

1 **Coated Stainless Steel Bipolar Plates for Proton Exchange Membrane Electrolyzers**

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7 **Keywords**

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10

11 **Abstract**

12 Given its rapid response to fluctuating currents and wide operation range, proton exchange
13 membrane (PEM) water electrolysis is utmost suitable for generation of hydrogen from
14 renewable power. However, it is still hindered by the high cost of the stack components
15 compared to those used in the alkaline technology. In particular, the titanium bipolar plates
16 (BPP) are an issue and the replacement of this metal by stainless steel is a challenge, due to the
17 highly corrosive environment inside PEM electrolyzer stack. Herein, we coat stainless steel BPPs
18 with 50-60 μm Ti and 1.5 μm Pt coatings by vacuum plasma spraying (VPS) and magnetron
19 sputtering physical vapor deposition (PVD), respectively. The BPPs are evaluated at constant 1
20 A cm^{-2} for more than 1000 h. The thermally sprayed Ti coatings fully protect the stainless steel
21 substrate during this period of time, and the Pt surface modification allows achieving a cell
22 performance comparable to the baseline.

23

24 1. Introduction

25 In 1800, William Nicholson and Anthony Carlisle discovered the electrolysis of water into H₂
26 and O₂, by applying direct current (DC) and for a long time was the main technique for hydrogen
27 production for industry.¹ Over 200 years later, the splitting of water is experiencing a renaissance
28 due to energy applications and proton exchange membrane (PEM) electrolysis is the most
29 dynamic technique, which was reported in 1973 by Russell and coworkers.² In this context,
30 hydrogen is nowadays expected to act as a carbon neutral energy vector to introduce renewable
31 electricity into other sectors.³ Compared to the well-established alkaline technology, PEM
32 electrolyzers have several advantages such as high efficiency, rapid response, compact system
33 design, and extended dynamic operation range.⁴⁻⁹ Moreover, gas purities up to 99.995 % can be
34 achieved with the PEM technology while only 99.5% for alkaline electrolyzers.¹⁰ Conversely, for
35 small production rate, PEM technology is more expensive than alkaline.^{11,12} However, it
36 becomes more competitive and likely cheaper in large production rates, especially in the
37 Megawatt input power range.

38 The stack, which is assembled with several cells connected in series, is the key part of the PEM
39 electrolyzer unit.⁶ The membrane electrode assembly (MEA) is one core component of a PEM
40 cell. Current collectors (CC) on both sides of the MEA, which are permeable for water and the
41 product gases, allow current to flow to and from the electrodes.¹³⁻¹⁵ The two half-cells are
42 surrounded by so called bipolar plates (BPP) or separators, which usually have flow fields that
43 allow the reactant water to be transported to the CC and the product gases to be removed
44 efficiently.^{16,17}

45 The stack comprises about 60% of the total cost of the PEM electrolyzer and the titanium bipolar
46 plates (BPP) are responsible for half the cost of the stack.⁸ The BPPs are manufactured from
47 titanium, which is highly stable to corrosion in oxidative environments, but machining this metal
48 is complicated and expensive.^{18,19} Furthermore, semi-conductive oxides form on its surface as a
49 result of anodization, and this passive layer affects negatively the performance and durability of
50 the electrolyzer.²⁰⁻²³ Thereby, the reduction or total replacement of massive Ti in PEM
51 electrolyzers by low cost materials is a pressing issue for the industry.

52 The use of stainless steel as base material for manufacturing BPPs of proton exchange membrane
53 fuel cell (PEMFC) has been extensively reported. When used in fuel cells, it requires a high
54 corrosion resistance coating with excellent electronic properties.²⁴⁻²⁶ In this context, conductive
55 coatings such as C,²⁷⁻²⁹ Au,³⁰ TiN,³¹ TiN/C,³² TaN,³³ CrN,³⁴ and SnO₂:F³⁵ have been extensively
56 evaluated for corrosion protection of PEMFC stainless steel bipolar plates. Nevertheless, these
57 coated-BPPs are not currently used in PEM electrolyzers. The reason is that the high cell voltage,
58 at which the electrolyzer operates in nominal conditions (2 V, 40-60 °C, 1 x 10⁵ Pa or higher),
59 accelerates corrosion, which might not be avoided with PEMFC coatings.

60 An approach for developing protective coatings for BPPs of PEM electrolyzers can be: (i)
61 Deposition of a thick Ti coating by thermal spraying³⁶⁻⁴⁰ for corrosion protection of stainless
62 steel; (ii) Surface modification of the Ti coating to decrease contact resistance.^{21,41,42} We have
63 recently shown that a coating of Ti with a subsequent surface modification with Pt (Pt/Ti)
64 protects stainless steel from corrosion over an extended period of time, while maintaining its
65 electrical properties.³⁹ In our work the corrosion evaluation was performed in a simulated
66 environment of PEM electrolyzer for short periods. However, long-term testing of the coatings in
67 a commercial PEM electrolyzer is crucial to demonstrate their capability for industrial

68 applications. In this work, we report the results of a 1000 h test on a stack with Ti and Pt/Ti
69 coated stainless steel bipolar plates in a commercial PEM electrolyzer. Neither decrease in the
70 electrolyzer performance nor degradation of the stainless steel substrate was observed, proving
71 that this metal can be used as base material for manufacturing low cost bipolar plates.

72 **2. Experimental**

73 *2.1. Coating process and stack assembly*

74 The development of the Ti and Pt coatings on stainless steel was reported elsewhere.³⁹ The
75 coatings were deposited on 120 cm² active area 316L stainless steel round BPP from
76 Hydrogenics. The plates were previously **sand-blasted** with SiO₂ powder to increase the surface
77 roughness of the support thus the adherence of the Ti coating to it is improved. A feedstock of
78 titanium powder (grade 1, grain size < 45 μm, TLS Technik Spezialpulver) was used. The
79 coating was applied on both sides of the plates. The chamber pressure was 50 mbar. A plasma
80 enthalpy of 21.3 MJ kg⁻¹ was achieved by carefully controlling the flow rates of H₂, He and Ar,
81 The presence of H₂ decreases the partial pressure of O₂ and its reduction by H₂ takes place, thus
82 preventing the oxidation of Ti into TiO₂. The former increases the electrical resistance of the Ti
83 coating. Thereafter, a step of capillary sealing procedure allowed to fully densify the Ti coatings.
84 Finally, the area of the flow field that is in contact with the current collectors was sanded with
85 SC4000 paper and rinsed with **deionized (DI) water**. **No abrasives were used**. An additional layer
86 of Pt was deposited on some of the Ti-coated stainless steel BPP, by magnetron sputtering
87 physical vapor deposition (PVD). The BPP were assembled in a rainbow stack and in which all
88 cells had the same commercial membrane electrode assemblies MEAs (Greenerity E300,
89 N115CS membrane), metallic current collectors and carbon-based gas diffusion layers (GDL).

90 Table 1 enlists the configuration of the cell coatings in the stack. The first two cells, which had
91 Ti bipolar plates with proprietary coatings from Hydrogenics, were used as a baseline for
92 comparison purposes.

