

1 Characterization Methodology for Anode Starvation in HT-PEM Fuel 2 Cells

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8 9 Abstract

10 Degradation caused by fuel starvation may be an important reason for limited fuel cell
11 lifetimes. In this work, we present an analytical characterization of the high
12 temperature polymer exchange membrane fuel cell (HT-PEM FC) behavior under
13 cycled anode starvation and subsequent regeneration conditions to investigate the
14 impact of degradation due to H₂ starvation. Two membrane electrode assemblies
15 (MEAs) with an active area of 21 cm² were operated of up to 550 minutes, which
16 included up to 14 starvation / regeneration cycles. Overall cell voltage as well as
17 current density distribution (S⁺⁺ unit) were measured simultaneously each minute
18 during FC operation. The cyclicity of experiments was used to check the long term
19 durability of the HT-PEM FC. After FC operation, micro-computed tomography (μ-CT)
20 was applied to evaluate the influence of starvation on anode and cathode catalyst
21 layer thicknesses.

22 During starvation, cell voltage and current density distribution over the active area of
23 the MEA significantly differed from nominal conditions. A significant drop in cell
24 voltage from 0.6 to 0.1 V occurred after approx. 20 minutes for the first starvation
25 step, and after 10 minutes for all subsequent starvation steps. By contrast, the
26 voltage response is immediately stable at 0.6 V during every regeneration step.
27 During each starvation, the local current density reached up to 0.3 A·point⁻¹ at the
28 area near the gas inlet (9 cm²) while near the outlet it drops to 0.01 A·point⁻¹. The
29 deviation from a balanced current density distribution occurred after 10 minutes for
30 the first starvation step, and after ca. 2 minutes for the subsequent starvation steps.
31 Hence, compared to the voltage drop, the deviation from a balanced current density
32 distribution always starts earlier. This indicates that the local current density
33 distribution is more sensitive to local changes in the MEA than overall cell voltage
34 drop. This finding may help to prevent undesirable influences of the starvation
35 process.

36 The μ-CT images showed that H₂ starvation lead to thickness decrease of ca. 20-
37 30 % in both anode and cathode catalyst layers compared to a fresh MEA. Despite of
38 the 14 starvation steps and the thinning of the catalyst layers the MEA presents
39 stable cell voltage during regeneration.

40 Key words:

41 HT-PEM FC, hydrogen starvation; regeneration; voltage; current density distribution;
42 μ-CT.

Nomenclature

P_{ac} – current density of an active point sufficiently supplied with H_2 (when current density $> 0.04 \text{ A}\cdot\text{point}^{-1}$), determined from S^{++} unit (Simulation Services®), $\text{A}\cdot\text{point}^{-1}$

i – operating current density, $\text{A}\cdot\text{cm}^{-2}$

I – operating current, A

n – number of electrons transferred per mole of reactant consumed

F – Faraday constant, $\text{s}\cdot\text{A}\cdot\text{mol}^{-1}$

\dot{m} – the rate of mass transfer by diffusion of reactants to the catalyst layer, $\text{mol}\cdot\text{s}^{-1}$

A_{ac} – sufficiently active area, cm^2

I_l – local current density, determined from S^{++} unit, $\text{A}\cdot\text{point}^{-1}$

ΣI_l – sum of local current densities, determined from S^{++} unit, $\text{A}\cdot\text{point}^{-1}$

43

44 **1. Introduction**

45 High temperature polymer exchange membrane fuel cells (HT-PEM FC) have
46 entered the market in the last decade [1]. This type of FC is considered as a clean
47 and efficient power source for portable and stationary applications such as combined
48 heat and power (CHP) application, stand-alone power, backup power and
49 uninterrupted power supply (UPS) [2-6]. In HT-PEM FC a polybenzimidazole (PBI)
50 membrane doped with phosphoric acid is used. The typical operating temperature of
51 HT-PEM is around 160-180 °C that results in improved electrochemical kinetics for
52 electrode reaction in comparison to the low temperature (LT) PEM FC. Other
53 advantages of HT-PEM related to the enhanced operating temperature are higher
54 tolerance to impurities like carbon monoxide [7, 8] and simpler water management
55 [1]. Zhang et al. [9] investigated the dependence of the FC performance on
56 temperature. They found that in the range of 120-180 °C, the enhanced temperature
57 decreases the membrane resistance leading to higher cell power density [10].

58 However, for this type of FC there are some challenges which need to be solved, for
59 example increased degradation rate at more demanding operating temperature [11-
60 13]. Possible stressors for the operation of a HT-PEM FC are mass transfer limitation
61 due to the presence of phosphoric acid in the catalyst layer [14, 15], electrochemical
62 cycling, the start/stop procedure, and fuel starvation [16].

63 Fuel starvation, which refers to hydrogen undersupply (H_2 starvation), occurs during
64 startup and shutdown due to the rapid load variation or as a consequence of
65 inhomogeneous H_2 distribution in a single cell or between assemblies of cells [17]. In
66 addition, an uneven distribution of phosphoric acid in the the HT-PEM FC [18, 19],
67 during MEA manufacturing and/or the activation process, can also flood the catalyst
68 and results in local hydrogen undersupply [20].

69 During H_2 starvation, the local depletion of H_2 leads to an inhomogeneous current
70 density distribution over the active surface area of the MEA [17], which can either

71 lead to active points (P_{ac}) being sufficiently supplied with H_2 or insufficiently supplied
72 parts of surface area defined as inactive points. The non-sufficient or inactive areas
73 may accelerate fuel cell degradation.

74 Previously, the behavior under H_2 starvation was investigated for LT-PEM FCs and
75 phosphoric acid fuel cells (PAFC). For example, Zhang et al. [21] investigated air and
76 H_2 starvation for LT-PEM FC under controlled current and voltage modifications.
77 They observed that current density and temperature distribution were
78 inhomogeneous across the FC depending on the location along the flow channel.
79 Song et al. investigated an influence of anode starvation on PAFC. The experimental
80 results show a 5 mV loss in cell voltage after H_2 starvation [22].

