Supporting information 1

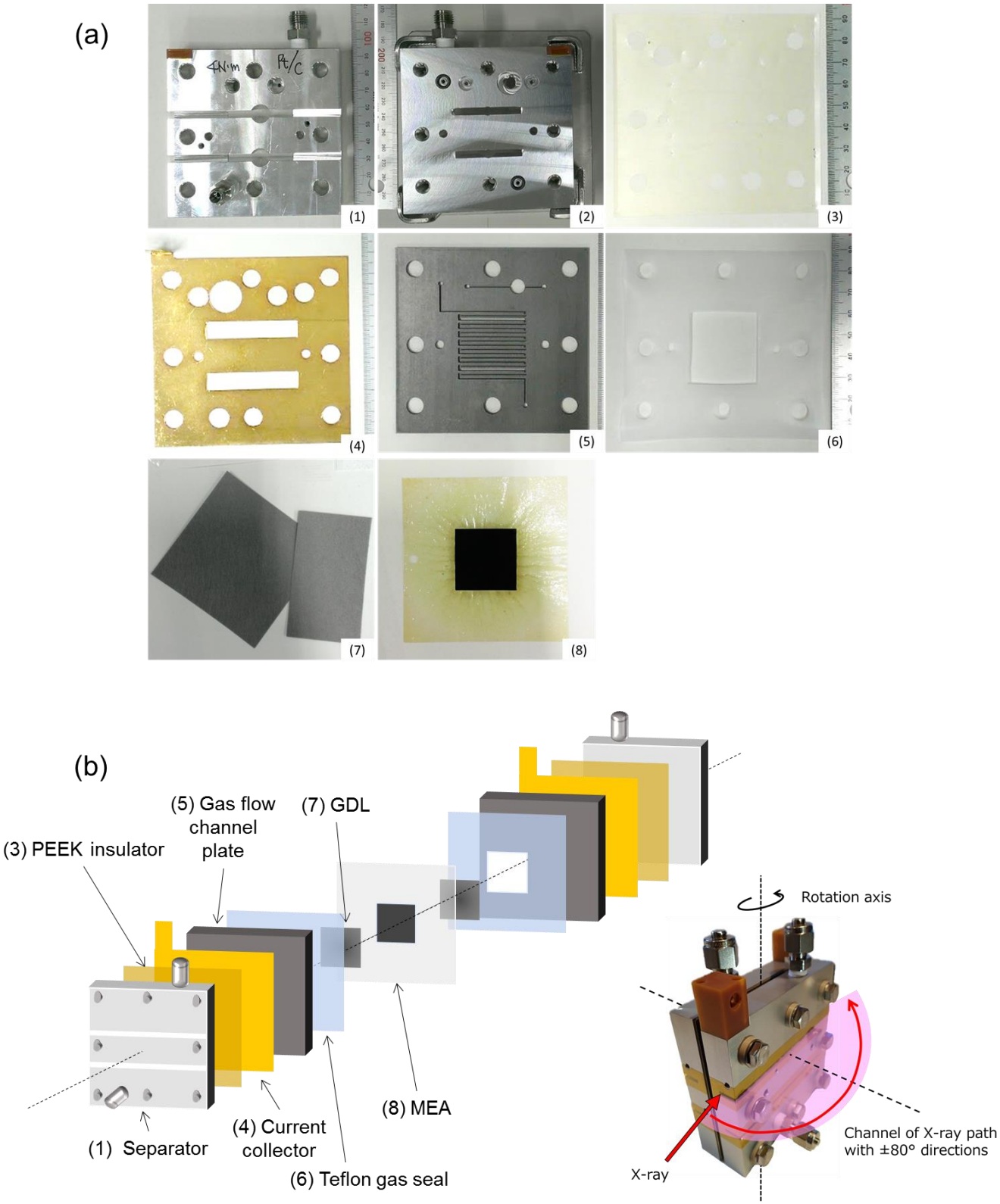

Figure S1. (a) Photographs of stacking components in the *operando* PEFC cell for CT-XANES: (1, 2) separators at the cathode and anode sides, (3) PEEK insulator film, (4) current collector, (5) serpentine gas flow channel plate, (6) Teflon gas seal, (7) GDL, and (8) MEA. (b) Schematic (left) and photograph (right) of the PEFC cell.