93 2.2. PEM electrolyzer and impedance tests

94 The stack (model 92E, Hydrogenics), Figure 1a, with coated stainless steel bipolar plates was
95 tested in a commercial PEM electrolyzer ($0.75\text{-}2.5 \text{ Nm}^3 \text{ H}_2 \text{ h}^{-1}$ Hylyzer Hydrogen Generator,
96 Hydrogenics), Figure 1b. The electrolyzer was running for several days as part of an activation
97 protocol until it reached a stable voltage at a given current density. Then the stack was evaluated
98 at constant 1 A cm^{-2} , for 1000 h, at $38 \text{ }^\circ\text{C}$, and $6.5 \times 10^5 \text{ Pa}$ balanced pressure system. This
99 current density was deliberately chosen to compare degradation rates with other reports, in which
100 PEM electrolyzers with Ti BPP were operated at least 100 h.^{18,43-46} Polarization curves were
101 recorded before, and after 500 and 1000 h, from 0.01 to 1 A cm^{-2} (rectifier step rate: 4.2 mA cm^{-2}
102 s^{-1}) at $29 \text{ }^\circ\text{C}$ and $6.5 \times 10^5 \text{ Pa}$ balanced pressure system. Temperature fluctuations were
103 negligible in this current density range. Likewise, electrochemical impedance spectroscopy (EIS)
104 measurements were carried out with a potentiostat/galvanostat (Zahner elektrik IM6) coupled
105 with a booster (Module PP240) for each cell at $27 \text{ }^\circ\text{C}$. Measurements were carried out at 20 A
106 with an amplitude of 3 A and frequencies between 0.1 and 750 Hz . The results were fitted to an
107 equivalent electrical circuit consisting of an ohmic resistance (R_1) connected in series with two
108 sections of resistance - constant phase element ($R_2\text{-CPE}$, $R_3\text{-CPE}$). The first element, R_1 ,
109 represents the ohmic behaving components of the cell, containing electrical and ionic resistances.
110 The second component, $R_2\text{-CPE}$, represents capacitive double layer effects in the electrode of
111 ionic and electric components, and the third component, $R_3\text{-CPE}$, correspond to the charge
112 transfer resistance of the oxygen evolution reaction.

113 The inlet water resistance of the stack was kept higher than $10 \text{ M}\Omega \text{ cm}^{-1}$ at all time, by means of
114 a DI water resin system, which traps transition metal ions as well as S, F and Si. Therefore, the
115 resin can be used to determine qualitatively stack degradation products from catalysts and
116 coatings. X-ray photon electron spectroscopy (XPS) was performed at the end of the 1000 h test
117 looking for Fe or other elements of the 316L.

118 2.3. *Contact resistance measurements*

119 Interfacial contact resistance (ICR) vs. compaction force measurements were performed after the
120 1000 h test to evaluate degradation effects due to formation of semiconducting oxide layers on
121 the surface of the coatings. This technique is widely used to determine ICR of BBP for
122 PEMFC.^{32,35,47-49} We assume that the ICR parameter of the coated stainless steel BPP before the
123 test is similar to the one determined on Ti and Pt/Ti coated dummy flat samples,³⁹ since the
124 coating parameters in this work were the same. The bipolar plates were placed between two
125 pieces of GDL carbon paper (280 μm thick) and two copper cylinders, which were previously
126 cleaned with 0.5 M H_2SO_4 . The ICR measurements were performed by applying a current of 5 A
127 and the contact pressure was varied from 20 to 200 N cm^{-2} . The separation between the channel
128 ribs and width of the rib is in both cases $\sim 1 \text{ mm}$ after coating. Therefore, the compaction force
129 was adjusted by a factor of two. The voltage was measured with the same potentiostat used for
130 the EIS measurements. An electrical circuit, which represents each interface by a resistor,⁴⁹ was
131 used to determine the ICR of each plate.

132 2.4. *Scanning electron microscopy (SEM)*

133 Analysis of the cross section of the coated-BPPs was carried with an ULTRA plus (Zeiss Corp.)
134 scanning electron microscope. The images were recorded with the secondary electrons an

135 integrated AsB GEMINI lens detector, separating the back scattered electron (BSE) signal. The
136 acceleration voltage was 15 kV (1 nm resolution) and the working distance 8.1 mm.

137 **3. Discussion of results**

138 *3.1. Coated stainless steel BPP*

139 One concern of every coating procedure is how well the layer can cover zones in the BPPs that
140 are more prone to corrosion than others. Cross-section SEM images of the Ti-coated stainless
141 steel BPPs, readily after being coated are presented in Figure 1c and 1d. The micrographs reveal
142 that the coating covers all the regions of the manifolds, the exposed 3D areas of the flow
143 field, inlet/outlet holes, edges, corners and even some regions of the backside of the BPP. It is
144 worthwhile noting that it was not necessary to tilt the plate to obtain a uniform thickness of the
145 coating on all the surface of the ribs of the BPP. The BPP with Pt/Ti coatings were not analyzed
146 by SEM prior the assembly of the stack, assuming that the morphology of the coatings is similar
147 coatings reported elsewhere.³⁹

148 *3.2. Cell performance*

149 The 92E stack with the coated-BPPs was mounted in the Hylyzer PEM electrolyzer and operated
150 for a few days as part of an activation process. Thereafter, current-voltage curves from 0.01 to 1
151 A cm⁻² were recorded for each cell at a rectifier step rate of 4.2 mA cm⁻² s⁻¹, maintaining a stack
152 temperature of 29 °C, Figure 2a. According to the cell configurations presented in Table 1, the
153 cells with Ti-coated cathodes without Pt, cell 4 and 5, showed the highest E_{cell} at 1 A cm⁻². The
154 Nyquist plots of the EIS measurements at 27 °C and 0.166 A cm⁻² are presented in Figure 2b. **It**
155 **needs to be mentioned, the the E_{cell} of the baseline and the Pt/Ti coated cells at 38 °C is high**

156 compared to what it has been reported with same stack technology.⁵⁰ The issue can originate
157 form an increase of water pressure in the flow field channels and sealing compression in the
158 grooves caused by the thick Ti coating, which affected the performance of the whole stack.
159 Consequently, the width of the flow field channels and sealing grooves should be adjusted if they
160 are to be coated with 50-60 μm Ti. As a result, our study can only compare the performance of
161 the Pt/Ti coated cells with the baseline in the same stack. Further work will address this issue.

162 First, the EIS results show that cell 4 and 5 have much higher ohmic resistance (R_1) compared to
163 the others. As it will be shown in the next section, the ICR of the Ti coating with the carbon-
164 based GDL is much higher than the ICR of the Pt coating with the same GDL. One can conclude
165 that the passivation of Ti is detrimental for the cell performance when using a carbon based GDL
166 in the cathode. Indeed, a significant improvement in the performance of unitized reversible fuel
167 cells (URFC) has been previously reported, when the Ti bipolar plates are coated with Pt²¹ or
168 Au.⁴² Second, the kinetic or activation resistance (R_2) is similar in all cells, since they all have
169 MEAs with similar catalysts. None of the cells presented mass transport issues, which accounts
170 for an excellent gas bubble management in the catalyst layers,⁵¹ thin current collectors with high
171 porosity^{13,52,53} and optimized flow field of the bipolar plate.¹⁶ Lastly, cell 6, having Pt/Ti coating
172 on anode and cathode side of the stainless steel BPP, showed the lowest E_{cell} at 1 A cm^2 .

