Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Supporting Information

## Visualization and Understanding of Degradation Behaviors of a PEFC Pt/C Cathode Electrocatalyst by a Multi-Analysis System Combining Time-Resolved Quick XAFS, Three-Dimensional XAFS–CT, and Same-View Nano-XAFS/STEM-EDS Techniques

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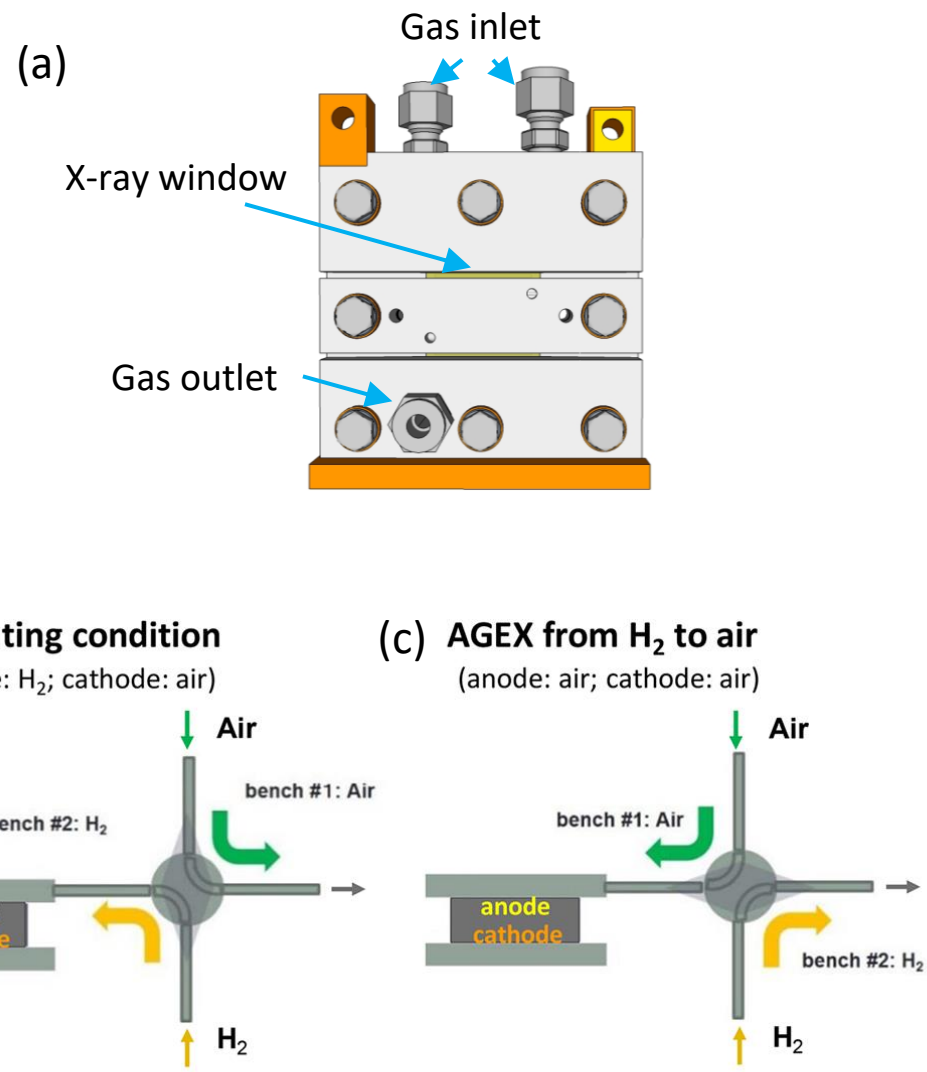


**Figure S1**. (a) Schematic of homemade PEFC single cell for SR X-ray based multi measurements; (b, c) AGEX setup for MEA in PEFC by a four-way valve.

