

Electronic Supplementary Information for

***In-situ* S-K XANES study on polymer electrolyte fuel cell: Changes in chemical state of sulfonic group depending on humidity**

Kazuhisa Isegawa,^a Tetsuo Nagami,^b Shinji Jomori,^b Masaaki Yoshida^a and Hiroshi Kondoh^{*,a}

^aDepartment of Chemistry, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama, Japan.

^bToyota Motor Corporation, 1 Toyota-cho, Toyota, Japan.

*To whom correspondence should be addressed.

E-mail: kondoh@chem.keio.ac.jp

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1. Photodecomposition of the Nafion membrane

On the course of this study we found from S-K XANES spectra that x-ray irradiation onto the Nafion membranes induces irreversible photodecomposition of the sulfonic groups. We performed continuous irradiation experiments of X rays onto the Nafion membranes at BL6N1 of AichiSR with a high photon density (I_0 current/irradiated area: 0.20 nA/mm²) and at BL-11B of PF with a low photon density (0.04 nA/mm²) for comparison. Both the experiments were carried out in a helium path using a silicon drift detector.

Time courses of S-K XANES spectra taken at AichiSR BL6N1 and PF BL-11B are shown in Fig. S1. Intensities of the shoulder structure and the main peak are compared as shown in Fig. S2. In the case of the high photon density shown in Fig. S2A, the main peak is decreased slightly, while the shoulder structure is readily increased. These irreversible changes are associated with photodecomposition of the sulfonic groups of Nafion. The difference spectrum between the 1st and last spectra of Fig. S2A is shown as green line in Fig. S3. Since the peak position of the difference spectrum coincides with that of sulfuric acid, the main photodecomposition product is identified as sulfuric acid. On the other hand for the lower photon density shown in Fig. S2B no spectral changes are observed. Thus we could perform in-situ experiments without photodecomposition when we used a sufficiently low photon density. The data shown in the text were obtained under such sufficiently low photon density conditions.

To understand time dependence of the photodecomposition, the factor analyses were conducted to the XANES spectra shown in Fig. S2A by linear combination of the spectra of Nafion and the sulfuric acid (Fig. S4). The abundance ratio of the sulfuric acid varies almost linearly with time as shown in Fig. S4(c). If the measurement was carried out for a longer period, the abundance ratio would be asymptotic to a constant value.

The information on the structural changes in side chains of Nafion could be obtained by C-K and/or O-K XANES measurements, which is useful for understanding of the photodecomposition mechanism. However, in *in-situ* experiments using an actual fuel cell like our setup, the information might be obscured by background signals from carbon support, water, oxygen and so on. The microscopic capability is quite important to eliminate such background signals.

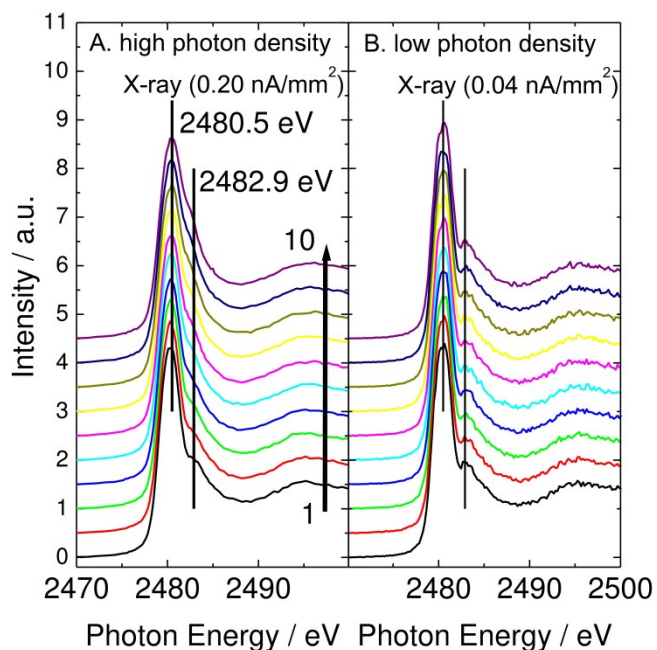


Figure S1. Comparison of S-K XANES spectra of Nafion membranes measured with high and low photon-density x rays; A: 0.20 nA/mm² taken at BL6N1 of the Aichi-SR and B: 0.04 nA/mm² at BL-11B of the Photon Factory.

