

1 **Life test of a high temperature PEM fuel cell prepared by electrospray**

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6 **Abstract**

7 A life test has been conducted to a PBI-based membrane-electrode assembly
8 (MEA) in which the anode and cathode catalyst layers were prepared by
9 electrospray and results were compared with a previous study in which the catalyst
10 layer was prepared by airbrushing. During the study, the average and local current
11 density were continually monitored and several diagnostic techniques were
12 periodically applied, including polarization curves, cyclic voltammetries,
13 electrochemical impedance spectroscopy and computational fluid dynamics
14 modeling (CFD). Results show that significantly better fuel cell performance is
15 achieved by the electrosprayed MEA, by about 40%, as compared with the MEA
16 prepared by traditional airbrushing with the same catalyst loading. According to the
17 experimental measurements, the higher electrochemical active surface area and
18 more favorable mass transport are the main responsible for the improved yield.
19 Modeling estimations agree with experimental observations and corroborate better
20 mass transport properties of the catalyst layer when using electrospray. This can be
21 explained by a more appropriate morphology of the layer. No evidence of positive
22 effects on the lifetime of the fuel cell was found out. At the end of the lifetest, the
23 local concentrations of platinum (Pt) and phosphorus (P) in the degraded MEA were
24 analyzed and a correlation between Pt loading profile and local current distribution
25 could be established.

26 **Keywords:** Electrospray, PBI, PEM fuel cell, life study, postmortem.

27 **1. Introduction**

28 One of the main problems that limit the introduction of fuel cells in the market
29 and their massive commercialization is their high price. Therefore, institutions such
30 as the European Commission and the Department of Energy of the U.S.A include in
31 their guidelines the reduction of production cost as one of the key points for fuel
32 cells to be commercialized in the near future [1, 2]. In the case of PEMFC there is
33 an item of the investment cost of great relevance: the catalyst. Doing a rough
34 estimation, platinum may represent around 40% of the total cost of a PEM fuel cell,
35 in both low and high temperature technologies.

36 The reduction of Pt loading without severely affecting fuel cell performance is
37 possible by several means, being one of them the improvement of electrode
38 preparation and Pt deposition [3]. There exists a number of different methods to
39 prepare electrodes (tape-casting, spraying, painting, sputtering, filtering, etc.) for a
40 PEM fuel cell [4-9] and all of them aim at achieving a proper morphology and
41 structure in order to attain better catalyst utilization. Amongst them, one of the
42 most promising is the electrospray deposition of a catalyst ink onto the gas
43 diffusion layer.

44 The electrospray deposition technique, which was applied to the preparation of
45 electrodes for low temperature PEM fuel cells by Baturina and Wnek [10] and
46 Benítez et al. [11, 12], consists of the generation of an aerosol phase from a
47 suspension of particles, thanks to the action of a strong electric field. When it is
48 employed to make PEMFC electrodes, the electric potential is applied between an
49 ejector needle and the substrate where the catalyst layer needs to be deposited. A
50 suspension containing the different components of the catalyst layer (ink) is
51 transferred into an aerosol, which is formed by highly disperse charged particles
52 that deposit on the substrate under the electrostatic interaction. Under appropriate
53 conditions, a film with high catalytic performance and porous dendritic morphology
54 can be obtained. Such film is characterised by a highly porous structure in the

55 meso- and macroporosity range, with pore volumes per gram of carbon of up to 12
56 $\text{cm}^3/\text{g}_\text{c}$, against 1.8-2.5 $\text{cm}^3/\text{g}_\text{c}$ for standard airbrushed layers, as measured with
57 mercury porosimetry [13]. Model estimations of the catalyst layer porosity in this
58 work corroborate the important porosity increase with electro sprayed films. A
59 recent localized reference electrode study has shown that the high porosity of the
60 catalyst layer favors lateral homogeneity of cell response as a consequence of
61 improved mass transport within the cell [14]. Ultra-low platinum loadings have
62 been used with promising results in Nafion-based fuel cells [15-17], obtaining a
63 comparable performance to electrodes prepared by sputtering.

