

# 1 **Revealing In-plane Movement of Platinum in PEFCs after Heavy-duty Vehicle Lifetime**

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14

## 15 **Abstract**

16 Fuel cell heavy-duty vehicles (HDVs) require increased durability of oxygen reduction reaction  
17 electrocatalysts making knowledge of realistic degradation mechanisms critical. Here, identical location  $\mu$ -  
18 X-ray fluorescence spectroscopy was performed on membrane electrode assemblies (MEAs). The results  
19 exposed heavy in-plane movement of electrocatalyst after HDV lifetime, suggesting that electrochemical  
20 Ostwald ripening may not be a local effect. Development of local loading hotspots and a preferential  
21 movement of electrocatalyst away from cathode catalyst layer cracks was observed. Heterogeneous  
22 degradation showed by a modified cathode gas diffusion layer MEA after HDV lifetime was successfully  
23 quantified thanks to the identical location approach. Further synchrotron  $\mu$ -X-ray diffraction and  
24 fluorescence experiments were performed to obtain currently unknown correlation between electrocatalyst  
25 nanoparticle size increase and loading change. A direct correlation was discovered which developed only  
26 after HDV lifetime. The work provides direction to engineer immediate system-level mitigation strategies  
27 and to develop structured cathode catalyst layers with durable electrocatalysts.

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33 To achieve zero carbon emissions, governments and industries across the world are implementing the use  
34 of clean hydrogen, targeting difficult to decarbonize sectors such as heavy-duty transportation, aviation,  
35 shipping and chemical manufacturing. Heavy-duty vehicles (HDVs) make up only 7 % of the total vehicles  
36 on-road<sup>1</sup> but produce nearly 26 % of the United States (US) transportation sector greenhouse gas emissions<sup>2</sup>.  
37 Polymer electrolyte fuel cells (PEFCs) are an excellent candidate to power emission free HDVs particularly  
38 due to their ability to increase driving range at a much smaller additional weight penalty. However, initial  
39 system cost remains a significant challenge for large scale adoption mainly due to the use of platinum-group  
40 metal (PGM) electrocatalysts to promote oxygen reduction reaction (ORR). For a projected manufacturing  
41 volume of 100,000 systems/year, the calculated PEFC stack cost is \$41.93/kW of which 53% is contributed  
42 by electrocatalyst and applications<sup>3</sup>. Current approach to reduce initial cost and improve performance by

43 utilizing highly dispersed PGM nanoparticles (2-3 nm) on carbon support adversely affects stack lifetime<sup>4</sup>  
44 <sup>6</sup>. Small well-dispersed nanoparticles result in improved PGM utilization by effectively increasing the  
45 electrochemically active surface area (ECSA). This boosts power density while reducing PGM loading and  
46 cost/kW. However, repeated oxidation-reduction of platinum (Pt) nanoparticles during HDV lifetime  
47 causes Pt dissolution in the cathode catalyst layer<sup>4,6</sup>. This dissolution leads to loss in the ECSA via  
48 deposition of Pt in the membrane and increase in Pt nanoparticle size through electrochemical Ostwald  
49 ripening and/or coalescence<sup>6,7</sup>. In addition, nanoparticles of Pt alloyed with transition metals such as cobalt  
50 (Co) and nickel (Ni) to reduce cost while enhancing ORR activity face significant leaching of transition  
51 metals within the voltage-pH range of PEFC operation<sup>8</sup>. Such transition metal leaching negates achieved  
52 improvement in ORR activity at the beginning of life. It also affects proton conduction and oxygen transport  
53 properties of ionomer causing loss in high current density performance<sup>9</sup>. The complex balance between  
54 cost, performance and durability of PEFCs coupled with the 2050 projection of 54% increase in HDV miles  
55 travelled<sup>10</sup> makes understanding electrocatalyst degradation a top priority to develop durable ORR  
56 electrocatalysts.

57  
58 Recently, *in situ* identical location transmission electron microscopy (IL-TEM) and *ex situ* identical  
59 location scanning transmission electron microscopy (IL-STEM) techniques using aqueous electrolyte  
60 rotating disk electrode (RDE) setup have been utilized to elucidate electrocatalyst degradation  
61 mechanisms<sup>11,12</sup>. The more common IL-STEM uses a gold coated TEM grid which allows atomic level  
62 imaging, energy dispersive X-ray spectroscopy (EDS) and electron energy-loss spectroscopy (EELS)  
63 analysis of electrocatalyst in the same region at different lifetime stages. Results from above discussed  
64 techniques combined with flow cell inductively coupled plasma mass spectroscopy (ICP-MS) have  
65 identified Pt dissolution as the primary and dominant degradation mechanism followed by Pt nanoparticle  
66 size increase through migration-coalescence and Pt nanoparticle detachment from carbon support.  
67 Contrarily, membrane electrode assembly (MEA) tests have shown that nanoparticle size increase by  
68 electrochemical Ostwald ripening is the dominant degradation mechanism<sup>13</sup>. Such disparity is caused by  
69 the complicated cathode catalyst layer operation environment within MEA, where multiple transport  
70 processes at the electrocatalyst-support-ionomer interface play a crucial role<sup>14</sup>. In addition to electrocatalyst  
71 and ionomer properties, the transport processes are also affected by the operating conditions, PEFC  
72 components and cathode catalyst layer morphology<sup>15,16</sup>. This is also the reason for poor translation of  
73 electrocatalyst ORR activity from RDE to MEA-scale<sup>14</sup>. Furthermore, electrocatalyst degradation is  
74 strongly influenced by loading, and RDE working electrodes employ ultra-low electrocatalyst loading  
75 deposited on either carbon or gold surface compared to MEA-scale where a much higher loading is  
76 deposited on membrane resulting in a 100x loading difference. This can lead to degradation rates that  
77 deviate substantially from realistic conditions. Various studies have attempted to eliminate this disparity by  
78 using different electrolyte flowrates, operating temperatures and electrode configurations in the RDE  
79 setup<sup>12,17</sup>. However, concerns regarding the relevance of identified RDE-scale degradation mechanisms to  
80 MEA-scale remain<sup>14</sup>. To date, MEA-scale AST studies commonly rely on *ex situ* TEM of scraped  
81 electrocatalyst from the cathode catalyst layer and SEM/EDS analysis of MEA cross-sections<sup>7,13</sup>. Although,  
82 this reveals nanoparticle size increase and through-plane changes like Pt band formation, the techniques  
83 fail to capture in-plane degradation phenomenon. Recently synchrotron  $\mu$ -X-ray diffraction studies revealed  
84 important in-plane heterogeneity in Pt nanoparticle size increase due to influence of operating conditions  
85 and PEFC components<sup>18,19</sup>. Thus, to mitigate the risk of misidentifying degradation mechanisms and  
86 misdirecting the electrocatalyst material development it is very important to validate the results with  
87 thorough MEA-scale analysis which captures realistic aspects of electrocatalyst degradation.

88  
89 Here, commercially available catalyst coated membranes (CCMs) designed for potential HDV application  
90 were subjected to accelerated stress tests (ASTs) simulating HDV lifetime. A simple method was utilized  
91 to achieve MEA-scale identical location  $\mu$ -X-ray fluorescence (IL- $\mu$ -XRF) spectroscopy maps before and  
92 after the AST. From the total three-dimensional movement, IL- $\mu$ -XRF mapping of the MEAs performed  
93 near the inlet and outlet regions of cathode gas flow field captured the two-dimensional in-plane movement

94 of Pt electrocatalyst. Analysis of identical locations revealed distinct changes in Pt loading strongly  
95 influenced by its initial distribution and by cathode catalyst layer morphology. A modified cathode gas  
96 diffusion layer (GDL) MEA was used to highlight the effect of PEFC components on electrocatalyst  
97 degradation. The resulting heterogeneous Pt degradation was successfully quantified using the developed  
98 method. Finally, synchrotron  $\mu$ -X-ray diffraction ( $\mu$ -XRD) and  $\mu$ -XRF experiments were performed  
99 successively on identical locations to establish a currently unknown correlation between nanoparticle size  
100 increase and changes in loading after the AST. Electrochemical characterization was performed at various  
101 stages of the AST to support the spectroscopic analysis.

## 102 **Simulating HDV lifetime**

103 Using a representative HDV drive cycle for Class 8 truck reported by the California Air Resource Board,  
104 the National Renewable Energy Laboratory simulated the cell voltages for a hybrid 250 kW fuel cell  
105 system/35 kWh battery traction power system with a minimum idle power of 20 kW to limit the upper  
106 potential limit (UPL) at 0.9 V<sup>20,21</sup>. Electrocatalyst degradation is severely impacted by high UPLs, thus UPL  
107 for HDV lifetime needs to be clipped at 0.9 V to ensure that US Department of Energy (DOE) interim and  
108 ultimate system lifetime targets of 25,000 and 30,000 hours are reached<sup>22</sup>. A further low value of UPL  
109 cannot be used as it decreases overall system efficiency while causing thermal management issues. Based  
110 on the simulated cell voltages and previous DOE recommended light-duty vehicle (LDV) AST equating to  
111  $\geq 5000$  hours of system lifetime<sup>22</sup>, a square cell voltage cycle as depicted in **Figure 1a** with lower potential  
112 limit (LPL) of 0.6 V and UPL of 0.9 V with a hold time of 3 seconds each was adopted in this study. To  
113 equate the AST to  $\geq 25,000$  hours of HDV lifetime, the 6 second square cell voltage cycle was repeated for  
114 90,000 times in a non-reactive cathode gas ( $N_2$ ) environment at 80°C in 100% relative humidity (RH) under  
115 atmospheric pressure, giving a total AST time of 150 hours (Methods). Although, real-world HDV  
116 operation is in a reactive cathode gas environment (air) at wide range of temperatures and in varying RH,  
117 the  $N_2$  environment AST was selected particularly to focus on electrocatalyst degradation. Detailed and  
118 extensive benchmarking of this AST reported in the literature ensures that mechanistic conclusions drawn  
119 in this study and their implications on real-world HDV operation are highly relevant. It is also crucial to  
120 mention that several efforts primarily led by the Million Mile Fuel Cell Truck consortium (M2FCT) are  
121 ongoing to meet the urgent need of ASTs better adapted for HDV applications.

