



Investigation of degradation effects in polymer electrolyte fuel cells under automotive-related operating conditions[☆]



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HIGHLIGHTS

- CO₂ increases exponentially in the anode/cathode exhaust in case of fuel starvation.
- A CO peak in addition to the significant CO₂ peak is detected in anode exhaust gas.
- PEFC performance reduces about 47% between BOL and EOL.
- ECSA reduces about 37.4% on cathode and 59.5% on anode.
- Anodic/cathodic charge transfer resistance as well as the cell resistance increases.

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ABSTRACT

The influence of artificial starvation effects during automotive-related operating conditions is investigated within a polymer electrolyte fuel cell (PEFC) using non-dispersive infrared sensors and a current scan shunt. Driving cycles (DC) and single load change experiments are performed with specific fuel and oxidant starvation conditions.

Within the DC experiments, a maximal CO₂ amount of 4.67 μmol per cycle is detected in the cathode and 0.97 μmol per cycle in the anode exhaust without reaching fuel starvation conditions during the DC.

Massive cell reversal conditions occur within the single load change experiments as a result of anodic fuel starvation. As soon as a fuel starvation appears, the emitted CO₂ increases exponentially in the anode and cathode exhaust. A maximal CO₂ amount of 143.8 μmol CO₂ on the anode side and 5.8 μmol CO₂ on the cathode side is detected in the exhaust gases. The critical cell reversal conditions only occur by using hydrogen reformate as anode reactant. The influence of the starvation effects on the PEFC performance is investigated via polarization curves, cyclic and linear sweep voltammetry as well as electrochemical impedance spectroscopy. The PEFC performance is reduced by 47% as a consequence of the dynamic operation.

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1. Introduction

Polymer electrolyte fuel cells (PEFCs) are promising alternatives to conventional combustion engines. For the use of PEFCs in automotive applications, an increased lifetime and durability as well as lower platinum loadings of the electrodes might be cited as examples in order to reach the automotive targets.

Pei et al. [1] have reviewed the main factors affecting the lifetime of PEFCs in automotive applications. Especially, start stop

cycles and the dynamic operation of PEFCs provoke a reduced lifetime and thus, load cycling is one of the main cause of PEFC degradation. The frequently changed load induces an increased water generation and leads to water management and flooding problems affecting the gas concentration at the electrode. The dynamic response of the PEFC is another important problem concerning the irreversible degradation effects. As a consequence of a sudden change of load, fuel and oxidant starvation can occur and induce irreversible degradation effects like carbon corrosion or platinum dissolution. Pei et al. [2] analyzed real driving cycles of PEFC buses and identified that 56.6% of the total PEFC degradation can be traced to dynamic load changes, while 33% of the degradation occurred under start–stop cycles, 5.8% under high power load and 4.7% of the degradation rate under idling. The transient response of PEFC under various operating conditions was also

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investigated by Cho et al. [3]. Several load changes under different operating conditions were performed and specific undershoot/overshoot behavior of the voltage were identified. Basically, a certain time delay is needed after a load change until a steady state operation is achieved. For the case of a load change from low to high current density, first, the voltage drops in the order of 1 s because of through-plane gas transport problems and diffusion mass-transfer limitations, especially within the gas diffusion layer (GDL). Second, a time delay in the order of 10 s is needed until the voltage reaches a new steady state after the load change. It is concluded in Ref. [3] that the voltage recovery time in the order of 10 s can be mainly traced to the delayed media supply, the inhomogeneous concentration distribution at the electrode, existing flooding issues as well as a delay in the water content recovery in the membrane, especially in the case of an insufficient water supply during a load change. In the case of load changes from high to low current densities, a faster response time in the range of a few seconds is obtained due to the better membrane humidification at the beginning of the load change at higher current densities [3]. A general overview of the response times of the processes occurring during PEFC operation can be found in the publication of Wagner et al. [4]. Due to the great impact of transient operating conditions on the PEFC degradation, further publications regarding the transient response of PEFCs are available in literature [5–7].

The occurrence of critical operating conditions under dynamic operation, e.g. flooding issues or fuel/oxidant starvation induces degradation effects like platinum dissolution and agglomeration as well as carbon corrosion. Within driving cycle experiments over 1200 h, Borup et al. [8] identified a growth in the platinum (Pt) particle size from 1.9 to 3.5 nm on the cathode electrode. As a conclusion of the experiments carried out, growth in Pt particle size is accelerated during cycling to high potentials, with increased operating temperature and increased humidification. The growth in Pt particle size as well as the Pt dissolution was also found in further publications [9,10]. A mechanistic explanation of the Ostwald ripening is given in the publication of Virkar et al. [11]. Besides this, the Pt dissolution decreases the electrochemical surface area (ECSA) and thereby, reduces the lifetime of the PEFC. Here, the metallic Pt is dissolved into portable Pt ions. Due to a concentration gradient, the dissolved Pt ions migrate in the direction of the electrode/membrane interface and existing crossover hydrogen reduces the Pt ions. The deposition of a metallic Pt band near the electrode/membrane interface is the result of the Pt dissolution. Because of repeated start–stop cycles, Yoda et al. [12] identified such a Pt band in the distance of 10–20 μm to the electrode/membrane interface using scanning electron microscope (SEM) measurement technique.