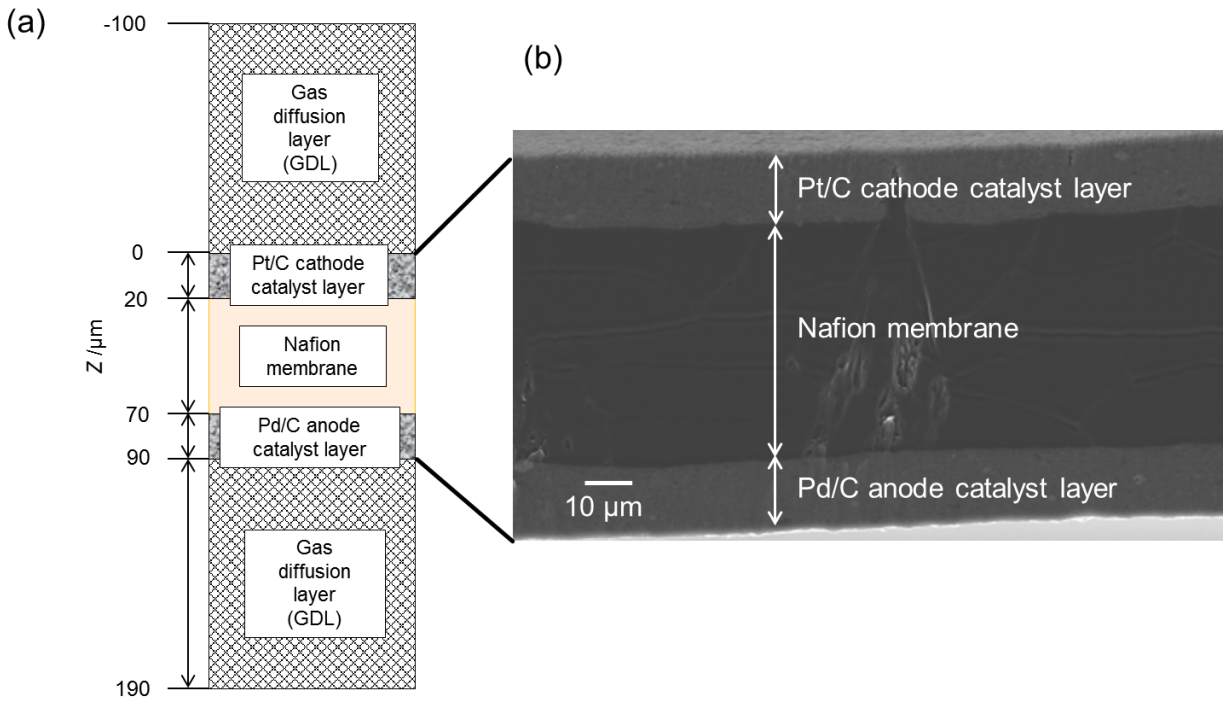

Figure S2. (a) Cross-sectional schematic of MEA and GDL. (b) *Ex situ* cross-sectional SEM image (SU6600, Hitachi High-technologies Co.) of the MEA.

Polymer electrolyte fuel cell operation

A commercial MEA was prepared as a sample (EIWA Co., Ltd.; 3 × 3 cm surface area). A Nafion membrane (NR-212, Sigma-Aldrich) was coated with 50 wt %-Pt/C (TEC10E50E, Tanaka Kikinzoku Kogyo K.K.) and 50 wt %-Pd/C (TECPd(ONLY)E50E, Tanaka Kikinzoku Kogyo K.K.) at the cathode and anode sides with a practical catalyst loading of 0.5 $mg_{\text{-Pt/Pd}}$ cm^{-2}. On both sides of the MEA, 100-μm-thick gas diffusion layers (GDLs; TGP-H-030, Toray Ind., Inc.) were inserted.

H_2 (99.99999%, supplied at the anode at 150 mL min^{-1}) and N_2 (99.99999%, supplied at the cathode during 3D CT-XANES measurements at 600 mL min^{-1}), or air (99.99999%, supplied at the cathode during aging at 600 mL min^{-1}) were supplied by mass-flow controllers and were bubbled through humidifiers set at a RH of 70% with a commercial gas supply kit (CNF52742, NF Co., Ltd.). The temperature of the PEFC cell was kept at 353 K.

A cell voltage between the anode and cathode was applied by a PG stat (VSP, BioLogic Science Instruments Co. Ltd.) with a current amplifier (VMP3B-20, BioLogic Science Instruments). The as-prepared MEA was aged 150 times in 23 fixed current steps (0 → 0.01 → 0.04 → 0.12 → 0.16 → 0.22 → 0.27 → 0.33 → 0.48 → 0.66 → 1.31 → 1.95 → 2.60 → 3.25 → 3.82 → 4.56 → 5.20 → 5.85 → 6.50 → 7.15 → 7.80 → 8.44 → 9.20 A; for each 6 s step). Then, a CV was measured with H_2 flow (anode) and N_2 flow (cathode). ECSA was estimated from the charge density of absorbed/desorbed hydrogen in the CV (Figure S3).

The degradation of the MEA was performed by ADT cycles with rectangular voltage cycling steps at 0.6–1.0 V for 3 s with H_2 (anode) and air (cathode) flows. The ADT was repeated for 5000, 10,000 and 20,000 cycles during the CT measurements, and CVs and CT data were recorded after each cycle.