173 A 1000 h test at 1 A cm^{-2} was carried out readily after the initial electrochemical characterization
174 of the stack. The resulting E_{cell} vs. time characteristics of cell 1 - 6 are presented in Figure 3. The
175 electrolyzer was shut down after \sim 500 h of operation and it was kept in this mode for almost 100
176 h to determine degradation effects when the electrolyzer is turned off. These conditions will
177 necessarily occur in any application when H_2 is not constantly required. Current potential curves
178 and EIS were recorded at the end of the stand-by period, Figure 4a and 4b, respectively. Once the

179 electrolyzer was brought back in operation, the voltage of cell 4 and 5 was more than 100 mV
180 higher than before the shutting down, while for the other four cells such changes did not occur.
181 By fitting the equivalent circuit proposed in Section 2.2, the changes of the ohmic resistances of
182 each cell can be quantified. The ohmic resistance of the surface modified cells decreases almost
183 homogeneously by an average value of $45 \text{ m}\Omega \text{ cm}^{-2}$. Conversely, cell 4 and cell 5 increased their
184 ohmic resistance by 243 and $117 \text{ m}\Omega \text{ cm}^{-2}$, respectively. Post-mortem analysis (Section 3.3) will
185 show that not only the anode side of the Ti coated plate oxidized, but also the cathode side
186 experienced degradation. The negative effect might have occurred during the stand-by period as
187 concluded from the time equivalence of degradation and stand-by period, although it was not
188 directly proven.

189 The change of E_{cell} and R_1 for all the cells is summarized in Figure 5a and 5b, respectively. In
190 overall, cell 1 (baseline) and cell 6 (Pt/Ti coating on anode and cathode) showed the highest
191 performance and no increase in E_{cell} . The main difference between them is that cell 1 is made of
192 Ti, while cell 6 uses stainless steel as based material for its manufacture. Except for cells 4, the
193 performance of the cells improved slightly overtime, which can be explained by a progressive
194 decrease of the ohmic (R_1), Figure 5b. Cell 4 and cell 5 improve significantly their performance
195 in the initial 100 h until reaching a steady state. From Figure 3 one can only observe the
196 improvement of their performance in the initial 100 h, which is a complex activation process
197 (recovering) not yet fully explored in the literature of PEM electrolysis. Both cells progressively
198 continue degrading and in particular after the shut down period, which can be well appreciated
199 from Figure 4a (Increase in E_{cell}) and Figure 5a (decrease in R_1). The performance of both cells
200 did not recover anymore for the subsequent 900 h. From the polarization curves of Figure 2a and

201 4a (as well as in Figure 5b: high increase in R_1) one can observe that Cell 4 degraded more than
202 Cell 5 after the 1000 h test.

203 Moreover, other works have reported a concomitant increase in E_{cell} has as result of
204 degradation^{18,43–46} and the cause is mostly attributed to poisoning of the MEA with metallic
205 cations such as Fe.^{54–57} This metal is present in the DI water in small amounts and it increases its
206 concentration over time in the O₂ separator due to the electrolysis process. Therefore, a DI water
207 resin is necessary for trapping the Fe ions and it needs to be replaced regularly. The effect of Fe
208 poisoning in PEM electrolyzers is not well studied so far but it is expected that Fe will decrease
209 the ionic conductivity and deposit on the cathode.⁵⁸ As a result, the E_{cell} will increase over time.
210 In our study, we did neither observe rise of E_{cell} of the cells with Pt/Ti/ss bipolar plates nor
211 abnormal increase of iron concentration in the DI water resin, and nor pitting corrosion after the
212 1000 h test.

213 From the results discussed in this section, it can be concluded the following: (i) The titanium
214 coating does not need further surface modification on the anode side if it is in contact with a
215 metallic collector; (ii) The titanium coating should be modified, with Pt for example, if carbon
216 paper GDL is to be used as cathode current collector; (iii) The stainless steel BPP might not
217 require a Ti coating on the cathode side. Further investigations are necessary in order to
218 demonstrate (iii), as corrosion of stainless steel might occur in the periods when the electrolyzer
219 is turned off.

220 3.3. Degradation and post-mortem analysis

221 After disassembling of the stack, a noticeable darkness of the surface of the Ti coating in the
222 cathode and anode side of the plate was observed. The grayish surface of the coating on the

223 anode side reappeared after sanding it for a few minutes with SC4000 paper, thus removing the
224 oxide layer. The ICR vs. compaction force measurements were carried on areas of the BPP
225 before and after sanding procedure to evaluate the effect of degradation. Figure 6 summarizes the
226 results on Ti/ss while Pt/Ti/ss is included for comparison. First, one can observe that the Pt
227 surface modification reduces the contact resistance of Ti with the carbon paper almost 2 orders
228 of magnitude at 120 N cm^{-2} and does not change with the compaction pressure, which was
229 already observed in our previous work.³⁹

230 Secondly, the surface of the cathode degraded more than the anode side. If the cause was
231 oxidation of the Ti coating, certainly, it did not take place during operation of the electrolyzer,
232 but most likely during the stand-by period in which the electrolyzer was turned off. One must
233 also consider the possibility of degradation of the cathode Ti coating by H_2 embrittlement.^{59,60}
234 The results of ICR vs. compaction force suggest that the cathode side might not necessarily need
235 to be coated with Ti as austenitic stainless steels are more resistant to hydrogen
236 embrittlement.^{61,62} In the case of the Pt/Ti-coated stainless steel BPP, the Pt coating peeled off in
237 some areas of the grooves of the BPP in which the sealing is inserted. However, no signs of
238 degradation of the Pt coating were observed in the contact area with either the metallic CC
239 (anode) or carbon-based GDL (cathode). The peeling of the thermally sprayed Ti coating was
240 neither observed for the Ti/ss nor Pt/Ti/ss BPPs.

241 Samples of the DI water resin were collected at the beginning (fresh) and the end (used) of the
242 1000 h and they were analyzed by X-ray photon electron microscopy (XPS). Table 2 enlists the
243 elements that were detected, and in particular Ti and Fe concentration in the resin increased by
244 0.3 and 0.1 wt%, respectively, after the 1000 h test. The former might originate in the
245 degradation of the Ti BBPs (cell 1-2) or the Ti coating (cell 3 - 4). Yet, the element of interest is

246 iron, which is a product of pitting corrosion of stainless steel. The increase of this metal in the
247 resin is negligible and even higher amounts have been observed for other E92 stacks having only
248 Ti BPPs (measurements not shown). Therefore, the traces of Fe in the resin can only arise from
249 inlet water for the entire system, as corrosion of stainless 316L steel pipes and valves in DI water
250 is unlikely.⁶³ Finally, Figure 7a shows a SEM cross-section of optical image of the Ti coating on
251 the stainless steel BPPs after the 1000 h test. A close up image of the Pt/Ti coating deposited on
252 the anode side of the BPP is presented on in Figure 7b. Neither peeling off the coatings nor
253 corrosion of the substrate (pinholes) was observed in any plate. The electrochemical and post-
254 mortem physical analysis clearly support the use of stainless steel as base material for BPPs of
255 PEM electrolyzers.

256 **4. Conclusions**

257 Thermally sprayed Ti-coated stainless steel bipolar plates of PEM electrolyzer were tested for
258 more than 1000 h at constant 1 A cm^{-2} . The coating fully protected the stainless steel substrate;
259 however it degraded when used in the cathode and in contact with the carbon-based GDL,
260 resulting in a significant increase of cell voltage (E_{cell}). The oxidation of the Ti coating on the
261 anode side did not pose a negative effect. The problem was solved by modifying the surface of
262 the Ti coating with a $1.5 \text{ }\mu\text{m}$ Pt layer (Pt/Ti). The highest performance of the PEM electrolyzer
263 was achieved with this dual coating deposited on the anode and cathode side. Additional results
264 suggest that no coating is necessary on the cathode side, if stainless steel is to be use as base
265 material for manufacturing the BBPs. Furthermore, cheaper steels, Cu, or Al can possibly be
266 used instead of stainless steel since corrosion was not observed. However, the BPP made of these
267 metals would require a coating on both sides to protect against any possible corrosion
268 phenomena, in particular during the stand-by periods.

