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Methods to determine degradation in fuel cells

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Abstract

Polymer electrolyte fuel cells are a promising technology for converting the chemically bound energy of hydrogen into power. In order to establish fuel cells as a commercially viable product, the durability of membranes and electrodes in practical applications such as electric vehicles needs to be extended. The degradation mechanisms over lifetime are investigated by subjecting fuel cells to accelerated stress tests. Decomposition of the polymer electrolyte significantly affects the ionic conductivity and therefore the fuel cell performance. Cracks and tears form due to the thinning of the membrane, leading to reactant crossover and fluoride emissions. Electrochemical methods for characterizing degradation include polarization curves, electrochemical impedance spectroscopy and hydrogen diffusion current measurements. Local effects like flooding and dry-out of fuel cells are investigated using impedance spectroscopy in combination with total harmonic distortion analysis.

Keywords: accelerated stress test; polymer electrolyte fuel cell; electrochemical impedance spectroscopy; hydrogen diffusion current; fluoride emission rate; total harmonic distortion; flooding, dry-out;

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Nomenclature

AST	accelerated stress test
BoL	begin of life
CEET	Institute of Chemical Engineering and Environmental Technology
CV	cyclic voltammetry
DoE	US Department of Energy
DLSEC	dynamic large signal equivalent circuit
EoL	End of Life
EIS	electrochemical impedance spectroscopy
ESCA	electrochemically active catalyst area
FER	fluoride emission rate
GDL	gas diffusion layer
IMD	intermodulated
MEA	membrane electrode assembly
OCV	open cell voltage
PE(M)FC	polymer electrolyte (membrane) fuel cell
PITM	platinum band in the membrane
SSEC	small signal equivalent circuit
THD(A)	total harmonic distortion (analysis)

1. Introduction

Due to the rapid increase in greenhouse gas emissions mankind is confronted with the threat of climate change nowadays. In order to decrease greenhouse gases and achieve the goals of The Paris Agreement more renewable energy sources have to be introduced. One of such technologies is the PEFC which is an ideal candidate for the mobile and transport sector.

There are many advantages of the initiation of PEFCs. Firstly, PEFCs are capable of converting the chemical energy, bound in hydrogen, without harmful emissions into power. Secondly, the energy conversion efficiency is higher than in gasoline or diesel operated heat engines and it has a high power density. Unfortunately, one of the biggest drawbacks is the rather short lifetime of these fuel cells in practical applications that prevent them from being commercially available on large scale up to now. This is especially the case under strongly fluctuating load conditions which can be encountered in cars. Therefore, the degradation mechanisms causing performance loss have to be investigated in order to develop methods for mitigation. The Fuel Cell Systems Group at the CEET at Graz Technical University uses different approaches in order to characterize the different degradation conditions and mechanisms. ASTs are used to either selectively induce certain degradation modes or to portray harmful conditions, which can occur during real operation [M. Bodner et al. (2017)].

Voltage cycling is one possible approach for accelerated stress testing. Within the electrodes, the carbon based support material can undergo oxidation, leading to the emission of CO₂, a loss of electric conductivity and electrochemically active catalyst surface area. Off-gas analysis can be utilized to identify operating points, accelerating carbon support corrosion. Structural changes can be visualized ex-situ by various means. X-ray computed tomography, transmission electron spectroscopy and scanning electron spectroscopy are powerful tools therefore. If the latter is combined with energy dispersive X-ray spectroscopy, the local chemical composition of the electrode can be determined [M. Bodner et al. (2015)].

Voltage cycling also leads to platinum oxidation and dissolution. In dependence on the conditions within the fuel cell, platinum ions can be washed out or redeposited, forming agglomerates. This is driven by the high surface energy of the nanoparticles and results in a loss of ECSA. At high potentials and in the presence of hydrogen on the anode, ions are transported into the polymer electrolyte membrane, where they are reduced by crossover hydrogen, forming a PITM. Even though this represents a loss of ECSA as well, studies have indicated a mitigating effect of PITM on ionomer degradation [M. Bodner et al. (2015); M. Bodner, B. Cermenek et al. (2015); N. Macauley et al. (2015)].