81 Zhou et. al. [17] studied the effect of H_2 starvation in HT-PEM FC on voltage and
82 local current density measured simultaneously under different stoichiometries ($\lambda_A <$
83 1.0) and at different current loads. They observed that the current density under H_2
84 starvation is highest in the upstream (inlet) regions, decreasing along the flow
85 channel direction and lowest in downstream (outlet) regions due to high mass
86 transfer resistances.

87 The consequences of H_2 starvation are reported differently. Liang et al. [23] observed
88 that under H_2 starvation water electrolysis and carbon corrosion take place at the
89 anode side of the FC. Carbon corrosion may lead to the irreversible loss of the
90 electrochemical catalyst surface area (ECSA) [24]. Those undesirable reactions
91 could have an influence on changes inside the MEA, e.g. in thickness and / or on the
92 morphology [25, 26]. Therefore, to increase the lifetime of HT-PEM FCs the effects of
93 H_2 starvation need to be investigated in more detail.

94 In this work we present H_2 starvation / regeneration cycles up to 550 minutes for 2
95 identical HT-PEM FC MEAs under operation. The regeneration step allows the
96 evaluation of (ir)reversible degradation after each starvation step. To the best of our
97 knowledge such a repeated combination of starvation / regeneration procedures has
98 not yet been reported. The cyclicity of experiments was used to study the long term
99 durability of the HT-PEM FC. Both, voltage and current density mapping were
100 measured each minute simultaneously, allowing the evaluation of changes in FCs as
101 a function of time and the optimization of the operational strategies to prevent FC
102 lifetime reduction.

103 2. Basics

104 A FC produces electricity at the fixed current density i ($A \cdot cm^{-2}$). When the current is
105 applied the electrochemical reaction leads to the depletion of the reactants at the
106 catalyst layer. Then i can be calculated using the following equation

$$107 \quad i = n F \dot{m} / A_{ac} \quad (1)$$

108 whereas n is the number of electrons transferred per mole of reactant consumed, F is
109 Faraday constant, $s \cdot A \cdot mol^{-1}$, \dot{m} is the rate of mass transfer by diffusion of reactants to
110 the catalyst layer, $mol \cdot s^{-1}$ and A_{ac} is active area, cm^2 . The operating current (I) can be
111 then calculated by:
112
113

$$114 \quad I = i A_{ac}; \quad (2)$$

116

117 Under H₂ starvation, A_{ac} will be reduced due to insufficient gas flow. Meanwhile,
118 under the H₂ undersupply, the reduction of A_{ac} or respectively the inhomogenous
119 current density distribution can be measured with local current densities (I_l), for
120 example if the A_{ac} is divided over 100 points of the flow field. In case of a full
121 homogeneity the current density is equal at all the 100 points and shall be higher
122 than 0.04 A·point⁻¹. The explanation of the chosen 0.04 A·point⁻¹ current density will
123 follow in chapter 3.

124 In order to evaluate inhomogenous current density distribution, the 100 points can be
125 divided into two categories: the active points (P_{ac}) with a current density greater than
126 or equal to 0.04 A·point⁻¹ and the inactive points corresponding to less than 0.04
127 A·point⁻¹. From the sum of active points (count of P_{ac}) the active area can be
128 calculated with with the assumption below:

129

$$130 \quad A_{ac} \propto \sum P_{ac} \text{ (if } P_{ac} \geq 0.04 \text{ A);}$$

131

132 The gas flow through the bipolar plate channels can be characterized by the gas
133 partial pressure gradient which is strongly determined by the flow field design. If
134 continuous gas consumption is assumed, there is a common depletion gradient of
135 reactor gas partial pressure from inlet to the outlet [27, 28] (Fig. 1a, white arrow).
136 There is almost no difference in the partial pressure of neighboring channels (e.g. 1.-
137 5., Fig. 1a, b) compared to the adjacent channels (with opposite flow directions)
138 along the flow channel (e.g. 1. and 6., Fig. 1b), which is due to the fuel consumption
139 in the cell reaction. The partial pressure difference between two channels forces H₂
140 transport through the gas diffusion layer under the rib, which leads to an
141 improvement of the local current density.

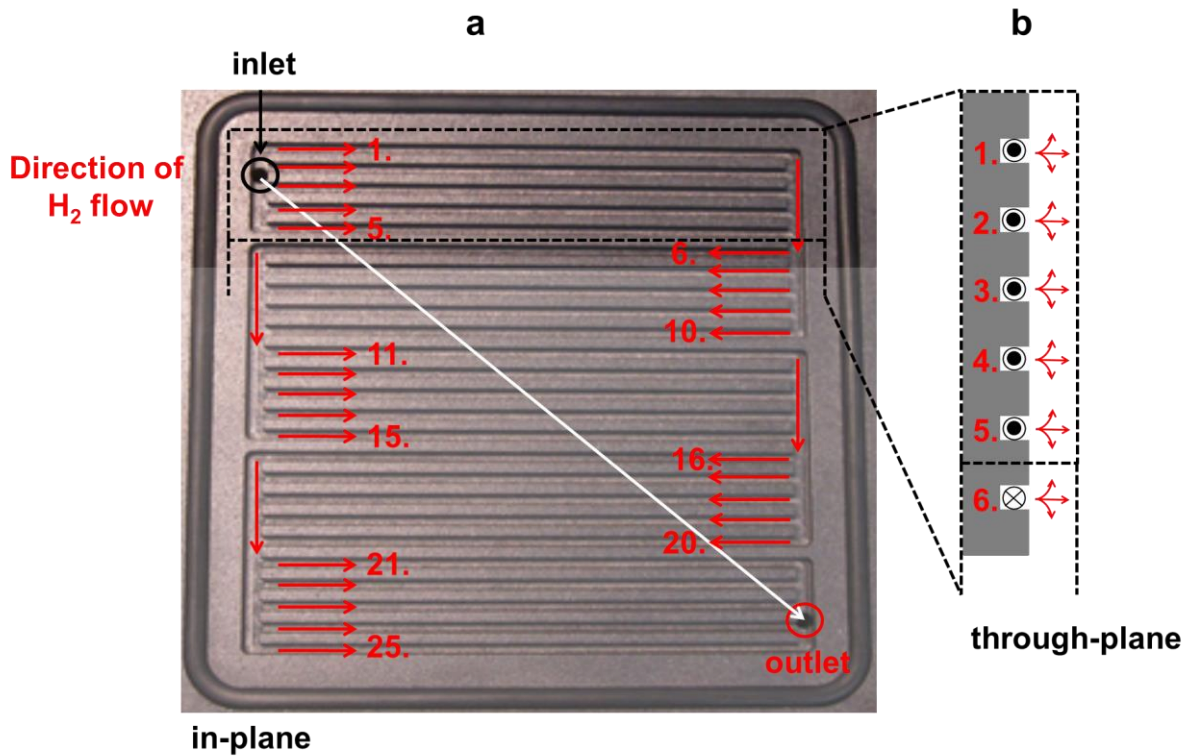
142 The decrease in H₂ partial pressure at the catalyst surface may increase anodic
143 mass transport resistance, leading to an increase in the anode overpotential [17].
144 Therefore H₂ starvation typically results in a significant drop in cell voltage.