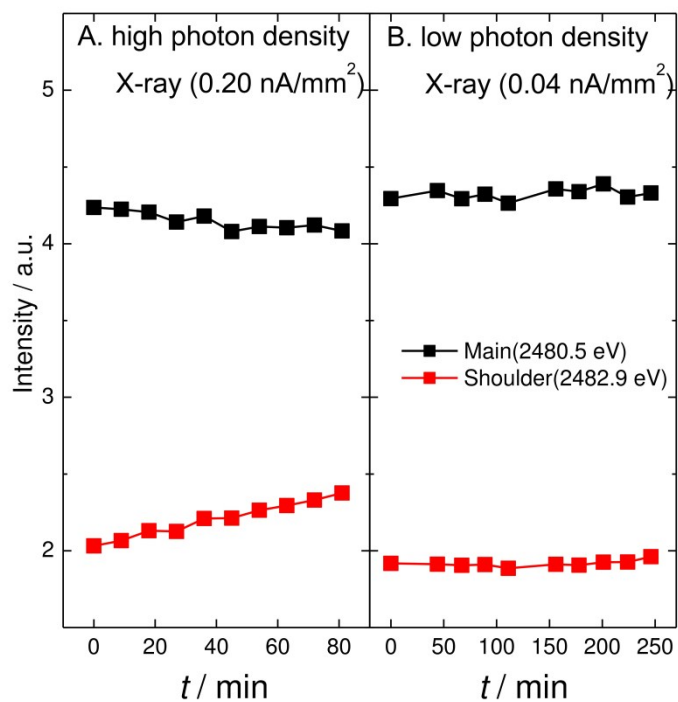


Figure S2. Plots of intensities of the main peak and the shoulder structure of the S-K XANES spectra taken under continuous x-ray irradiation shown in Fig. S1.