Decomposition of the polymer electrolyte can significantly affect the fuel cell performance due to a decreased ionic conductivity and can be monitored by effluent water analysis, as fluorine is emitted in the process. Ex-situ, fluoride emission rate, stemming from electrolyte decomposition, can be determined by fluoride ion selective electrode measurement. Changes in the polymer structure due to fragmentation of the polymer are investigated by nuclear magnetic resonance. Cracks and tears may form as the membrane is thinned; leading to reactant crossover and thus mixed potentials, locally increased temperatures by chemical oxidation and thus further degradation [M. Bodner et al. (2015); Q. Chen et al. (2007); Q. Chen et al. (2004)].

Different means are available for fuel cell characterization, including electrochemical methods such as polarization curves, electrochemical impedance spectroscopy, cyclic voltammetry and hydrogen diffusion current measurements. The combination with segmented current collector plates, which are able to spatially resolve the temperature distribution as well, additionally gives information on the local conditions. Degradation faults like flooding and dry-out of fuel cells are investigated using EIS in combination with THDA.

EIS is applied for single cells and stacks at different operating points. The direct current of the fuel cell is superimposed with a sinusoidal alternating current. With the help of electrical equivalent circuits, the impedance spectra are fitted and the electrolyte resistances as well as the cathode and anode resistances at different operating conditions are determined [A. Schenk et al. (2014); B. Andreaus et al. (2002); C. Brunetto et al. (2009); J. Zhang et al. (2008)].

For monitoring degradation on system level, impedance spectra are recorded in-situ at different operating points. The direct current of the fuel cell is superimposed by a sinusoidal alternating current. Based on the voltage response, the impedance, the electrolyte resistance and the cathode and the anode resistances are determined. If the sinusoidal current is applied in the non-linear region, distortions of the sinusoidal output voltage are observed. The total harmonic distortion of the output voltage signal is recorded with small input amplitudes at different frequencies or IMD current signals. The THD signal corresponds to the occurrence of local, critical operating conditions (flooding, dry-out) inside the stack [E. Ramschak et al. (2006); S. Thomas et al. (2013)].

This paper will concentrate on chemical membrane degradation by OCV hold testing using EIS, hydrogen diffusion current measurements and FER analysis on the one hand. On the other hand the detection of flooding and dry-out events in PEMFCs using EIS and THDA will be presented.

2. Experimental

2.1. OCV hold tests

For OCV holding tests, a 25 cm² single cell with a MEA (IRD, Odense, Denmark) for stationary applications was operated at the conditions according to [US DoE (2013)]. The temperature was set to 90 °C with a relative humidity of 30% and a stoichiometry of 10 calculated for a reference current density of 0.2 A cm⁻² for both anode and cathode, respectively. A pressure of 0.1 bar on anode and cathode was applied.

The cell was characterized at the beginning as well as after 500 hours of testing under the conditions stated above [M. Bodner et al. (2015)]. Using EIS, the high frequency resistance, which resembles the membrane resistance, as well as the hydrogen diffusion current, were recorded every 24 hours along with effluent water samples being taken for FER analysis.

2.2. EIS and THDA

Measurements concerning the online monitoring of degradation by EIS and THDA were taken using a PEMFC stack (ZBT, Duisburg, Germany) consisting out of five 50 cm² fuel cells (see Fig. 1).

On the anode side hydrogen with a mass flow of 1.2 l h⁻¹ and a stoichiometry of 1.5 was provided, on the cathode side synthetic air with a mass flow of 3 l h⁻¹ and a stoichiometry of 2.5 was set. All experiments were conducted under ambient pressure.