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150 **Fig. 1: a)** In-plane view of serpentine flow field and **b)** schematic representation of
 151 the gas transport in serpentine flow field (through-plane view). Red arrows show the
 152 H₂ flow directions; ● indicates the gas flow perpendicular to the paper from the
 153 bottom upwards, and ⊗ indicates the flow perpendicular to the paper from the bottom
 154 downwards.

155

156 2. Experimental setup

157 2.1 Hardware setup

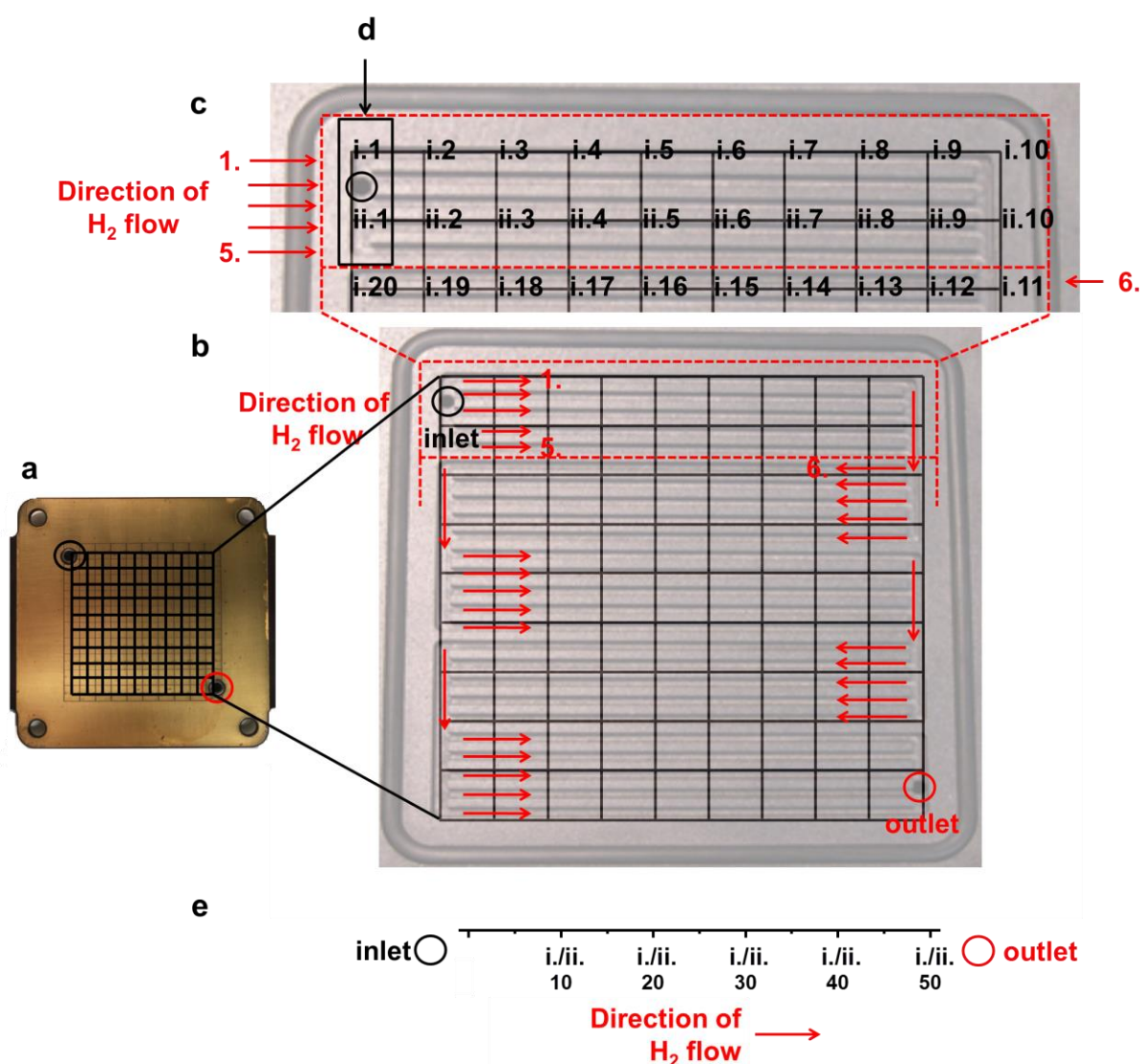
158 In this work, three identical MEAs Dapozol® G77 (Danish Power Systems®), were
 159 chosen for testing. This type of MEA is based on a PBI/H₃PO₄ membrane with an
 160 active area of 21 cm². The membrane was placed between two gas diffusion
 161 electrodes (GDE). The assembly with a thickness of around 0.6 mm was inserted
 162 between two graphite flow fields with five quintuple serpentine flow channels (Fig.
 163 1a). The MEAs were tested on a FC test station FuelCon AG (Evaluator-C 70316).

