Elucidating the degradation mechanism of the cathode catalyst of PEFC by a combination of electrochemical methods and X-ray fluorescence spectroscopy

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Table of contents

Section 1. Microscopic confirmation of homogeneous catalyst layer.
Section 2. Experimental design to determine Pt content within the catalyst layer.
Section 3. Calibration curve and limit of detection for Pt content.
Section 4. Calibration curve and limit of detection for TaC content.
Section 5. Particle size distribution of Pt-Nps.
Section 6. Compositional analysis of Pt/TaC by XRF.
Section 7. Physical characterization of Pt/Vulcan catalyst.
Section 8. ORR Tafel plots of the catalysts: Pt-Nps, Pt/Vulcan and Pt/TaC.
Section 9. Study of the mechanical stability of the Nafion-free catalyst layer.
Section 10. Fluorescence spectra of the catalyst layer as a function of number of cycles during the load cycle protocol.
Section 11. Average of the particle size of each catalyst as a function of number of cycles during the load cycle protocol and shut-up/shut-down protocol.
Section 12. ORR Tafel plots as a function of number of cycles during the load cycle protocol.
Section 13. Fluorescence spectra of the catalyst layer as a function of number of cycles during the start-up/shut-down protocol.
Section 14. Fluorescence spectra of Pt/TaC (Ta₃₇₄) layer as a function of number of cycles during the start-up/shut-down protocol.
Section 15. ORR Tafel plots of catalysts as a function of number of cycles during the start-up/shut-down protocol.
Section 1. Microscopic confirmation of homogeneous catalyst layer.

Figure SI1. Optical micrograph of the film obtained using (A) the one-drop casting method and (B) the film obtained using the multi-drop casting method proposed in this work.
Section 2. Experimental design to determine Pt content within the catalyst layer.

In order to establish a relationship between the electrochemical surface area (ECSA) and Pt content, to distinguish between associative and dissociative processes, the Pt content of the catalyst layer on the disk was determined by X-ray fluorescence (XRF). After a well-defined number of degradation cycles, the working electrode was placed in a XRF spectrometer and the Pt content was resolved. To reduce the background noise, the best scan quality provided by the equipment was employed for all the measurement carried out in this work. These measurements took 25 minutes each under helium atmosphere.

After the Pt content characterization, the carbon disk was polished with 0.05 µm alumina to remove all the catalyst from the carbon disk surface. After the polishing, the carbon disk was sonicated for 10 minutes and dried in an air-flow oven at 55 ºC. In order to confirm the absence of any remaining catalyst on the carbon surface, the disk was characterized by XRF prior to its next use. Then, a new thin catalyst layer was prepared to proceed with the degradation protocols.
Section 3. Calibration curve and limit of detection for Pt content.

In order to establish a relationship between the XRF response and the Pt content, an experimental calibration curve was constructed. A certain volume of Pt solution with a well-known concentration of Pt (125 µg mL\(^{-1}\)) was deposited on a zero response carbon disk and allowed to evaporate in air. The dried carbon disk was then analysed by XRF with each Pt loading on the disk investigated in triplicate (table SI1).

**Table SI1. Experimental data for Pt calibration curve.**

<table>
<thead>
<tr>
<th>Mass Pt ± 0.1 (µg)</th>
<th>Net intensity ± 1 (Cps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.0</td>
<td>1464  1515  1634</td>
</tr>
<tr>
<td>6.9</td>
<td>1408  1427  1339</td>
</tr>
<tr>
<td>5.9</td>
<td>1195  1253  1199</td>
</tr>
<tr>
<td>4.8</td>
<td>951   868   960</td>
</tr>
<tr>
<td>3.7</td>
<td>729   762   799</td>
</tr>
<tr>
<td>2.6</td>
<td>618   515   614</td>
</tr>
<tr>
<td>1.5</td>
<td>315   335   355</td>
</tr>
<tr>
<td>0.7</td>
<td>234   167   177</td>
</tr>
<tr>
<td>1.2</td>
<td>275   290   230</td>
</tr>
<tr>
<td>2.2</td>
<td>399   490   465</td>
</tr>
</tbody>
</table>

Figure SI2 shows the calibration plot using the net intensity of Pt\(_{L\alpha}\) signal (9.45 KeV) as a function of the mass of Pt deposited on the carbon disk. As can be seen, the response of the intensity is linearly proportional to the mass of Pt with a correlation coefficient of 0.996.
Figure SI2. Calibration data for Pt detection by XRF spectrometer (gradient = 199 ± 3 Cps µg⁻¹, R² = 0.998).
Section 4. Calibration curve and limit of detection for TaC content.

In order to establish a relationship between the XRF response and the TaC content, an experimental calibration curve was constructed. The protocol followed was the same used for the calibration curve of detection of Pt, section 3.

*Table SI2. Experimental data for TaC calibration curve.*

<table>
<thead>
<tr>
<th>Mass $m_t \pm 0.1$ (µg)</th>
<th>Net intensity $\pm 1$ (Cps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>23.5</td>
<td>1464 1515 1634</td>
</tr>
<tr>
<td>19.3</td>
<td>1408 1427 1339</td>
</tr>
<tr>
<td>34.5</td>
<td>1195 1253 1199</td>
</tr>
<tr>
<td>41.4</td>
<td>951  868  960</td>
</tr>
</tbody>
</table>

Figure SI3 shows the calibration plot using the net intensity of TaC$_{L\alpha}$ signal (8.45 KeV) as a function of the mass of TaC deposited on the carbon disk.
**Figure SI3.** Calibration data for TaC detection by XRF spectrometer (gradient = $144 \pm 4$ Cps $\mu$g$^{-1}$, $R^2 = 0.999$).
Section 5. Particle size distribution of Pt-Nps.