EIS experiments were conducted at different stack temperatures (50 °C, 60 °C, 70 °C). For simulating flooding and dry-out events, the temperature of the humidifiers at anode and cathode side was changed in 10 °C steps from 50 °C up to 80 °C, respectively.

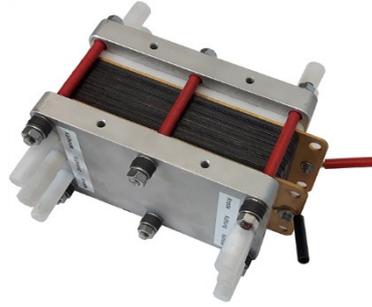


Fig. 1 PEMFC stack with five fuel cells

EIS measurement series at different operating points were performed in galvanostatic mode at alternating current amplitude of 500 mA within a frequency range between 10 kHz and 100 mHz with a power potentiostat PP240 and the software THALES (Zahner Elektrik, Kronach, Germany). While recording impedance spectra the harmonic distortion signals were also logged. With this data THDA was performed using Equation 1.

$$THD_n = \frac{\sqrt{\sum_{i=2}^n U_i}}{U_1} \quad (1)$$

2.3. Effect of Pinhole formation determined by segmented cell analysis

A rectangular 25 cm² single cell with an in-house designed 4-fold serpentine flow field on both sides and a segmented cathode was used to investigate the effects of pinholes on MEA degradation. At each segment, currents were measured separately using shunt resistors. The MEA consisted of an 18 μm thick commercially available catalyst coated Nafion type membrane with a symmetric Platinum loading of 0.4 mg cm⁻², sandwiched between Sigracet GDL with a microporous layer.

After conditioning, polarisation curves, EIS and current distribution measurements were recorded before and after gradual introduction of pinholes at various locations seen in Figure 2. Load cycling induced fuel starvation was performed while adding nitrogen to the anode gas flow to allow off gas analysis with an online gas analyser (ABB). The ECSA was monitored using CV before and after pinhole introduction and operation with pinholes

3. Results and Discussion

3.1. OCV hold tests

At BoL the value of the OCV was 970 mV and successively decreased over the test period of 500 hours. After each testing period the voltage partially recovered, but the overall trend showed a clear decline (see Fig. 3a). Looking at the polarization curves at BoL and EoL (see Fig. 3b), a clear reduction of the maximum current density and the maximum power density can be observed, which indicates severe degradation after the test.

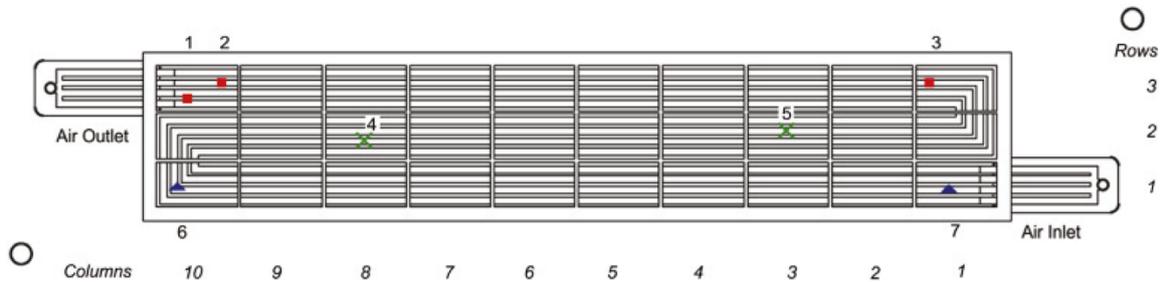


Fig. 2 Location of the pinholes on the flowplate, with ■ the first set of pinholes (1-3) near anode inlet, x second set of pinholes (4,5) in the middle section, and ▲ third set of pinholes (6,7) near the cathode inlet