164 A current density and temperature distribution device (S⁺⁺ Simulation Services®) was
 165 installed during the whole experiment on the anode side under the flow field (Fig. 2a).
 166 The schematic representation of the S⁺⁺ unit location under the serpentine flow field is
 167 presented in Fig. 2b (overlapped view of S⁺⁺ unit and the flow field; Fig. 1a). The S⁺⁺
 168 unit consists of 100 points (intercepts) and each of them provides information about
 169 local current density (i_l), which builds up a 2D distribution map of current densities.
 170 Fig. 2b and Fig. 2c present the locations and numbering principle of 100 points from
 171 S⁺⁺ unit at the flow field.

172 The flow channel from inlet to outlet can be divided into 50 sections (Fig. 2d) while
 173 each section corresponds to two points at S⁺⁺ unit (e.g. i.1 and ii.1). Those 50

174 sections enable gas flow from one side the other (e.g. i/ii.1 - i/ii.50). However, at the
 175 intercepts i.1 / ii.1 and i. / ii.50 where MEA was fixed to the S⁺⁺ device, there is
 176 always zero current density, therefore, those values were neglected for further
 177 calculations. The result of current density mapping will be visualized as a segmented
 178 surface, each segment consists of four adjacent points of about 0.25 cm² size.

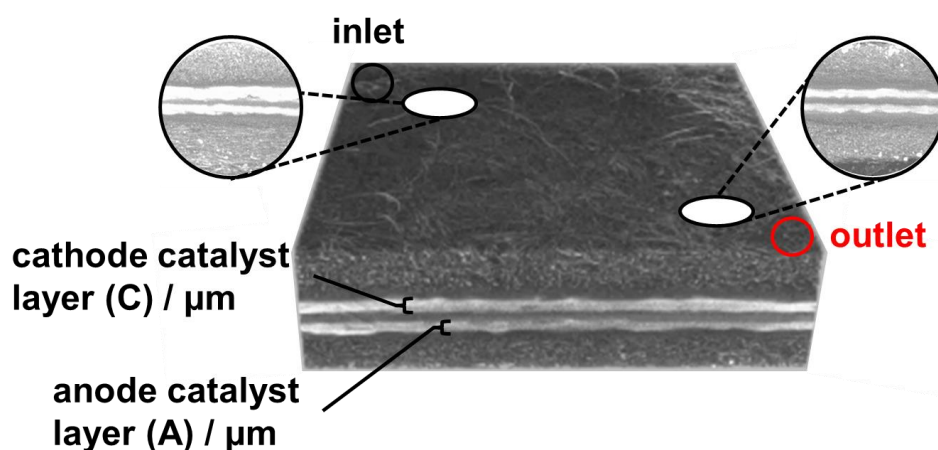
179 Beside the 2D distribution map over the MEA, the current density was also plotted as
 180 an “unfolded” view along the flow direction from inlet to outlet, as normal in simulation
 181 work (Fig. 2e) [29]. Since each section along the flow direction corresponds to two
 182 points of the S⁺⁺ unit, there are two current density values at each section of the
 183 unfolded view.



184
 185 **Fig. 2: a)** Current density distribution device (S⁺⁺ unit), **b)** serpentine flow field
 186 schematically overlapped with the S⁺⁺ unit (location of S⁺⁺ points (intercepts) -
 187 “folded” view, **c)** zoom into intercept locations from i.1 to i.20, **d)** exemplary section
 188 at the flow channel (points: i.1 and ii.1) and **e)** “unfolded” view of the sections (S⁺⁺
 189 serpentine pattern) at the flow channel (from inlet to outlet).

190 Micro-computed tomography (μ -CT) allows a non-destructive view into HT-PEM FC
 191 components and was conducted to measure the thicknesses of different layers of the

192 MEA. Measurements were carried out with the microcomputed X-ray tomography
 193 system (Skyscan 1172 Desktop-Micro-CT, Bruker, Belgium). The samples were
 194 prepared with a hole-puncher (\varnothing 4 mm). Those samples were cut from two different
 195 locations on the MEAs (1-near inlet; 2-near outlet) (Fig. 3). In order to receive
 196 comparable results the geometrical resolution of each measurement was held
 197 constant by $1.23 \mu\text{m}\cdot\text{px}^{-1}$. The thickness of defined layers, such as cathode catalyst
 198 layer and anode catalyst layer of the investigated location was measured with the
 199 help of the software Dataviewer (Fig. 3). The values for thicknesses were calculated
 200 by averaging ten values of five sagittal or coronal 2D-images [30]. The settings used
 201 for these investigations are summarized and shown in Table 1 [25].



202
 203 **Fig. 3:** Schematic presentation of an exemplary 3D μ -CT image.

204
 205 **Tab. 1:** Operational settings in μ -CT.

Parameter	Value	Unit
Acceleration voltage	78–82	kV
Source current	96–102	μA
Sample size \varnothing	4-5	mm
Rotation step	0.2	$^{\circ}$
Random movement	10	-
Averaging	4	-
Optical resolution	1.23	$\mu\text{m}\cdot\text{px}^{-1}$
Duration	140-180	min

206

207 2.2. Experimental procedure

208 Prior to the electrochemical experiments the assembled HT-PEM FC was activated
 209 [31] by heating up the cell under N_2 supply to a temperature of $120 \text{ }^{\circ}\text{C}$. Subsequently
 210 reactant gases were fed: hydrogen with a stoichiometric factor of 1.5 for the anode

211 ($\lambda_A = 1.5$) as fuel, and oxygen with a stoichiometric factor of 9.5 for the cathode ($\lambda_C =$
212 9.5) as oxidant while the temperature was increased to 160 °C. Shortly after, the load
213 current was increased stepwise up to 6.35 A. The stoichiometry factor is based on
214 the ratio between the available gas at the inlet and the required gas necessary for the
215 reaction [32].

216 The intended oversupply of oxygen avoids any influences from the cathodic side of
217 the FC and for clear separation of degradation phenomena on the anode side. The
218 following activation procedure was conducted for each cell. From the time when
219 stable operation was reached (0.3 A/cm² with $\lambda_A = 1.5$ and $\lambda_C = 9.5$), such condition
220 was kept constant for 168 h in order to reach constant voltage.