## 122 **Fundamentals of Pt degradation**

123 The standard Nernst equilibrium potential of direct dissolution reaction of Pt ions when corrected for the  
124 increased surface energy of nanoparticles can decrease to  $\sim 0.5$  V (1 nm and  $10^{-6}$  M of  $Pt^{2+}$ ) compared to  $\sim$   
125 1 V of bulk Pt. This is commonly known as the Kelvin or Gibbs-Thompson effect<sup>4</sup>. This effect can also be  
126 observed for dissolution of Pt ions during reduction reaction of Pt oxide. The equilibrium potential for  
127 dissolution of Pt ions from nanoparticles is further lowered by decreasing concentration of Pt ions<sup>4</sup>. Thus,  
128 purely based on thermodynamic analysis, significant degradation of Pt nanoparticles occurs via Pt  
129 dissolution within PEFC operational voltage (0.6 V to 1 V) and pH ( $\sim 1$  to 4) range. This also means that  
130 degradation is affected not only by electrocatalyst properties such as nanoparticle size<sup>23</sup>, distribution<sup>23,24</sup>,  
131 crystalline orientation, dispersion and carbon support type but also by the local cathode catalyst layer  
132 environment<sup>25</sup>. The local environment can be affected by operating conditions like cell temperature, RH,  
133 reactant flow rates and by PEFC components like micro-porous layer (MPL) of GDL and flow field. Cell  
134 temperature and RH are serious Pt degradation stressors which can be influenced in the local environment  
135 by cathode catalyst layer morphology. These include but are not limited to features like porosity, in-  
136 plane/through-plane Pt loading distribution and catalyst layer cracks<sup>26</sup>. Liquid water flux in the cathode  
137 catalyst layer, affected by the interplay between operating conditions, PEFC components and morphology  
138 also plays crucial role to control local RH and Pt ion concentration consequently influencing electrocatalyst  
139 degradation<sup>12,16</sup>.

144 Besides the ECSA loss due to migration-coalescence, dissolution of Pt ions results in three additional ECSA  
145 loss pathways as shown in **Figure 1b** where firstly, the Pt ions can reduce on nearby larger nanoparticles  
146 with lower surface energy. The Pt ions can also diffuse towards anode and get reduced in the membrane by  
147 crossover hydrogen to form a Pt band<sup>5,7</sup>. Physical location of such Pt band is governed by the partial  
148 pressures of hydrogen and oxygen during the AST<sup>27</sup>. For a non-reactive cathode gas (N<sub>2</sub>) environment, Pt  
149 band is located near the membrane-cathode interface. And lastly, Pt ions can completely leave the system  
150 with effluent water. This ECSA loss pathway is less explored although ICP-MS reports of effluent water  
151 have detected concentration of Pt ions<sup>12</sup>. The dominant ECSA loss pathway of course depends on the  
152 thermodynamics of Pt dissolution, but it also depends heavily on the convoluted interplay between kinetics  
153 of Pt oxidation, dissolution and reduction<sup>28</sup>. As a result, the effects of UPL, LPL and time spent at each  
154 potential limit during the AST emerge. Electrochemical analysis of MEA tests coupled with *in situ* ICP-  
155 MS studies suggest that the cathodic step of AST cell voltage cycle (i.e. stepping from UPL to LPL) causes  
156 maximum dissolution of Pt ions followed by direct dissolution during the anodic step<sup>28</sup>. The cathodic  
157 dissolution is attributed to reduction of Pt oxide (~ 0.8 V) formed at the UPL. The formation rate and  
158 coverage of Pt oxide is greatly affected by the UPL and the hold time<sup>4,28,29</sup>, respectively. Therefore, a higher  
159 value of UPL with longer hold time will result in increased Pt oxide formation and consequently higher  
160 dissolution during the cathodic step. Dissolution during the cathodic step also makes Pt degradation a  
161 function of number of AST cycles<sup>29</sup>. The rate of reduction of Pt ions is reported to be relatively high  $\leq \sim$   
162 0.6 V<sup>30</sup>. Thus, a higher value of LPL also affects the amount of Pt oxide formed at UPL during the next  
163 cell voltage cycle as less clean Pt surface is available for oxide formation. For Pt-alloy catalysts, both the  
164 time spent, and value of LPL is of higher importance since reduction potential of the base metal is  
165 involved<sup>31</sup>. Ratio of Pt dissolution during the anodic vs cathodic step is a strong function of the UPL.  
166 Anodic step dissolution is important for low UPLs, cathodic step dissolution for high UPLs and dissolution  
167 during both steps for intermediate UPLs<sup>4,28</sup>. Several studies are still ongoing to fully understand the effects  
168 of above discussed properties, conditions and parameters on electrocatalyst degradation.

## 169 170 **Electrochemical characterization**

171  
172 Polarization curves with high frequency resistance (HFR) collected at 80°C in 100% RH under 150 kPa of  
173 absolute pressure in H<sub>2</sub>-air (anode-cathode) differential conditions during various stages of the AST are  
174 plotted in **Figure 2a**. Except a very small drop within first 10,000 AST cycles, the cell HFR remains  
175 unchanged throughout the AST. Such slight initial decrease in HFR has been previously reported<sup>15</sup> and is  
176 usually attributed to additional cell conditioning. As the AST progresses and the electrocatalyst undergoes  
177 degradation, a monotonic increase in kinetic and mass transport cell overpotentials can be observed. An  
178 overpotential increase of ~ 25 mV and ~ 33 mV is seen at geometric current densities of 0.8 A.cm<sup>-2</sup> and 1.5  
179 A.cm<sup>-2</sup> respectively. Thus, the MEA achieved set DOE target of  $\leq 30$  mV<sup>32</sup> of increase in overpotential at  
180 0.8 A.cm<sup>-2</sup>. A small change in the slope of polarization curves can be noticed between 60,000 and 90,000  
181 AST cycles. As the HFR is constant, this change in slope could be due to increase in oxygen mass transport  
182 resistance usually caused by the decrease of Pt roughness factor (rf) below a threshold value<sup>33</sup>. **Figure 2b**  
183 shows ECSA (calculated by integrating the hydrogen underpotential deposition region from cyclic  
184 voltammograms in Supplementary Figure 1) plotted at different stages of the AST. The ECSA decreased  
185 by ~ 32% after 90,000 AST cycles. The loss in ECSA agrees well with the observed increase in cell  
186 overpotentials. Tafel plots generated from data collected in operating conditions same as the polarization  
187 curves but in O<sub>2</sub> cathode environment are plotted in **Figure 2c**. The ORR Tafel slope is close to literature  
188 reported value of 70 mV.dec<sup>-1</sup> in MEAs<sup>34-36</sup> and does not change through the AST. Plot inset **Figure 2c**  
189 shows the mass activity at 0.9 V calculated from the Tafel plots. A ~ 45% decrease is observed in mass  
190 activity which follows a loss trend similar to the ECSA.

## 191 192 **Identical location $\mu$ -X-ray fluorescence spectroscopy**

193

194 Using a thin polytetrafluoroethylene (PTFE) template with alignment markers (Methods), IL- $\mu$ -XRF  
195 spectroscopy was performed on MEA before and after HDV lifetime. The spectroscopy was performed in-  
196 plane on an area of 2048  $\mu\text{m}$  by 2048  $\mu\text{m}$  with a resolution of 2  $\mu\text{m}$  by 2  $\mu\text{m}$  near inlet and outlet of the  
197 serpentine cathode flow field. **Figure 3a** and **b** show the 2D IL- $\mu$ -XRF maps near inlet and outlet  
198 respectively. Corresponding loading histograms are shown in **Figure 3c** and **d**. Marked locations A,B,C in  
199 the inlet map before AST and A',B',C' after AST establish successful mapping of identical locations. Only  
200 one location is marked hereafter to signify identical location. A total average Pt loading of  $559 \pm 11 \mu\text{g.cm}^{-2}$   
201 was quantified in the before AST inlet map with presence of several local hotspots within initial  
202 distribution of Pt loading. The size of such local loading hotspots may differ, but it is a recurring feature  
203 found in various commercially available and in-house made CCMs fabricated using completely different  
204 techniques. One reason for development of such local loading hotspots is attributed to agglomeration of the  
205 carbon support influenced by solvent ratios, ionomer, drying conditions and dispersion methodology<sup>37</sup>. The  
206 before AST outlet map also shows features similar to the before AST inlet map with a total average Pt  
207 loading of  $553 \pm 11 \mu\text{g.cm}^{-2}$  which falls within the observed spatial variation of  $\pm 2\%$  (Methods). The after  
208 AST inlet and outlet maps show a total average Pt loading of  $551 \pm 11 \mu\text{g.cm}^{-2}$  and  $548 \pm 11 \mu\text{g.cm}^{-2}$   
209 respectively. A clear increase in the intensity of local loading hotspots and development of cracks can be  
210 noticed in both the inlet and outlet after AST maps. However, a higher degree of cracking can be observed  
211 in the outlet map suggesting some heterogeneous degradation between inlet and outlet. The loading  
212 histograms of inlet and outlet before AST show a unimodal initial distribution of Pt loading. The distribution  
213 stays unimodal after the AST with a negligible change in the total average Pt loading as it falls within the  
214 observed spatial variation. A larger representative area of  $\sim 4 \text{ cm}^2$  out of the  $5 \text{ cm}^2$  active area was also  
215 mapped with a resolution of 20  $\mu\text{m}$  by 20  $\mu\text{m}$  (Supplementary Figure 2a). A total average Pt loading of  $559$   
216  $\pm 11 \mu\text{g.cm}^{-2}$  and  $550 \pm 11 \mu\text{g.cm}^{-2}$  was quantified for the  $4 \text{ cm}^2$  before and after AST maps respectively.

