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Transient limiting current measurements for characterization of gas diffusion layers

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HIGHLIGHTS

- In-situ characterization of GDLs.
- Transient limiting current measurement for prediction of oxygen transport resistance.
- Quasi in-situ synchrotron X-ray computed tomography and radiography measurements on GDLs.
- Visualization of liquid water inside GDL microstructure.

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ABSTRACT

The water management in proton exchange membrane fuel cells (PEMFC) is strongly influenced by the design of the gas diffusion layers (GDL). Limiting current measurements in small-scale cells operating at high stoichiometries are useful to determine the oxygen transport resistance. The oxygen transport resistance increases, once water condenses inside the GDL.

In this study a new electrochemical method for voltage loss estimation of GDL induced oxygen transport losses are presented. This new method, referred to as “transient limiting current” (TLC), is compared with the literature method. TLC allows a direct estimation of oxygen transport resistance at an arbitrarily conditioned state.

This study also presents a case study of liquid water visualization of a PEM fuel cell with varying GDLs types. With the help of quasi in-situ synchrotron X-ray computed tomography and time resolved radiography measurements we investigate appearance and distribution of liquid water inside the GDLs under limiting current conditions.

1. Introduction

Low temperature polymer electrolyte fuel cells (PEMFC) are a promising technology for clean power sources and are applicable to automobile systems. Key challenges of this technology still remain, notably the required improvements of power density, durability as well as costs. The trend for automotive applications is to increase current densities in order to achieve higher volumetric power densities, where the gas diffusion layer (GDL) plays a significant role [1–4]. The GDL enables the transport of reactants from the flow fields to the catalyst-coated membrane (CCM) and excess liquid water to the gas channels. It also conducts electrons and heat between the flow fields and the CCM [5,6]. A typically automotive GDL consists of a paper- or non-woven felt-based carbon substrate with an additional microporous layer (MPL), which is facing towards the electrode. The GDL microstructure and the composition of the carbon fiber substrate have a significant

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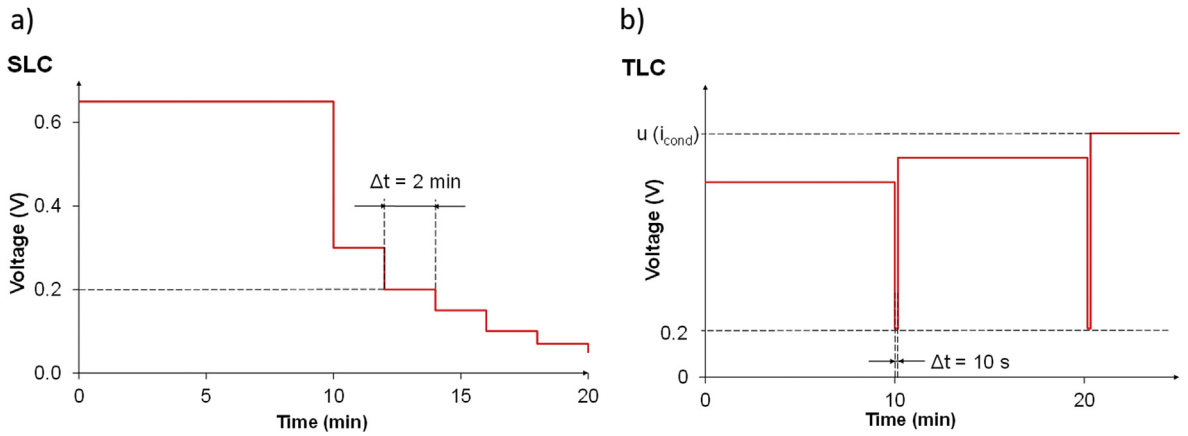

Fig. 1. A) SLC: Continuous ramp to limiting current for different oxygen concentrations, b) TLC: quick jump to limiting current for different conditioned load point.

influence on water accumulation and transport properties. The influence of microstructure was discussed by various authors [7–10]. An in-situ measurement for characterizing GDLs in terms of oxygen transport resistance has been presented in literature by Baker and Caulk [11,12]. They described a change in oxygen transport resistances depending on the water content. For paper-like GDLs a clear distinction between a dry state (entire pore volume can be used for oxygen transport) and a wet state (reduced pore volume due to liquid water saturation) are shown. Oppositely, felt-based GDLs displayed an increase of oxygen transport resistance - under conditions where no flooding was expected [12]. We refer to this method as stationary limiting current (SLC). The basic principle of the method is to lower the cell voltage until the amount of oxygen transported to the catalyst equals the amount of oxygen consumed in the reaction. The related current is the limiting current. The reason for the phrase “stationary” in the term is that in the experiments the temperature profile in the MEA, as well as the saturation profile is in steady state as each voltage niveau is held for 2 min before the limiting current is extracted. In this paper an alternative limiting current method is introduced. In contrast to the SLC, we condition generally-arbitrary load points before the current is tracked after a sudden jump to 0.2 V. From the current trend the transient limiting current (TLC) is extracted that characterizes the oxygen transport resistance linked with the conditioned state.