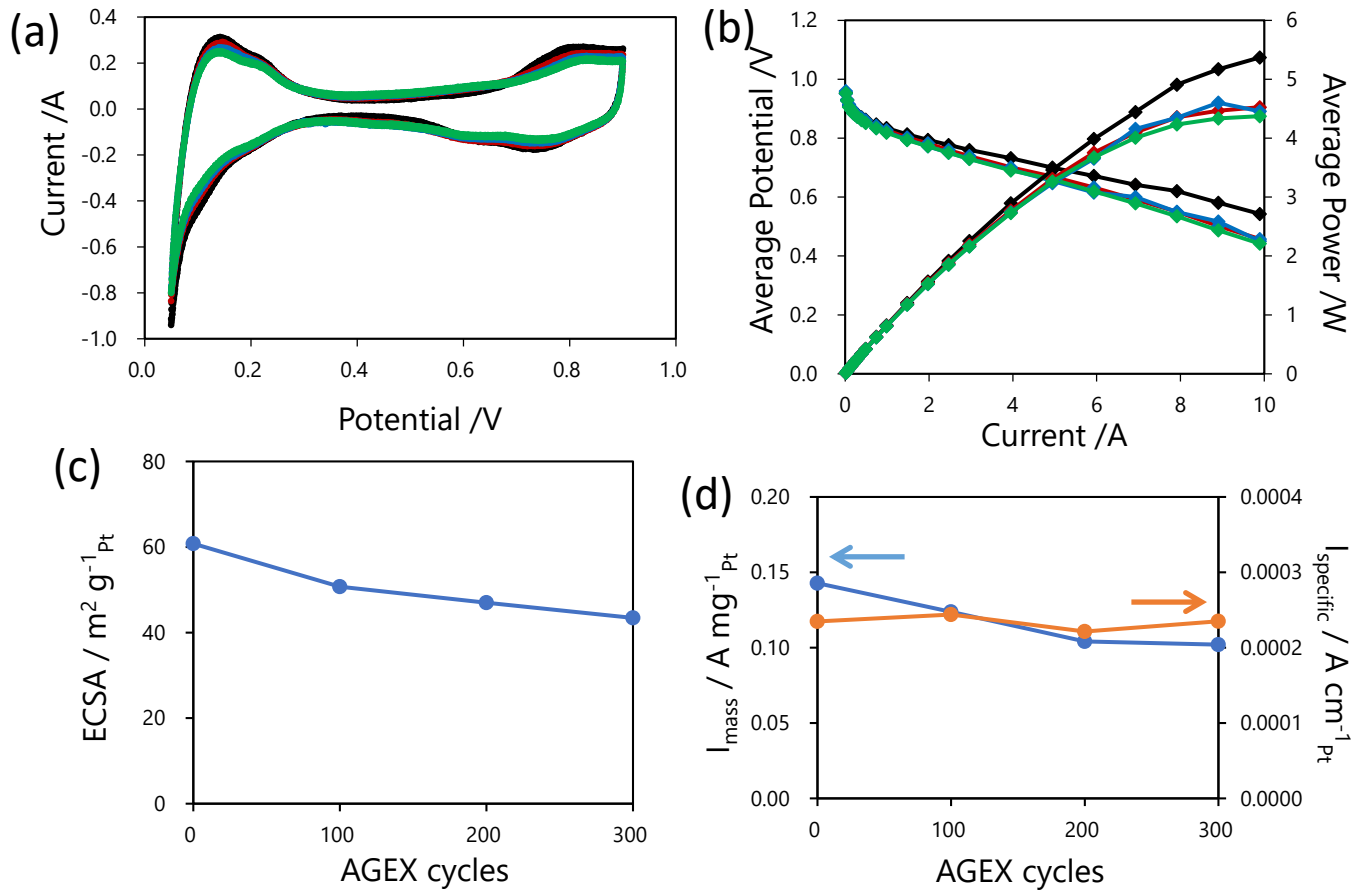


**Figure S2.** Electrochemical data. (a) cyclic voltammograms (CVs), (b) I-V polarization curves, (c) electrochemical active surface areas (ECSA), (d) mass activities (MA) and surface specific activities (SA) of the MEA Pt/C samples after aging (before AGEX) and after 100, 200 and 300 AGEX cycles.

Electrochemical experiments in the AGEX treatments were controlled and monitored using a combination of AUTOLAB302N PGSTAT and BOOSTER20A with NOVA software (Metrohm Autolab B.V.). Cyclic voltammograms (CVs) for the MEAs were conducted between 0.05 and 0.9 $V_{RHE}$ at 20 and 50 mV $s^{-1}$ in $H_2$ (anode) and $N_2$ (cathode) operating atmospheres. The hydrogen adsorption charge determined from the CV (at 50 mV $s^{-1}$) was used to calculate the electrochemical surface area (ECSA) after correction for the double-layer charge in the potential region between 0.05–~0.4 V, assuming 210 µC $cm^{-2}$ as hydrogen adsorption charge for polycrystalline Pt. Following the CVs, MEA performances were examined under the galvanostatic conditions by applying stepwise increasing constant currents for 1 min followed by a frequency response analysis (FRA) at 10 mA AC amplitude and 1000 Hz frequency to measure the real part of the fuel-cell impedance to obtain the iR-free cell potentials. Performance tests (MA and SA) were carried out using air as cathode feed gas as described previously. [refs. 48,70] Fuel cell temperature was kept at 80°C and gas humidifier at 78°C, resulting in a relative humidity of about 92% during all experimental procedures. In AGEX, starting from the PEFC operating conditions ($H_2$–air) and when the anode $H_2$ gas was switched to air, which corresponds to the shutdown conditions (air–air).