221 Starvation / regeneration cycles were repeated for up to 550 minutes. Each cycle
222 consisted of a starvation process with $\lambda_A = 1.0$ at 6.35 A (equals 0.3 A/cm²) and
223 subsequent regeneration process with $\lambda_A = 1.5$ at 8.46 A (equals 0.4 A/cm²). λ_C was
224 kept at a value of 9.5 in all conditions. The load of 6.35 A was chosen for the
225 starvation step, representing a standard value for typical FC operation [33]. After that
226 the FC was held under 0.4 A/cm² for 20 minutes for regeneration to assure full FC
227 recovery after starvation.

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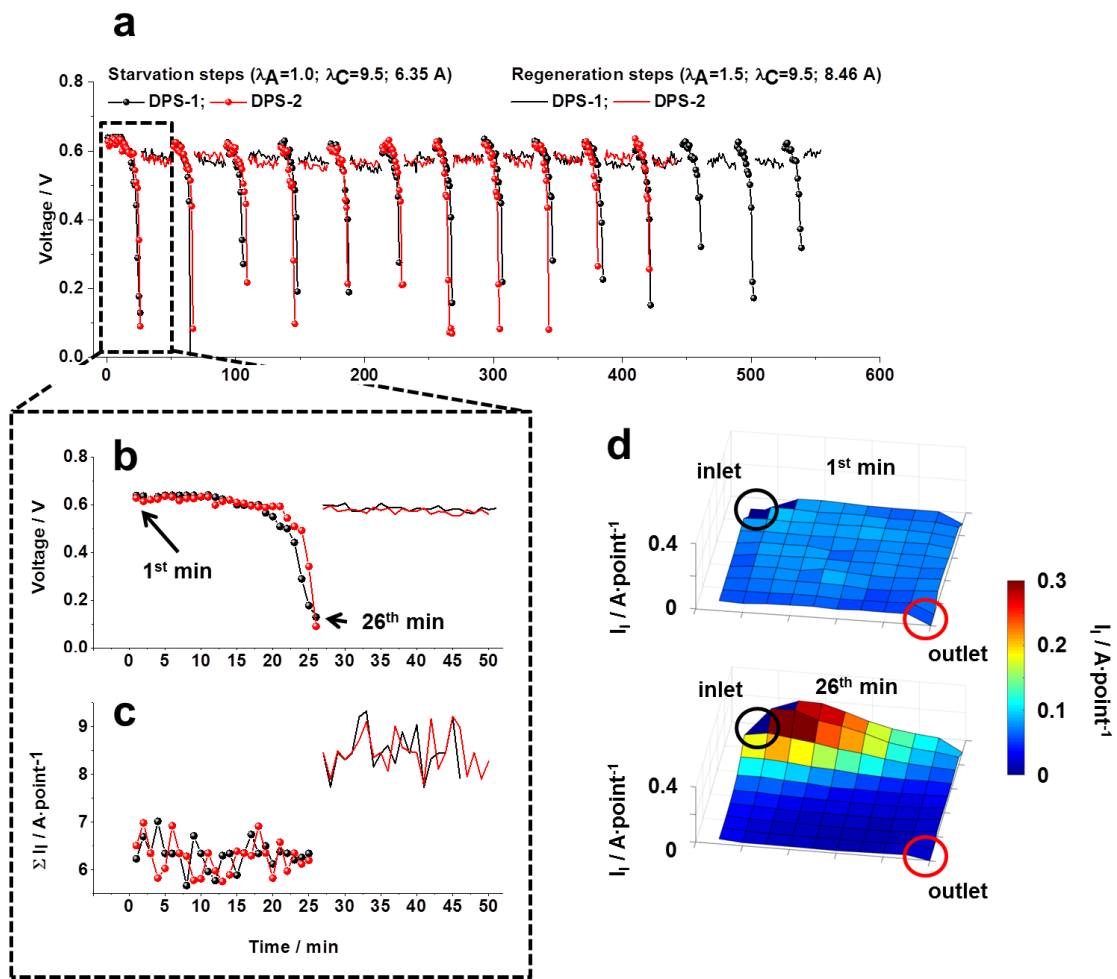
229 3. Results and discussions

230 Previous experiments were performed under different anode stoichiometries: $\lambda_A =$
231 0.9, $\lambda_A = 1.0$ and $\lambda_A = 1.1$. At $\lambda_A = 0.9$ the FC immediately lost performance and the
232 gas supply was automatically turned off due to test bench security thresholds, while
233 at $\lambda_A = 1.1$ the FC ran stable. At $\lambda_A = 1.0$ the cell operated for several minutes,
234 followed by a sharp voltage drop to test bench safety limits and the system was
235 turned off. Hence, for the detailed study of starvation processes the stoichiometry λ_A
236 = 1.0 was chosen.

237 As shown in Fig. 4a the starvation steps repeatedly induced a significant voltage
238 drop. However, the immediate response during regeneration was a stable and
239 constant voltage at 0.6 V. This could indicate that, if degradation by H₂ starvation
240 occurred during the first starvation step it would have probably been insignificant.

241 In particular, the first starvation step lasted ca. 25-26 minutes for both DPS (Fig. 4b),
242 and as expected, at $\lambda_A = 1.0$ voltage starts to drop from ca. 0.6 V after around 20
243 minutes down to minimal safety limits (ca. 0.1 V). Despite the voltage drop, the sum
244 of local current densities of 100 points from the S⁺⁺ unit (ΣI_l) yielded 6.35 ± 0.30 A
245 throughout the whole starvation step (as well as 8.46 ± 0.45 A during regeneration;
246 Fig. 4c). The visible fluctuations in ΣI_l in Fig. 4c likely occurred due to single point
247 current density fluctuations.

248 Figure 4d shows the current distribution at minutes 1 and 26 in the first starvation
249 step for DPS-1. At minute 1 the current is well distributed all over the A_{ac}. Except for
250 the few points directly at the inlet and outlet the current is 0.07 A·point⁻¹ (0.639 V).
251 However, at minute 26 there is a clear deviation in current distribution, with points
252 near the inlet reaching about 0.3 A·current⁻¹ and points near the outlet decreasing to
253 about 0.01 A·point⁻¹. The H₂ concentration is higher near the inlet than near the
254 outlet, which corresponds to the common gradient within the serpentine flow field
255 (Fig. 1, white arrow) [27].



