

Electronic Supplementary Information

**Spatial Imaging of Catalyst Poisoning with SO<sub>2</sub> on Pt/C PEFC  
Electrocatalyst by *Operando* Pt L<sub>III</sub>-edge XAFS-CT Imaging**

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## ***Supporting information 1: sample and electrochemical processes***

### ***MEA***

MEAs with a 50 wt% Pt/C catalyst (TEC10E50E, Tanaka Kikinzoku Kogyo K.K. (TKK); 0.5 mg<sub>Pt</sub> cm<sup>-2</sup> for electrochemical analysis and *operando* XAFS analysis; 1.5 mg<sub>Pt</sub> cm<sup>-2</sup> for *operando* XAFS-CT analysis) at the cathode and a 50 wt% Ru/C catalyst (TECRu(ONLY)50E, TKK; 0.5 mg<sub>Ru</sub> cm<sup>-2</sup>) at the anode were commercially prepared by Eiwa Co., Ltd. The catalyst layers of 3 cm × 3 cm were hot-pressed onto a Nafion membrane (NR-212, Sigma-Aldrich) of 7 cm × 7 cm size. The set of the MEA with two gas diffusion layers (GDLs; TGP-H-030, Toray Ind., Inc.) was inserted in an *operando* PEFC cell, consisting of Al-Mg-made separators, Kapton-made thin film heaters, Au-coated Cu-made current collectors, and carbon-made gas flow channel plates (1 mm × 1 mm, serpentine pattern).<sup>S1</sup>

### ***PEFC operation and electrochemical measurements***

The PEFC cell was operated at 353 K by supplying humidified H<sub>2</sub> at the anode (99.99995%, 150 mL min<sup>-1</sup>, relative humidity (RH) = 92%) and humidified 20% O<sub>2</sub>/N<sub>2</sub> (99.99995%, 1000 mL min<sup>-1</sup>, RH = 92%) at the cathode. The cell voltage was controlled by a potenti/galvano stat (VSP-300, BioLogic Science Instruments Co. Ltd.) with two sets of 10 A booster boards. In the following experiments, the cell voltage was applied using the anode acting as a reference electrode. The as-prepared MEA in the PEFC cell was conditioned by the 150 cycles of IV scan (0–1.1 A cm<sup>-2</sup>, 14 steps, 6 s for each). Following, the cathode gas was purged with N<sub>2</sub> gas, and CV cycles were recorded (0.05–0.90 V at 0.05 V s<sup>-1</sup> speed). ECSA was calculated by the average charge in hydrogen adsorption and desorption peaks of the CV (0.05–0.4 V range). IV profiles were measured under similar conditions for the conditioning of MEA and power density was calculated.

### ***SO<sub>2</sub>-poisoning and electrochemical treatment for catalyst recovery***

An on-site SO<sub>2</sub>-poisoning system was constructed inside the experimental hutch of the SPring-8 BL36XU station for *operando* XAFS measurements as shown in Fig. S2.<sup>S2</sup> To supply humidified gas with SO<sub>2</sub> contaminant to the cathode, 200 ppm of SO<sub>2</sub>/N<sub>2</sub> was added to the humidified cathode gas (N<sub>2</sub> or 20% O<sub>2</sub>/N<sub>2</sub>, 99.99995%, relative humidity (RH) = 92%) before the inlet of the cathode side of the PEFC cell.<sup>S3</sup> 4 ppm of SO<sub>2</sub> balanced with the humidified 20% O<sub>2</sub>/N<sub>2</sub> (for electrochemical measurements) or N<sub>2</sub> (for XAFS measurements) was supplied to the PEFC cell at the total flow rate of 1000 mL min<sup>-1</sup>. During the SO<sub>2</sub>-poisoning treatment, the cell voltage was kept at 0.4 V, and the time-course change in the cell current was monitored by chronoamperometry (CA).

For *operando* XAFS-CT experiments, due to the limitation of beamtime at SPring-8, the high concentration of 50 ppm SO<sub>2</sub> balanced with humidified 20% O<sub>2</sub>/N<sub>2</sub> (RH = 92%) was supplied with the total flow rate of 1000 mL min<sup>-1</sup> at the PEFC cathode, applying the cell voltage of 0.4 V for 100 min.

Then, the cell voltage was kept constant at 0.4 V and the cathode gas was switched from 20% O<sub>2</sub>/N<sub>2</sub> to humidified N<sub>2</sub> (RH = 92%). The total time of the SO<sub>2</sub> flow was 120 min (20% O<sub>2</sub>/N<sub>2</sub>: 100 min, N<sub>2</sub> 20 min). The catalyst poisoning with SO<sub>2</sub> was evaluated by CV and a decrease in ECSA (6.7 m<sup>2</sup> g<sub>Pt</sub><sup>-1</sup> for 4 ppm SO<sub>2</sub>, 5.7 m<sup>2</sup> g<sub>Pt</sub><sup>-1</sup> for 50 ppm SO<sub>2</sub>) was found to be independent of the SO<sub>2</sub> concentration (Fig. S3(c)).