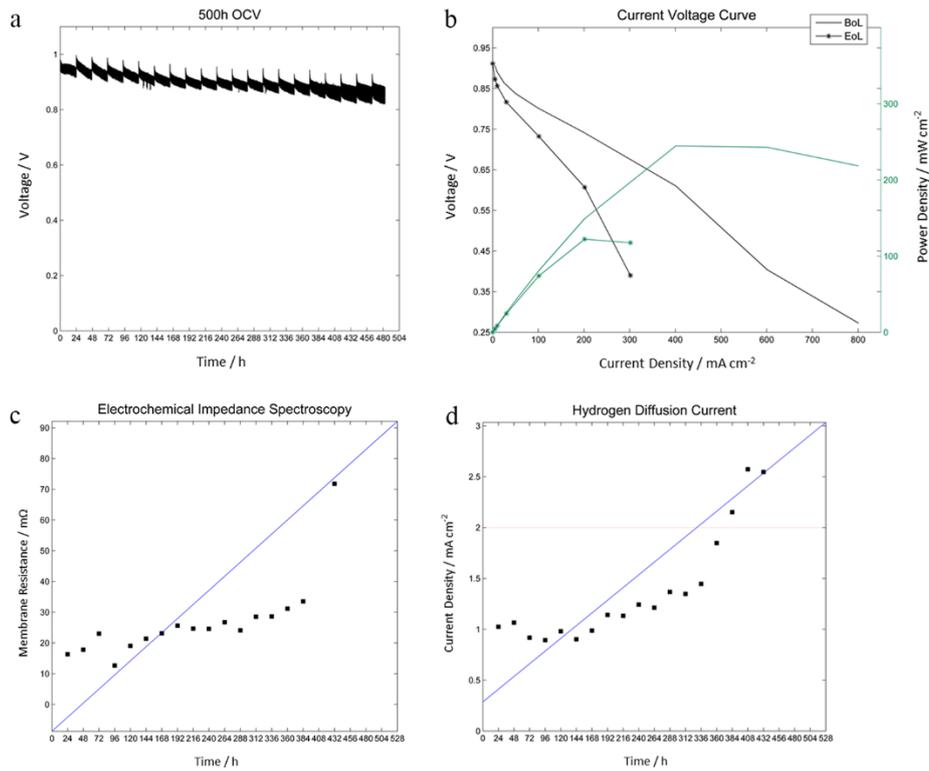


Fig. 3 (a) OCV over the duration of 500 hours under OCV hold conditions; (b) polarization curve before (BoL) and after (EoL) 500 hours of OCV hold conditions; (c) high frequency resistance and (d) hydrogen diffusion current, measured every 24 hours over the duration of 500 hours of OCV hold test

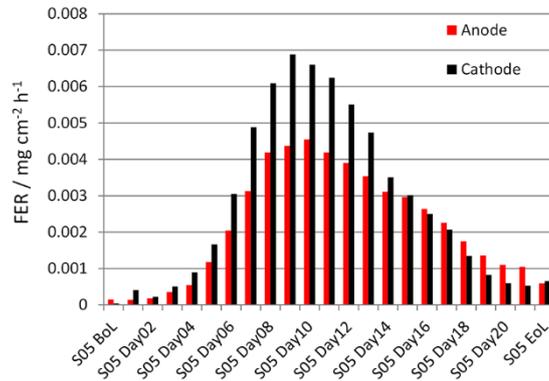


Fig. 4 FER, determined every 24 hours over the duration of 500 hours of OCV hold testing

In Figure 3c the development of the high frequency resistance over the duration of the test is presented. As can be seen the membrane conductivity shows a rather steady decrease most of the time of testing, however at the end a sharp drop arises. The corresponding hydrogen diffusion current illustrated in Figure 3d follows a similar pattern. The light red line in Figure 3d denotes the target value of a maximum hydrogen diffusion current density of 2 mA cm^{-2} given by the test protocol [US DoE (2013)] and is exceeded after extensive testing.