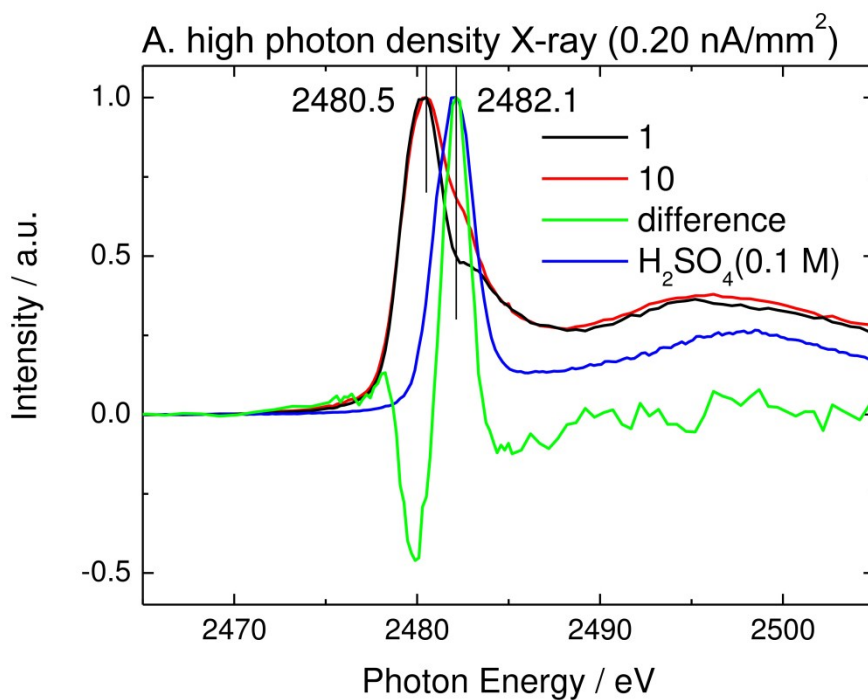


Figure S3. Difference spectrum of S-K XANES (green) between the 1st spectrum (black) and the 10th spectrum (red) taken under continuous x-ray irradiation onto a Nafion Membrane with a high photon density (0.20 nA/mm^2). As a reference, an S-K XANES spectrum of sulfuric acid in aqueous solution (0.1 M) is also indicated (blue).

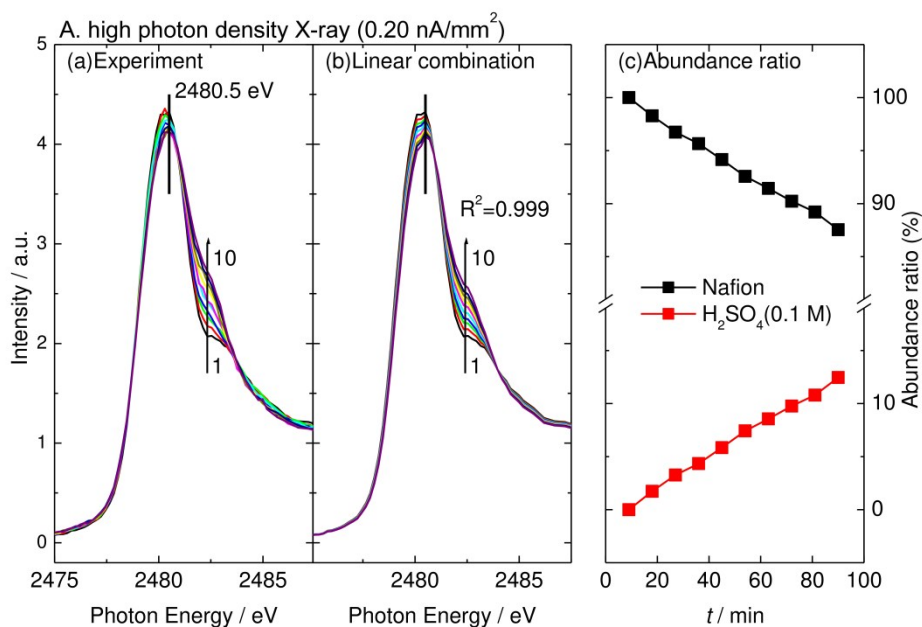


Figure S4. Estimation of abundance ratio of sulfuric acid produced by the photodecomposition as a function of a time. (a) experimental spectra; (b) reproduced spectra by linear combination of Nafion and sulfuric acid spectra; (c) time evolution of the abundance ratio.

2. Simulated S-K XANES spectra for the standard samples

We simulated S-K XANES spectra for alkyl sulfonate ions on the basis of the density functional theory transition potential (DFT-TP) calculations¹ using StoBe-deMon program² with the GGA/PBE functional as shown in Fig. S5 and compared with those for the observed spectra for the corresponding alkyl sulfonic acids in solution taken as the standard samples shown in Fig. 2. It is confirmed that the observed spectra are well reproduced in the simulated spectra.