The electrochemical recovery of the SO<sub>2</sub>-poisoned MEA was processed by supplying 1000 mL min<sup>-1</sup> of 20% O<sub>2</sub>/N<sub>2</sub> (RH = 92%) at the cathode and applying 1.0 V for 1 h. After each treatment, the cathode gas was sufficiently exchanged by N<sub>2</sub>, and CV measurements were performed to evaluate the poisoning and subsequent recovery of the Pt electrocatalyst in the MEA.

### ***Operando Pt L<sub>III</sub>-edge XAFS measurements and curve-fitting analysis***

*Operando* Pt L<sub>III</sub>-edge XAFS measurements were performed at the BL36XU beamline of SPring-8 (8 GeV, 100 mA) as illustrated in Fig. S2.<sup>S2</sup> Hard X-rays were monochromatized by a Si(111) channel-cut compact monochromator, and monochromatized X-rays were detected by ion chambers filled with N<sub>2</sub>/Ar (95/5) for I<sub>0</sub> and N<sub>2</sub>/Ar (50/50) for I<sub>1</sub> and I<sub>2</sub>, respectively. The *in-situ* PEFC cell with an X-ray transmission window (1 mm width) was set in the optical path between the I<sub>0</sub> and I<sub>1</sub> ion chambers. During the XAFS measurements of the SO<sub>2</sub>-treated MEA, 1000 mL min<sup>-1</sup> of 4 ppm SO<sub>2</sub> balanced with humidified N<sub>2</sub> (RH = 92%) was supplied to the cathode side to maintain the S-poisoned structures of the Pt electrocatalyst, while 1000 mL min<sup>-1</sup> of humidified N<sub>2</sub> (RH = 92%) was supplied for the measurement after the recovery process. The SO<sub>2</sub>-poisoned MEA suffered serious sample damage by long-time X-ray irradiation in the presence of O<sub>2</sub>, but we found that the XAFS measurements under an inert N<sub>2</sub> atmosphere at the cathode were efficient to avoid serious sample damage during the XAFS measurements. The measured Pt L<sub>III</sub>-edge XANES and EXAFS spectra were calibrated at E<sub>0</sub> of 11.559 keV and normalized by using an XAFS package software: Demeter (Athena). Phase shift and backscattering amplitude for each shell were calculated by FEFF8.5L code using structural parameters obtained from the crystalline structures of Pt (ICSD243678), PtO<sub>2</sub> (ICSD26599), and PtS (ICSD41375). S<sub>0</sub><sup>2</sup> for the EXAFS fitting was set at 0.94 by referring to our previous study.<sup>S4</sup>

### ***Particle size distribution analysis of the Pt electrocatalyst by TEM***

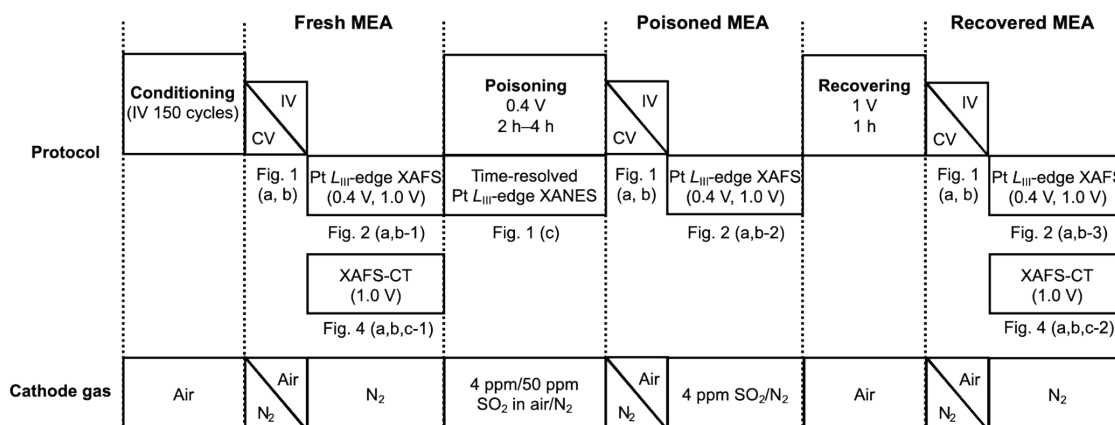
The MEAs were taken out from the PEFC cell and dried under a vacuum overnight. Then, the Pt electrocatalysts were scratched off from the cathode side of the MEAs and dispersed in acetone. The acetone dispersion was ultra-sonicated in an ice bath for 10 min (three times) and the small amount of the supernatant was dispersed in ethanol. 1.5 μL of the ethanol dispersion was dropped onto a Cu-made TEM grid to prepare TEM samples. The particle size of the Pt electrocatalyst was evaluated based on TEM images and using at least 200–300 particles, whose average particle sizes were estimated by Gaussian curve fitting.