217  
218 To study the increase in intensity of local loading hotspots, above IL- $\mu$ -XRF maps were closely examined  
219 before and after the AST. **Figure 4a** shows one of the many (Supplementary Figure 3) local 400  $\mu\text{m}$  by 400  
220  $\mu\text{m}$  areas from inlet which delineates development of such local hotspots after AST. Marked locations A  
221 and A' in **Figure 4a** clearly indicate in-plane movement of Pt which led to evolution of a hotspot where the  
222 average total Pt loading increased from  $\sim 750 \mu\text{g.cm}^{-2}$  to  $\sim 1100 \mu\text{g.cm}^{-2}$ . An average increase of  $\sim 32\%$   
223 can be seen for formation of hotspots specifically observed in **Figure 4a**. Such hotspots evolved selectively  
224 in locations with local loading already  $\geq 750 \mu\text{g.cm}^{-2}$  confirming that initial Pt loading distribution plays a  
225 crucial role in how the Pt distribution will evolve during AST. Thus, formation of such hotspots could be  
226 driven by relatively low inter-nanoparticle distance in the initial stages and later by the (resulting) larger Pt  
227 nanoparticle sizes. The striking in-plane movement of Pt on the scale of tens of  $\mu\text{m}$  after AST may signify  
228 that electrochemical Ostwald ripening in the cathode catalyst layer is not a local effect as currently believed.  
229 **Figure 4b** shows another local 400  $\mu\text{m}$  by 400  $\mu\text{m}$  area before and after AST from the outlet. Such maps  
230 also revealed a preferential movement of Pt away from the cracks making them more prominent after AST.  
231 The preferential movement of Pt could be thermodynamically driven between the regions. The transmission  
232 images (Supplementary Figure 4) showed that cracks are present before AST and become more prominent  
233 after AST. Most likely, the cracks formed during the drying step of CCM fabrication and caused sparse  
234 distribution of Pt loading within. Different studies have reported that cracks result in low breakthrough  
235 pressure for removal of liquid water<sup>38</sup>. This can cause high liquid water flux in the cathode catalyst layer  
236 cracks consequently decreasing the local concentration of Pt ions. The sparse loading distribution within  
237 cracks coupled with low local Pt ion concentration can intensify Pt degradation in and around cracks<sup>39,40</sup>.  
238 The heavy in-plane movement of Pt along with the presence of loading hotspots within  $\sim 0$  to 5  $\mu\text{m}$  of a  
239 crack certainly substantiates the role of cathode catalyst layer morphology on Pt degradation. Cracks can  
240 also aid the through-plane movement of Pt ions either towards the membrane (via ionomer phase) or out of  
241 the cathode catalyst layer (via effluent water).

242  
243 To understand if Pt degradation can be impacted by MEA components and to confirm if the developed  
244 identical location method could quantify such effects, a GDL with modified MPL was used on the cathode

245 of MEA subjected to HDV lifetime. Cracks of width  $\sim 30\text{-}50\ \mu\text{m}$  were milled in the MPL (Methods) with  
246 a pitch of 1 mm in a direction perpendicular to the land/channels of the flow field and were confirmed by  
247  $\mu\text{-X}$ -ray computed tomography (Supplementary Figure 5). **Figure 5a** and **b** show IL- $\mu\text{-XRF}$  maps of inlet  
248 and outlet (before and after AST) respectively. Like the standard MEA, significant changes in Pt loading  
249 can be observed between maps before and after AST of both inlet and outlet regions of the modified MEA.  
250 However, in contrast to the standard MEA a substantial heterogeneous degradation after AST was noted  
251 between the inlet and outlet most likely due to poor thermal and water management of the modified GDL.  
252 A loss in the total average Pt loading of inlet from  $545 \pm 11\ \mu\text{g}\cdot\text{cm}^{-2}$  to  $477 \pm 10\ \mu\text{g}\cdot\text{cm}^{-2}$  was effectively  
253 quantified before and after AST. This  $\sim 13\%$  loss in the total average Pt loading is significantly higher than  
254 the observed  $\pm 2\%$  spatial variation (Methods). Thus, it may be assigned to the loss of Pt ions out of the  
255 mapped area. To understand if this loss from the mapped area was not due to Pt redistribution to the other  
256 parts of the active area caused by an in-plane movement of Pt,  $4\ \text{cm}^2$  out of the  $5\ \text{cm}^2$  active area was also  
257 mapped (Methods and Supplementary Figure 2b). A similar trend of decrease in average total Pt loading  
258 from  $558 \pm 11\ \mu\text{g}\cdot\text{cm}^{-2}$  to  $498 \pm 10\ \mu\text{g}\cdot\text{cm}^{-2}$  was quantified equating to  $\sim 10\%$ . Thus, the heterogeneous  
259 degradation resolves the small  $\sim 3\%$  drop observed in the loss of total average Pt loading between the large  
260  $4\ \text{cm}^2$  and local inlet area. On the other hand, the total average Pt loading of the outlet was  $547 \pm 11\ \mu\text{g}\cdot\text{cm}^{-2}$   
261 and  $535 \pm 11\ \mu\text{g}\cdot\text{cm}^{-2}$  before and after AST, respectively. The decrease was negligible compared to the  
262 inlet and fell quite close to the observed spatial variation confirming heterogeneous degradation between  
263 the inlet and outlet was caused by the modified GDL.

264  
265 A remarkably high difference in crack development can be observed between inlet and outlet after AST  
266 with modified GDL explaining the  $\sim 13\%$  loss in total average Pt loading and the heterogeneity. The crack  
267 formation for the outlet is close to that observed within standard MEA after AST, all of which show minimal  
268 change in the total average Pt loading. This further elucidates the role of cracks in through-plane and in-  
269 plane transport of Pt ions. **Figure 5c** and **d** show inlet and outlet loading histograms for the modified MEA  
270 respectively. The initial unimodal distribution stays the same after the AST for both however, histogram  
271 for inlet after the AST shifts left owing to the observed loss in total average Pt loading. The identical  
272 location approach allowed successful quantification of evolution of cracks, inlet-outlet degradation  
273 heterogeneity and the effect of MEA components on electrocatalyst degradation. Although out of scope for  
274 this study, it must be noted that observed loss of Pt loading if via effluent water can be corroborated by  
275 ICP-MS of it.

276  
277 Additional TEM and STEM/EDS analysis of both MEAs after AST at different through-plane locations of  
278 the cathode catalyst layer was performed to confirm and complement the observations above.  
279 Supplementary Figures 6, 7 and 8 show Pt nanoparticle size growth throughout the cathode catalyst layers  
280 of both MEAs along with development of Pt loading hotspots.

281 Compared to the standard MEA, modified MEA (Supplementary Figure 9) before AST showed identical  
282 overpotentials in the kinetic and ohmic regions. Higher cell overpotentials observed in the mass transport  
283 region were most likely due to the MPL modification. After AST, cell overpotentials increased more for  
284 the modified MEA in all regions driven by relatively high Pt degradation. Cell overpotential increase of 33  
285 mV at  $0.8\ \text{A}\cdot\text{cm}^{-2}$ , 54 % loss in mass activity at 0.9 V and 41 % loss in ECSA was observed after AST for  
286 the modified MEA. Interestingly, after AST the  $\text{H}_2$  crossover saw an increase of 16% for the modified MEA  
287 indicating increased membrane degradation by combination of cathode catalyst layer and MPL cracks.

