

Development of Electrode Diagnostics for High-Temperature Polymer Electrolyte Fuel Cells

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High temperature polymer electrolyte fuel cells (HT-PEFCs) based on phosphoric acid doped polybenzimidazole (PBI) membranes (cf. Figure 1) as a gel-type proton transport medium benefit in several different ways from operating at elevated temperatures of around 160°C. First of all, they can be combined effectively with heating systems due to a higher working temperature, leading to overall higher system efficiencies in combined heat and power applications. Secondly, HT-PEFCs tolerate orders of magnitude larger amounts of the catalyst poison CO (up to 2% [1]) compared to low temperature perfluorosulfonic acid membrane fuel cells (LT-PEFC, approx. 10ppm [2]), which renders them more suitable to generate electricity from hydrogen-rich reformat gases without complex and energy intensive CO cleanup. Furthermore, it is not necessary to humidify the membrane or the process gases.

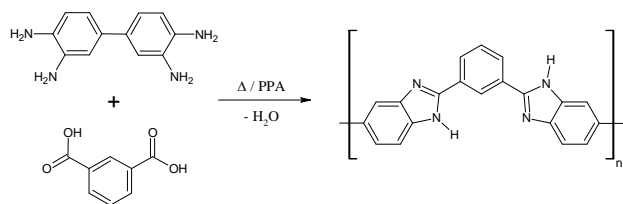


Figure 1. Synthesis of polybenzimidazole with tetra-aminobiphenyl and an aromatic dicarboxylic acid (e.g. isophthalic acid) as initial monomers in polyphosphoric acid (PPA) [2].

The HT-PEFC can be affected by a number of degradation effects at different locations of the membrane electrode assembly, e.g., pinhole formation, acid evaporation and membrane thinning. Electrodes can also represent a major degradation area. Interestingly, specific degradation mechanisms, such as carbon corrosion, catalyst detachment and catalyst particle growth can be found in the LT-PEFC as well. Additionally, structural changes and acid flooding of the gas diffusion layer of the cell can occur. All degradation effects are complex functions of the specific operational parameters, making it challenging to identify them individually. This in turn is necessary to gain insights into limitations in MEA lifetime and is the key to successful development of mitigation strategies to reach a desired lifetime of more than 40.000 hours for stationary applications.

One of the specific degradation triggers is known as “Start/Stop”- or “Reverse-Current Decay”-Mechanism [3], [4]. The mechanism is induced during the fuel cell startup or shutdown and is one of the main reasons for carbon degradation at the cathode. The number of start/stop cycles is closely related to the overall lifetime of the fuel cell. If, for example, a HT-PEFC is used in a CHP system, it is conceivable that several hundred cycles will be accumulated, which lead to a rapid and irreversible damage of the cell. Therefore, it is desirable to develop a reliable method to determine the amount of corroded carbon at the cathode.

Cyclic voltammetry (CV) is a well known tool for measuring the electrochemically active surface area (ECSA) of an electrode. This area is linked to the amount of carbon involved in the electrodes reactions. If one can determine the change in the ECSA, it is therefore possible to estimate the loss of carbon based on the start/stop degradation mechanism. For LT-PEFCs it is a rather standard procedure to obtain the ECSA with the help of hydrogen under potential deposition (H_{upd}) or CO-stripping [5]. The excessive amount of phosphate anions in the HT-PEFC, which are strongly bound to the electrode, makes it difficult to work with the H_{upd} method. Therefore CO-stripping voltammetry is the diagnostic tool of choice including the drawback that the CO-peak is not very well defined.

This contribution will tackle this particular problem by providing insights on how to determine the ECSA based on electrochemical analysis and real-time exhaust gas analysis during CV measurements (cf. Figure 2). The experiments are carried out at laboratory conditions with hydrogen or reformat at different temperatures and are supported by ex-situ analysis. In summary, the combined findings lead to an improved understanding of carbon corrosion during start/stop and provide a powerful diagnostic tool for measuring ECSA in HT-PEFCs.

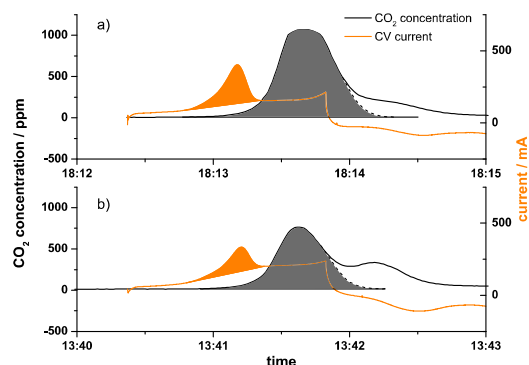


Figure 2. Estimation of the ECSA with help of CO-stripping and real-time exhaust gas CO_2 analysis. a) represents the measurements before and b) the measurements after start/stop cycling.

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