Figure 4 illustrates the FER measured every 24 hours for anode and cathode, respectively, during OCV hold testing. During the whole test the values on the cathode are significantly higher than on the anode most of the time. Especially, this is the case when the values on both sides traverse a maximum. After the maximum and at the end the FER of the anode starts to exceed the respective values of the cathode.

All results stated above signal a severe degradation of the polymer electrolyte membrane. Multiple degradation mechanisms are responsible. On the one hand, the decreased OCV and the increasing hydrogen diffusion current indicate membrane thinning and pinhole formation. On the other hand, the rising membrane resistance is the result of a loss of conductive moieties.

The results exhibit, that the conducted AST caused chemical degradation of the membrane. Both the dissociation of acidic ion conducting groups as well as the decomposition of the structure giving backbone take place in parallel [M. Bodner, J. Senn et al. (2017); M. Bodner et al. (2016); M. Rami (2017)].

3.2. EIS and THDA

The aims of these investigations are to detect local flooding and dry-out events inside a PEMFC stack and, in a second step, to differentiate between these two degradation conditions. Therefore, EIS measurements are taken under the conditions stated in the Experimental section. Using a SSEC the electrolyte membrane resistance as well as the charge transfer resistance and concentration resistance can be determined. Table 1 clearly demonstrates the effect of different relative humidity on the membrane resistance. At low relative humidity in the anode and cathode gas the resistance of the membrane is high because of the depletion of water molecules inside the membrane which help to transport hydrogen ions to the cathode. Then the resistance traverses a minimum where optimal conditions prevail and at flooding events the resistance slowly increases again due to flooding of the GDL and longer diffusion pathways to the cathode.

Table 1. Electrolyte membrane resistance in dependency of temperature of humidifier; Stack temperature: 70 °C; Operating point: 0.1 A cm⁻²

Temperature of humidifiers [°C]	Relative humidity [%RH]	Electrolyte membrane resistance [Ω cm ²]
50 (dry-out)	35.2	1.18
60 (dry-out)	61.8	1.02
70 (optimal)	100	0.81
80 (flooding)		0.82

THD measurements are based on the following principle. If sinusoidal alternating current signals with small amplitudes or IMD signals are applied at an operating point in the linear (ohmic) region at optimal conditions there should not be any harmonic distortion in the output voltage signal. Once one of the degradation conditions (flooding, dry-out) occurs, the polarization curve changes drastically and the operating point moves into the nonlinear region. After applying the aforementioned alternating current signals again, harmonic distortion signals at certain frequencies are going to be detected. One goal of the investigations is to assign frequencies, which show high harmonic distortions to respective degradation conditions.