### 288 289 **Correlation between Pt nanoparticle size and loading**

290  
291 **Figure 6a, b** and **c** show  $300\ \mu\text{m}$  by  $300\ \mu\text{m}$  synchrotron  $\mu\text{-X}$ -ray diffraction ( $\mu\text{-XRD}$ ) maps of CCM before  
292 AST, inlet-after AST and outlet-after AST respectively along with  $\mu\text{-XRF}$  maps of the same location  
293 (Methods). No correlation can be observed between Pt nanoparticle size and loading distribution for the  
294 CCM before AST. The average Pt nanoparticle size before AST is  $3.6 \pm 0.5\ \text{nm}$  with a Pearson's correlation  
295 of  $-0.07$  between the 2D maps of nanoparticle size and loading (Supplementary Table 1). A Pearson's

296 correlation of 0 means no linear relationship while a correlation of -1 or +1 indicates complete linear  
297 relationship between two maps. The inlet and outlet after AST show a direct linear correlation (positive  
298 correlation) between the Pt nanoparticle size and loading with a Pearson's correlation of +0.37 and +0.33,  
299 respectively. This means that increase in Pt nanoparticle size is driven by the local increase in Pt loading.  
300 The average inlet and outlet Pt nanoparticle size increased to  $5.8 \pm 1$  nm and  $6.8 \pm 1$  nm, respectively. Some  
301 local hotspots in the  $\mu$ -XRD maps show a nanoparticle size increase of almost 8 nm after AST. The  
302 synchrotron  $\mu$ -XRD and  $\mu$ -XRF maps of the modified MEA (Supplementary Figure 10) also show direct  
303 linear correlation with a Pearson's correlation of +0.42 for inlet. More interestingly, the average inlet Pt  
304 nanoparticle size increased to  $6.8 \pm 1$  nm even after  $\sim 13\%$  loss in the total average Pt loading was quantified  
305 from the IL- $\mu$ -XRF after AST. Thus, coupled with the established correlation above, for a large  $\mu$ m scale  
306 region in the cathode catalyst layer undergoing degradation, average Pt nanoparticle size increase and loss  
307 in average Pt loading can be mutually inclusive. This finding is extremely important as it provides a  
308 blueprint to prevent the depletion of Pt near the membrane-cathode interface in the through-plane direction  
309 by developing a hybrid cathode catalyst layer structure with targeted regions of larger Pt nanoparticle size  
310 and lower Pt weight % at locations which undergo exacerbated electrocatalyst degradation.

311  
312 To conclude, commercial CCMs designed for potential HDV applications were subjected to AST  
313 simulating HDV lifetime. A simple approach was used to facilitate IL- $\mu$ -XRF spectroscopy of MEAs before  
314 and after the AST. The results revealed striking in-plane movement of Pt strongly influenced by the initial  
315 loading distribution. Increase in the intensity and evolution of local loading hotspots with preferential  
316 movement of Pt away from the cathode catalyst layer cracks was observed and successfully quantified. A  
317 GDL with cracked MPL was used on the cathode to understand the effect of PEFC components on Pt  
318 degradation. The identical location approach exposed heterogeneous degradation between inlet-outlet and  
319 allowed quantification of  $\sim 13\%$  loss in total average Pt loading for the inlet after AST. Synchrotron  $\mu$ -  
320 XRD and  $\mu$ -XRF experiments showed a direct linear correlation between Pt nanoparticle size and loading,  
321 which developed only after AST. The increase in average Pt nanoparticle size to 6.76 nm for modified MEA  
322 inlet even after  $\sim 13\%$  loss in total average Pt loading suggested that nanoparticle size increase and loading  
323 loss are mutually inclusive for a cathode catalyst layer area undergoing degradation.

324  
325 Based on the findings, focused efforts must be put to prevent initial heterogeneous distribution of Pt loading  
326 and to avoid development of undesired morphological features in the cathode catalyst layer during the CCM  
327 fabrication step. Heterogeneous degradation, in-plane movement of Pt and correlation of nanoparticle size  
328 increase with loading loss provide fundamental understanding for development of durable cathode catalyst  
329 layers. A hybrid/structured cathode catalyst layer can effectively mitigate significant electrocatalyst  
330 degradation. Lastly, current electrocatalyst degradation models must be tuned for each MEA component in  
331 use or else the predicted PEFC system lifetime may deviate significantly from the real-world operation.

## 332 333 **Methods**

### 334 **CCM characterization**

335 CCMs with Pt/C electrocatalyst having anode Pt loading of  $50 \mu\text{g}\cdot\text{cm}^{-2}$  and cathode Pt loading of  $500 \mu\text{g}\cdot\text{cm}^{-2}$   
336 were procured. From SEM, the average anode and cathode catalyst layer thicknesses were measured to be  
337  $\sim 3 \mu\text{m}$  and  $\sim 14 \mu\text{m}$  respectively while the average membrane thickness was measured to be  $\sim 8 \mu\text{m}$   
338 (Supplementary Figure 11). Although not required for the scope of this study, it is important to highlight  
339 that features like ePTFE reinforcement and radical scavenging additives required for high membrane  
340 durability were absent. An average Pt nanoparticle size of  $3.8 \pm 1.2$  nm with unimodal distribution was  
341 calculated from TEM before AST (Supplementary Figure 12). The Pt nanoparticles can be observed to be  
342 uniformly dispersed over the low surface area carbon support (Supplementary Figure 6a) however  
343 elemental mapping does show some local heterogeneity (Supplementary Figure 8).

### 344 **MEA preparation and testing hardware**

345 Commercial CCMs were used to prepare two MEAs with 5 cm<sup>2</sup> active area. Freudenberg H23C6 was used  
346 as both anode and cathode GDL for the first standard MEA. Cracks were introduced in the MPL of only  
347 cathode Freudenberg H23C6 GDL to prepare the second modified MEA.

348 Fuel cell quick connect fixture (qCf) coupled with a cell fixture (cF) from balticFuelCells GmbH (Schwerin,  
349 Germany) was used. Two turn 5 cm<sup>2</sup> x7 serpentine channel graphite flow field was utilized<sup>41</sup>. The GDL  
350 compression in this setup is pneumatically controlled. The manufacturer recommended 1-1.1 MPa pressure  
351 of the GDL was achieved by a pneumatic compression pressure of ~ 0.9 bar. This resulted in an optimum  
352 20-22% of GDL compression. Polarization curves and mass activity measurements were performed using  
353 850e fuel cell test system from Scribner Associates (Southern Pines, NC). Cyclic voltammograms (CVs),  
354 linear sweep voltammograms (LSVs) and electrochemical impedance spectroscopies (EISs) along with the  
355 HDV AST all in nitrogen cathode environment were performed using Interface 5000 potentiostat from  
356 Gamry Instruments (Warminster, PA).

### 357 **AST and Electrochemical characterization**

358 The ASTs were performed at 80°C cell temperature in 100% RH under atmospheric pressure. **Figure 1a**  
359 shows the cell voltage cycle for the HDVAST comprising 0.6 V LPL and 0.9 V of UPL with a dwell time  
360 of 3 seconds at each potential. Gas flow rates of 0.2 slpm and 0.2 slpm (H<sub>2</sub>/N<sub>2</sub>) were used for anode and  
361 cathode, respectively. During the AST, each MEA was characterized after 0, 10000, 30000, 60000 and  
362 90000 AST cycles.

363 CVs after cleaning cycles were recorded with a potential scan from 0.1 V to 1.2 V at a scan rate of 100  
364 mV.s<sup>-1</sup>, while LSVs were collected from 0.05 V to 0.8 V at sweep rate of 1 mV.s<sup>-1</sup> to measure hydrogen  
365 crossover. EIS was collected at 0.2 V from 20 kHz to 0.1 Hz with 6 points/decade. All were collected in  
366 H<sub>2</sub>/N<sub>2</sub> environment at 80°C in 100% RH under atmospheric conditions with gas flow rates of 1 slpm/1 slpm  
367 on the anode/cathode, respectively. Cell conditioning was performed at 80°C in 100% RH under  
368 atmospheric pressure by cycling the voltage between 0.8 V, 0.6 V and 0.3 V (30 seconds each) for 200  
369 cycles in a H<sub>2</sub>/air environment. Voltage recovery consisted of voltage hold at 0.2 V for 1 hour at 40°C in  
370 150% RH under 150 kPa absolute pressure in a H<sub>2</sub>/air environment. Polarization curves in H<sub>2</sub>/air and H<sub>2</sub>/  
371 O<sub>2</sub> environments were collected in differential conditions at 80°C in 100% RH under 150 kPa absolute  
372 pressure with gas flow rates of 1 slpm/2.5 slpm at anode/cathode, respectively. For air, 4-minute holds from  
373 high current density (2 A.cm<sup>-2</sup>) to low current density (0 A.cm<sup>-2</sup>) were performed while for O<sub>2</sub> the holds  
374 consisted of 3 minutes with increments of 25 mV from 0.75 V to open circuit potential. The data of last  
375 minute was averaged and used to plot polarization curves (air) and Tafel plots (O<sub>2</sub>). A specific order of  
376 electrochemical experiments was followed (Supplementary Figure 13b) to get highly reproducible results.

### 377 **Modification of MPL**

378 Cracks of ~ 20 μm width were milled into the 35 μm thick free-standing MPL of Freudenberg H23C6 GDL  
379 using the ~ 15 μm wide tip of tungsten micro needle. The fabrication was done by hand under an optical  
380 microscope (x 20) with a pitch of 1 mm. μ-XCT was performed to confirm the morphology (Supplementary  
381 Figure 5). The MPL cracks provided a direct transport pathway between the gas diffusion substrate and the  
382 cathode catalyst layer for reactants and products.