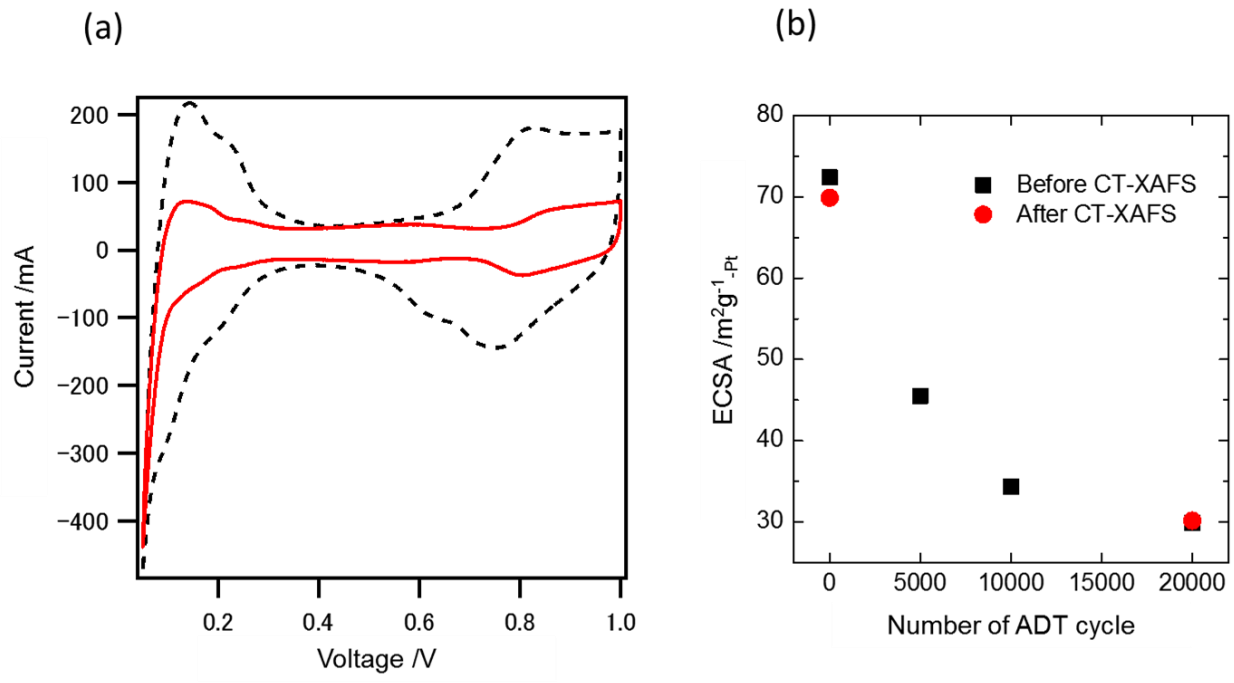

Figure S3. (a) Cyclic voltammograms before (black dashed line) and after (red solid line) the ADT. (b) ECSA changes after the 20,000 ADT cycles before (black square) and after (red circle) the CT-XANES measurements.

Supporting information 2

Experimental procedure for CT-XANES:

Operando CT measurements were conducted at the BL36XU undulator beamline at SPring-8 (8 GeV, 100 mA), Japan (Figure S4). The PEFC cell was irradiated with X-rays monochromatized by Si(111) channel-cut monochromator and passed through a paper rotation diffuser. Higher harmonic X-rays were rejected by two vertical mirrors between the monochromator and the diffuser. The X-ray transmission images of the sample were recorded by a high-resolution X-ray imaging unit (AA50, Hamamatsu Photonics K.K.) coupled with a low noise sCMOS camera (Orca-Flash 4.0, Hamamatsu Photonics, K.K.). The effective view size in the image was 300 nm pixel^{-1}. CT-XANES data were recorded under the PEFC operation conditions. A series of CT-XANES data before ADT was recorded at a constant cell voltage of 1.0 V with the flows of H_2 (anode) and N_2 (cathode). After 20,000 ADT cycles, next CT-XANES measurement was performed at 1.0 V with a similar gas flow.

Angle-limited CT-XANES data were measured as follows. The PEFC cell was rotated to the incident X-ray beam between ±80° angles at an angle interval of 0.1°, and 1600 X-ray projected transmission images of the sample ($I(E)$) were collected. In order to avoid serious sample damage by X-ray irradiation, we decided energy range for the CT-XANES measurements as 11.451-11.631 keV. The CT data measurements were conducted at 184 X-ray energies in the range around the Pt L_{III} edge. The incident X-rays images ($I_0(E)$) were measured at each energy with removing the PEFC from the X-ray beam. The dark signal of the sCMOS camera (I_d) was also considered. The total measurement time was 2.5 h (about 1 min for each energy).