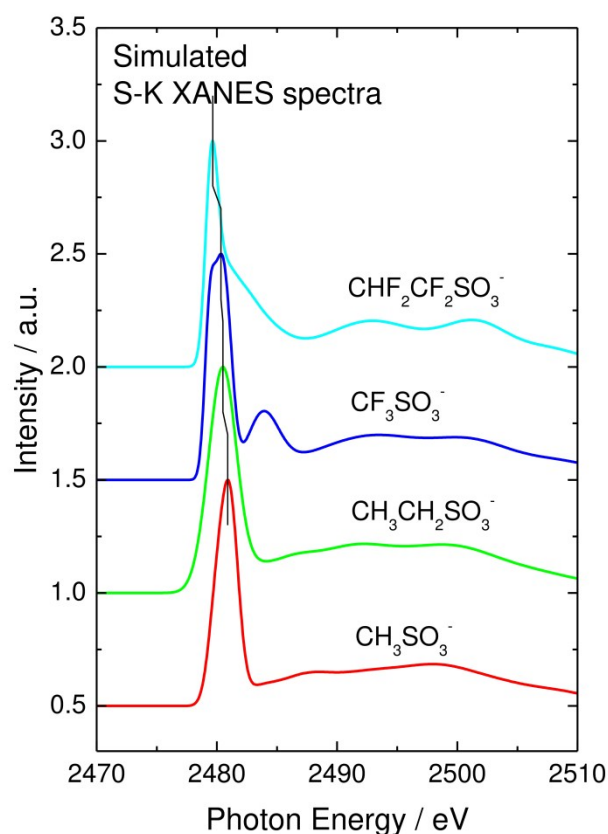


Fig. S5. Simulated S-K XANES spectra for alkyl sulfonate ions; CHF₂CF₂SO₃⁻, CF₃SO₃⁻, C₂H₅SO₃⁻, CH₃SO₃⁻ (Top to bottom).

3. Cyclic voltammetry curves for the MEAs depending on humidity

Figure S6 shows cyclic voltammetry (CV) curves for the MEAs recorded after keeping the MEAs under conditions indicated in the figure. For example, “wet, -0.2 V” means that the MEA was kept under the wet gas-flowing condition at a cathode voltage of -0.2 V vs. SHE until reaching the equilibrium and then a S-K XANES spectrum was measured and subsequently a CV curve was recorded for a potential range from 0 to 1.0 V at a scan rate of 10 mV/s with keep the humidity unchanged (i.e. wet in this case). Under the dry conditions the current is substantially reduced over the whole range of applied potential. Note that when the humidity was returned to wet after once drying the MEA, the CV curve (bleu) is not completely recovered to the original curve (black), indicating that an irreversible process takes place in the MEA under the dry condition. This is associated with decomposition of the sulfuric group into atomic sulfur adsorbed on the catalysts as shown in Fig. 6.

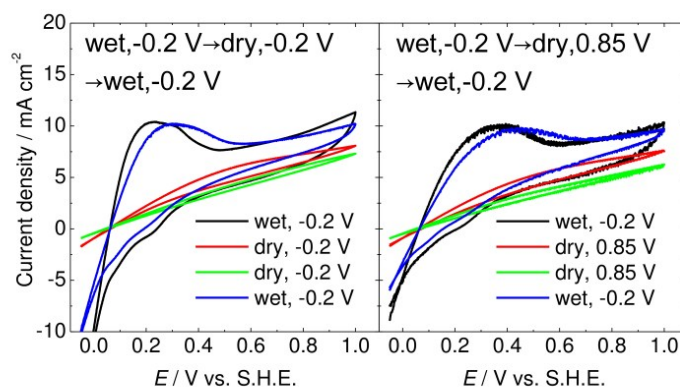


Figure S6. Cyclic voltammetry (CV) curves for the MEAs under wet and dry gas-flowing conditions. All the CV curve measurements were conducted at a scan rate of 10 mV/s.

4. Peak analysis of the main peak and the shoulder structure

In the main text, spectral changes depending on potential and humidity are discussed using the intensity changes at certain energies; peak maxima of the main peak (2480.5 eV) and the shoulder structure (2482.9 eV). However, there is a possibility that the peak maxima are also shifted. To check this possibility we conducted curve-fitting analyses for the *in-situ* S-K XANES spectra shown in Fig. 3 using three Gaussian functions corresponding to the main peak, shoulder structure and post-edge component. Peak areas of the main peak and the shoulder structure, and their ratios are shown in Fig. S7. Under dry condition, the area ratio decreases similarly to Fig. 4. Energy shifts of the features are shown in Fig. S8 (upper). Under dry condition, it is revealed that both the main and the shoulder structure shift to the high energy and the separation energies between the main peak and the shoulder structure also increases as shown in Fig. S8 (lower).