64 Most studies with electro sprayed catalyst layer have been mostly dedicated to
65 their application in low temperature PEMFC. The first study, to our knowledge, on
66 the use of electro spray-prepared electrodes in PBI-based PEM fuel cells has been
67 communicated in Ref. [18] showing improved performance with respect to
68 conventional layers prepared with airbrushing. The porous morphology of the
69 electro sprayed layers improves reactants accessibility and transport within the
70 catalyst layer also within a PBI based cell. However, no information was reported
71 about the stability of this cell type when using electro sprayed catalyst layer. A
72 change in stability is to be expected with catalyst layer morphology, since
73 degradation processes like carbon corrosion and platinum dissolution, also depend
74 on mass transport properties under certain conditions. For instances, in a cell
75 operated under high current density, corrosion reactions may exacerbate by
76 localized starvation phenomena and lateral inhomogeneities that appear as a
77 consequence of slow mass transport. Such phenomena are especially acute in low
78 temperature PEMFC due to the presence of liquid water that must be transported
79 through the porous medium at a high rate [19-21]. In PBI cells working at higher
80 temperatures, water transport in the vapor phase may be faster, although corrosion
81 reactions are accelerated by the higher working temperature. It is, therefore, of
82 high interest to analyse if there is an effect of the electro sprayed layer on the
83 durability of this type of cell.

84 In this paper, we aim at studying the break-in and degradation (typical life test)
85 of a PBI PEM fuel cell whose electrodes have been prepared by the electro spray
86 technique, identifying the reasons that cause it by means of experimental
87 characterization (including current density distribution, electrochemical
88 characterization with different techniques and physico-chemical characterization of
89 the MEA after the life test). Experimental results are complemented with modelling
90 based on computational fluid dynamics, as developed in previous works [22-24].

91 It is also of interest to compare the results obtained in this study with those of
92 the life test study performed to the MEA presented in Ref. [25], prepared by
93 manual airbrush.

94

95 **2. Experimental and modeling**

96 *MEA preparation*

97 To prepare the membrane-electrode assembly (MEA), two 49 cm² square
98 electrodes with 0.25 mg cm⁻² Pt loading, the same as that used in Ref. [25], were
99 fabricated. In the first place, a microporous layer constituted by carbon black
100 (Vulcan XC-72) and polytetrafluoroethylene was manually sprayed onto a piece of
101 carbon fiber paper (TORAY TGPH-90) until the desired carbon loading was achieved.
102 Next, the catalyst layer was deposited using the electro spray technique [13]. In
103 order to prepare the catalytic ink, Pt/C (E-TEK 40 wt. % Pt on carbon Vulcan XC-
104 72) and polybenzimidazole (PBI) were dispersed into a dimethylacetamide solution.
105 Then, the electrodes were assembled by hot-pressing them with a PBI membrane in
106 between. This membrane had previously been casted from a PBI solution and
107 immersed into a 75 wt. % H₃PO₄ bath until a doping level of around eight molecules
108 of acid per polymer repeating unit was reached.

109 *Fuel cell set-up*

110 The so-prepared MEA was inserted between two graphite end plates where 4-
111 step serpentine flow channels are mechanized. A sensor plate for current
112 distribution measurement (S++, Germany) was placed behind the end plate of the
113 cathode side. Finally two additional thick plates that provide with mechanical
114 support and allow for heating the device by means of integrated electric heaters
115 were also disposed. A detailed description of the arrangement is available in Ref.
116 [26].

117 *Lifetime study*

118 The lifetime study was performed respecting the procedure applied in Ref [25].
119 Essentially, this consisted of the operation of the fuel cell at 150 °C and at a
120 constant potential of 0.60 V while the average and local current density values were
121 recorded. Additional electrochemical tests were carried out periodically in order to
122 assess at different times the global performance of the fuel cell and its components.
123 Thus, the continuous operation was regularly interrupted to perform polarization
124 curves, cyclic voltammetries, hydrogen crossover measurements and
125 electrochemical impedance spectroscopy (EIS). A potentiostat/galvanostat
126 (Ecochemie, The Netherlands) coupled with a Frequency Response Analyzer (FRA)
127 was used for this purpose.