### 383 **Identical location μ-X-ray fluorescence**

384 A thin 25 μm PTFE template was prepared with alignment markers. Using the cathode flow field as  
385 reference, holes were cut out in the template near the inlet and outlet (Supplementary Figure 13a). The



386 diameter of the holes was kept equal to the diagonal of the 2048  $\mu\text{m}$  by 2048  $\mu\text{m}$  area to be mapped. This  
387 ensured automatic alignment of the mapped areas when the template was placed (matching the alignment  
388 markers simultaneously) on the MEAs only during  $\mu$ -XRF mapping before and after the AST. Similarly, a  
389 PTFE template with square cut out of 4 $\text{cm}^2$  area was prepared to facilitate identical location mapping of the  
390 larger areas.

391 *Ex situ*  $\mu$ -XRF measurements were performed using the XGT-9000 Horiba XRF microscope. A 10  $\mu\text{m}$   
392 capillary was utilized to map an area of 2048  $\mu\text{m}$  by 2048  $\mu\text{m}$  near inlet and outlet with 1024 pixels of  
393 detector resolution in both x and y directions giving a final resolution of 2  $\mu\text{m}$   $\times$  2  $\mu\text{m}$ . The larger 20.48  
394 mm  $\times$  20.48 mm ( $\sim$  4  $\text{cm}^2$ ) area was also mapped using the 10  $\mu\text{m}$  capillary with 1024 pixels of detector  
395 resolution in both x and y directions giving a final resolution of 20  $\mu\text{m}$   $\times$  20  $\mu\text{m}$ . The x-ray energy was set  
396 to 50 keV. As the x-ray penetrates the full MEA (anode GDL, CCM and cathode GDL), the reflected x-ray  
397 signal to the detector includes Pt contribution from both anode and cathode. Thus, the quantified total  
398 average Pt loading is the sum of anode and cathode loading. Changes in the total average Pt loading are  
399 dominated by the cathode since negligible changes occur in anode (dynamic reference electrode). This  
400 allows to reliably obtain information about quantitative changes in the cathode. 2D colormaps were  
401 generated in MATLAB using fluorescence images generated by the microscope and the quantified total  
402 average Pt loading. The total average Pt loading was quantified for the CCMs using a calibration curve  
403 generated from 10  $\mu\text{m}$  capillary maps of calibration samples with known Pt loading. For Pt loading  
404 quantification L alpha peak was used. Supplementary Figure 14c shows representative spectrum of a 2048  
405  $\mu\text{m}$  by 2048  $\mu\text{m}$  map.

406 To further understand variation and to confirm that quantified data reflected true change, the total average  
407 Pt loading of each area was reconfirmed by using a larger 1.2 mm capillary at multiple spots (Supplementary  
408 Table 2). A variation of  $\pm$  2% was observed between the two capillaries. No GDLs were removed from the  
409 CCM after AST. The GDLs also made sure that the CCM was completely flat during mapping before and  
410 after AST. To make certain that observed in-plane movement of Pt was not due to distortion of the CCM  
411 when placed under vacuum, an equilibrium time of  $\sim$  3 hours was provided before any mapping. Lastly, the  
412 inlet and outlet were marked on the cathode GDL for further after AST synchrotron experiments.

### 413 **$\mu$ -X-ray computed tomography**

414 Ex-situ  $\mu$ -XCT of standard and modified Freudenberg H23C6 GDL was performed at Beamline 8.3.2 at  
415 Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory (LBNL), Berkeley, California  
416 using 25 keV energy monochromatic x-rays. 50  $\mu\text{m}$  LuAg:Ce scintillator, 10x lenses and sCMOS  
417 PCO.Edge camera were used to achieve an image with 0.65  $\mu\text{m}$   $\text{pix}^{-1}$ . Exposure time of 200 ms was used  
418 to collect 1300 images per scan. Image processing was done using ImageJ.

### 419 **Synchrotron $\mu$ -X-ray diffraction and fluorescence**

420 The synchrotron  $\mu$ -XRD mapping was conducted at Beamline 12.3.2 of the ALS. A monochromatic X-ray  
421 beam (10 keV) was focused to 2 $\times$ 5  $\mu\text{m}^2$  by a pair of Kirkpatrick–Baez mirrors. The CCM samples were  
422 mounted on a high-resolution x–y scan stage and tilted 20° relative to the incident X-ray beam. 2D X-ray  
423 diffraction images were recorded in reflection mode with a two-dimensional Pilatus-1 M detector mounted  
424 at 60° to the incoming X-ray, approximately 150 mm from the probe spot. Exposure time at each position  
425 was 8 s. Calibrations for distance, center position, and tilt of detector were performed based on  $\sim$ Al<sub>2</sub>O<sub>3</sub>  
426 powder reference taken at the same geometry. For high resolution mapping of each 0.3 mm  $\times$  0.3 mm area  
427 of each MEA samples. A 2D scan of 30  $\times$  30 points was performed with a step size of 10  $\mu\text{m}$ . Supplementary  
428 Figures 14a and b show representative  $\mu$ -XRD diffraction pattern and integrated intensity vs 2 $\theta$  single peaks  
429 (Pt 220), respectively. The X-ray diffraction data was processed by XMAS<sup>42</sup>. Change in average Pt

430 nanoparticle size before and after AST is dominated by the cathode. As negligible nanoparticle size growth  
431 occurs at the anode, quantitative information about changes in the cathode can be obtained.

432 The synchrotron  $\mu$ -XRF mapping was carried out at the exact identical location using identical raster scan  
433 step of the diffraction mapping (start and end point, step size and scan area). The Vortex-EM detector is  
434 positioned at an angle to the incoming X-ray beam. The monochromatic X-ray energy was increased to 12  
435 keV for XRF measurements.

#### 436 **Transmission electron microscopy**

437 Samples extracted from before AST (Control) MEA, near the inlet of standard MEA, and near the inlet of  
438 modified MEA were embedded into an epoxy mixture using an Araldite 6005 epoxy mixture kit (use of  
439 approximately 10.7 g Araldite 6005, 7 g Dodecyl Succinic Anhydride (DDSA) and 0.23 g (DMP-30)  
440 2,4,6, -Tris-(dimethylaminomethyl) phenol) and cured for 16 hours at 68 °C. A Leica EM Trim2 was used  
441 to trim a straight section of the embedded MEA with epoxy on both sides. Ultramicrotomy was done to  
442 the block to produce cross-sections of the MEA using a Leica EM UC7 (set to 6 ° and a cutting speed of 1  
443 mm s<sup>-1</sup>) and a Diatome diamond knife with an edge length of 2.5 mm and a knife angle of 35 °. Ultrapure  
444 deionized water was used in the diamond knife assembly to collect the cross-sections where they were  
445 placed onto SPI 3 mm diameter Cu TEM grids (400 mesh slim bar).

446 Imaging was conducted on a JEOL NEOARM 200CF probe-corrected TEM operated at 200 kV. Elemental  
447 mapping was done in STEM mode with EDS using a 70  $\mu$ m aperture and C-6 spot size setting. Elemental  
448 maps were collected at a magnification of 25 kx for ~ 5 minutes using two 100 mm<sup>2</sup> JEOL SDD EDS  
449 detectors. Post processing of the maps was done using Oxford Instruments AZtec EDS software. Several  
450 images acquired at 80 kx, 150 kx, and 500 kx in conventional TEM mode were used to capture through-  
451 plane information on the observed degradation phenomena and for nanoparticle size analysis. A 100  $\mu$ m  
452 aperture and a spot size of C-5 was used. Several images were acquired at different locations of the cathode  
453 catalyst layer, including areas at the membrane-cathode catalyst layer interface, approximately in the middle  
454 of the catalyst layer, and areas at the gas diffusion layer-catalyst layer interface. Nanoparticle size analysis  
455 of before AST (Control) sample was done manually on images taken at 500 kx using imageJ's freehand  
456 tool to measure the area of the selected nanoparticle's region. It should be noted that measurements were  
457 only made to nanoparticles that could be distinguished; agglomerates or overlapping nanoparticles were not  
458 analyzed. The equivalent diameter was back calculated assuming a circular particle shape. The measured  
459 equivalent diameters were then analyzed using MATLAB's 'Distribution Fitter' application (MATLAB  
460 2022a). The bin size was preset to 0.5 nm width and a probability distribution function (PDF) analysis was  
461 used to fit a lognormal distribution to the measured equivalent diameters. To better estimate the localized  
462 nanoparticle size, a minimum of 3 images and 200 nanoparticles were used in general as a guideline at each  
463 region. An iterative approach was used at each region until the mean value of the nanoparticle size did not  
464 change significantly. A total of 1241 nanoparticles were measured for the before AST (Control) MEA. An  
465 overall PSD combining the measurements of all three regions is reported.

#### 466 **Scanning electron microscopy**

467 MEA samples were potted in epoxy to prepare cross sections. The MEA samples were first placed in  
468 between and supported by stainless steel foil in the epoxy. The samples were then polished using a Buehler  
469 EcoMet 30 polishing paper gradually progressing from grit number 320 to 1200. Images of the polished  
470 cross-section were recorded using a scanning electron microscope (JEOL SEM 7200F) in secondary  
471 electron mode with 5-15kV accelerating voltage.

#### 472 **Data availability**

473 The authors declare that the data supporting the findings of this study are available within the paper and its  
474 Supplementary Information. Source data are provided with this paper.