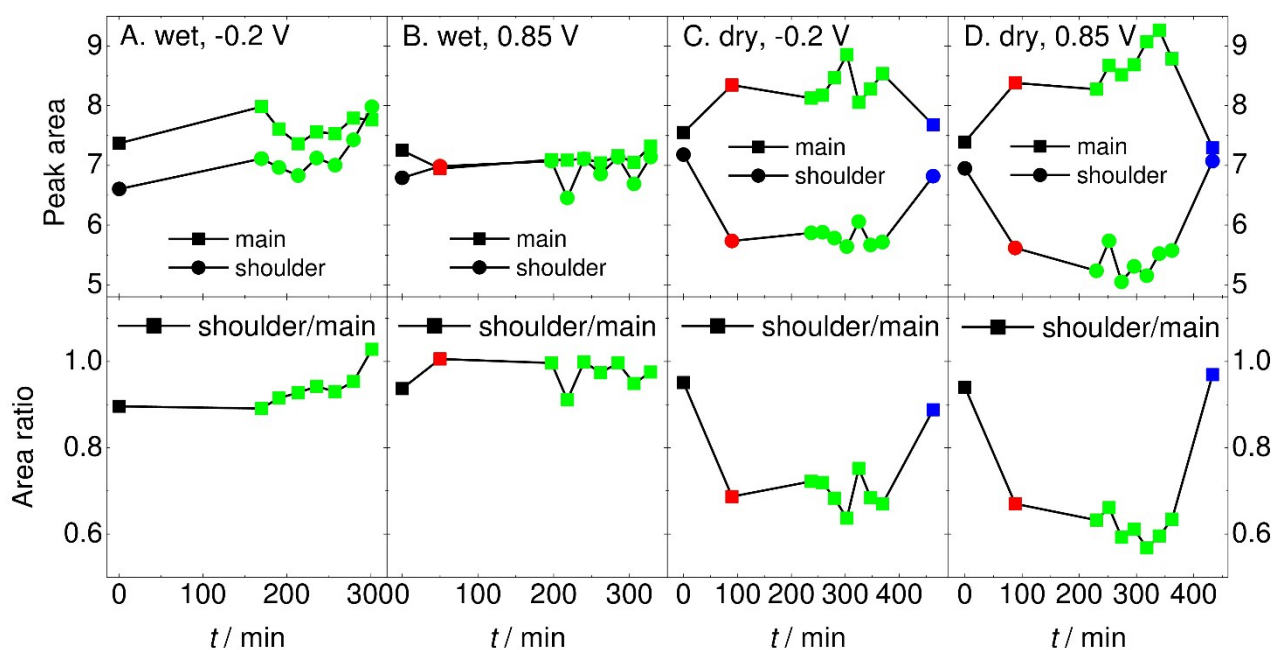


Figure S7. Peak areas of the main peak and the shoulder structure in the spectra shown in Fig. 3 are plotted as a function of elapsed time (upper); area ratio of the main peak and the shoulder structure (lower). The color code is the same as that in Fig. 3.