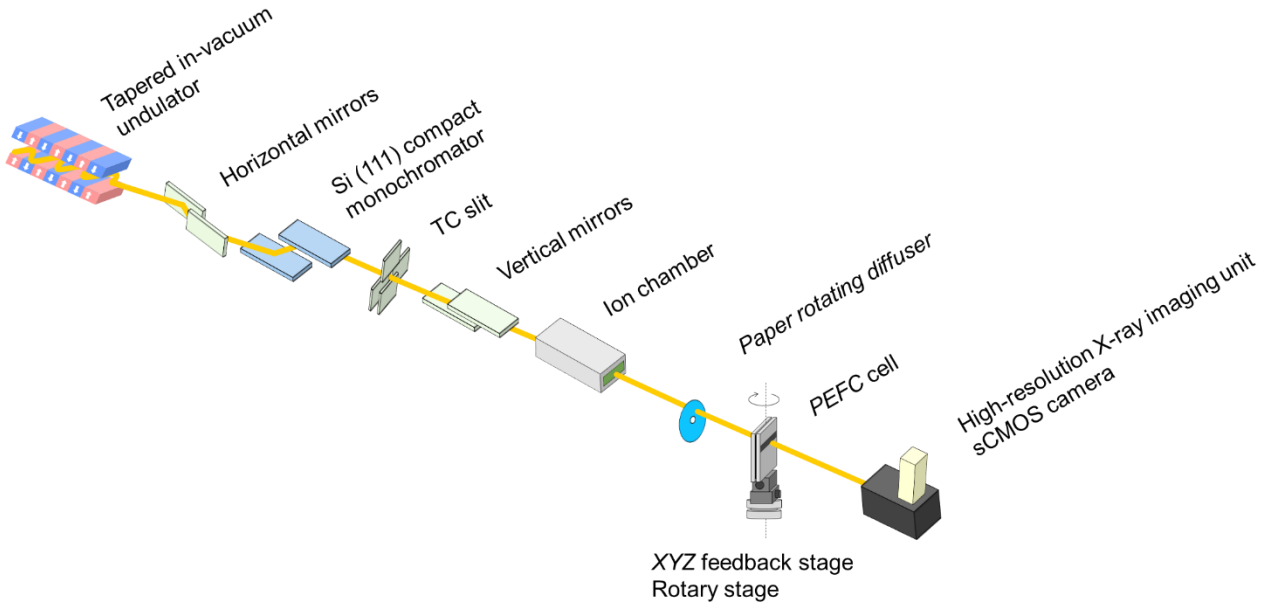

Figure S4. Schematic of the CT-XANES setup at the SPring-8 BL36XU undulator beamline.

Supporting information 3

Reconstruction of CT-XANES

The CT-XANES analysis was performed by the following protocol. The two-dimensional (2D) X-ray transmission images $I(E)$ were converted to the absorption coefficient (μt) by Beer's law with the $I_0(E)$ and $I_d(E)$ images (eq. 1).

$$\mu t = -\ln\left[\frac{I(E) - I_d}{I_0(E) - I_d}\right] \quad \text{(eq. 1)}$$

To correct differences in X-ray transmission in a flat sample from each projection angle (±80°), an image filter was adapted by considering the reciprocal trigonometric function to the sample thickness. The series of X-ray transmission images at different X-ray energies were converted to a four-dimensional matrix. The slight misalignments of the field of view in the data stack were corrected precisely. The Pt L_{III}-edge XANES spectra were separated at each pixel, and were independently curve-fitted (E = 11.50–11.62 keV) with a function (eq. 1 in the paper).

For the 3D matrix of edge jump height ($\boldsymbol{b}_1$) or white-line peak height ($\boldsymbol{c}_1$) in the xy-projection coordinates and projection angles (θ), a sinogram consisting of the x–θ cross section was obtained. The sinogram of $\boldsymbol{b}_1$ or $\boldsymbol{c}_1$ was respectively reconstructed into a 3D matrix of $\widehat{\boldsymbol{b}}_1$ or $\widehat{\boldsymbol{c}}_1$ by angle-limited CT calculation with the ordered-subset expectation maximization (OS-EM) method [*, ref. S1]. To reduce the artifacts, we approximated intensities coming from the outside of the reconstruction area to the average intensity of the reconstruction area. Although small artifact still remained in the outline of the reconstructed image, the agreement of the reconstructed images was confirmed for the present missing-wedge calculation. Finally, the 3D matrix of $\widehat{\boldsymbol{b}}_1$ or $\widehat{\boldsymbol{c}}_1/\widehat{\boldsymbol{b}}_1$ was obtained in the real-space XYZ coordinates. $\widehat{\boldsymbol{c}}_1/\widehat{\boldsymbol{b}}_1$ was converted to the absolute Pt valence state by using the white-line heights of Pt foil (Pt^0) and Pt acetylacetonate (Pt^{2+}) as standard. All calculations were parallelized by GPGPU code and were computed within several days.