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476  
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## 481 Author contributions

482  
483 K.K. and A.Z. were chiefly responsible for most of the experiments. L.C. and N.T. performed combined  
484 XRD and XRF experiments at the synchrotron. M.C. and S.P. performed microscopy experiments. P.A.,  
485 L.C, J.B., C.J. and I.Z. helped with data interpretation and did conception of the study. K.K. produced the  
486 first manuscript draft and all the authors edited it. L.C., C.J., P.A. and I.Z. obtained funding support and  
487 oversaw the study.

## 489 Competing Interests

490 The authors declare no competing interests.

## 494 Figure Captions (for main text figures)

495  
496 **Figure 1| Single cell voltage cycle of the accelerated stress test (AST) and ECSA loss pathways.** **a**, Square cell voltage cycle  
497 consisting of 0.6 V lower potential limit (LPL) and 0.9 V upper potential limit (UPL) with a hold time of 3 seconds each. To  
498 simulate heavy-duty vehicle lifetime equivalent to  $\geq 25,000$  hours, the square cell voltage cycle is repeated 90,000 times. **b**,  
499 Schematic of three ECSA loss pathways caused by dissolution of  $\text{Pt}^{\text{X}+}$  ions from Pt nanoparticles.

500 **Figure 2| Electrochemical characterization after 0, 10k, 30k, 60k and 90k AST cycles.** **a**, Polarization curves with high  
501 frequency resistance (HFR) collected at 80°C in 100% RH under 150 kPa of absolute pressure in  $\text{H}_2$ -air differential environment.  
502 **b**, ECSA calculated from CVs collected at 80°C in 100% RH under 100 kPa of absolute pressure in  $\text{H}_2$ - $\text{N}_2$  environment. **c**, Tafel  
503 plots generated from  $\text{H}_2$ - $\text{O}_2$  differential environment data collected at 80°C in 100% RH under 150 kPa of absolute pressure. (Inset)  
504 Mass activity at 0.9 V calculated from the corresponding Tafel plots.

505 **Figure 3| Identical location- $\mu$ -XRF spectroscopy of the standard membrane electrode assembly.** **a, b** In-plane Pt loading maps  
506 of inlet (**a**) and outlet (**b**) with regions marked to establish identical location before and after the accelerated stress test (AST). **c, d**  
507 Corresponding histograms of the inlet and outlet respectively showing the unchanged unimodal Pt loading distribution before and  
508 after the AST. Scale bars, 500  $\mu\text{m}$ .

509 **Figure 4| In-plane movement of Pt.** **a, b** Local  $\sim 400 \mu\text{m} \times 400 \mu\text{m}$  areas before and after the accelerated stress test (AST) from  
510 inlet (**a**) and outlet (**b**) Identical location- $\mu$ -XRF maps of the standard membrane electrode assembly. Marked regions highlight  
511 evolution of local loading hotspots and preferential movement of Pt away from cracks after the AST. Scale bar, 100  $\mu\text{m}$ .

512 **Figure 5| Identical location- $\mu$ -XRF spectroscopy of the modified membrane electrode assembly.** **a, b** In-plane Pt loading maps  
513 of inlet (**a**) and outlet (**b**) before and after the accelerated stress test (AST). **c, d** Corresponding Pt loading distribution histograms  
514 of the inlet and outlet respectively. Unimodal distribution was unchanged before and after the AST however a loss in inlet average  
515 total Pt loading was observed. Scale bars, 500  $\mu\text{m}$ .

516 **Figure 6| Synchrotron  $\mu$ -XRD and  $\mu$ -XRF spectroscopy of standard membrane electrode assembly (MEA) identical**  
517 **locations after accelerated stress test (AST).** **a**, Before AST 300  $\mu\text{m} \times 300 \mu\text{m}$  maps showing no correlation between Pt  
518 nanoparticle size and loading distribution. **b, c** Inlet and outlet of the standard MEA respectively showing a strong linear correlation  
519 between Pt nanoparticle size and loading distribution after AST. Scale bar 50  $\mu\text{m}$ .

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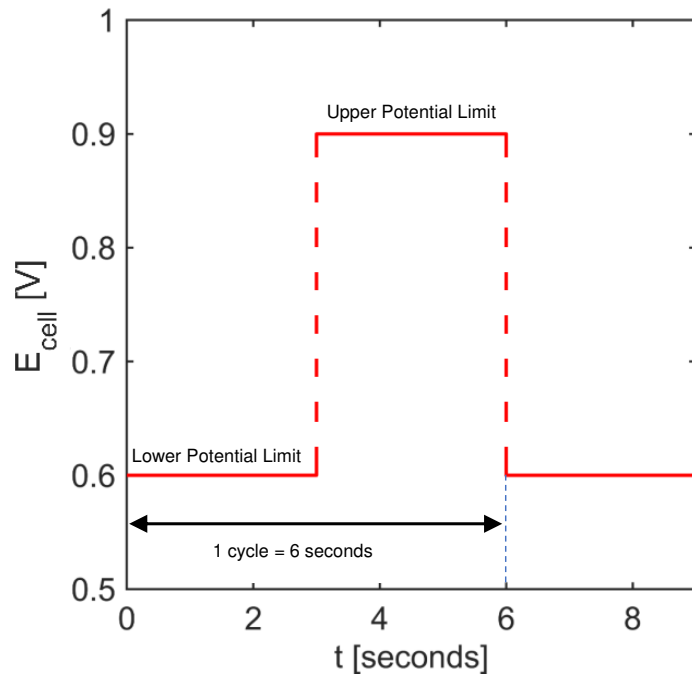
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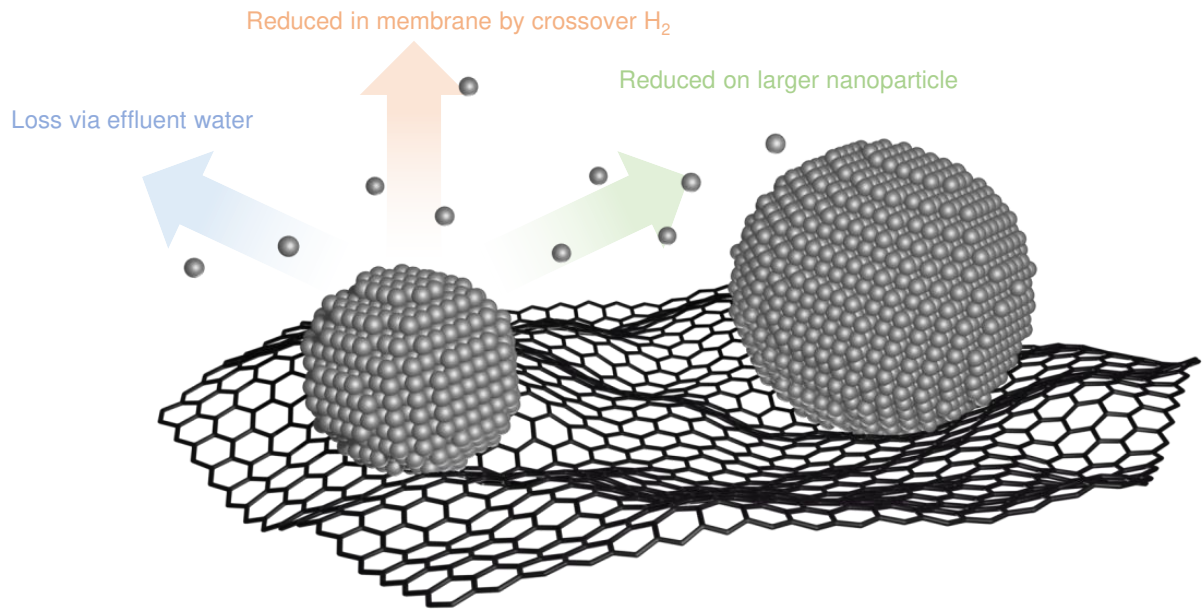
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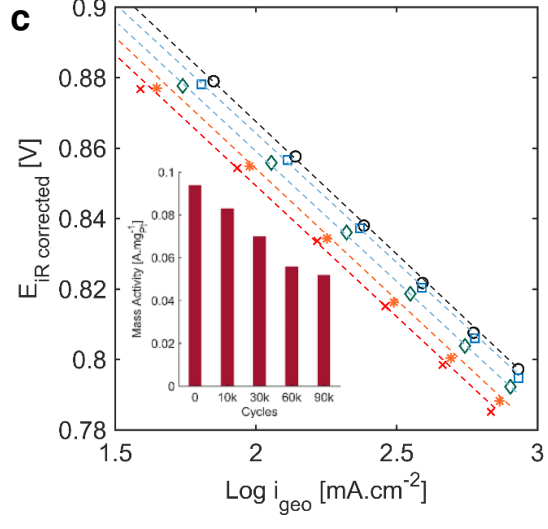
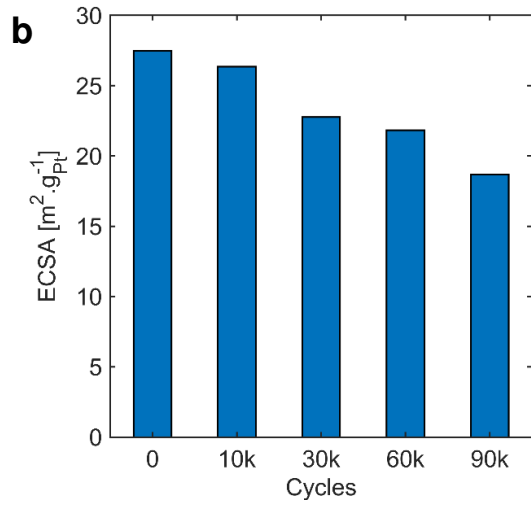
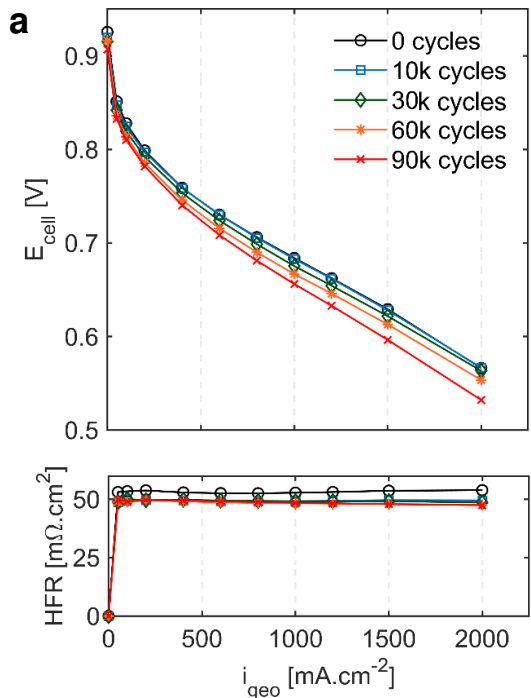
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**a**