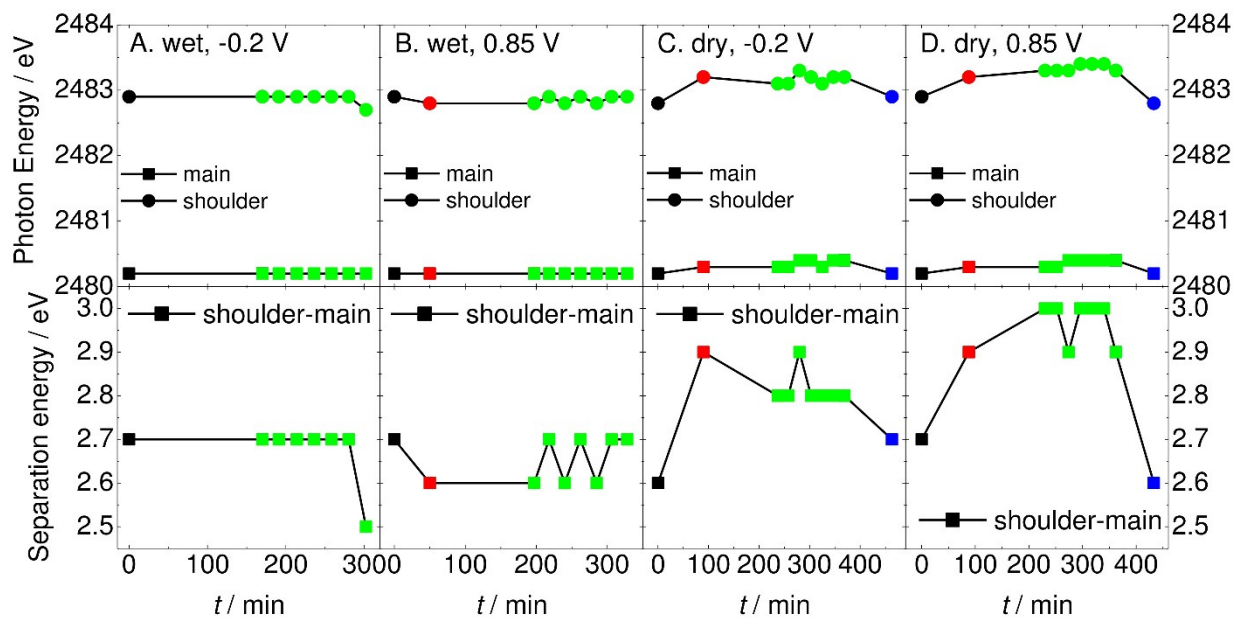


Figure S8. Peak energies of the main peak and the shoulder structure in the fitted spectra of Fig. 3 are plotted as a function of elapsed time (upper); energy differences between the main peak and the shoulder structure (lower). The color code is the same as that in Fig. 3.

5. Thermal effects on the XANES spectra

The humidity of the cell was controlled by temperatures of the cell and bubblers on the gas lines as described in the experimental section. For the wet condition the temperature of the cell was kept at 20 °C, while for the dry condition it was increased to 60 °C. From the experimental results obtained under these conditions it cannot be excluded that the observed changes in XANES spectra might include thermal effects. To check this possibility we conducted the same experiments except for the cell temperature, where the temperature of the cell was kept at 20 °C both for the wet and dry conditions and afterward it was increased to 60 °C to check thermal effects.

Figure S7 shows in-situ XANES spectra for the MEA (cathode) of the PEFC under gas flow (H_2 for anode and He for cathode) with changing humidity under applying potential to the cathode (A: -0.2 V, B: 0.85 V). Intensity ratios of the main peak and the shoulder structure are shown in Fig. S8. It is confirmed that similar humidity-dependent spectral changes are observed (from black to red) even at a constant temperature of 20 °C. Note that the increase in temperature from 20 °C to 60 °C under the dry condition (from red to green) causes only a small change, which indicates that the thermal effect on the cell is not significant.

Figure S9 shows low-energy region of the S-K XANES spectra taken under gas-flowing conditions shown in Fig. S7 on a magnified scale. A peak is clearly observed at 2471 eV, which is attributed to atomic sulfur adsorbed on the Pt catalysts. Although the formation rate of the atomic sulfur is higher at -0.2 V, it is formed even at 0.85 V. This is more clearly seen in the intensity plots as a function of elapsed time as shown in Fig. S10. The formation rate of the Pt-adsorbed atomic sulfur is independent of temperature, but it was found to depend on the applied potential. The drying-induced decomposition of the sulfuric group into atomic sulfur could be accelerated on the Pt catalyst surfaces biased at -0.2 V.