Figure S14. Particle size distribution of Pt-Nps obtained from TEM measurements. The relative abundance of each particle size was calculated from a total of 175 nanoparticles.
Section 6. Compositional analysis of Pt/TaC by XRF.

A layer of Pt/TaC was deposited on the surface of a zero background response carbon disk. Then, this carbon disk was placed in a XRF spectrometer, acquiring the composition of this prepared catalyst. The compositional analysis was done in triplicate, resulting in a composition of $(19.6 \pm 0.8) \% \text{Pt}$ and $(80.4 \pm 0.8) \% \text{Ta}$.

![X-ray fluorescence spectra of Pt nanoparticles supported on TaC. The signals at 8.45 keV and 9.45 keV are associated to $\text{Ta}_{L\alpha}$ and $\text{Pt}_{L\alpha}$ respectively. In order to present clear results, the original data was digitalized using the GraphClick software. Original data is available upon request.](image)

**Figure S15.** X-ray fluorescence spectra of Pt nanoparticles supported on TaC. The signals at 8.45 keV and 9.45 keV are associated to $\text{Ta}_{L\alpha}$ and $\text{Pt}_{L\alpha}$ respectively. In order to present clear results, the original data was digitalized using the GraphClick software. Original data is available upon request.

Section 7. Physical characterization of Pt/Vulcan catalyst.
Figure SI6. (A) XRD pattern, (B-C) TEM images and (D) particle size distribution of Pt/Vulcan catalyst. The relative abundance of each particle size was calculated from a total of 175 nanoparticles.
Section 8. ORR Tafel plots of the catalysts: Pt-Nps, Pt/Vulcan and Pt/TaC.

Figure SI7. Mass activity, $j_k$, for the ORR on Pt-Nps, Pt/Vulcan and Pt/TaC, data are shown for the positive-going sweep at 20 mVs$^{-1}$ in O$_2$-saturated 0.1 M HClO$_4$ at 1600 rpm.
Section 9. Study of the mechanical stability of the Nafion-free catalyst layer.

Figure SI8. Voltammetric profiles of Pt-nps (A), Pt/Vulcan (B) and Pt/TaC (C) before (black line) and after (red dashed line) mechanical stress evaluation. The catalysts were rotated at 300 rpm in 0.1 M HClO₄ during 5 hours at open circuit potential. The voltammograms were carried out in 0.1 M HClO₄ at 50 mVs⁻¹.
Section 10. Fluorescence spectra of the catalyst layer as a function of number of cycles during the load cycle protocol.

**Figure SI9.** X-ray fluorescence spectra (Pt$_{l_{\alpha}}$) of Pt-Nps (A), Pt/Vulcan (B) and Pt/TaC (C) at different stages of the load cycle protocol; 0 cycles (black line), 2000 (blue line), 6000 cycles (red line) and 10000 cycles (green line). The scale bar corresponds to 100 Cps intensity. In order to present clear results, the original data was digitalized using the *GraphClick* software. Original data is available on request.
Section 11. Average of the particle size of each catalyst as a function of number of cycles during the load cycle protocol and shut-up/shut-down protocol.

Figure SI 10. Average particle size of the Pt nanoparticles calculated from the mass of platinum and the ECSA as a function of the number of cycles for (A) load cycle protocol and (B) start-up/shut-down protocol. Pt-Nps (black), Pt/TaC (blue) and Pt/Vulcan (red).
Section 12. ORR Tafel plots as a function of number of cycles during the load cycle protocol.

Figure SI11. Mass activity, $j_k$, for the ORR on Pt-Nps (A), Pt/Vulcan (B) and Pt/TaC (C) as a function of number of degradation cycles during the load cycle protocol. Data are shown for the positive-going sweep at 20 mVs$^{-1}$ in O$_2$-saturated 0.1 M HClO$_4$ at 1600 rpm.
Section 13. Fluorescence spectra of the catalyst layer as a function of number of cycles during the start-up/shut-down protocol.

**Figure SI12.** X-ray fluorescence spectra of Pt-Nps (A), Pt/Vulcan (B) and Pt/TaC (C) at different stages of the start-up/shut-down protocol. 0 cycles (black line), 500 cycles (blue line), 1000 cycles (red line), 2000 cycles (green line), 3000 cycles (orange line) and 5000 cycles (purple line). The scale bar corresponds to 100 Cps intensity. In order to present clear results, the original data was digitalized using the GraphClick software. Original data is available on request.
Section 14. Fluorescence spectra of Pt/TaC (Ta\textsubscript{Lα}) layer as a function of number of cycles during the start-up/shut-down protocol.

\textbf{Figure SI13.} X-ray fluorescence spectrum of Pt/TaC at different stages of the start-up/shut-down protocol. 0 cycles (black line), 500 cycles (blue line), 1000 cycles (red line), 2000 cycles (green line), 3000 cycles (orange line) and 5000 cycles (purple line). The scale bar corresponds to 500 Cps intensity. In order to present clear results, the original data was digitalized using the GraphClick software. Original data is available on request.
Section 15. ORR Tafel plots of catalysts as a function of number of cycles during the start-up/shut-down protocol.

**Figure SI14.** Mass activities, $j_k$, for the ORR on Pt-Nps (A), Pt/Vulcan (B), and Pt/TaC (C) as a function of number of cycles during the start-up/shut-down protocol. Data are shown for the positive-going sweep at 20 mVs$^{-1}$ in O$_2$-saturated 0.1 M HClO$_4$ at 1600 rpm.