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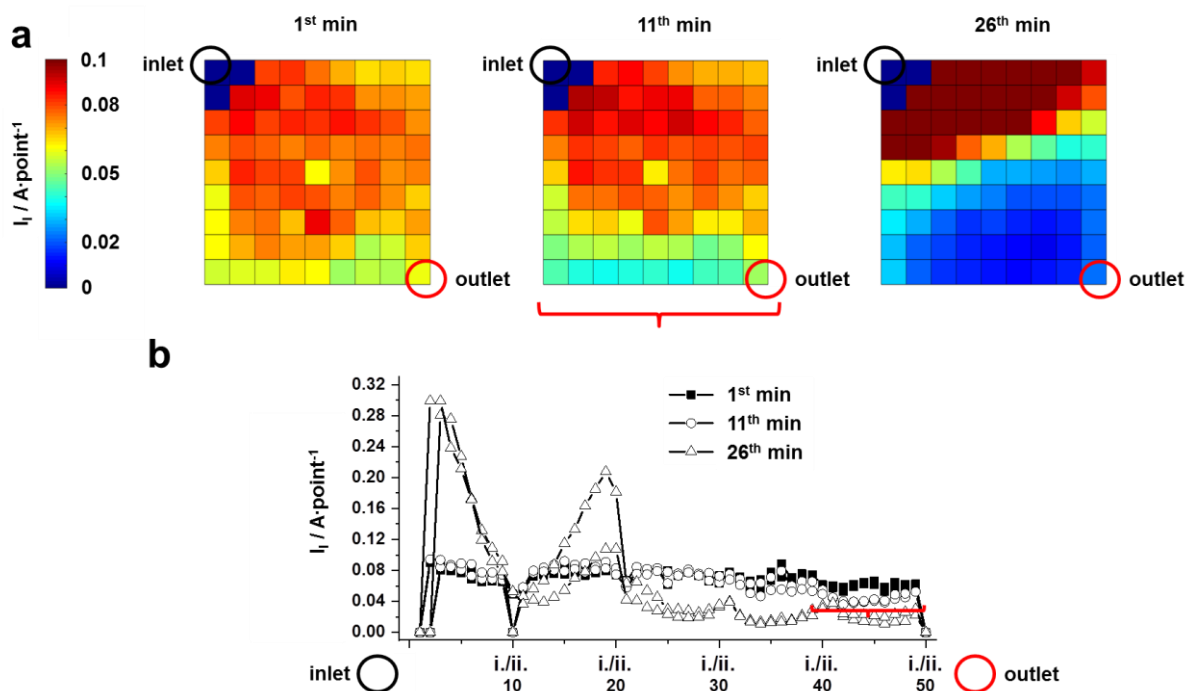
258 **Fig. 4: a)** Cell voltage of DPS-1 and 2 during ca. 550 min operation, **b)** zoom of
 259 voltage and **c)** sum of local current densities of 100 points from the S^{++} unit for
 260 starvation / regeneration step 1 vs. time as well as **d)** 3D local current density
 261 distribution for minutes 1 and 26 in DPS-1 during starvation step 1.

262 For a better differentiation of the processes near the outlet the density distribution is
 263 shown as a 2D map in more detail for the lower current ranges for the minutes 1, 11
 264 and 26 (Fig. 5a) and as current density values extracted from every point of the map
 265 in the “unfolded” view (Fig. 5b). At minute 1 the current is around $0.07 \text{ A} \cdot \text{point}^{-1}$,
 266 which indicates a balanced operation and distribution over the whole area. Hence,
 267 during the first 10 minutes the system operates stable only with marginal differences
 268 in voltage and local current densities. However, at minute 11 the intercepts from
 269 i./ii.41 to i./ii.50 close to the outlet operated with a current density $\leq 0.04 \text{ A} \cdot \text{point}^{-1}$
 270 while at minute 26 more than half of A_{ac} operated below $0.04 \text{ A} \cdot \text{point}^{-1}$ (Fig. 5). Next
 271 to the observed drop to $0.01 \text{ A} \cdot \text{point}^{-1}$ at minute 26 the current densities near the inlet
 272 significantly increase up to $0.3 \text{ A} \cdot \text{point}^{-1}$ (Fig. 4c). However, the sum of local current
 273 densities yielded the nominal current (6.35 A) such as in minutes 1 and 11.

274 To compensate for the two times lower current and to reach the nominal current in
 275 total (6.35 A) the remaining intercepts (80 points) increased their current densities by
 276 more than $0.07 \text{ A} \cdot \text{point}^{-1}$. Therefore, the minute 11 is taken as the onset of deviation
 277 from the balanced current density distribution during starvation. The current density

278 of $0.04 \text{ A}\cdot\text{point}^{-1}$ indicates the instability of A_{ac} at minute 11. However, at that time the
279 respective voltage value is still the same as in minute 1 (Fig. 4a).

280 The outliers (current density decrease) at the points i./ii.10 and i./ii.11 of the gas flow
281 from inlet to outlet (Fig. 5) can be explained with the channel geometry of the flow
282 field, since at those points the H_2 gas flow is constricted (Fig. 1a). The outlier of gas
283 flow from inlet to outlet (e.g. intercept i.25; Fig. 5) at which current density repeatedly
284 increased after the decrease in previous intercepts can be due to an in-plane cross-
285 over effect passing over the geometry of flow channels [34].



286 **Fig. 5: a)** 2D current density distribution maps during starvation step 1 at minutes 1,
287 11 and 26, **b)** Unfolded view of the current densities ($\text{A}\cdot\text{point}^{-1}$) for minutes 1, 11 and
288 26 extracted from the 2D maps (Fig. 5), red bracket points to current decrease at
289 minute 11.
290

291 The number of points, where the local current density is $> 0.04 \text{ A}\cdot\text{point}^{-1}$ represents
292 an area with sufficient H_2 supply (P_{ac}), which balance A_{ac} to the actual operational
293 current. The residual points ($< 0.04 \text{ A}\cdot\text{point}^{-1}$) have insufficient H_2 supply, and the
294 partial pressure balance of the system is disturbed. In order to balance the low H_2
295 partial pressure against ambient pressure, undesirable air may back-feed into the
296 anode side of the assembly (air front) from the open outlet, which may further expand
297 to about i./ii.20th (Fig. 4a; 5b). As soon as an H_2 and air front builds up on the anode
298 side, the MEA acts not only as the fuel cell (hydrogen oxidation reaction (HOR) –
299 anode side / oxygen reduction reaction (ORR) - cathode side), but also as the
300 galvanic cell (HOR and oxygen evolution reaction (OER) –anode side / ORR –
301 cathode side) [35].

