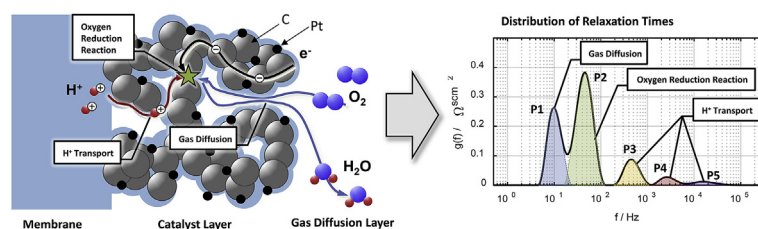
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HIGHLIGHTS

- Impedance study of a PEM fuel cell at clearly defined operating points.
- Identification of loss processes by the distribution of relaxation times.
- Analysis of process dependencies on current density, gas compositions and humidity.
- Separation and quantification of anode and cathode polarization contributions.
- Unambiguous process assignment to the underlying physical mechanisms.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Polymer electrolyte membrane fuel cell
Electrochemical characterization
Electrochemical impedance spectroscopy
Distribution of relaxation times
Polarization contribution

ABSTRACT

Electrochemical impedance spectroscopy data of a polymer electrolyte membrane fuel cell are compiled across a wide range of operating conditions. In all cases, homogeneous operating conditions are applied over the entire cell area to set a clearly defined operating point and to derive unambiguous parameter dependencies. As a novelty, this diverse set of impedance spectra is deconvoluted by the distribution of relaxation times (DRT) method in the frequency range from 0.5 Hz to 60 kHz. In H_2 /air-operation five polarization contributions with different time constants are registered. The assignment to gas diffusion in the gas diffusion layer and catalyst layer, the oxygen reduction reaction at the Pt-catalyst and proton transport processes in the cathode catalyst layer is supported by a systematic analysis of parameter dependencies.

Furthermore, DRT deconvolution in H_2/H_2 -operation reveals three “new” anode contributions, usually hidden by the dominating cathode contributions. They are assigned to gas diffusion and hydrogen oxidation, including charge-transfer and proton transport in the anode catalyst layer. It is confirmed that the polarization contributions at the cathode side sum up to 96% for typical operating conditions, but the share changes to 80% cathode and 20% anode at low hydrogen partial pressure.

1. Introduction

Researchers commonly use polarization curve characterization to compare the efficiency and performance of polymer electrolyte membrane fuel cell (PEMFC) single cells. However, in order to identify and quantify the individual performance-related polarization processes, and to set up a physicochemical meaningful model, a precise analysis is

necessary at each operating point along the polarization curve.

Electrochemical impedance spectroscopy (EIS) is a suitable in-situ technique for recording polarization processes with individual time constants. EIS measurements have so far been widely applied in literature in order to determine the membrane resistance, which is used for ohmic drop corrections of polarization curves [1–4]. Beyond that, several research groups have studied PEMFC impedance spectra in

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<https://doi.org/10.1016/j.jpowsour.2018.09.004>

Received 24 July 2018; Received in revised form 30 August 2018; Accepted 3 September 2018

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more detail. Typically, literature reports two pronounced arcs for PEMFC impedance spectra, accounting for charge transfer at medium frequencies and gas diffusion at low frequencies [1,5–8]. Charge transfer decreases with increasing current density, whereas gas diffusion becomes progressively more dominant. The low-frequency arc can even vanish, if low current densities or high stoichiometries are applied. In this case, the spectrum is reduced to one semicircle. In contrast to that, Xie et al. reported gas diffusion to be dominant at open circuit conditions (OCC) [5]. Sometimes an additional high-frequency feature can be detected as a third semicircle [2,9] or 45° branch [6,7,10]. Although this shape of spectrum is reported several times, it is not consistently assigned. This feature is sometimes assigned to proton transport processes in the catalyst layer [2,7,11], to distributed ionic resistance in the catalyst layer [6], to the construction of the MEA [9] or to charge transfer kinetics at the anode [1,12]. Furthermore, literature generally agrees that the identified polarization processes are mainly caused at the cathode side, although there is no precise analysis as to which extent the anode contributes.

Commonly the obtained impedance spectra are analyzed by a complex nonlinear least square fit (CNLS) approximation to a model function represented by an equivalent circuit model (ECM) [1,5,13–15]. In this case the ECM has to be defined *a priori*, without knowing the eventual number, size and time constants of the contributing polarization processes. The assessment of a physicochemically motivated ECM remains challenging, especially if polarization processes with close time constants occur. This leads to processes overlapping in the frequency domain and thus hinders clarification, which may result in incorrect model assumptions and instable and/or ambivalent fitting results. A more meaningful physical process identification is given by an alternate approach, where ECM and starting parameters for the CNLS algorithm are obtained by a pre-identification of the impedance response aided by the distribution of relaxation times (DRT) [16,17]. This approach was established in the framework of our solid oxide fuel cells research [18] and successfully transferred to lithium-ion batteries [19]. More recently, the DRT method was partially demonstrated on high temperature polymer electrolyte fuel cells (HT-PEMFC) [20].

In this paper, DRT analysis is applied to the impedance spectra of a PEMFC single cell, across a wide range of operating conditions (see Section 2.2 for details). In all cases, homogeneous operating conditions are applied over the entire cell area to set a clearly defined operating point and to derive unambiguous parameter dependencies. A suitable measurement setup will be introduced below.