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275 References

- 276 1. Royal Society of Chemistry, *Chem. World*, 2003, *Enterp. electrolysis* (2003)
277 <http://www.rsc.org/chemistryworld/Issues/2003/August/electrolysis.asp>.
- 278 2. J. H. Russell, L. J. Nuttall, and A. P. Fickett, *Am. Chem. Soc. Div. Fuel Chem. Prepr.*, **18**, 24–33 (1973).
- 279 3. A. Sternberg et al., *Energy Environ. Sci.*, **8**, 389–400 (2015) <http://xlink.rsc.org/?DOI=C4EE03051F>.
- 280 4. K. E. Ayers, C. Capuano, and E. B. Anderson, *ECS Trans.*, **41**, 15–22 (2012)
281 <http://ecst.ecsdl.org/content/41/10/15.abstract>.
- 282 5. K. E. Ayers, L. Moulthrop, E. B. Anderson, E. C. S. Transactions, and T. E. Society, *ECS Trans.*, **41**, 75–83
283 (2012) <http://ecst.ecsdl.org/content/41/46/75.abstract>.
- 284 6. M. Carmo, D. L. Fritz, J. Mergel, and D. Stolten, *Int. J. Hydrogen Energy*, **38**, 4901–4934 (2013)
285 <http://www.sciencedirect.com/science/article/pii/S0360319913002607>.
- 286 7. F. Barbir, *Sol. Energy*, **78**, 661–669 (2005).
- 287 8. L. Bertuccioli et al., *Study on development of water electrolysis in the EU by E4tech Sàrl with Element Energy*
288 *Ltd for the Fuel Cells and Hydrogen Joint Undertaking*, (2014).
- 289 9. K. E. Ayers et al., *ECS Trans.*, **33**, 3–15 (2010) <http://ecst.ecsdl.org/content/33/1/3.abstract>.
- 290 10. K. Zeng and D. Zhang, *Prog. Energy Combust. Sci.*, **36**, 307–326 (2010)
291 <http://www.sciencedirect.com/science/article/pii/S0360128509000598>.
- 292 11. Fuel Cells and Hydrogen Joint Undertaking, *Commercialisation of energy storage in europe, A fact-based*
293 *analysis of the implications of projected development of the European electric power system towards 2030 and*
294 *beyond for the role and commercial viability of energy storage*, p. 52, (2015).
- 295 12. K. A. Friedrich, *Studie über die Planung einer Demonstrationsanlage zur Wasserstoff - Kraftstoffgewinnung*
296 *durch Elektrolyse mit Zwischenspeicherung in Salzkavernen*, p. in press, (2015).
- 297 13. S. A. Grigoriev, P. Millet, S. A. Volobuev, and V. N. Fateev, *Int. J. Hydrogen Energy*, **34**, 4968–4973 (2009)
298 <http://www.sciencedirect.com/science/article/pii/S0360319908015528>.
- 299 14. H. Ito et al., *Int. J. Hydrogen Energy*, **37**, 7418–7428 (2012)
300 <http://www.sciencedirect.com/science/article/pii/S0360319912001917>.
- 301 15. M. A. Hoeh et al., *Electrochem. commun.*, **55**, 55–59 (2015)
302 <http://www.sciencedirect.com/science/article/pii/S1388248115000776>.
- 303 16. H. Ito et al., *Int. J. Hydrogen Energy*, **35**, 9550–9560 (2010)
304 <http://www.sciencedirect.com/science/article/pii/S036031991001284X>.

- 305 17. A. S. Tijani, D. Barr, and A. H. A. Rahim, *Energy Procedia*, **79**, 195–203 (2015)
306 <http://www.sciencedirect.com/science/article/pii/S1876610215021943>.
- 307 18. H. G. Kim, L. K. Kwa, W. Han, L. K. Kwac, and W. Han, in *International Conference on Power and Energy*
308 *Systems Lecture Notes in Information Technology, Vol.13.*, vol. 13, p. 373–379 (2012) <http://www.ier->
309 [institute.org/2070-1918/lnit13/v13/373.pdf](http://www.ier-institute.org/2070-1918/lnit13/v13/373.pdf).
- 310 19. C. K. Jin, M. G. Jeong, and C. G. Kang, *Int. J. Hydrogen Energy*, 1–9 (2014)
311 <http://dx.doi.org/10.1016/j.ijhydene.2014.03.013>.
- 312 20. J.-T. T. Wang, W.-W. W. Wang, C. Wang, and Z.-Q. Q. Mao, *Int. J. Hydrogen Energy*, **37**, 12069–12073 (2012)
313 <http://www.sciencedirect.com/science/article/pii/S0360319912010798>.
- 314 21. H.-Y. Jung, S.-Y. Huang, and B. N. Popov, *J. Power Sources*, **195**, 1950–1956 (2010)
315 <http://www.sciencedirect.com/science/article/pii/S0378775309017352>.
- 316 22. S. S. Dhrab, K. Sopian, M. A. Alghoul, and M. Y. Sulaiman, *Renew. Sustain. Energy Rev.*, **13**, 1663–1668
317 (2009) <http://www.sciencedirect.com/science/article/pii/S1364032108001676>.
- 318 23. D. R. Hodgson, B. May, P. L. Adcock, and D. P. Davies, *J. Power Sources*, **96**, 233–235 (2001).
- 319 24. R. A. Antunes, M. C. L. Oliveira, G. Ett, and V. Ett, *Int. J. Hydrogen Energy*, **35**, 3632–3647 (2010)
320 <http://linkinghub.elsevier.com/retrieve/pii/S0360319910001308>.
- 321 25. M. C. L. de Oliveira, G. Ett, and R. A. Antunes, *J. Power Sources*, **206**, 3–13 (2012)
322 <http://dx.doi.org/10.1016/j.jpowsour.2012.01.104>.
- 323 26. L. Peng, P. Yi, and X. Lai, *Int. J. Hydrogen Energy*, **39**, 21127–21153 (2014)
324 <http://www.sciencedirect.com/science/article/pii/S0360319914024549>.
- 325 27. H. Husby, O. E. Kongstein, A. Oedegaard, and F. Seland, *Int. J. Hydrogen Energy*, **39**, 951–957 (2014)
326 <http://www.sciencedirect.com/science/article/pii/S0360319913026281>.
- 327 28. W. J. Pech-Rodríguez, D. González-Quijano, G. Vargas-Gutiérrez, and F. J. Rodríguez-Varela, *Int. J. Hydrogen*
328 *Energy*, **39**, 16740–16749 (2014) <http://www.sciencedirect.com/science/article/pii/S0360319914009379>.
- 329 29. Z. Wang et al., *Int. J. Hydrogen Energy*, **41**, 5783–5792 (2016)
330 <http://www.sciencedirect.com/science/article/pii/S0360319915314944>.
- 331 30. A. Kumar, M. Ricketts, and S. Hirano, *J. Power Sources*, **195**, 1401–1407 (2010)
332 <http://linkinghub.elsevier.com/retrieve/pii/S037877530901564X>.
- 333 31. Y. Wang and D. O. Northwood, *J. Power Sources*, **191**, 483–488 (2009)
334 <http://linkinghub.elsevier.com/retrieve/pii/S0378775309002845>.
- 335 32. H. Sun, K. Cooke, G. Eitzinger, P. Hamilton, and B. Pollet, *Thin Solid Films*, **528**, 199–204 (2013)
336 <http://www.sciencedirect.com/science/article/pii/S0040609012013776>.
- 337 33. C. Choe, H. Choi, W. Hong, and J.-J. Lee, *Int. J. Hydrogen Energy*, **37**, 405–411 (2012)
338 <http://dx.doi.org/10.1016/j.ijhydene.2011.09.060>.
- 339 34. Y.-C. Park et al., *Int. J. Hydrogen Energy*, **38**, 10567–10576 (2013)
340 <http://www.sciencedirect.com/science/article/pii/S0360319913014493>.
- 341 35. H. Wang and J. A. Turner, *J. Power Sources*, **170**, 387–394 (2007)
342 <http://linkinghub.elsevier.com/retrieve/pii/S0378775307007574>.
- 343 36. J. Kawakita et al., *Surf. Coatings Technol.*, **201**, 1250–1255 (2006)
344 <http://www.sciencedirect.com/science/article/pii/S0257897206001034>.
- 345 37. T. Valente and F. P. Galliano, *Surf. Coatings Technol.*, **127**, 86–92 (2000)
346 <http://www.sciencedirect.com/science/article/pii/S0257897200005491>.
- 347 38. H. Ji and P. M. Marquis, *Surf. Coatings Technol.*, **45**, 121–127 (1991)
348 <http://www.sciencedirect.com/science/article/pii/025789729190214H>.
- 349 39. A. S. Gago et al., *J. Power Sources*, **307**, 815–825 (2016)
350 <http://www.sciencedirect.com/science/article/pii/S0378775315306832>.