128 Throughout the lifetime study, 100 mL min⁻¹ (STP) dry hydrogen and 100 mL
129 min⁻¹ (STP) dry pure oxygen were fed. Polarization curves were performed at a scan
130 rate of 1 mV s⁻¹ at the same operating temperature as the lifetest. Inlet flow rates
131 were 675 mL min⁻¹ (STP) dry air and 211 mL min⁻¹ (STP) dry hydrogen. Current
132 density distribution was simultaneously measured, recording a map every 0.5 s,
133 which allowed the obtaining of local polarization curves as well as the evolution of
134 local current density. Cyclic voltammetries were carried out at a scan rate of 100
135 mV s⁻¹ and again at operating temperature. Measuring the areas at high
136 temperature gives rise to lower absolute values due to thermodynamics and
137 kinetics changes [27] but it allows following area changes without altering the

138 degradation process. Humidified N₂ was fed to the cathode side, while dry hydrogen
139 was introduced in the anode side. The integration of hydrogen desorption peak was
140 the way used to evaluate the cathode electrochemical active surface area. The
141 same cell configuration was used to measure hydrogen crossover current at 0.5 V.
142 Impedance spectra experiments at $i=0.02$ A cm⁻² and at $E_{cell}=0.70$ V were
143 performed to measure membrane resistance and charge transfer resistance. Dry
144 pure oxygen and dry hydrogen were used.

145 *Post-mortem analysis*

146 A physico-chemical study of the degraded MEA was carried out. This post-
147 mortem analysis was performed by taking the MEA out from the fuel cell once the
148 life study was completed and dividing it into 16 portions. Then, the platinum (Pt)
149 and phosphorus (P) content of each piece were measured. To this end, they were
150 separately treated in aqua regia (HNO₃/HCl 1:3) and heated up in a microwave
151 oven (Ethos Plus, Milestone, U.S.A.) to boost the acid attack. The thermal
152 treatment consisted of a temperature ramp from 25 °C to 190 °C, finishing with a
153 10 min period at this temperature. The samples were cooled at room temperature
154 for 24 h to finally measure P and Pt concentration by the use of ICP-AES (Liberty
155 Sequential, VARIAN, U.S.A.). The results obtained were related to the Pt and P
156 loading of the MEA portion.

157 *Modelling*

158 A simulation tool was applied to assess the conditions of the different
159 components of the fuel cell during the lifetime study. This tool is based on the
160 implementation of a high temperature full-cell model in COMSOL Multiphysics v 3.5.
161 After a thorough sensitivity analysis applied to the relevant parameters, a
162 methodology to evaluate the most representative properties of the fuel cell at local
163 level could be proposed. References [22-24] can be consulted if more information is
164 desired.

165

166 **3. Results and discussion**

167 Figure 1 shows the average current density measured at $E_{cell}=0.60$ V throughout
168 the life test. For comparison purposes, the study commented in Ref. [25] (MEA
169 made by airbrushing) has been overlaid.

170 **Figure 1 over here**

171 The average current density measured to the MEA prepared by electropray was
172 significantly higher. The performance improvement with respect to the airbrush
173 assembly is around 40% in terms of output power density. In the new assembly,
174 the conditioning-degradation trend can be clearly observed also. Like for the
175 airbrush assembly, the maximum average current density is reached after 37 h.
176 Apparently, the best performance is kept for some hours, and then a decay is
177 observed.

178 The curves show periodic transient steps which correspond to start-stop events
179 to proceed with characterization. Each peak matches with the restart of normal
180 operation after the interruption to perform additional measurements. According to
181 Cleghorn et al. [28], this performance recovery would correspond to reversible
182 losses whose sources are removed during the interruption periods. Formation of Pt
183 oxides and adsorption of poisons in the catalyst (which are removed while
184 performing the complementary tests) are probable causes for this behavior. In the
185 airbrush cell curve, the performance recovery when restarting operation, if any,
186 occurred to a much lower extent.