It will be demonstrated that DRT analysis facilitates the deconvolution of five individual polarization processes (P1–P5) in full-cell mode (H_2 /air) and three minor anode polarization processes (P1A – P3A) in anodic half-cell mode (H_2/H_2). For the first time, the contributions of both electrodes will be precisely quantified and correlated. The identified processes will then be assigned to the underlying physicochemical mechanisms.

2. Experimental

2.1. Cell assembly

This study investigates commercial membrane electrode assemblies (MEA) of type Greenerity® H500EL2 with platinum loadings of $0.4 \text{ mg}_{Pt} \text{ cm}^{-2}$ (cathode) and $0.2 \text{ mg}_{Pt} \text{ cm}^{-2}$ (anode). Single cells with an active surface area of 1 cm^2 were prepared by cutting 25 cm^2 MEAs and welding them into a PVDF foil for better handling and mechanical stability (Fig. 1b). The thus prepared MEAs were assembled with gas diffusion layers (GDL 29 BC from SGL®) and placed into an in-house developed fuel cell housing (Fig. 1a).

The housing and test bench were designed according to our established SOFC-testing facilities [21,22]. The cell is sandwiched in between gas distribution plates (anode: stainless steel; cathode: PEEK).

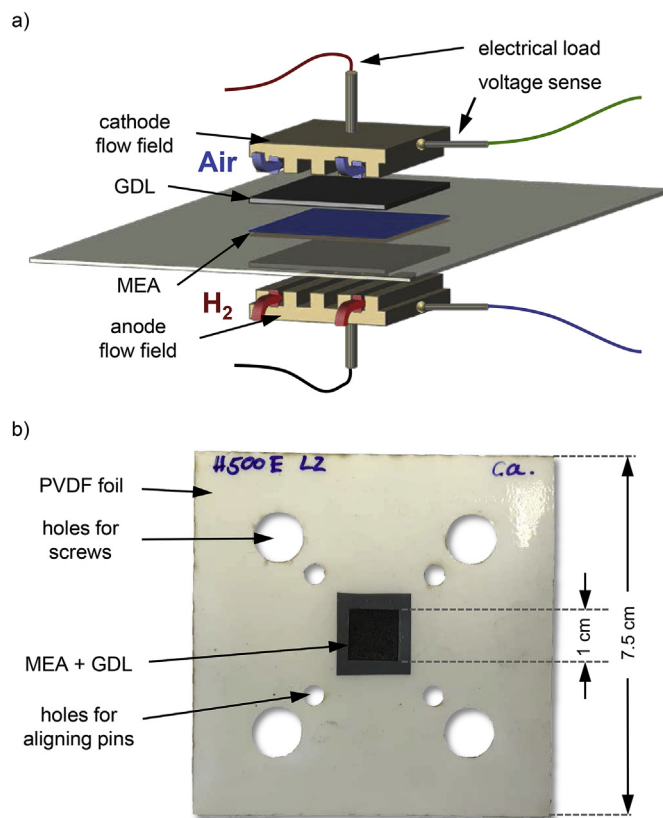


Fig. 1. (a) Cell setup with gold flow fields and contacting for 1 cm^2 MEAs. (b) Investigated cell with platinum loadings of $0.4 \text{ mg}_{Pt} \text{ cm}^{-2}$ (cathode) and $0.2 \text{ mg}_{Pt} \text{ cm}^{-2}$ (anode). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

The active electrode area contacting is realized by gold flow fields with parallel flow channels (cross-section: $1 \text{ mm} \times 1 \text{ mm}$). The high electrical and thermal conductivity of gold prevents gradients over the cell area and ensures a very low contact resistance vs. the GDL (see Section 3.1 for detailed description). In addition, ohmic losses caused by contacting and wiring are kept at a minimum using four point measurement. As expected, short-circuit measurements resulted in a resistance value of less than $1 \text{ m}\Omega \text{ cm}^2$. Furthermore, the use of twisted pair cables achieves low inductivity, which is beneficial for high resolution impedance measurements.

PTFE gaskets (thickness: $150 \mu\text{m}$) are used for sealing between the gas distribution plates and the cell. The housing is compressed by stainless steel heat exchanger plates containing a thermal fluid. The cell temperature is controlled by a Julabo F32-ME thermostat. Thermocouples attached to the rear of the gold flow fields provide information about temperatures close to the anode and cathode. In our setup the GDL contact pressure is independent from the sealing pressure and continuously adjustable from 0 to 200 N. The actual contact pressure is continuously logged by a force sensor. This ensures reproducible measuring conditions for varying cell dimensions. All following measurements have been conducted by applying a contact pressure of 50 N, which correlates to 1 MPa with respect to the land area of the flow field.

The gas is supplied by mass flow controllers enabling the supply of a well-defined mixture of oxygen, nitrogen and hydrogen to anode and cathode. The humidity in oxidant and fuel is generated in a catalytic burner chamber ahead of the cell by reacting hydrogen and oxygen [23]. The gas lines to the cell are heated. The humidities at the gas inlet and outlet (of cathode and anode, respectively) are monitored by four Driesen + Kern DKRF-400 humidity sensors.

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