302 The air - filled part of the anode side shifts the potential in the adjacent cathode
303 electrode (ca. 1.5 V vs. reversible hydrogen electrode (RHE)). Such potential is high
304 enough to start OER and lead to carbon oxidation currents. The electrochemical

305 oxidation of the carbon catalyst support (Eq. 3) is thermodynamically achievable at
306 potential $> 0.2 V_{\text{RHE}}$.



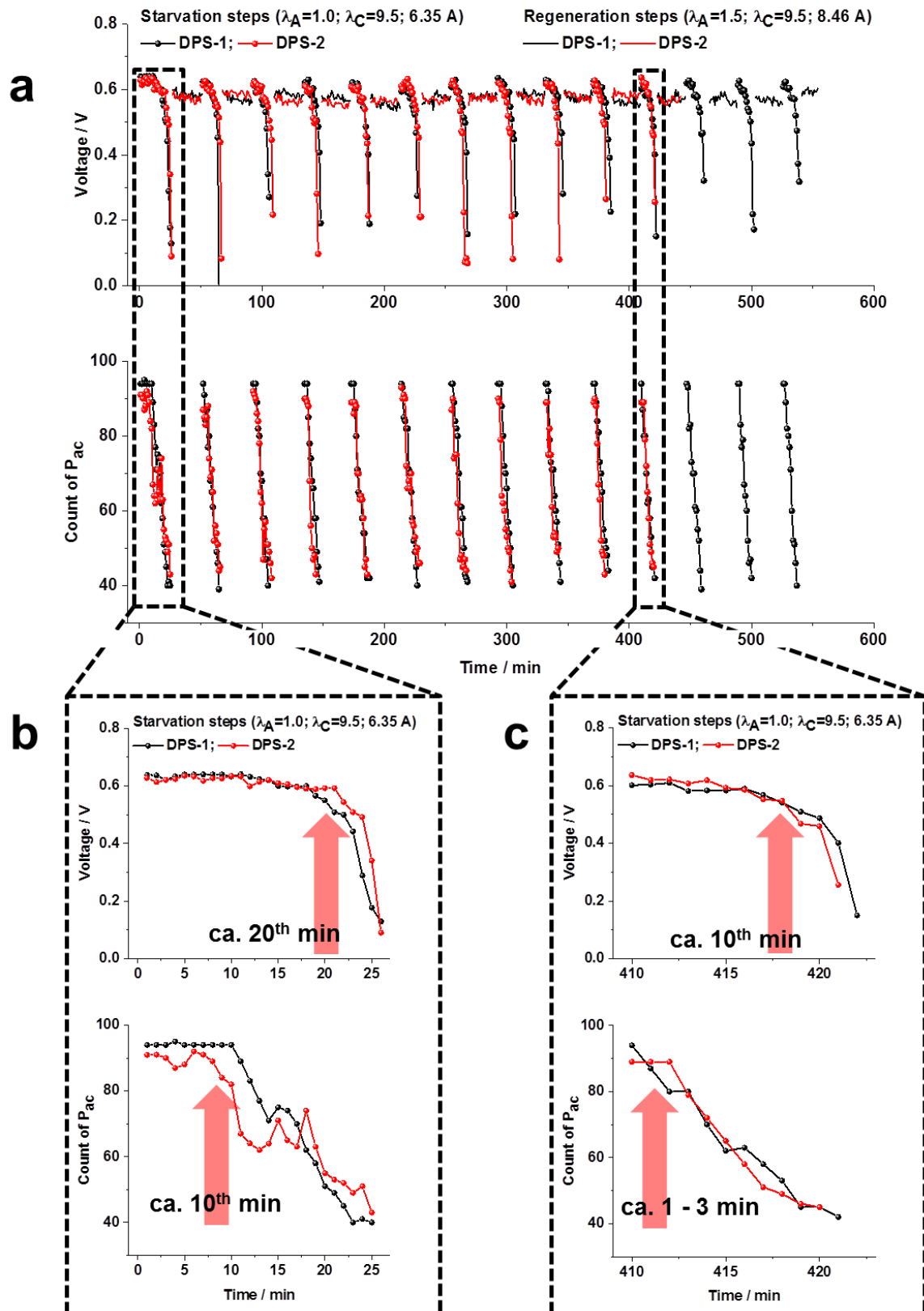
308 The consequence of the carbon oxidation of the carbon electrodes is cathode
309 thinning i.e. loss of void volume within the cathode catalyst layer and a concomitant
310 decrease in cathode layer thickness as reported in [36].

311 The anode catalyst layer may also suffer from air fronts on the anode side. Engl et al.
312 [37] reported carbon corrosion in HT PEM FC along with a loss of a Pt
313 electrochemical surface area (ECSA). The authors attributed this to the difference of
314 the anode potential due to change of MEA operation between fuel cell and the
315 galvanic cell. Similar findings of anode catalyst layer local thinning were also
316 observed by our group [38].

317 As a consequence, both anode and cathode sides can undergo degradation due to
318 anode starvation.

319

320



321

322 **Fig. 6:** a) Voltage behavior and P_{ac} for the 14 and 11 starvation steps and voltage
 323 behavior during regeneration step for DPS-1 and DPS-2 respectively, vs. time, **b)**
 324 zoom into the first starvation step of DPS-1 and DPS-2 and **c)** zoom into the 11th
 325 starvation step of DPS-1 and DPS-2.