187 At 197 h, the average current density generated decayed 10% with respect to
188 the initial value, which indicates improved durability for the electropray-prepared
189 MEA. In fact, the initial improvement during the break-in is larger for this cell,
190 which makes that 90% of the initial current density is reached at later time. The
191 average current density decay rate from the end of the activation stage until the

192 end of the experiment was 0.246 mA cm⁻² h⁻¹, whereas for the assembly prepared
193 by airbrush was 0.254 mA cm⁻² h⁻¹, which apparently indicates that the deposition
194 method does not significantly affect the performance loss rate.

195 Localized current measurements give more insight into the response of the cells.
196 These measurements were also obtained during the entire life test, so the evolution
197 of local current density is available. The sensor plate for current distribution
198 measurement counts with 100 segments (0.25 cm² each), but, for the sake of
199 clarification, the cell has been (fictitiously) divided into 16 regions only,
200 representing each one the average current density of the group of segments
201 comprised in the region in question. Figure 3 shows the local evolution of current
202 density in the different regions. Again, the assembly prepared by airbrushing has
203 been included in the figure for comparison.

204 **Figure 2 over here**

205 **Figure 3 over here**

206 All the regions show the same general trend of activation-degradation, as
207 observed in Fig.1. Curves appear, however, shifted vertically indicating that the
208 current density generated in each region is different, and there are also some
209 differences in their activation and degradation rates. Central segments (6,7,10,11)
210 show higher response over time. Figure 4 shows relative standard deviation of the
211 average current density during the break-in. The results obtained in Ref. [25] have
212 also been included with grey markers and dashed grey line. (This colour code will
213 be repeated in the rest of figures where a comparison is made between the airbrush
214 and the electrospray-prepared MEAs). Relative Standard Deviation (RSD) is defined
215 in Equation (1).

216

217
$$RSD = \sqrt{\frac{\sum(i_s - i)^2}{n}} / i \quad (1)$$

218

219 Except for a slight increase at the beginning of the experiment, the relative
220 standard deviation of the average current density remains constant in this period,
221 demonstrating the same behaviour as in the previous assembly studied. Thus, it
222 could be concluded that the RSD of the average current density does not change
223 during the activation stage.

224 Figure 5 shows images of the current density distribution, expressed as relative
225 deviation from the average current density, during the first 37 h of experiment for
226 the electro spray cell. This representation type allows to follow lateral inhomogeneity
227 in current response.

228 **Figure 4 over here**

229 **Figure 5 over here**

230 The central zone of the electrode is the most active, namely Regions 7 and 11,
231 whereas the corners show poorer performance. Although some minor changes can
232 be observed, the map essentially keeps its profile during the whole period,
233 repeating this assembly the behaviour observed for the airbrush MEA.

234 Figure 6 shows the RSD of the average current density during the degradation
235 stage. For the MEA prepared by electro spray, the observation is an increase of the
236 RSD at the final time with respect to the beginning of the stage. However, the
237 evolution is different to the previous assembly, since in this case the RSD is stable
238 until 120 h approx. and starts to increase then. The lower RSD values observed
239 throughout the life study for the assembly prepared by electro spray reveal that
240 current density distribution is more uniform in relative terms.

241 **Figure 6 over here**

242 Figure 7 shows the current distribution maps during the degradation period. The
243 relative differences between regions keep almost invariable until 117 h of
244 experiment, moment when red colours move towards the right side of the
245 electrode, indicating lower degradation rates of Regions 4, 8 and 12. On the other

246 hand, the appearance of lighter colours in Regions 6 and 8 denotes that they loss
247 their activity more quickly than the rest. The time when shifts in Figure 7 start to
248 be noticed coincides with the beginning of RSD increase observed in Figure 6, in the
249 same way that occurred with the airbrush assembly. This leads to associate a
250 change in the Relative Standard Deviation of the average current density with a
251 shift in the current density distribution map and with a decrease in the fuel cell
252 performance. For the reader's convenience, the evolution of current density
253 distribution during the lifetime study performed to the airbrush assembly is
254 presented in Figure 8.