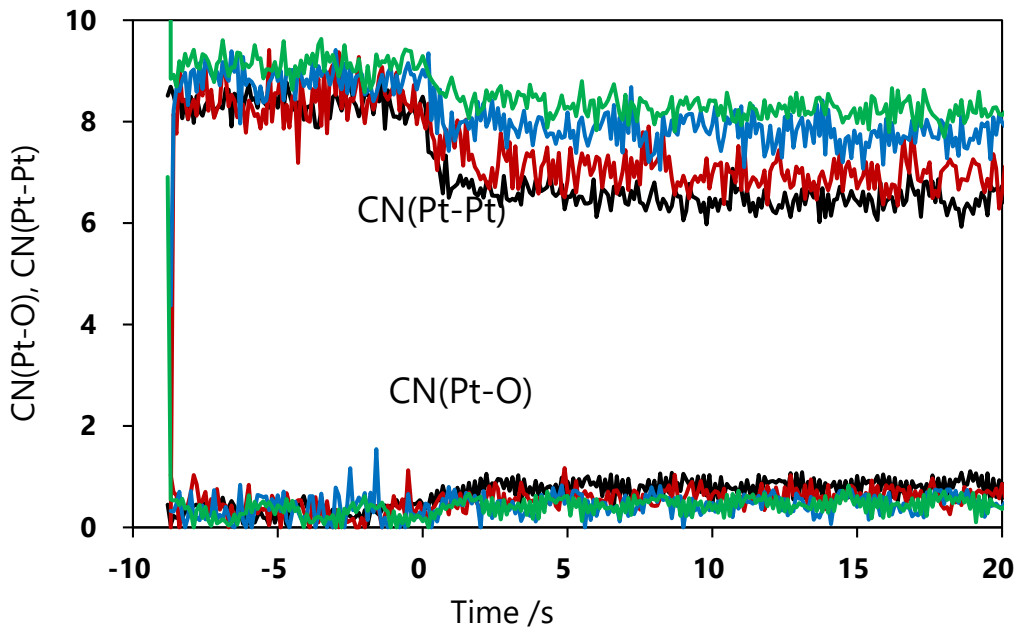


**Figure S3.** Transient response curves of the CN(Pt-O) and CN(Pt-Pt) for the MEA Pt/C cathode catalysts under the voltage operation 0.4 → 1.0 $V_{RHE}$. black: after aging (before AGEX); red: 100 AGEX cycles; blue: 200 AGEX cycles; green: 300 AGEX cycles; yellow: exponential fit. Under $H_2$ (anode)–$N_2$ (cathode); cell temp.: 353 K, relative humidity: ~93%. Data acquisition: every 100 ms.