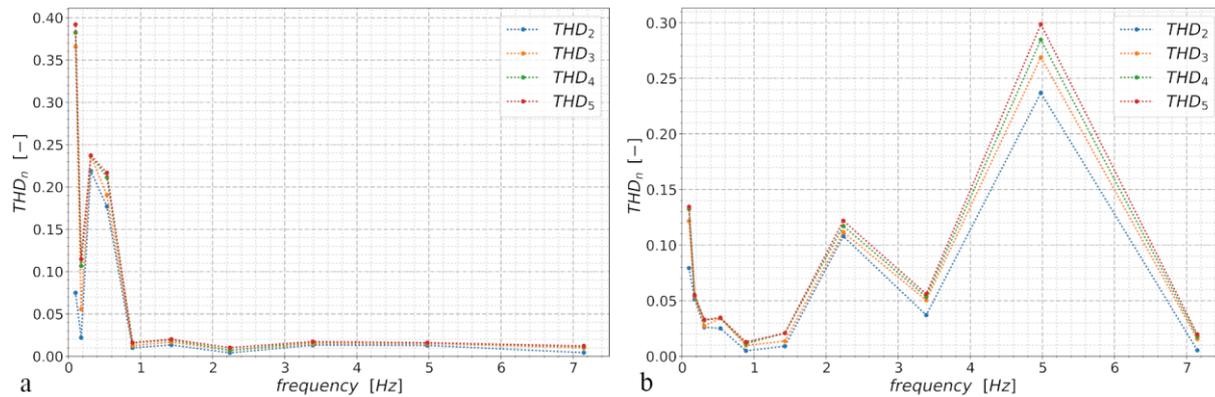


Fig. 5 THDA of (a) dry-out event (b) flooding event; THD_n see Equ. 1

In addition to impedance spectra, THD values are recorded and plotted over the frequency (see Fig. 5). Measurements at different temperatures of the stack and humidifiers show the same behaviour as can be seen in Figure 5a and 5b. In the low frequency range high peaks of the THD signals can be detected at certain frequencies.