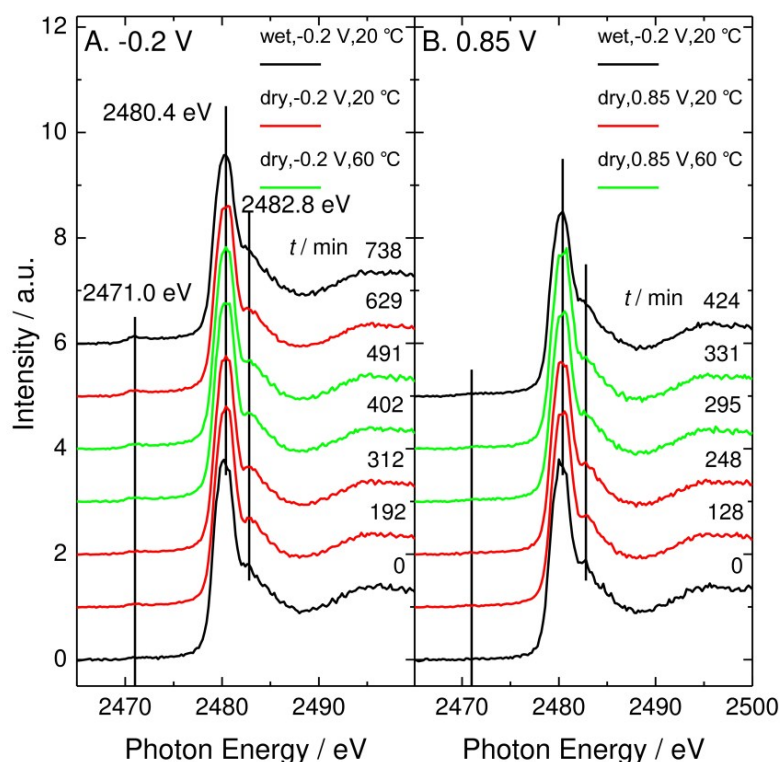


Figure S9. S-K XANES spectra of the cathode of PEFC under gas-flowing conditions at a constant temperature of 20 °C with changing humidity under applying potential to the cathode (A: -0.2 V, B: 0.85 V). Black curves are spectra measured at -0.2 V in the wet condition at 20 °C. Red curves are spectra taken under the dry condition at 20 °C, while green curves are those at 60 °C. The elapsed time from the initial measurement is shown at the right-hand side.

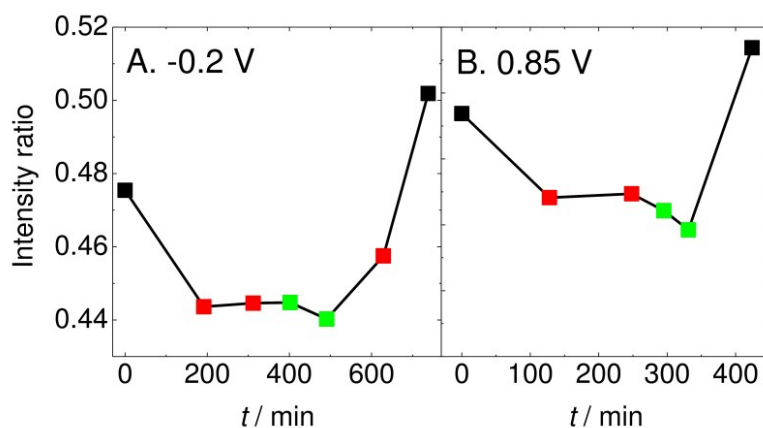


Figure S10. Plots of the intensity ratios of the main peak (2480.4 eV) and the shoulder structure (2482.8 eV) in the spectra shown in Fig. S7 as a function of elapsed time. The color code is the same as that in Fig. S7.