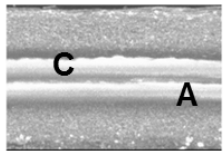
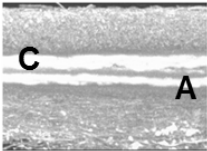
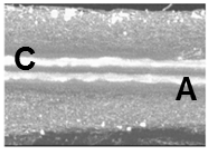
326 Accordingly, the A_{ac} is divided into sufficient and insufficient H_2 supply, and 0.04
327 $A \cdot \text{point}^{-1}$ is taken as the threshold value. The number of points with sufficient H_2
328 supply (P_{ac}) was determined for both DPS-1 and 2 (Fig. 6a) and, like the voltage
329 drop, highly reproducible and essentially the same for both MEAs. Both DPS-1 and
330 DPS-2 consist at the start of each starvation of ca. 95 sufficiently supplied points (ca.
331 21 cm^2), the number of which decreases during the starvation to ca. 40 points.
332 Hence, in the last minute of starvation the critical surface area is ca. 9 cm^2 . However,
333 if one compares the first starvation of DPS-1 and DPS-2 and the rest of starvation
334 steps, the time until voltage drops to below 0.2 V is in the first starvation period for
335 both MEAs (26 min; determined by safety shut-down) about twice as long as the later
336 starvation steps (10-15 min). The closer look at the first (Fig. 6b) and last starvation
337 (Fig. 6c) of both DPS-1 and DPS-2 shows that the significant voltage drop starts at
338 the first starvation step after 20 min and for the last starvation step after 10 min.
339 Further, the decrease in P_{ac} starts after ca. 10 minutes during the first starvation step
340 and after 1-3 minutes during the last starvation step for both DPS-1 and DPS-2. This
341 shows that the deviation of the current distribution starts earlier than the significant
342 drop in voltage during each starvation step. Therefore, the current distribution
343 analysis is more sensitive to the changes occurring in MEAs and suitable for the early
344 prediction of H_2 starvation.

345 The identical response in voltage and P_{ac} during H_2 starvation as well as the identical
346 voltage response during the regeneration steps allow a first assessment of
347 degradation effects. Since all regeneration steps showed a stable voltage at ca. 0.6 V
348 (Fig. 6a) it can be assumed that no severe degradation took place during the
349 starvation / regeneration steps. However, according to published experimental results
350 possible degradation mechanisms caused by H_2 starvation may consist of (i) back-
351 feeding processes and/or (ii) water electrolysis with subsequent corrosion processes
352 at the anode side [37]. Those may lead to irreversible changes in MEAs, such as
353 layer thickness and morphology [36, 39]. Therefore, in order to evaluate the impact of
354 starvation on the catalyst layers μ -CT measurements were conducted for both anode
355 and cathode sides, for the areas located at the inlet and the outlet. Table 2 shows the
356 comparison of catalysts layer thicknesses obtained for the fresh MEA from the same
357 batch (DPS-0, not been assembled in the FC test station) with those of DPS-1.

358 As shown in Table 2 the thicknesses of both cathode and anode catalyst layers were
359 reduced by about 30 % ($8\text{-}11 \mu\text{m}$) compared to a fresh MEA. Apparently, H_2
360 starvation has a thinning effect on the layers of DPS-1. The anode catalyst layer
361 thickness is slightly lower than the cathode catalyst layer at both inlet and outlet after
362 H_2 starvation. However, there is almost no thickness difference between inlet and
363 outlet of the same catalyst layers. This could be due to the fact that the total time
364 under starvation conditions (about 550 min) was too short to have significant
365 influence on the thickness of catalyst layer at two different places of the MEA surface.
366 It can be concluded that after the 14 starvation steps the overall thickness of the
367 anode and cathode catalyst layers are only slightly affected. Even if the layer
368 thickness appears to be reduced (Table 2) the performance of the DPS remained
369 unchanged (Figs. 4-6). Results on starvation / regeneration experiments extending
370 the number of cycles to further days of measurement (DPS-2) will be published soon
371 in a separate paper.

372 **Tab. 2:** Catalyst layer thicknesses as well as μ -CT images showing through-plane
 373 morphology of a fresh MEA (DPS-0) and the MEA of DPS-1 after operation. Mean
 374 values of layer thicknesses are calculated from 10 data points with single standard
 375 deviation.

376

Sample	DPS-0	DPS-1	
Sample status	Fresh MEA	Starvation / Regeneration	
Measurement duration / min	0	ca. 550	ca. 550
Location		inlet	outlet
μ -CT image			
cathode catalyst layer thickness (C) / μ m	35.3 ± 4.0	27.2 ± 6.2	28.6 ± 5.6
anode catalyst layer thickness (A) / μ m	35.6 ± 6.0	24.5 ± 4.0	24.3 ± 4.5

377

378

379 4. Conclusions

380 In this work, two identical MEAs from a DPS of a HT-PEM FC were cycled under
 381 anode starvation / regeneration conditions for up to 550 min, which included up to 14
 382 starvation steps. The results show that during starvation, cell voltage and current
 383 density distribution over the active area of the MEAs significantly differed from
 384 nominal conditions. The significant drop in cell voltage from 0.6 to 0.1 V occurred after
 385 ca. 20 minutes for the first starvation step, and after 10 minutes for all subsequent
 386 starvation steps. Compared to that the voltage response of both MEAs is immediate,
 387 stable and constant at 0.6 V during all subsequent regeneration steps.

388 Further, during each starvation, the local current density reached up to $0.3 \text{ A}\cdot\text{point}^{-1}$
 389 at the area near the gas inlet (9 cm^2) while near the outlet it drops to $0.01 \text{ A}\cdot\text{point}^{-1}$.
 390 The deviation from a balanced current density distribution occurred after 10 minutes
 391 for the first starvation step, and after ca. 2 minutes for the subsequent starvation
 392 steps. Hence, compared to the voltage drop the deviation from a balanced current
 393 density distribution always starts earlier. This indicates that the local current density
 394 distribution is more sensitive to local changes in the MEA than the cell voltage drop,
 395 which is an averaged measurement. Such conclusion is applicable for various types
 396 of MEAs with different active areas. This finding may help to prevent undesirable
 397 influences of the starvation process.

398

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403

404 **5. References**

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