3.3. Effect of Pinhole formation determined by segmented cell analysis

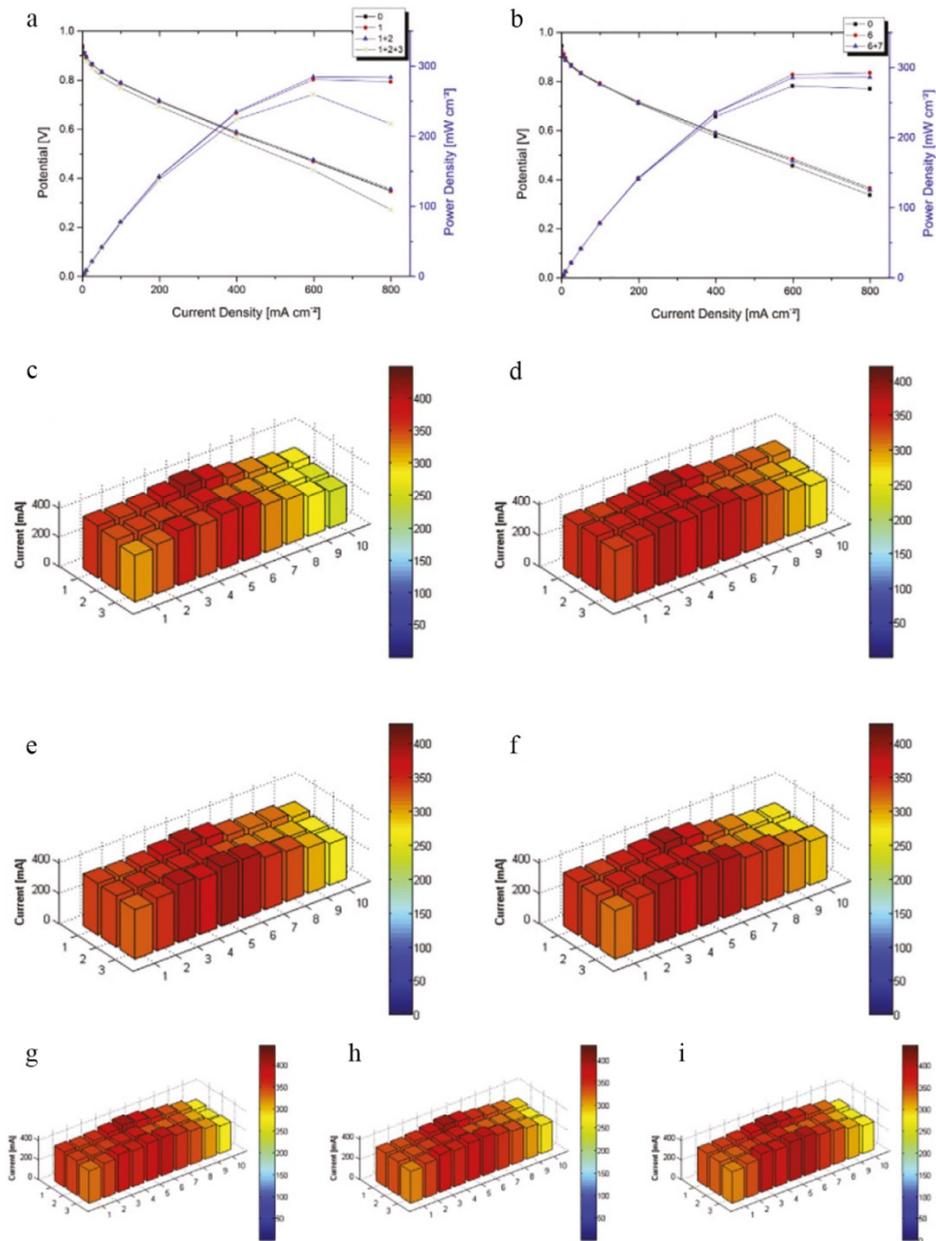


Fig. 6 Polarisation curves (a) with no pinhole, with pinhole at location number 1, 1 and 2 and 1 to 3; (b) with no pinhole, with pinhole at location number 6 and 6 and 7. Current distribution at 400 mA cm^{-2} (c) with no pinholes; (d) after the first perforation at the anode inlet (position 1); (e) after the second perforation (position 2); (f) after the additional perforation (position 3); (g) without pinholes; (h) after the first perforation (position 6); (i) after the additional perforation (position 7) at the cathode inlet [M. Bodner et al. (2015)].

Figure 6 shows that the influence of a pinhole on power density or performance of the whole cell can be insignificant or even cause a performance increase. This is caused by the local temperature rise, caused by the chemical oxidation of hydrogen near the pinhole. The corresponding current distribution measurement in Fig. 6 c)-f) confirmed this phenomenon, as the current is locally increased at the affected segment after the first perforation (segment 1). Additional perforations show only minor decrease in current densities of the affected segments.

In Figure 7 the current distributions of the intact and perforated MEA are shown during starvation cycles. After the first pinhole near the anode inlet, no effect could be observed while the introduction of a second pinhole resulted in a steep current gradient along the flow channels due to local fuel starvation. The third pinhole intensified the effect. Pinholes in the middle section have a similar effect, while pinholes near the cathode inlet showed only minor effects.