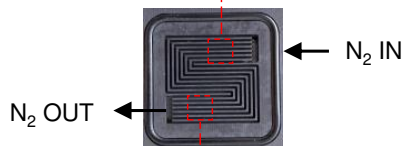
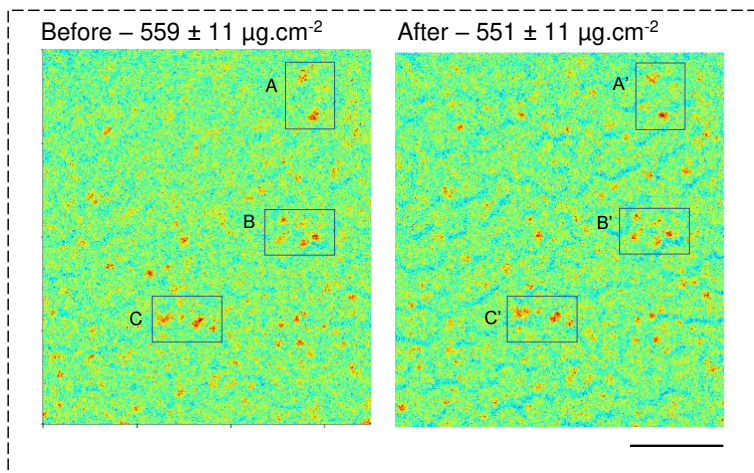
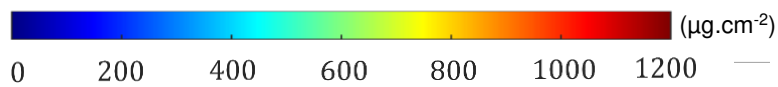
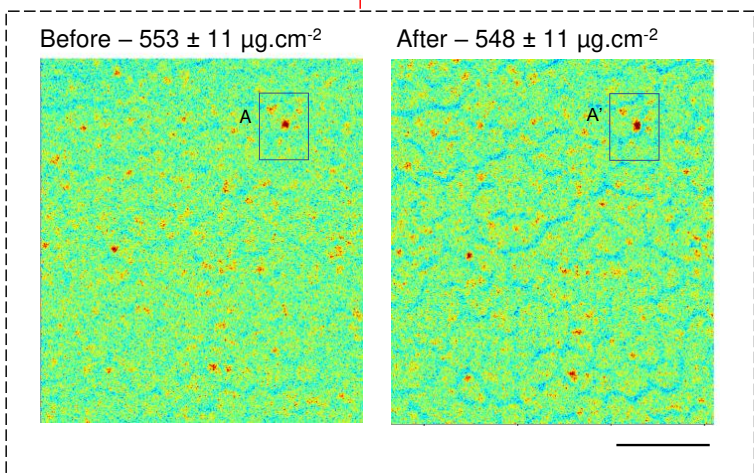
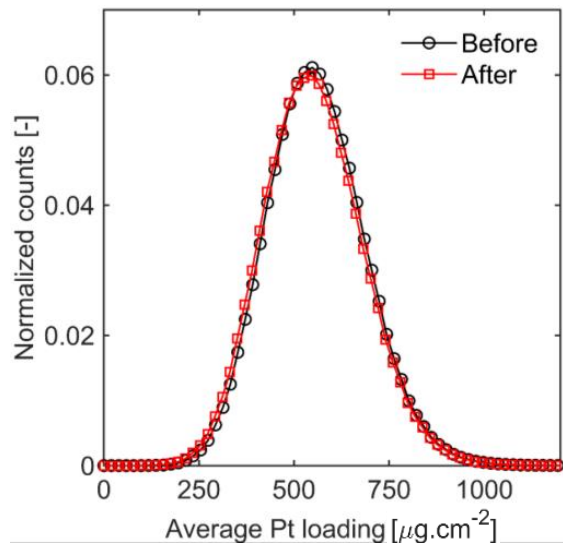
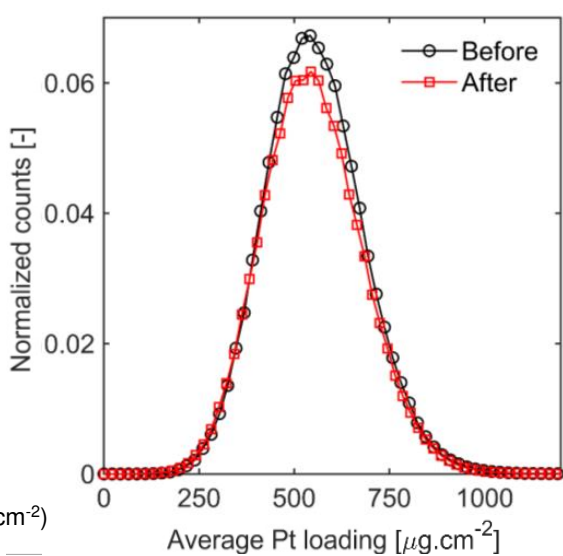