- 351 40. A. S. Gago et al., *ECS Trans.*, **64**, 1039–1048 (2014) <http://ecst.ecsdl.org/cgi/doi/10.1149/06403.1039ecst>.
- 352 41. T. J. Toops et al., *J. Power Sources*, **272**, 954–960 (2014)
- 353 <http://www.sciencedirect.com/science/article/pii/S0378775314014220>.
- 354 42. H.-Y. Jung, S.-Y. Huang, P. Ganesan, and B. N. Popov, *J. Power Sources*, **194**, 972–975 (2009)
- 355 <http://linkinghub.elsevier.com/retrieve/pii/S0378775309010441>.
- 356 43. S. P. S. Badwal, S. Giddey, and F. T. Ciacchi, *Ionics (Kiel)*, **12**, 7–14 (2006)
- 357 <http://link.springer.com/10.1007/s11581-006-0002-x>.
- 358 44. S. A. Grigoriev, K. A. Dzhus, D. G. Bessarabov, and P. Millet, *Int. J. Hydrogen Energy*, **39**, 20440–20446
- 359 (2014) <http://www.sciencedirect.com/science/article/pii/S0360319914013913>.
- 360 45. M. K. Debe et al., *J. Electrochem. Soc.*, **159**, K165–K176 (2012) <http://jes.ecsdl.org/content/159/6/K165.full>.
- 361 46. Ö. F. Selamet, F. Becerikli, M. D. Mat, and Y. Kaplan, *Int. J. Hydrogen Energy*, **36**, 11480–11487 (2011).
- 362 47. W. Yoon, X. Huang, P. Fazzino, K. L. Reifsnider, and M. A. Akkaoui, *J. Power Sources*, **179**, 265–273 (2008)
- 363 <http://www.sciencedirect.com/science/article/pii/S0378775307027024>.
- 364 48. L. Wang et al., *J. Power Sources*, **195**, 3814–3821 (2010).
- 365 49. H. Wang, M. A. Sweikart, and J. A. Turner, *J. Power Sources*, **115**, 243–251 (2003).
- 366 50. P. Lettenmeier et al., *Electrochim. Acta*, in press (2016)
- 367 <http://www.sciencedirect.com/science/article/pii/S0013468616310167>.
- 368 51. I. Dedigama et al., *Int. J. Hydrogen Energy*, **39**, 4468–4482 (2014)
- 369 <http://www.sciencedirect.com/science/article/pii/S0360319914000755>.
- 370 52. P. Lettenmeier, S. Kolb, F. Burggraf, A. S. Gago, and K. A. Friedrich, *J. Power Sources*, **311**, 153–158 (2016)
- 371 <http://www.sciencedirect.com/science/article/pii/S0378775316301008>.
- 372 53. F. Arbabi et al., *J. Power Sources*, **258**, 142–149 (2014)
- 373 <http://www.sciencedirect.com/science/article/pii/S0378775314002262>.
- 374 54. X. Wang et al., *Electrochim. Acta*, **158**, 253–257 (2015).
- 375 55. S. Sun, Z. Shao, H. Yu, G. Li, and B. Yi, *J. Power Sources*, **267**, 515–520 (2014)
- 376 <http://linkinghub.elsevier.com/retrieve/pii/S0378775314008106>.
- 377 56. P. Millet, F. Andolfato, and R. Durand, *Int. J. Hydrogen Energy*, **21**, 87–93 (1996)
- 378 <http://www.sciencedirect.com/science/article/pii/0360319995000054>.
- 379 57. G. Wei et al., *Int. J. Hydrogen Energy*, **35**, 3951–3957 (2010)
- 380 <http://linkinghub.elsevier.com/retrieve/pii/S0360319910002648>.
- 381 58. J. Mo et al., *Int. J. Hydrogen Energy*, **40**, 5–10 (2015)
- 382 <http://linkinghub.elsevier.com/retrieve/pii/S0360319915018340>.
- 383 59. M. . Louthan, G. . Caskey, J. . Donovan, and D. . Rawl, *Mater. Sci. Eng.*, **10**, 357–368 (1972)
- 384 <http://www.sciencedirect.com/science/article/pii/0025541672901097>.
- 385 60. D. S. Shih, I. M. Robertson, and H. K. Birnbaum, *Acta Metall.*, **36**, 111–124 (1988)
- 386 <http://www.sciencedirect.com/science/article/pii/0001616088900326>.
- 387 61. M. B. Whiteman and A. R. Troiano, *Corrosion*, **21**, 53–56 (1965)
- 388 <http://www.corrosionjournal.org/doi/abs/10.5006/0010-9312-21.2.53>.
- 389 62. E. Herms, J. . Olive, and M. Puiggali, *Mater. Sci. Eng. A*, **272**, 279–283 (1999)
- 390 <http://www.sciencedirect.com/science/article/pii/S0921509399003196>.
- 391 63. B. A. Johnson, *Corrosion of Metals in Deionized Water at 38°C (100 °F)*, National Aeronautics and Space
- 392 Administration (NASA) Report, NASA TM X-1791, (1969).

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395 **Tables**

396 Table 1. Arrangement of coated stainless steel (ss) bipolar plates in the stack.

Cell	Anode bipolar plate	Cathode bipolar plate
1	Baseline ^a	Baseline ^a
2	Baseline ^a	Baseline ^a
3	Ti/ss	Baseline ^a
4	Ti/ss	Ti/ss
5	Pt/Ti/ss	Ti/ss
6	Pt/Ti/ss	Pt/Ti/ss

397 ^aCoated titanium bipolar plate. The coating (non-disclosed) is proprietary technology of Hydrogenics

398 Table 2. XPS analysis of the DI water resin in the anode cycle of the PEM electrolyzer system
 399 before (fresh) and after (used) 1000 h constant performance at 1 A cm⁻².

Element	Fresh	Used
	[wt%]	[wt%]
O	10.9	18.5
C	79.6	72.9
S	7.2	6.2
Si	0	1.8
Fe	0	0.1
Ti	0	0.3
Ir	0	0.2
N	2.4	-

400

401

402 **Figure captions**

403 Fig. 1. a) Stack (E92, Hydrogenics) 120 cm² 6-cell stack tested in b) a 0.75-2.5 Nm³ H₂ h⁻¹
404 “Hylyzer” PEM electrolyzer unit (Hydrogenics). c) Cross-section SEM image of a Ti-coated
405 stainless steel bipolar plate before sanding; d) Cutaway of a corner between the channel of the
406 flow field and contact area with the current collector.