*OS-EM method is an accelerated expectation maximization (EM) method, which processes the data in subsets within iteration. The OS-EM method provides the correction of non-uniform attenuation, spreading to the depth, less noisy, and streak free, compared to the general filter back projection (FBP) method.

Ref. S1. (a) L. A. Shepp, Y. Vardi, *IEEE Trans. Med. Imaging*, **1982**, *1* 112; (b) K. Lange, R. J. Carson, *Journal of Computer Assisted Tomography*, **1984**, *8*, 306; (c) H. M. Hudson, R. S. Larkin, *IEEE Trans. Med. Imaging*, **1994**, *13*, 601.

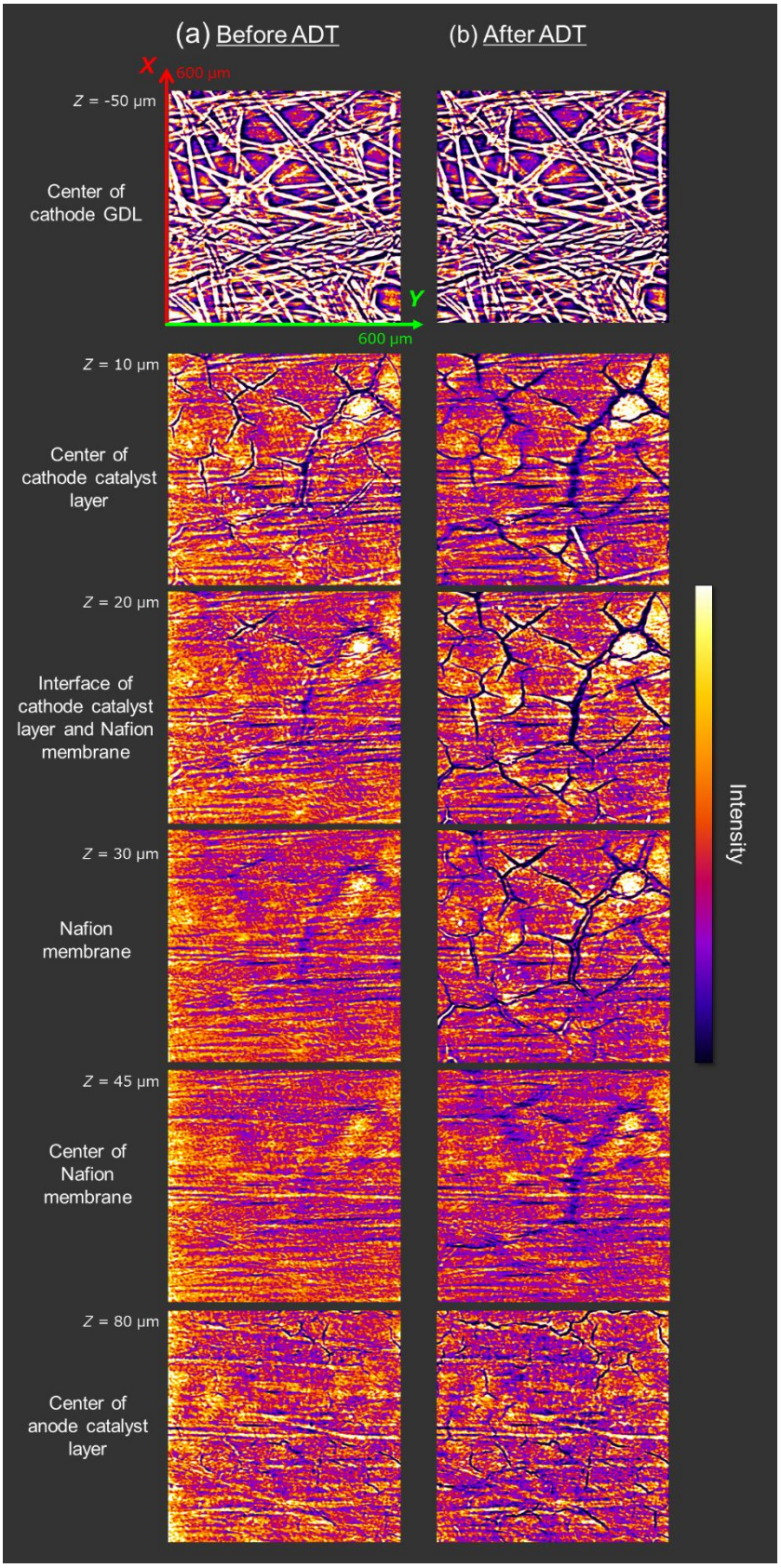

Figure S5. (a, b) Cross-sections of morphology images obtained from the CT data measured at 11.497 keV. (a) MEA before ADT and (b) MEA after the 20,000 ADT cycles.