Besides the Pt agglomeration and dissolution, carbon corrosion also reduces the ECSA. Maass et al. [13] investigated the potential transients as occurring during automotive PEFC operation. For the cathodic Pt/C electrodes, five specific carbon dioxide (CO_2) evolution maxima can be identified within the potential range between 0 and 1.2 V. At low cathodic potential limits (<0.3 V) and the presence of oxygen, chemical oxidation of carbon induced by hydrogen peroxide is the main process leading to carbon corrosion. Due to the catalytic activity of Pt, electrochemical carbon corrosion is basically possible at potentials higher than 0.3 V [13,14]. The highest CO_2 corrosion rates exist at higher cathodic potential ranges (>0.8 V). In presence of Pt, carbon monoxide (CO) is not detectable on cathode due to the CO adsorption on the Pt surface at lower potentials (<0.55 V) and the oxidation of CO to CO_2 at potentials higher than 0.55 V [13]. The main driving force for the carbon corrosion is the potential range at anode and cathode. Especially in dynamic operation, fuel and oxidant starvation is the main cause for critical cell potentials during PEFC operation. In the case of

oxidant starvation, the cell voltage drops to a value slightly under 0 V (approximately -0.1 V) [15]. As described above, the chemical oxidation of carbon due to the hydrogen peroxide formation is favored at potentials close to 0 V on cathode side. Taniguchi et al. [16] investigated the impact of fuel starvation regarding the electrocatalyst degradation. In the case of fuel starvation, cell reversal conditions occurred when the PEFC is loaded. The cell voltage can drop to values of -2 V [16]. Especially, the cell reversal conditions provoke permanent damage to the electrodes. Reiser et al. [17] identified the so called “reverse current decay mechanism” in the case of massive fuel starvation as occurring mainly in start–stop cycles. Due to the fuel starvation and the presence of oxygen on anode, the cathodic potential raises to high potentials (>1.4 V) [17]. The carbon corrosion on cathode which is induced by the anodic fuel starvation, can also be found in further publications in the literature [18–21]. The carbon corrosion reduces mainly the ECSA of the electrode due to the oxidation of the catalyst carbon support. Furthermore, the oxidation of carbon within the GDL is also possible, especially within the micro porous layer (MPL) which is in direct contact to the electrode. Spornjak et al. [22] investigated the influence of the MPL on carbon corrosion in the electrode using an accelerated stress test (AST) for carbon support corrosion. The contribution of the carbon corrosion within the MPL to the total amount of carbon corrosion was found to be in the range between 10 and 15% over short corrosion times [22]. The loss of ECSA induced by platinum agglomeration and carbon corrosion also increases the internal cell resistivity [22]. Due to the irreversible degradation effects, the PEFC performance decreases during the operation resulting in a shorter lifetime of the PEFC. A general overview of the PEFC degradation can be found in literature within the review articles [23–27].

The investigation of automotive-related operating conditions and their impact on the PEFC degradation is the main effort in the experiments carried out. Especially, the impact of fuel and oxidant starvation on the PEFC degradation is investigated in-situ. Therefore, the media supply times (forerun times) in front of dynamic load changes are varied on anode, cathode as well as on both sides in parallel inducing starvation effects within the PEFC operation. The “boxed” Driving Cycle (DC) as well as single load changes from 0.2 to 1.0 A cm^{-2} are used as automotive-related (dynamic) operating conditions. The induced carbon corrosion during the dynamic operation is analyzed using non-dispersive infrared (NDIR) sensors in order to detect CO and CO_2 in the anode and cathode exhaust gases. In addition, a current scan shunt (S++ Simulation Services) is used to analyze the current density distribution during the load changes. The loss of the ECSA due to the PEFC degradation is investigated by comparing the PEFC performance at the begin of life (BOL), at the middle of life (MOL) in between the dynamic measurements and at the end of life (EOL) after the dynamic measurements. Therefore, a basic cell characterization is performed using polarization curves, cyclic voltammetry (CV) as well as electrochemical impedance spectroscopy (EIS) measurements.

2. Experimental

A PEFC single cell with graphitic bipolar plates (BPP) was used within the experiments carried out. An overview of the meander-shaped flow field design and the orientation of the inlets and outlets (Fig. 1(a)) as well as the current scan shunt (Fig. 1(b)) which is used for analyzing the current density distribution, is shown in Fig. 1. The current scan shunt is fabricated by S++ Simulation Services and is designed for dynamic measurements with a signal resolution time in the range of 10 ms. The segmentation of the current scan shunt is 12 by 12, thus having 144 segments for the current distribution measurement over the whole active area.

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