255 **Figure 7 over here**

256 **Figure 8 over here**

257 As explained in Section 2, the normal operation was periodically interrupted in
258 order to acquire more information on the performance of the fuel cell. Polarization
259 curves allowed for the evaluation of the global and local performance under
260 different loads, while cyclic voltammetries enabled to follow the evolution of
261 electrochemically active surface area during the lifetime of the cell. Finally, EIS
262 analysis was employed to measure the evolution of charge transfer and ohmic
263 resistance.

264 Figure 9 shows the polarization curves obtained at different times of the life
265 study. The evolution of the maximum power yielded by the fuel cell essentially
266 agrees with the degradation trend observed in Figure 1. The polarization curves
267 suggest that the degradation process of the two assemblies is caused by a
268 combination of loss of catalytic activity, increase of ohmic resistance and worsening
269 of mass transport properties. However, the degradation appears to be more
270 intensive under higher loads for the airbrush assembly, which could be due to a
271 quicker deterioration of mass transport properties.

272 **Figure 9 over here**

273 Figure 10 shows the most relevant results of the voltamperometric and EIS tests
274 performed in order to study the catalyst conditions during the life study. Thus, the
275 electrochemically active surface area (*ESA*) determined by cyclic voltammetry and
276 the charge transfer resistance at 0.70 V determined by EIS analysis are plotted vs.
277 operation time.

278 **Figure 10 over here**

279 The charge transfer resistance is lower in the electrodes prepared by
280 electrospray and the values of *ESA* are significantly higher. This verifies that the
281 better general performance observed in Figure 1 is in part due to better catalyst
282 features when the catalyst layer is built-up by electrospray.

283 Figure 11 shows the evolution of electrolyte resistance at $i=0.02 \text{ A cm}^{-2}$
284 (measured by EIS) as well as the crossover current density during the life test.

285 **Figure 11 over here**

286 It can be checked that the initial and final electrolyte resistance are comparable
287 in both cases. However, the decrease observed in the electrospray assembly during
288 the activation stage is much less important than in the airbrushed one. It is not
289 expected that the deposition technique has such a strong influence on the
290 conductivity of the system, hence the differences measured and estimated in the
291 absolute values and their evolution must lie in some non-controlled variable due to
292 the manual production of membranes. The crossover current observed in Figure
293 11(b) is very similar in both cases and stable during the whole operation time,
294 which helps ascertain that membrane catastrophic failure did not occur.

295 With the experimental local polarization curves acquired during the life test and
296 the assistance of CFD simulation, it was possible to assess the value of the
297 characteristic parameters related to the fuel cell performance in the 16 regions
298 considered and at different times of the experiment. The process involved the

299 tuning of these parameters in order to fit the local polarization curves predicted by
300 a validated model to those experimentally measured. The model predictions show
301 trends for the cathode exchange current density and the electrolyte conductivity
302 that agree well with their respective related parameters experimentally measured
303 and presented in Figures 10 and 11. The estimations are particularly of interest in
304 the case of the porosity of the electrode, parameter linked to the morphology of the
305 catalyst layer that could not be experimentally measured during the test. According
306 to the model, porosity is higher for the electrospray assembly (ca. 0.3 vs 0.23 at t=
307 0 h). Furthermore, soon after the test starts, the porosity of the airbrush assembly
308 decreases significantly, contrasting with the higher stability predicted for the
309 porosity of the electrosprayed one (ca. 0.25 vs 0.1 at t=227 h). These results
310 indicate that the electrospray assembly has a catalyst layer with more appropriate
311 morphology for mass transport that is also more stable, which explains the
312 observations made in Figure 9 at higher current loads. The complete model results
313 can be consulted in Appendix A.