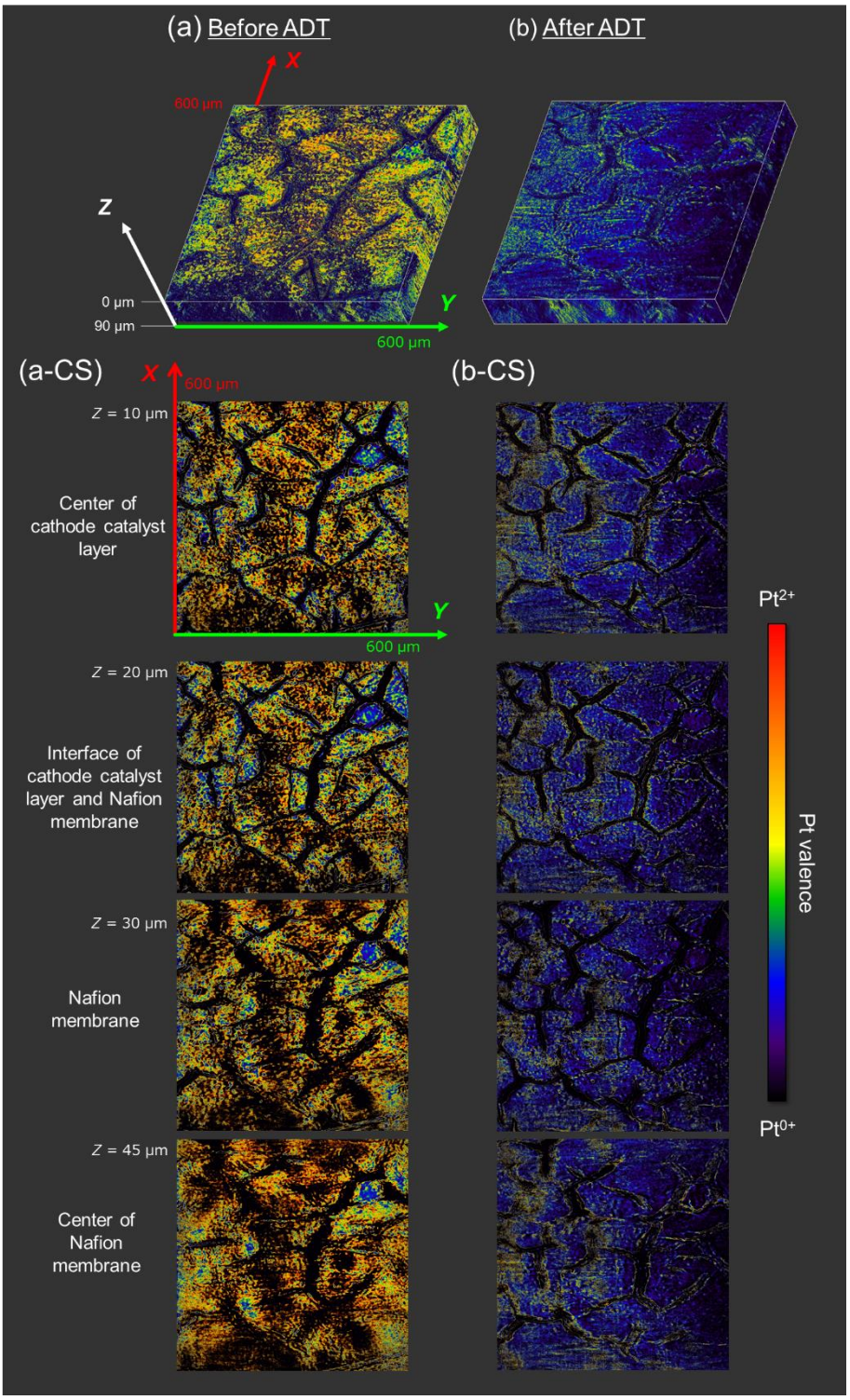

Figure S6. 3D images and (CS) cross-sectional images of Pt valence state in the MEA (a) before ADT and (b) after the 20,000 ADT cycles. Color bar is scaled between Pt^0 and Pt^{2+}. Cell voltage = 1.0 V.