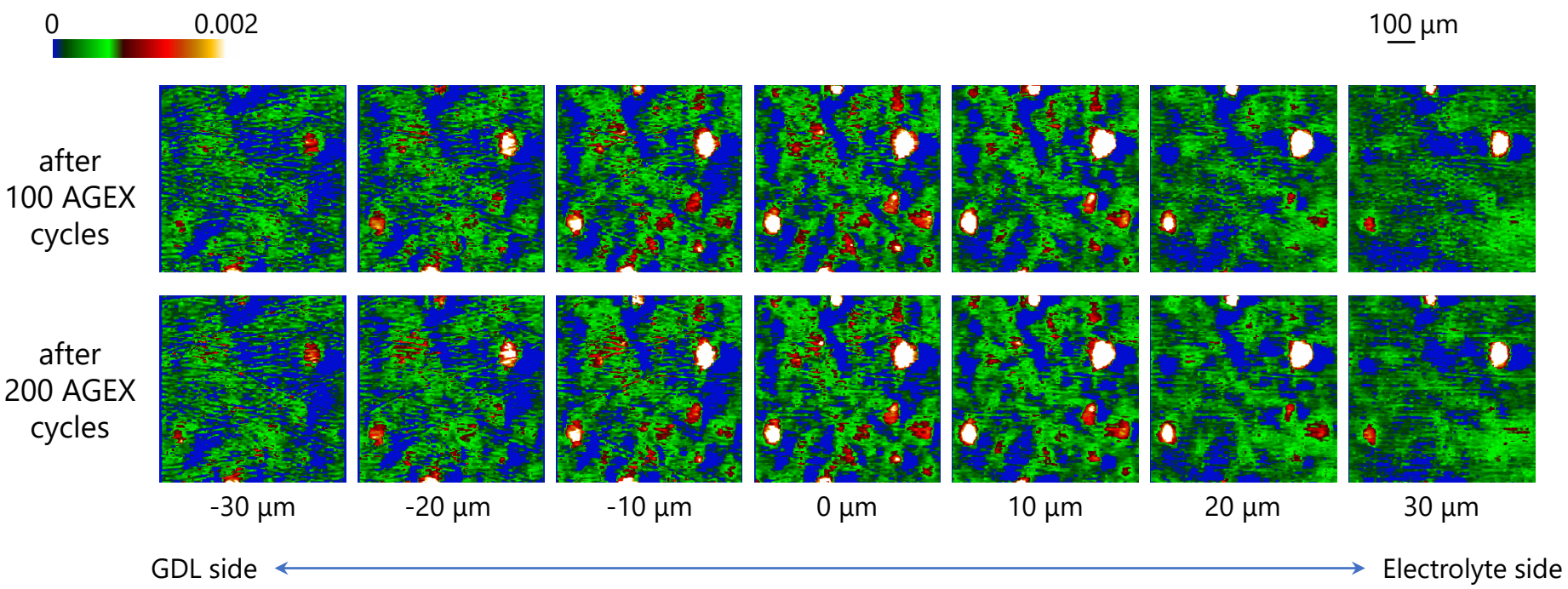


**Figure S4.** Cross-sectional images of Pt amount distribution at each depth of the cathode catalyst layer after 100 and 200 AGEX cycles at a cell potential of 1.0 $V_{RHE}$.