314 After the end of life of the assembly, the steps detailed in Section 2 were
315 followed in order to obtain platinum and phosphorus distributions. These, together
316 with the current density distribution map at the final time (Figure 7, t=227 h) in a
317 resolution of 4x4 have been represented in Figure 12.

318 **Figure 12 over here**

319 The platinum loading distribution shows a particular pattern, with higher
320 concentration in the central zone getting lower towards the corners. This
321 characteristic profile is a consequence of the electrospray process that has favoured
322 deposition on the centre of the substrate than on the corners, following changes in
323 the electric field intensity and creating a distribution as that shown in Figure 11(b).
324 Although the Pt loading measured corresponds to the total amount (anode +
325 cathode), it is very likely that the two electrodes had a very similar distribution

326 given that Pt was deposited by an automatized procedure. Then, the combination of
327 both should result in a pattern of the same shape. Thus, the catalyst relative
328 loading distribution shown in Figure 12(b) can be considered a good approximation
329 of the catalyst distribution of both cathode and anode separately.

330 The current density map (Figure 12(a)) has significant similarities with Pt
331 distribution, with the difference that the center of activity is shifted towards the
332 upper right-hand corner.

333 Figure 13 shows the parameter i_c^{ex} calculated by the mathematical model plotted
334 at four times of the life study. It is remarkable that the cathode exchange current
335 density profiles at t=0 h and t=37 h are almost identical to the Pt loading
336 distribution observed in Figure 12(b). This similarity is not so evident at t=121 h
337 and t=227 h, which indicates that the catalyst activity at these times is not only
338 determined by Pt concentration. Thus, the possibility of a strong link between Pt
339 loading distribution in the cathode and current density distribution is evident,
340 especially at the beginning of the lifetime of the MEA. The post-mortem analysis
341 carried out to the airbrushed MEA did not reveal this connection because it was not
342 possible to guess the Pt loading profile in the cathode from the measured total Pt
343 distribution.

344 **Figure 13 over here**

345 The PBI membrane thickness before assembly is shown in Figure 14. Thinner
346 regions are not the most active, so apparently membrane unevenness is not a key
347 issue in performance heterogeneity.

348 **Figure 14 over here**

349 The conductivity profile evaluated with the simulation tool, shown in Figure 15,
350 does not undergo important relative changes during the life time of the fuel cell. In
351 this case, the less conductive regions apparently coincide with the thicker zones of

352 the membrane (Figure 14), but no resemblances with the P distribution can be
353 observed.

354 **Figure 15 over here**

355 **4. Conclusions**

356 The application of the electrospray technique to build up the catalyst layers of a
357 PBI-based high temperature PEMFC results in a remarkable performance
358 improvement if compared with a MEA prepared by traditional airbrushing. According
359 to experimental and modelling diagnostic tools applied, the improvement was due
360 to better catalyst utilization and enhanced mass transport properties of the catalyst
361 layer. In terms of durability, no relevant advances were achieved. The performance
362 decay was found to be mainly caused by progressive loss of electrochemical active
363 surface area, which suggests that catalyst agglomeration took place during the
364 lifetime of the fuel cell. The catalyst distribution in the electrodes was not uniform
365 and showed higher concentration in the center than in the corners. A very similar
366 contour of local current density was measured during the life test, which revealed
367 the correlation between local catalyst loading and local performance. No such a
368 correlation could be inferred for phosphorus distribution or membrane thickness
369 and the measured current density. Thus, further improvements in the catalyst
370 deposition technique that lead to uniform Pt distribution could result in notable
371 enhancement of fuel cell performance.

372

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467

468 **NOMENCLATURE**

469

470 E potential (V)

471 i current density ($A\ m^{-2}$)

472 n number of segments

473 R resistance ($Ohm\ cm^{-2}$)

474

475 **Greek letters**

476 α transfer coefficient

477 ε porosity

478 κ conductivity (S m^{-1})

479

480 **Subscripts and superscripts**

481

482 c cathode

483 $cell$ cell

484 ct charge transfer

485 ex exchange

486 l electrolyte phase

487 mem membrane

488 s segment