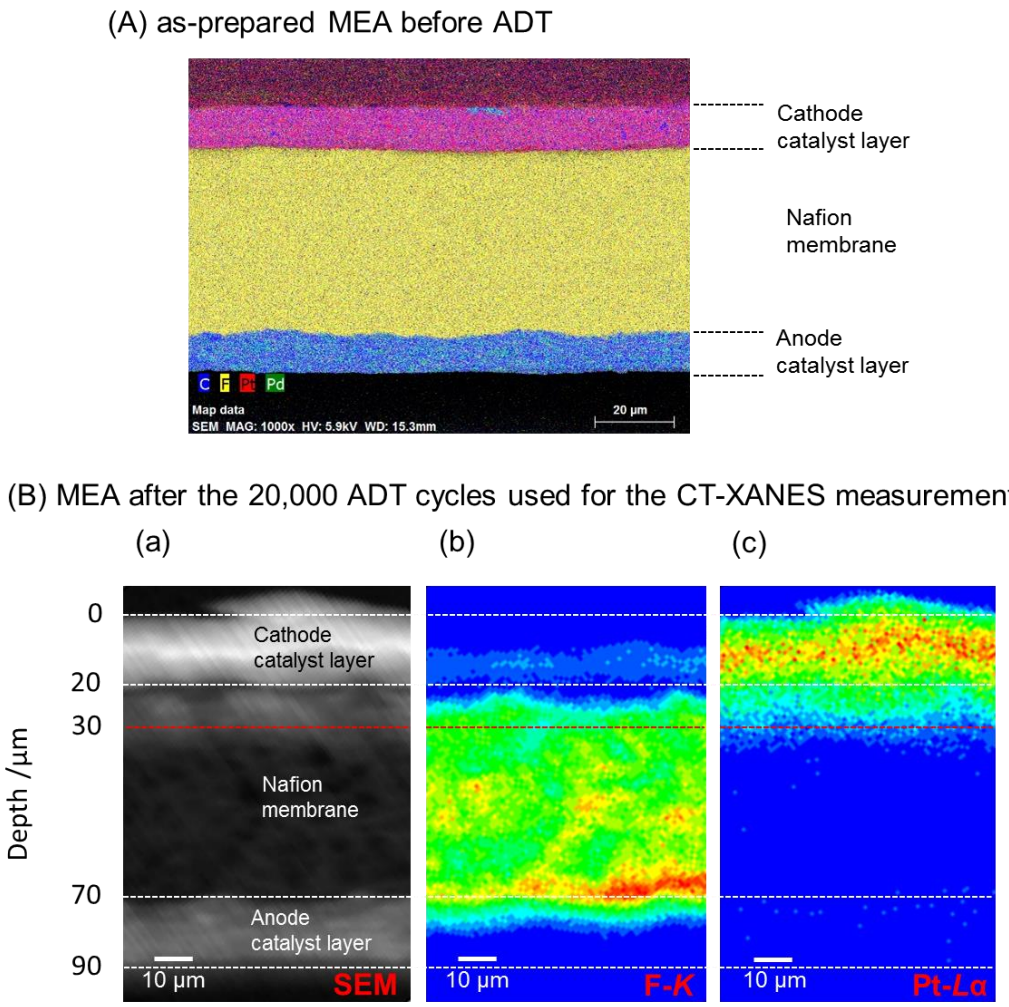

Figure S7. (A) *Ex situ* cross-sectional SEM-EDS image (SU6600, Hitachi High-tech. Co.) of another as-prepared MEA before aging and ADT. Blue, yellow, red, and green colors indicate C-*K*, F-*K*, Pt-*Mα*, Pd-*Lα* intensities, respectively. (B) (a) *Ex situ* cross-sectional SEM image (EPMA-1610, Shimadzu Co.) of the MEA after the 20,000 ADT cycles used for the CT-XANES measurements together with (b, c) SEM-EDS mappings of F-*K* and Pt *Mα* X-rays. White dashed lines present the interfaces of each layer. Red dashed line presents $Z = 30$ μm.