Through advancements in X-ray tomography and radiography technologies, it has recently become possible to obtain in-situ visualizations of water accumulation and water distribution [13–38]. Two common techniques for measuring the liquid water accumulation in operando are synchrotron X-ray imaging and neutron imaging [39]. Synchrotron X-ray radiography has been established as a useful technique for detecting liquid water behavior with high resolutions. Various studies performing in-situ visualization of liquid water have supported the link between oxygen transport resistance and liquid water saturation inside GDL [40,41]. Owejan et al. [40] shows the importance of the liquid water saturation distributions on oxygen diffusion transport modeling. Water distribution in different GDLs between land and channel regions has been observed by multiple studies [2,42–44]. Bazylak [45,46] investigated liquid water accumulation and oxygen mass transport resistance at high current densities using synchrotron X-ray.

In this study, we use synchrotron X-ray and radiography for visualization of water saturation and compare those with SLC and TLC measurements. We use SLC to generate different water saturation levels in various GDL types and detect those by quasi in-situ synchrotron X-ray tomography and radiography measurements. Two different structure types of GDL were analyzed, a paper and a non-woven felt based GDL substrate with MPL. Different saturation behavior of microstructure can be shown and are linked to limiting current measurements results.

2. Experimental

2.1. Equipment and operation conditions

Experiments were executed using the 50 cm^2 graphite composite flow field with an active area of 5 cm^2 as used in the study of Baker and Caulk [11,12]. The anode and cathode flow fields were identical (channels were 0.5 mm wide by 0.8 mm deep and spaced 0.5 mm apart). Commercial 5 cm^2 membrane electrode assemblies (MEAs) with a membrane thickness of 15 µm and a total loading of 0.5 mg_{Pt} cm^2_{MEA} (cathode loading of 0.4 mg_{Pt} cm^2_{MEA}) were used (platinum on a high surface area carbon on both electrodes). At these high loadings, oxygen transport losses of the electrode are negligible [47–49]. Two commercial GDLs (SGL 28BC and Freudenberg H14C7) were used, each type for both sides. GDL compression was controlled by pneumatic hardware with flexible sealing to set a compression of about 1.5 MPa at the landings. The cell temperature was controlled by heaters in the cell hardware and external fans in response to the temperature measured in the cathode flow field directly over the active area. In this study all experiments are done at 80 °C and 100% relative humidity at the inlet of anode and cathode. Back pressures were held constant at 3 bara on both sides. To maintain uniform along-the-channel conditions, high stoichiometries were used. On the anode side, 1.0 slpm of hydrogen was used at all test points, which resulted in stoichiometries greater than ten at all current densities. Also, oxygen stoichiometries exceeded 10 at all test points with a 4.0 slpm oxygen/nitrogen mixture flow rate. Pressure drops were below 50 mbar over the active area for liquid water disposal. High frequency resistance (HFR) measurements at 10 kHz (max. amplitude: 7.4 mA) were logged at all times with a digital ohm meter (Tsuruga Model 3566).

2.2. SLC

The SLC-method is schematically depicted in Fig. 1a. Dry oxygen mole fractions in nitrogen, ranging from 0.005 to 0.21, were used to measure the limiting current for each concentration. In SLC, the cell voltage was stepped down from 0.65 V to 0.05 V (with 2 min hold time) to gain the vertical trend near 0.2 V, thus indicating that a limiting current has been reached. At limiting current the oxygen concentration at the electrode approaches zero. These test conditions and analysis correspond to the work of Caulk and Baker [11,12].

From the limiting current value i_{lim} (at 0.2 V) the total oxygen transfer resistance $R_{O2,\,T}$ is derived, according to equation (1):

$$R_{O2,\,T} = \frac{(p_{O2,channel} - 0)\cdot 4\cdot F}{R\cdot T\cdot i_{lim}} = \frac{p_{O2,channel}\cdot 4\cdot F}{R\cdot T\cdot i_{lim}} \quad (1)$$

with F being the Faraday constant, $p_{O2,\,channel}$ the oxygen partial