407 Fig. 2. a) Initial current-potential curves of cell 1 - 6 from 0.01 to 1 A cm⁻² and a scanning rate
408 of 4.2 mA cm⁻² s⁻¹, 29 °C and balanced pressure system of 6.5 x 10⁵ Pa; b) Nyquist plot of the
409 initial EIS measurement at 27 °C, 0.166 A cm⁻² and an amplitude current of 3 A. The apex of the
410 frequency is indicated on top.

411 Fig. 3. Cell potential (E_{cell}) during the 1000 h test on cell 1 - 6 at 1 A cm⁻², at 38 °C and balanced
412 pressure system of 6.5 x 10⁵ Pa.

413 Fig. 4. a) Current- potential curves of cell 1 to cell 6 from 0 to 1 A cm⁻² and at 29 °C after 1000 h
414 test at constant 1 A cm⁻²; b) Nyquist plot of the EIS measurement at 27 °C, 0.166 A cm⁻² and an
415 amplitude current of 3 A after 1000 h constant operation at 1 A cm⁻². The apex of the frequency
416 is indicated on top.

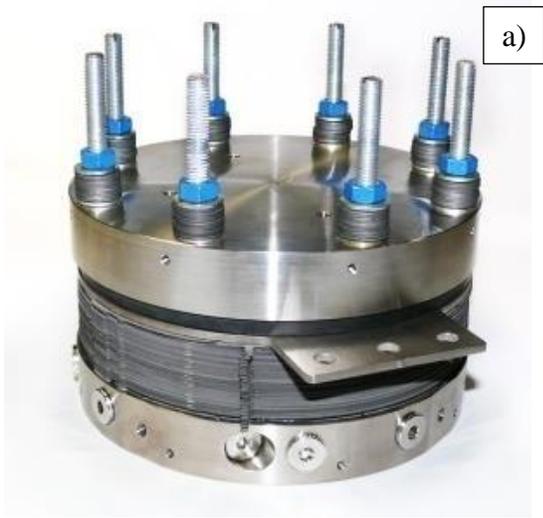
417 Fig. 5. a) Cell potential of cell 1 to cell 6 at 1 A cm⁻², 29°C, 6.5 x 10⁵ Pa and at three time steps,
418 initial, after 500 h and after 1000 h constant performance at 1 A cm⁻². b) Initial ohmic resistance
419 (R1) of cell 1 to cell 6 and after 1000 h constant performance at 1 A cm⁻² at 27°C.

420 Fig. 6. Interface contact resistance (ICR) with respect of compaction pressure of plate 4 (Ti/ss)
421 and plate 6 (Pt/Ti/ss) after 1000 h constant performance at 1 A cm⁻² at 38 °C. The anode and
422 cathode sides of the Ti/ss BPP were sanded to remove any oxide layer.

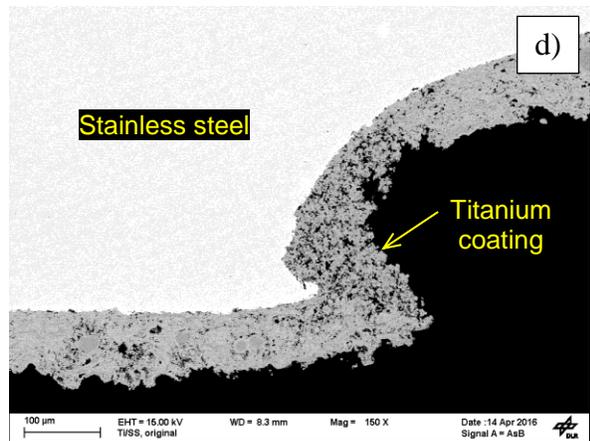
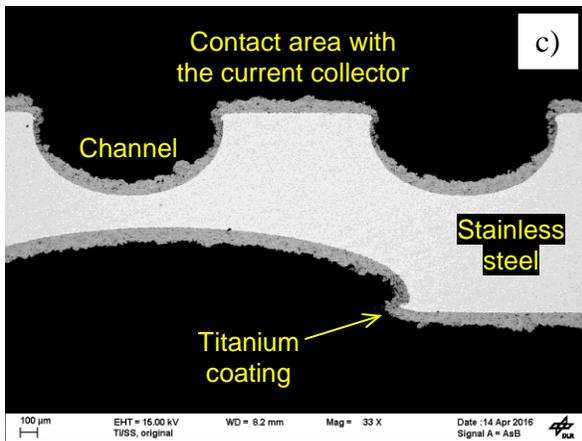
423 Fig. 7. Post-mortem cross-section SEM images a) Ti and b) Pt/Ti coatings on stainless steel
424 BPPs after the 1000 h test at constant 1 A cm^{-2} .

425

426 **Fig. 1.**



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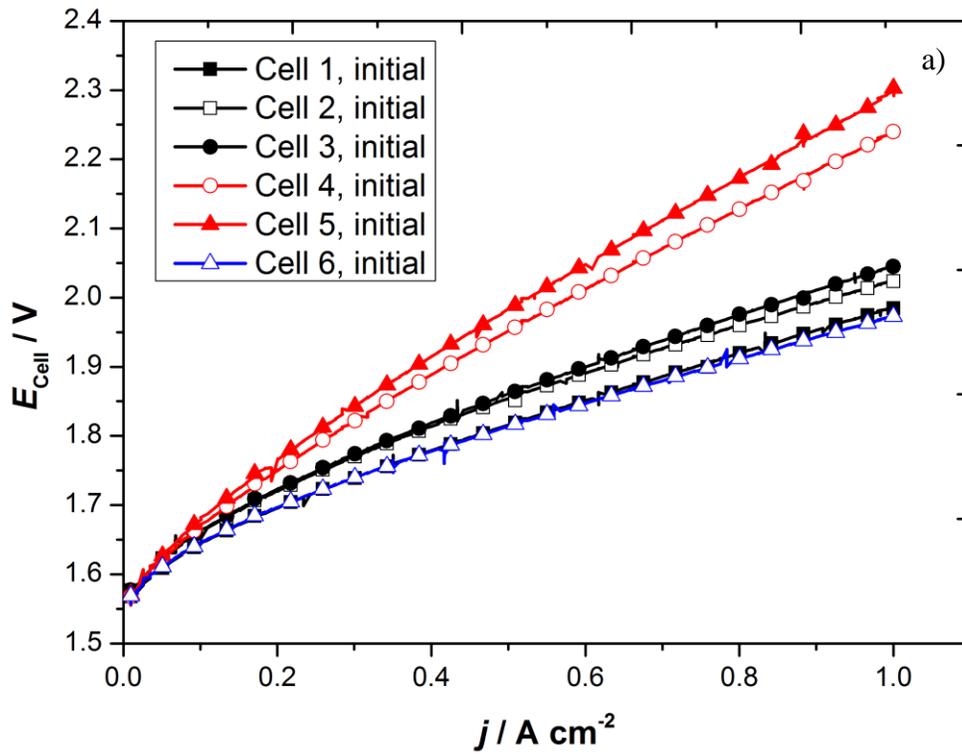