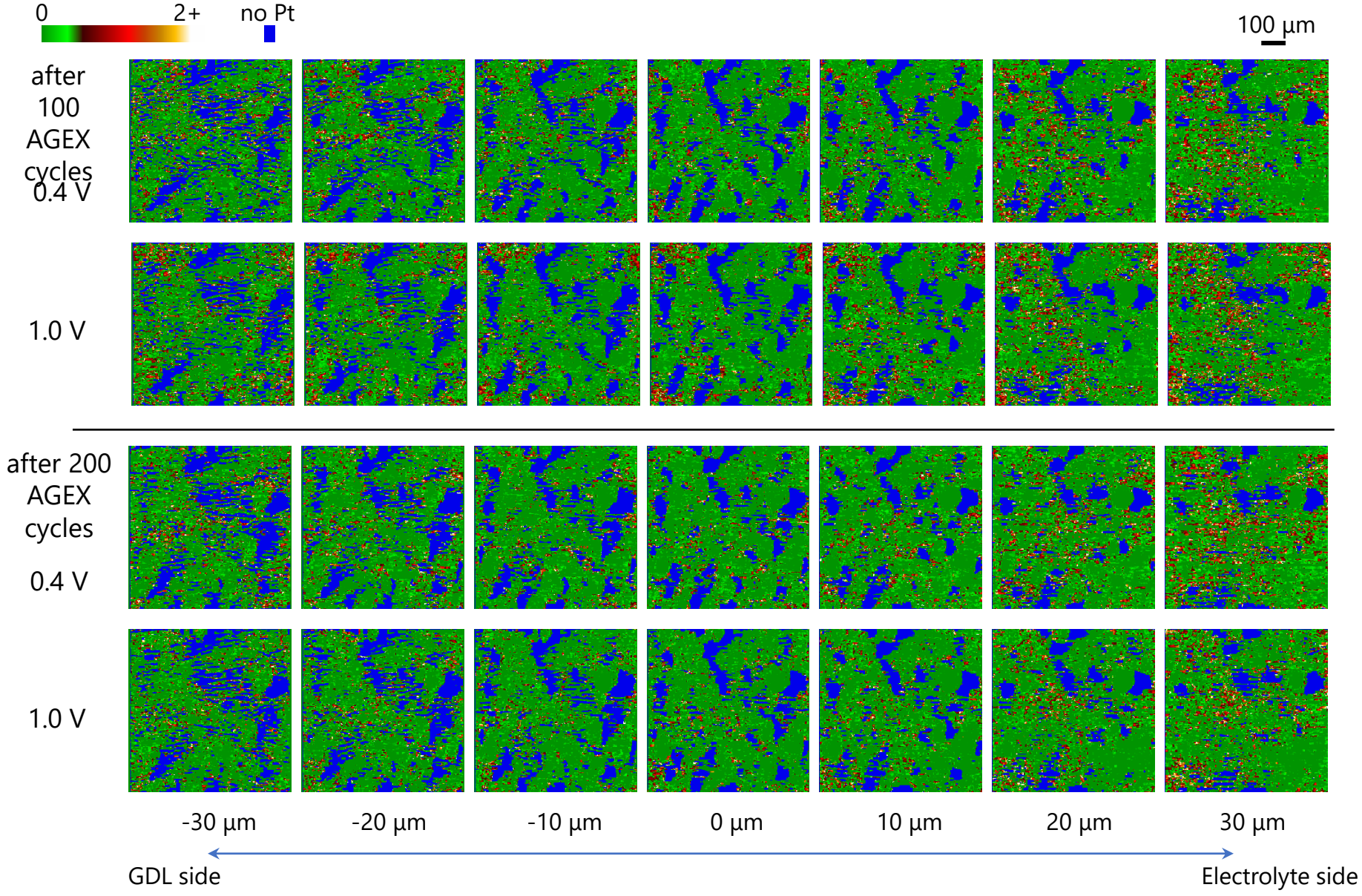


**Figure S5.** Cross-sectional images of Pt valence distribution determined by the white line peak intensity at each depth of the cathode catalyst layer after 100 and 200 AGEX cycles at a cell potential of 0.4 or 1.0 $V_{RHE}$.

