Improved electrochemical in-situ characterization of polymer electrolyte membrane fuel cell stacks

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HIGHLIGHTS

- A method for measuring hydrogen crossover currents in PEMFC stacks is presented.
- Quantitative characterization of membrane and electrode in stacks has been achieved.
- The method shows good quantitative agreement for all individual cells.

ARTICLE INFO

ABSTRACT

In-situ diagnostics for single polymer electrolyte membrane fuel cells are well known and established. Comparable stack level techniques are urgently needed to enhance the understanding of degradation during real system operation, but have not yet reached a similar level of sophistication. We have therefore developed a new method for the quantification of the hydrogen crossover current in stacks, which in combination with a previously published technique now allows a clear quantitative characterization of the individual cells' membranes and electrodes. The limits of the reported methods are theoretically assessed and application is then demonstrated on automotive short stacks. The results prove to be highly reproducible and are validated for individual cells of the respective stacks by direct comparison with cyclic voltammetry results, showing good quantitative agreement for the hydrogen crossover current, the double layer capacitance and the electrochemically active surface area.

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1. Introduction

Despite an extensive and ever increasing research effort, both the reduction of costs and the enhancement of durability remain significant challenges for manufacturers of polymer electrolyte membrane (PEM) fuel cells and fuel cell systems. Additionally, these problems are coupled, e.g. by the price of the membrane and catalyst materials [1].

In order to (a) improve the general understanding of degradation, (b) progressively decouple these challenges and (c) provide a precise ageing prognosis, the evolution of certain descriptive degradation parameters of membrane electrode assembly (MEA) needs to be known along their lifetimes as a function of load profile and operating conditions. These parameters comprise

- the membrane gas permeability, represented by the hydrogen crossover current density (i_{H2}),
- the amount of corrosion of the carbon catalyst carrier, represented by the double layer capacitance c_{DL} and
- the electrochemically active surface area (ECSA)

For single cell testing, the corresponding quantifications can be executed by potentiodynamic cyclic voltammetry (CV) [2]; however, these specimens are usually used on a laboratory scale, e.g. for benchmarking purposes. For stack testing, determination of these parameters in the past was typically carried out by disassembly of the stack, sequential characterization of each cell and reassembly [3], which can be laborious and difficult depending on stack design. Fuel cell manufacturers are thus in need of test procedures capable of a quick and reliable quantification of the above mentioned parameters of all individual cells in assembled stacks.

Although the need for such methods is obvious, only very few researchers have reported on such methods. Both Brightman et al.

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[4] and Lee et al. [5] independently presented similar galvanostatic methods. These methods enable a characterization of the electrode by assigning specific parts of the applied current to the above mentioned parameters using analogies to CV measurements. Both groups derived and applied these methods on single cells first, comparing the results with conventional CV measurements. Then the methods were demonstrated at the stack level, yielding plausible yet not fully validated results for the double layer capacitance and the ECSA. The main difference between both publications lies in the treatment of the hydrogen crossover current, which needs to be accounted for to precisely characterize the working electrode. While Lee et al. present a method of estimating the hydrogen crossover current by comparing results obtained at different applied current densities (an approach followed as well by Ref. [6]), Brightman et al. propose to simply minimize its effect (and thus the resulting error) by minimizing the hydrogen concentration gradient across the membrane, e.g. by dilution of the employed hydrogen.

In this publication, the original galvanostatic procedure is extended with a new test method (herein referred to as electrode and membrane characterization, respectively) specifically designed to measure the hydrogen crossover current of each cell. The combination of both methods is demonstrated on a short stack and afterwards validated by direct comparison with cyclic voltammograms of the very same cells after disassembling the stack. Additionally, the reproducibility of the procedure is assessed and its limitations are discussed.