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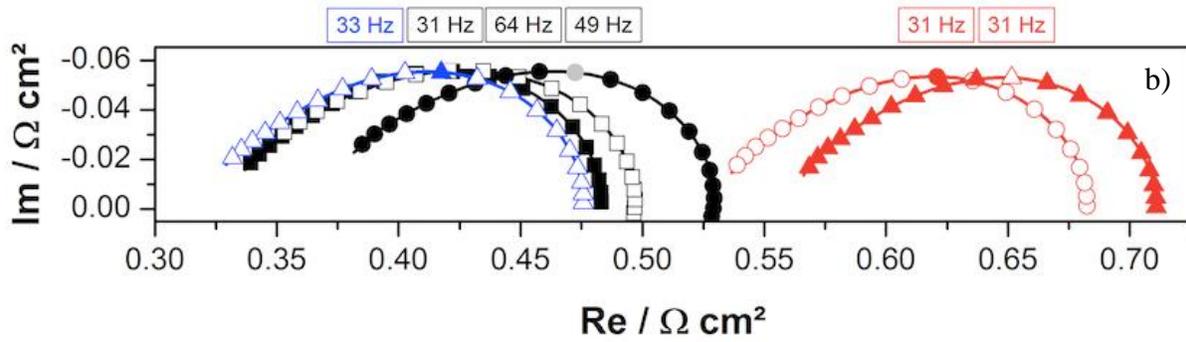
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431 **Fig. 2.**



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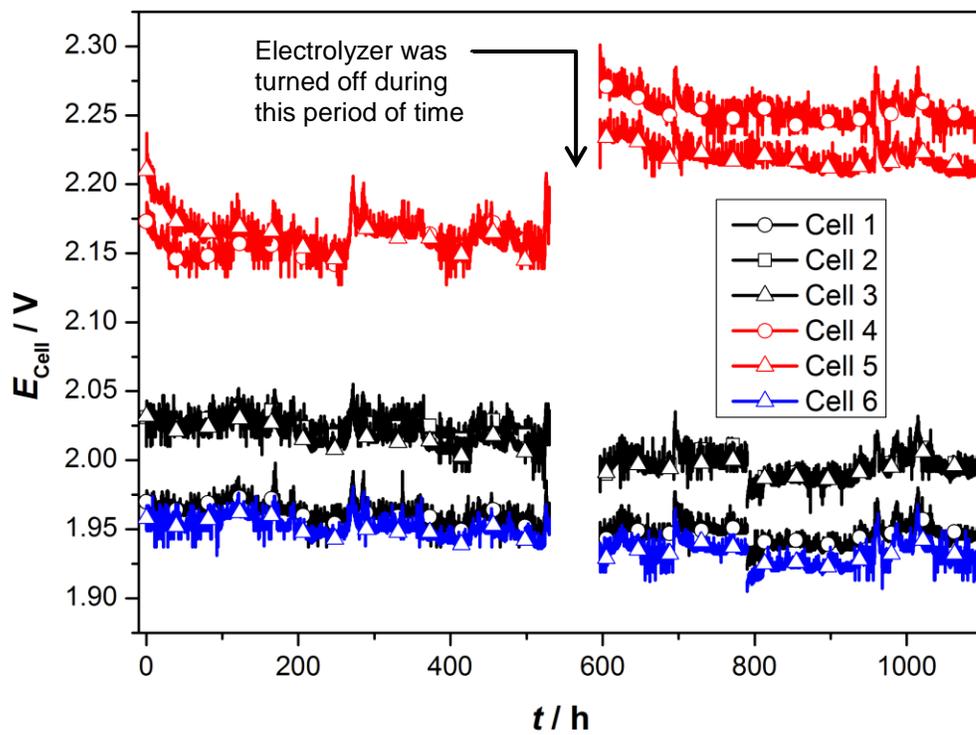


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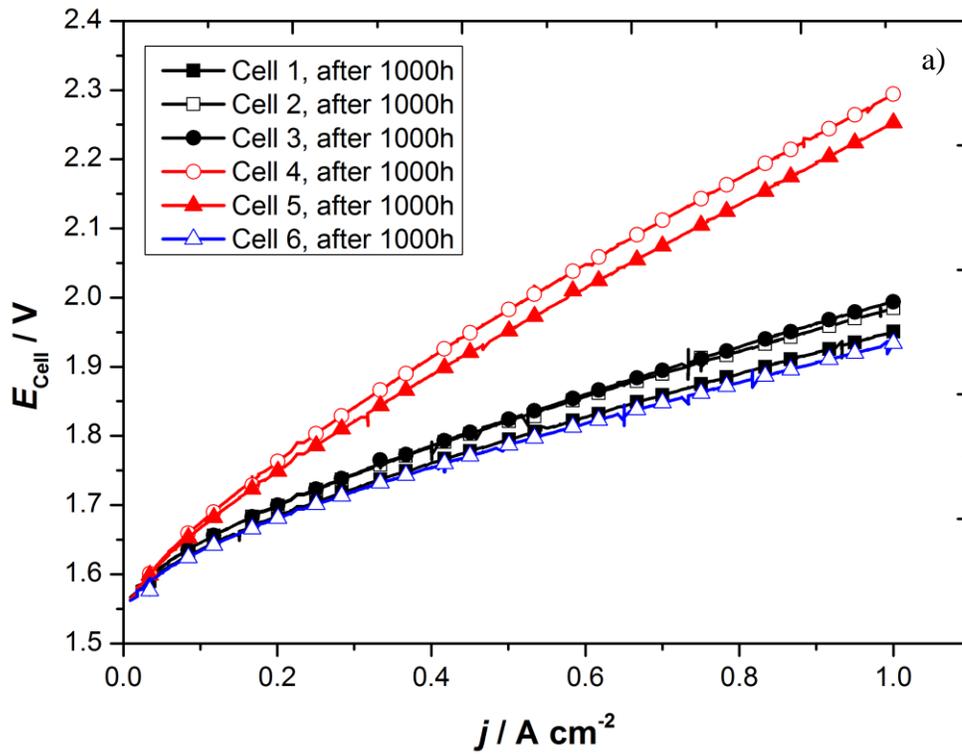
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437 **Fig. 3.**

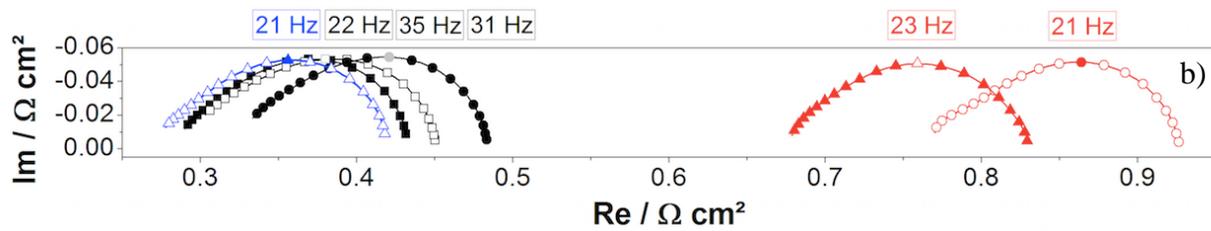


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439 Fig. 4.