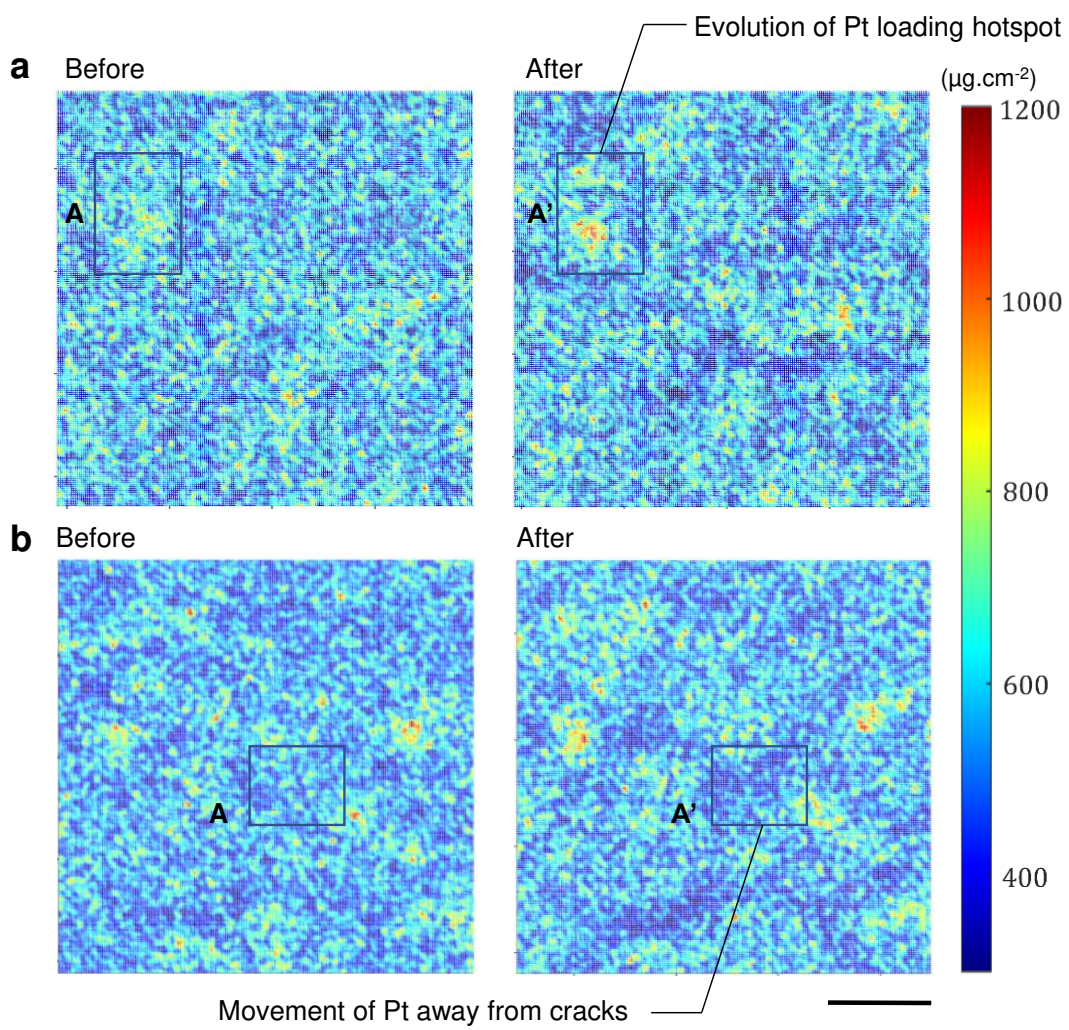
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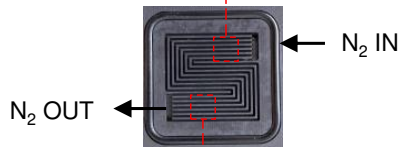
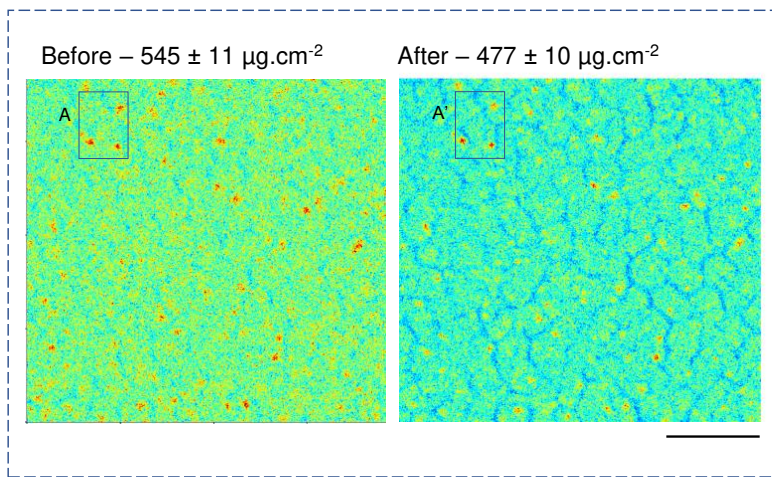
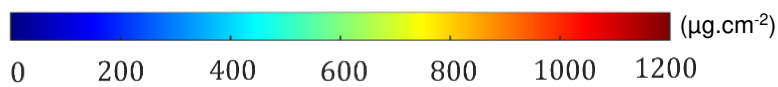
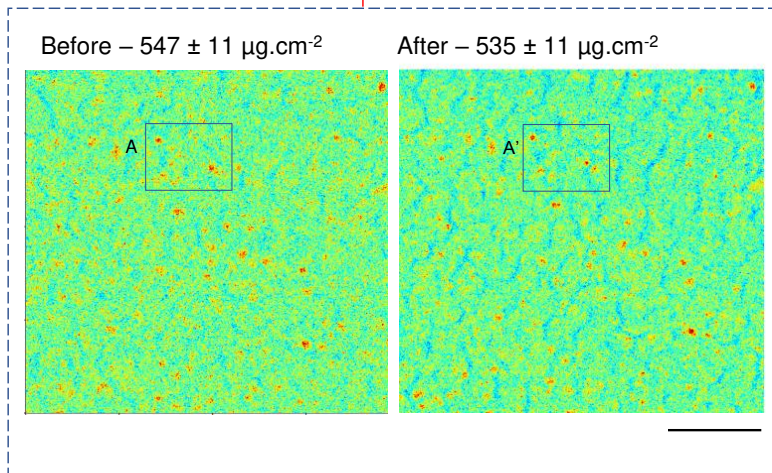
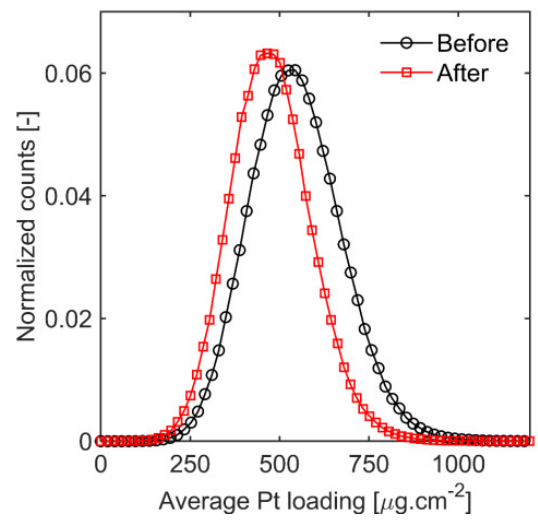
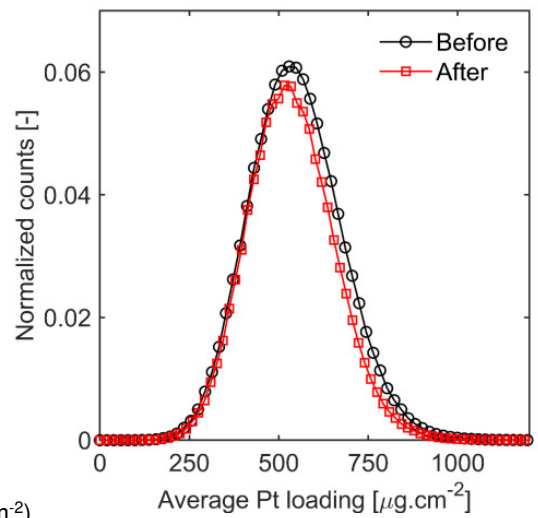


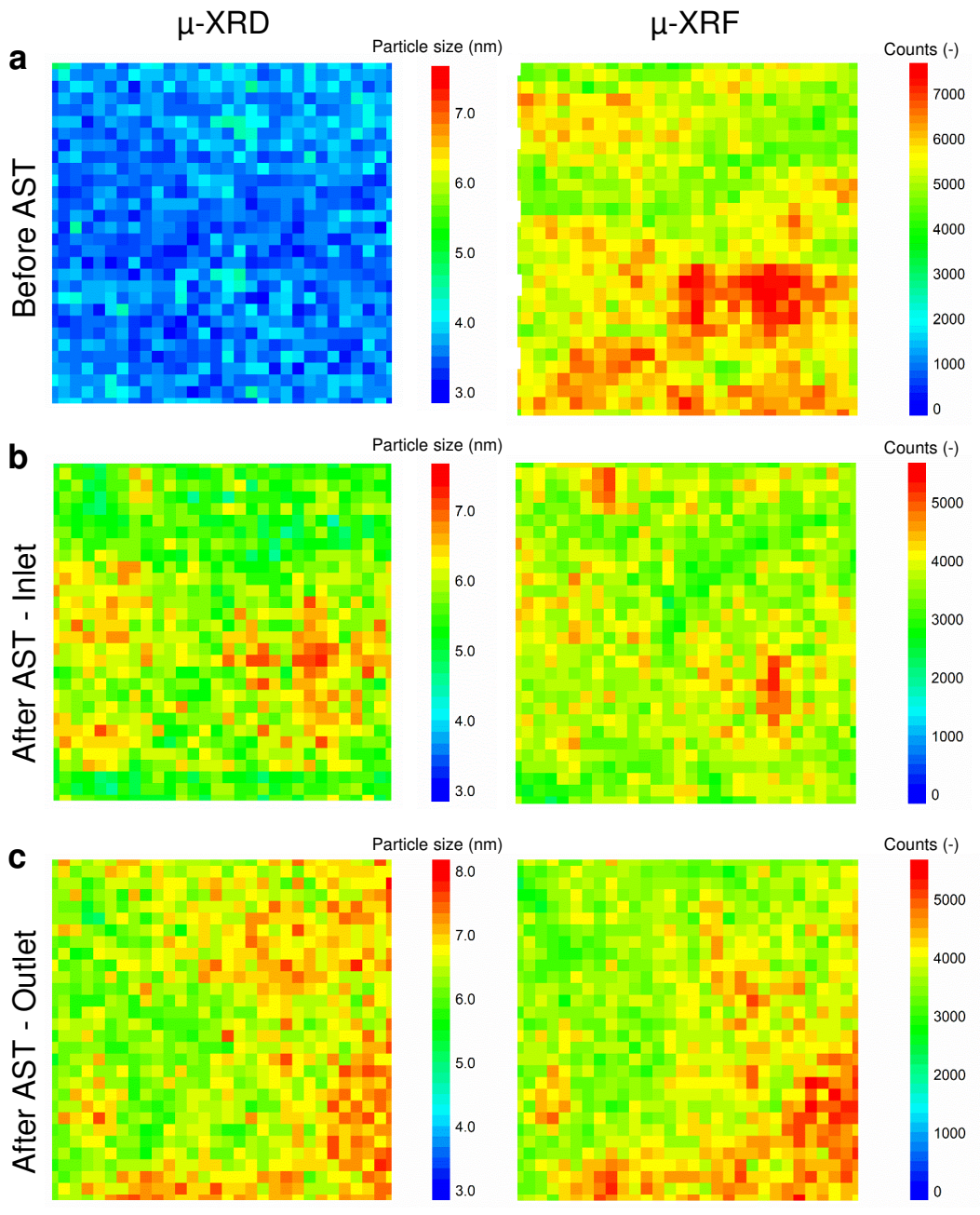




**a** INLET**b** OUTLET**c****d**



**a** INLET**b** OUTLET**c****d**



### Evolution of Pt loading hotspots