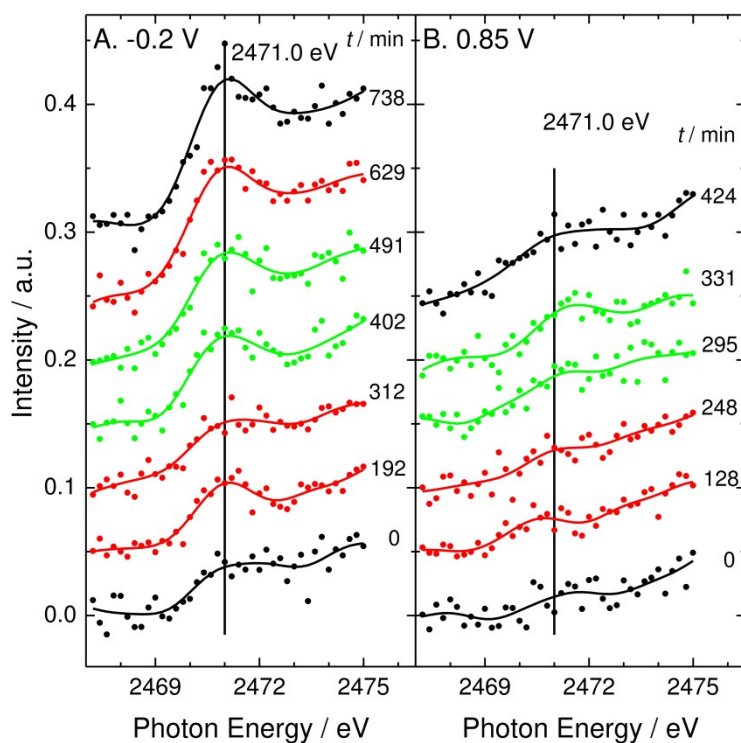


Figure S11. Low-energy region of the S-K XANES spectra taken under gas-flowing conditions shown in Fig. S7 on a magnified scale (dots: observed points, solid lines: smoothed curves). The elapsed time from the initial measurement is shown at the right-hand side. The vertical line corresponds to the energy position where the atomic sulfur adsorbed on Pt surfaces gives the main peak.³

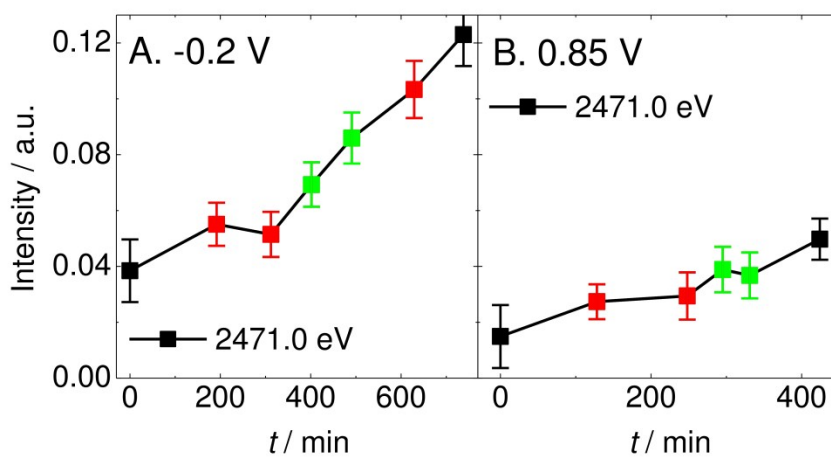


Figure S12. Plots of the intensity averaged over 5 points around 2471.0 eV of the XANES spectra shown in Fig. S9 as a function of elapsed time. The color code is the same as that in Fig. S7.

References

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3. O. A. Baturina, B. D. Gould, A. Korovina, Y. Garsany, R. Stroman and P. A. Northrup, *Langmuir*, 2011, **27**, 14930-14939.