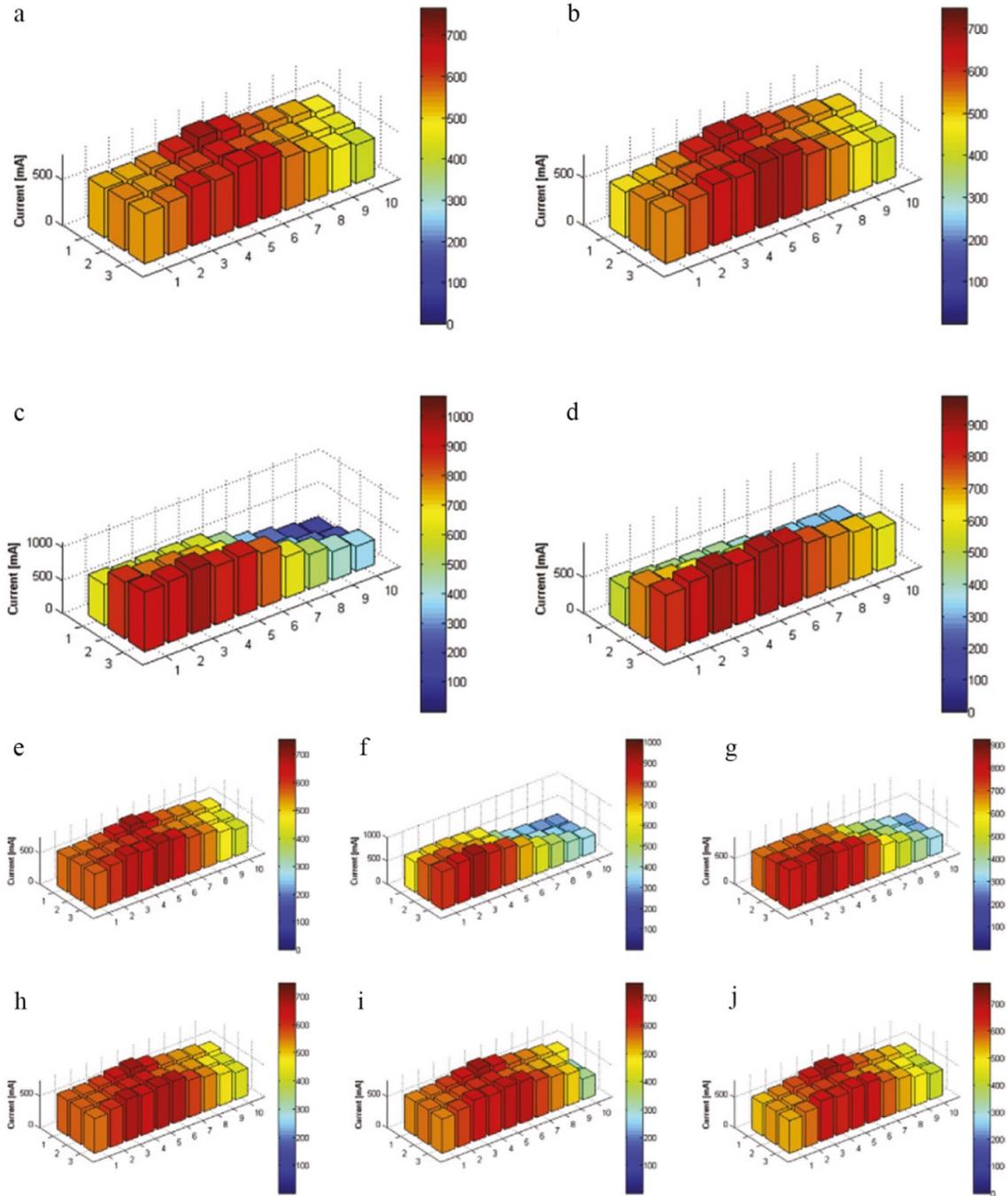


Fig. 7 Current distribution during fuel starvation (a) without pinholes; (b) after the first perforation at the anode inlet (position 1); (c) after the second perforation at the same segment (position 2); (d) after the additional perforation (position 3). (e) Without pinholes; (f) after the first perforation at position 4; (g) after the additional perforation at position 5 at the cathode inlet. (h) Without pinholes; (i) after the first perforation at position 6; (j) after the additional perforation (position 7) at the cathode inlet [M. Bodner et al. (2015)].

The membrane resistance determined by EIS decreased after the introduction of pinholes near the cathode inlet probably due to increased water generation from chemical hydrogen oxidation (see Table 2). Pinholes in the middle section lead to increased electrolyte resistance probably due to degradation of the membrane.

Pinholes near the anode inlet and in the middle section showed the highest carbon emission rates during gas analysis, indicating a promotion of carbon corrosion. Near the cathode inlet the pinholes had no effect on the carbon emission.

Table 2: Effects of pinhole location on electrochemical characteristics and carbon emission rates [M. Bodner et al. (2015)]

	Anode inlet	Middle section	Cathode inlet
OCV	Mild decrease	Mild decrease	Stronger, yet still mild decrease
Power density	Gain to intermediate loss	Mild decrease	Gain to mild loss
Membrane resistance	Mildly alternating results	Mild increase	Mild decrease
Carbon corrosion during starvation on anode	Increasing high emission	High emission	Decreasing low emission
Carbon corrosion during starvation on cathode	low to intermediate carbon corrosion	intermediate to low carbon corrosion	low carbon corrosion
Loss of ECSA	Low to vast loss	Intermediate to cast loss	Low loss

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