2. Theory

Since the individual cells in PEM fuel cell stacks are electrically connected in series, it is not possible to influence the individual cell voltages independently, which makes application of cyclic voltammetry unsuitable. However, both the procedures for membrane and electrode characterization presented below rely on the charging of the double layers of the individual cells and are thus closely related to standard cyclic voltammetry (CV). The new test method will therefore be explained by use of these analogies.

Both procedures will first be explained for single cell conditions, using the analogies to typical CVs. This is done in the first of the following subsections. In the second subsection, the practical and theoretical constraints for usage with stacks are analysed and a mitigation is outlined.

2.1. Derivation of the test procedure

In a PEM fuel cell CV setup the counter and working electrodes are usually under hydrogen/inert gas atmospheres, respectively. A typical result is shown in Fig. 1(a), where the applied current density i_{DC} can generally be split up into five components:
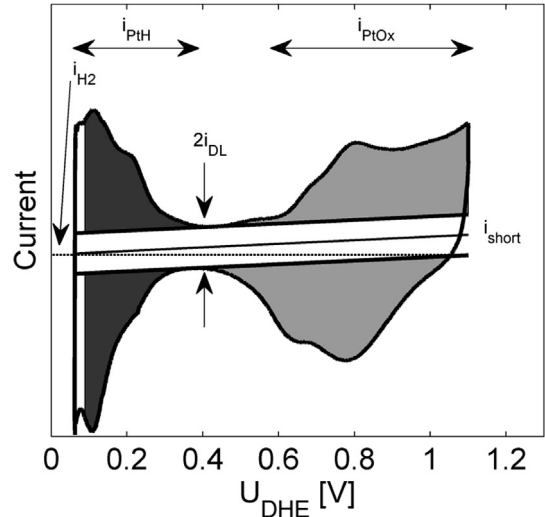
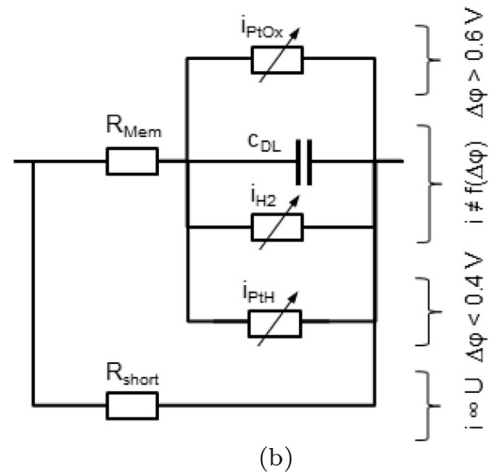- The current oxidizing the molar hydrogen crossover flux (i_{H2}),

$$H_2 \rightarrow 2H^+ + 2e^-$$
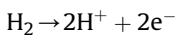
- The current oxidizing previously adsorbed hydrogen on the catalyst (i_{PtH}),

$$PtH \rightarrow Pt + H^+ + e^-$$
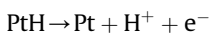
- The current needed to form any catalyst oxides during the measurement (i_{PtOx}), e.g.
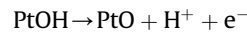

(a)

(b)

Fig. 1. Decomposition of the applied current during characterization (a) Typical CV as measured in a PEM fuel cell. (b) Equivalent circuit for an individual cell with DHE.

$$Pt + H_2O \rightarrow PtOH + H^+ + e^-$$

$$PtOH \rightarrow PtO + H^+ + e^-$$

- The double layer charging current (i_{DL})

$$i_{DL} = c_{DL}\frac{dU}{dt} \tag{1}$$

- The electrical shorting current (i_{short}),

$$i_{short} = \frac{U}{R_{short}}$$

When using a Dynamic Hydrogen Electrode (DHE) as counter electrode, its contributions are assumed to be negligible due to the fast hydrogen kinetics. The cell can then be visualized as the equivalent circuit depicted in Fig. 1(b), where the different current paths all are distinctly viable w.r.t. the working electrode's half-cell voltage. For the following derivation of the test procedure, it will