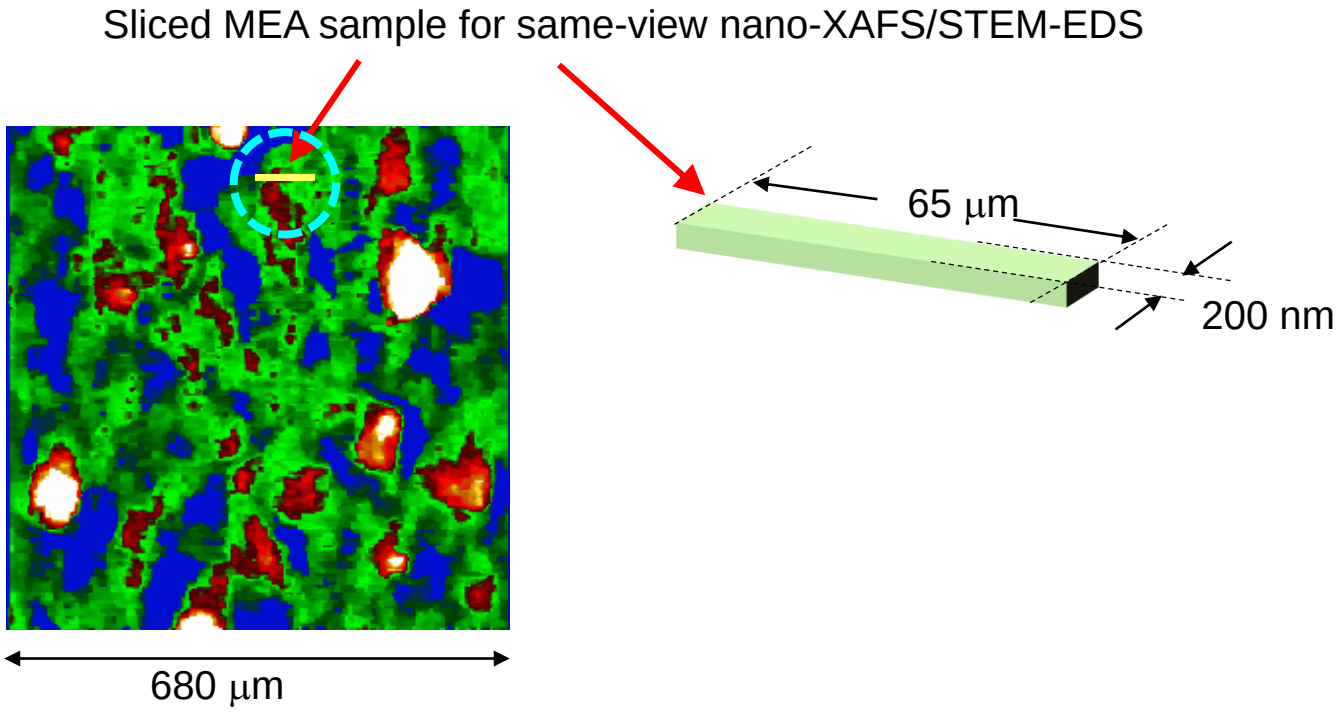


**Figure S6.** A sliced MEA sample area in a cross-sectional Pt-quantity imaging of the cathode catalyst layer after 300 AGEX cycles for same-view nano-XAFS/STEM-EDS.

**Table S1.** Statistics of voids of the MEA Pt/C cathode layer after 300 AGEX cycles in each region in Figure 10.

| | Electrolyte boundary area | GDL boundary area | Center area |
|---|---|---|---|
| Numbers of voids | 539 | 316 | 472 |
| Average void sizes / nm | 387 | 283 | 276 |
| Void fractions / % | 16.7 | 5.2 | 7.4 |

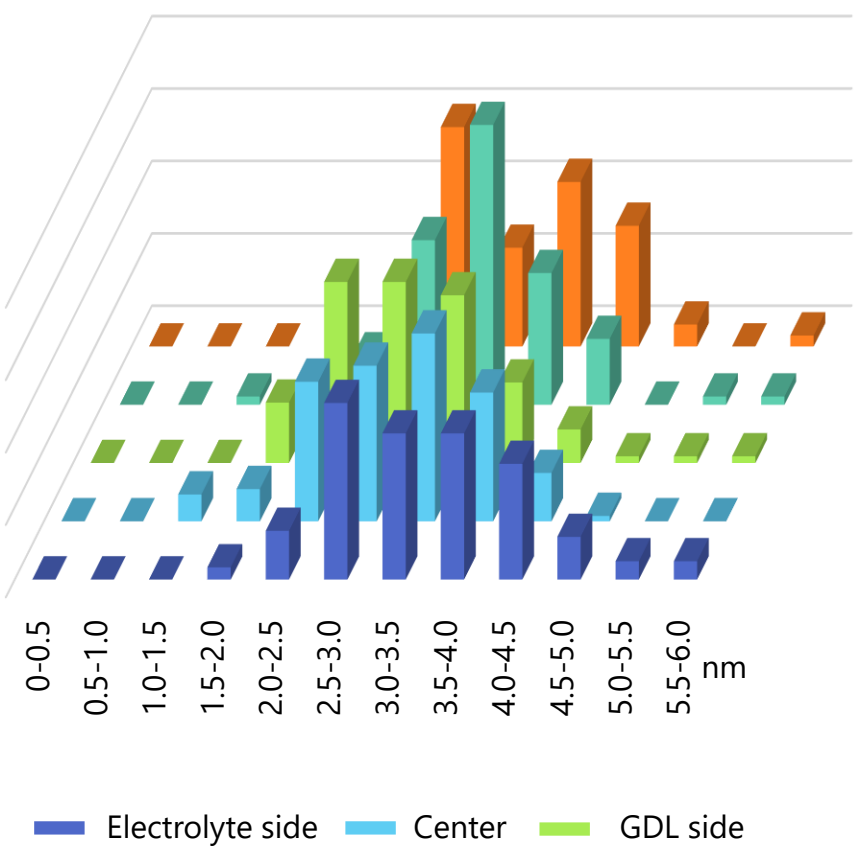


**Figure S7.** Histograms of Pt particle sizes of the MEA Pt/C cathode layer after 300 AGEX cycles by STEM images. Areas up to 5 µm from the electrolyte boundary (blue), GDL boundary (green), and center area (light blue). and areas around voids (blue green) and inside voids (orange).

**Table S2.** Statistics of Pt particle sizes in the MEA Pt/C cathode layer after 300 AGEX cycles in each region in Figure S7.

| | Pt particle / nm | C support / nm |
|---|---|---|
| Electrolyte side | 3.5 | 41.0 |
| Center | 3.0 | 41.2 |
| GDL side | 2.9 | 40.1 |
| Around void | 3.3 | 32.0 |
| In void | 3.3 | - |