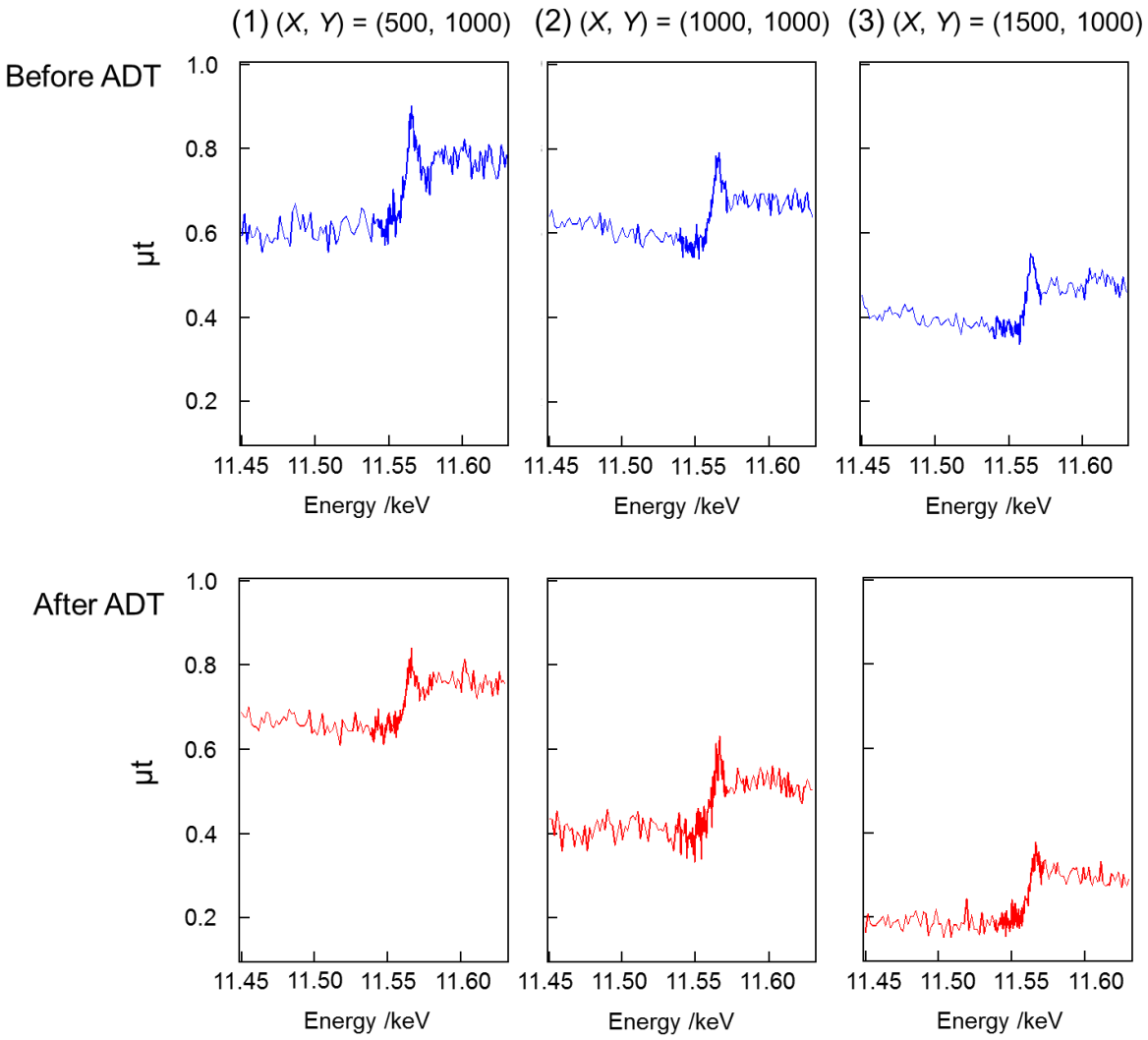

Figure S8. Examples of Pt L_{III}-edge XANES spectra obtained from the CT transmission images before reconstruction. XANES spectra separated at (X, Y) = (500, 1000), (1000, 1000), (1500, 1000) pixels on the 2D transmission of MEA before ADT and after the 20,000 ADT cycles (projection angle: θ = 20°). Cell voltage = 1.0 V.

The CT-XANES measurements with sample rotation take longer measurement time compared to conventional XANES measurements, and we found the degradation of the MEA by X-ray irradiation during the *operando* CT-XANES measurements. To avoid serious sample damage, we recorded the CT images at three different energies of 11451 (back ground), 11566 (white-line peak top), and 11572 eV (isosbestic point) only for the MEA after the 5,000 and 10,000 ADT cycles. After reconstructing the 3D images at each energy, the images of Pt density were roughly calculated by the subtraction of background image (11451 eV) from isosbestic image (11572 eV).

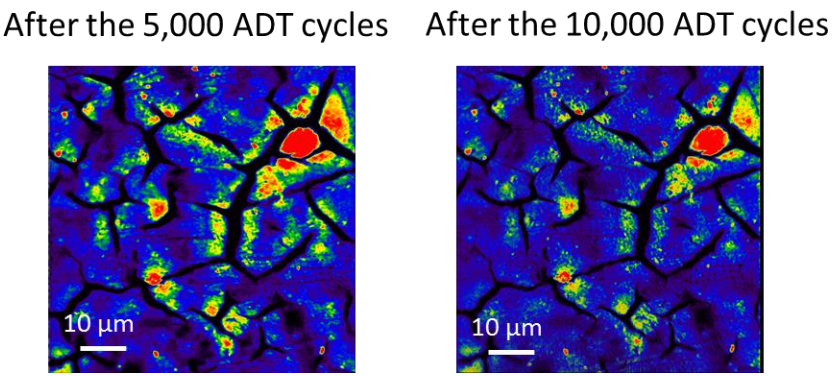

Figure S9 The Pt density images at Z = 10 µm (the center of cathode catalyst layer) calculated by the CT images measured at 11451 and 11572 eV for the MEA after the 5,000 (left) and 10,000 (right) ADT cycles.