### ***Same-view XAFS-CT measurements for the fresh and recovered MEA***

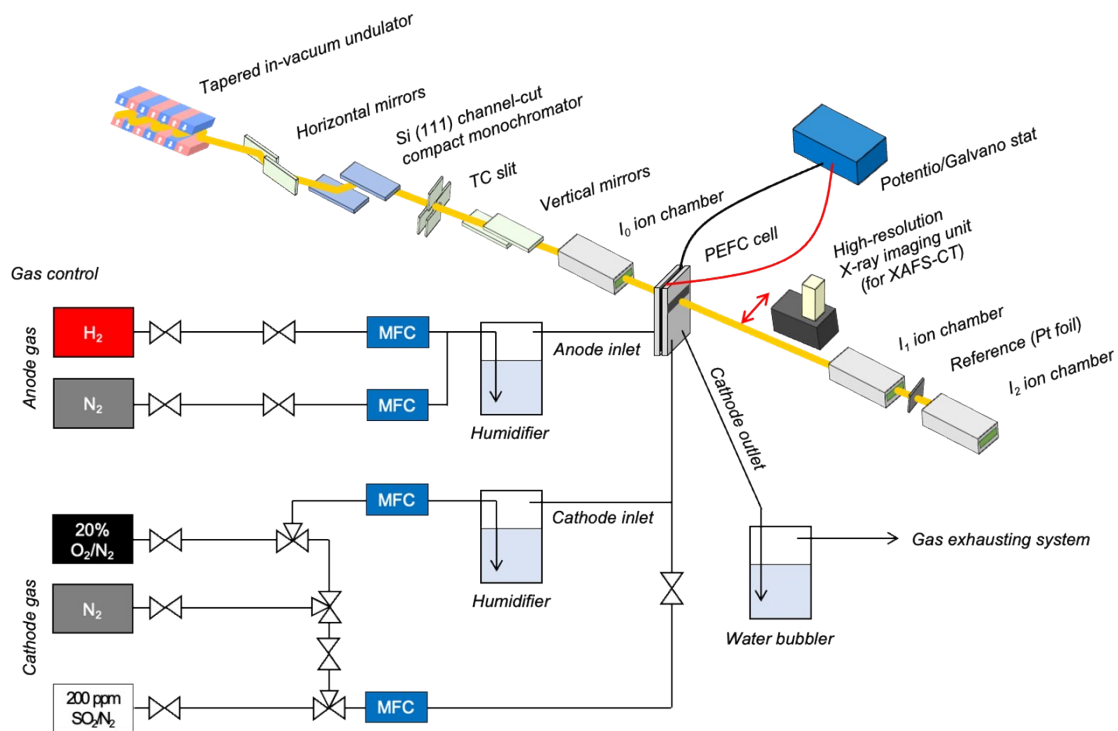
*Operando* XAFS-CT spectroimaging measurements were conducted at the BL36XU undulator beamline at SPring-8, as illustrated in Fig. S2.<sup>S2</sup> Hard X-rays monochromatized by Si(111) channel-cut monochromators were irradiated to the PEFC cell through a paper-made rotation diffuser. The PEFC cell was mounted onto a set of feedback stages ( $X$ ,  $Y$ , and  $Z$ ) and a rotary stage ( $\theta$ ). Stage axes were defined as parallel to the horizontal direction of the membrane surface ( $X$ ), the vertical direction of the membrane surface ( $Z$ ), and parallel to the direction of the X-ray optical path, the same as the depth direction of the membrane ( $Y$ ), respectively. The perpendicular irradiation of X-rays to the membrane sample was defined as  $\theta = 0^\circ$ .

As schematic of the data construction is shown in Fig. S6, the series of the X-ray transmission images of a sample ( $I(E)$ ) were measured at Pt  $L_{III}$ -edge ( $E = 11.274\text{--}11.855$  keV, 1250 pts) using a high-resolution X-ray imaging unit (scintillator; single crystalline CeGAGG, lens; AA50, Hamamatsu Photonics, K.K.) coupled with a low-noise sCMOS camera (2048 pixels  $\times$  2048 pixels, Orca-Flash 4.0 V2, Hamamatsu Photonics, K.K.). The monochromator was scanned by a quick mode and then the projection angle  $\theta$  was changed between  $\theta = \pm 80^\circ$  in  $1^\circ$  step. X-ray intensity images ( $I_0(E)$ ) were simultaneously measured for the energy range by a quick-energy scan without the sample. The dark signal of the sCMOS camera ( $I_{\text{dark}}$ ) was measured by closing an X-ray optical shutter. The effective pixel size of the images was  $0.325 \mu\text{m} \times 0.325 \mu\text{m}$  in the field of view of  $665.6 \mu\text{m} \times 665.6 \mu\text{m}$ . The rate of XAFS data acquisition at a single projection angle was 50 Hz and the overall time of the XAFS-CT measurements with 161 angles was about 1.5 h. The analysis of XAFS-CT data was described in Supporting information 3.