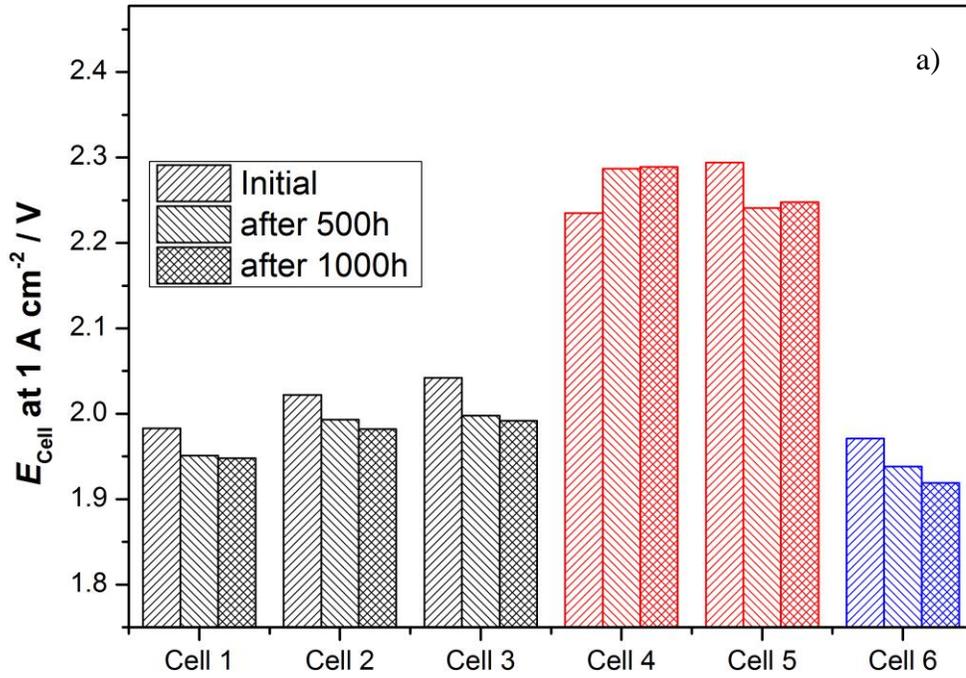
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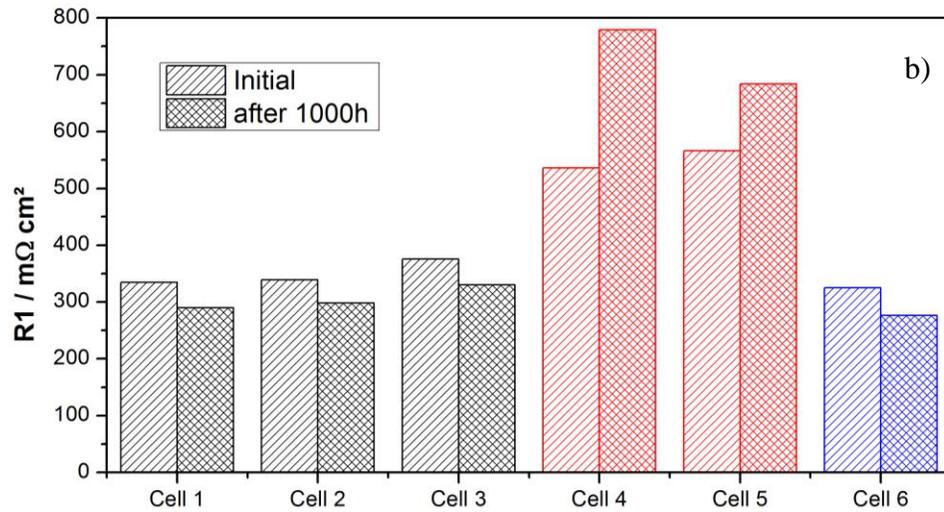
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443 **Fig. 5.**

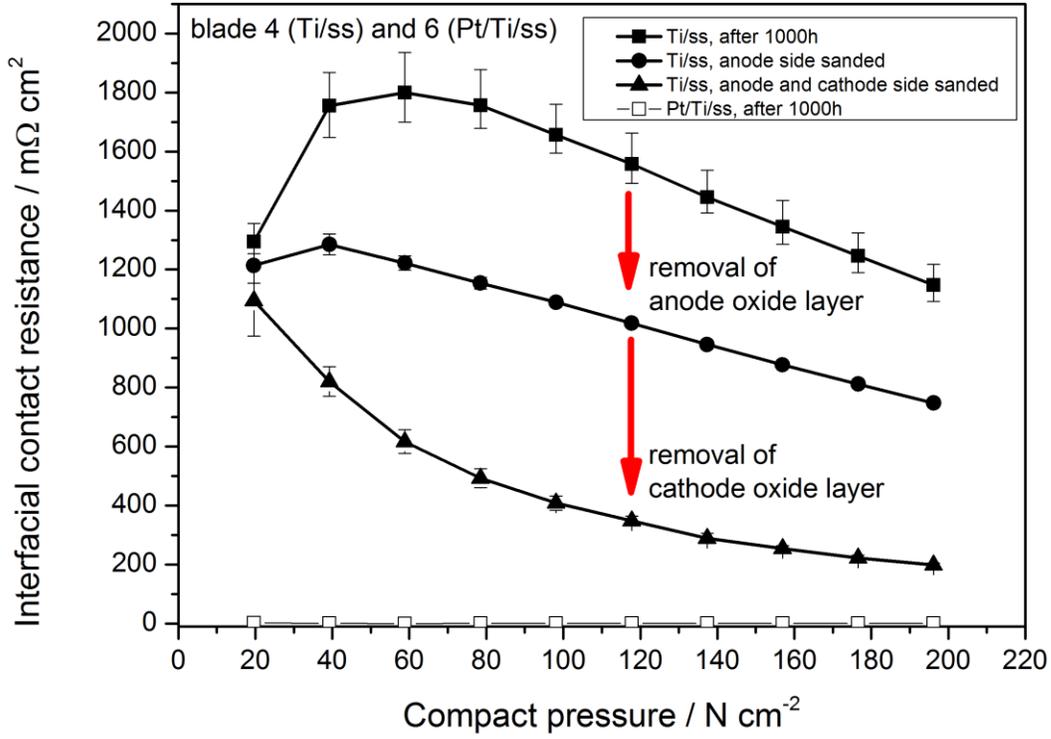


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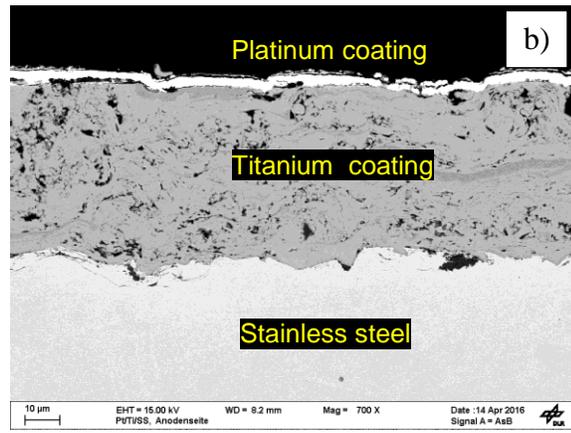
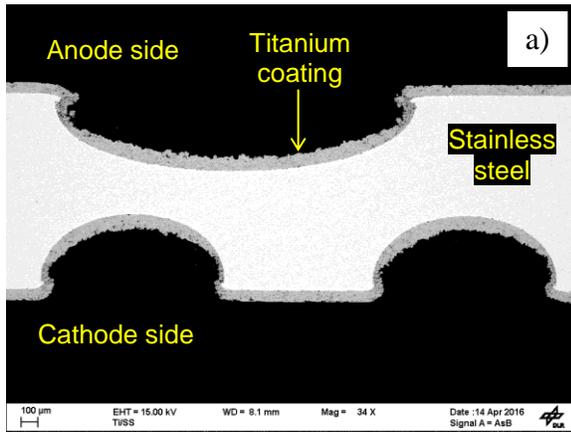
446 **Fig. 6.**



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449 **Fig. 7.**



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