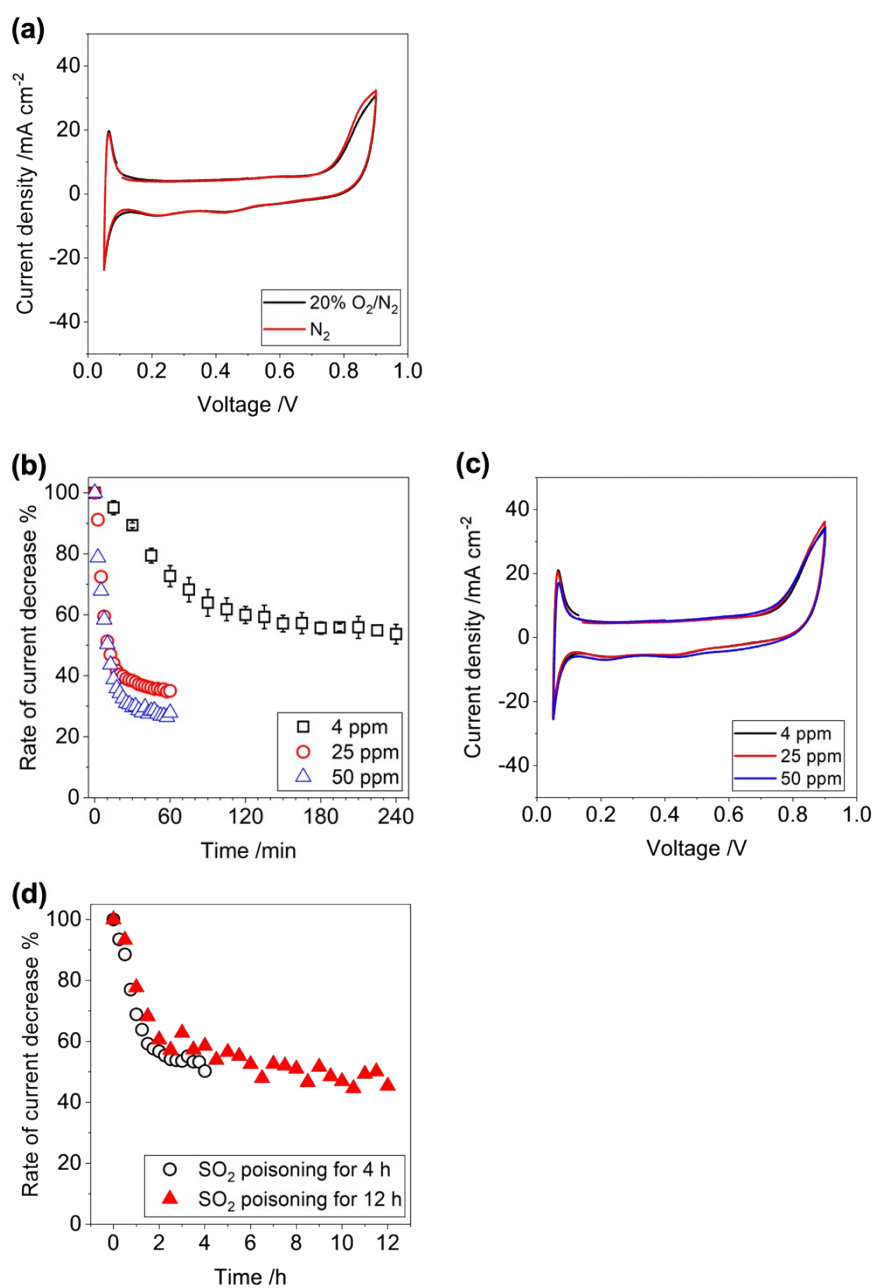
The XAFS-CT data sets were measured for the same MEA after the conditioning (fresh MEA) and after the catalyst poisoning with  $\text{SO}_2$  and the subsequent recovery process (recovered MEA). The catalyst poisoning was conducted with 50 ppm of  $\text{SO}_2$  and the final deactivation (loss of ECSA) was found to be comparable to that of 4 ppm of  $\text{SO}_2$  (see in Fig. S3 (c)). During the measurements, humidified  $\text{N}_2$  was supplied in  $1000 \text{ mL min}^{-1}$  at the cathode.



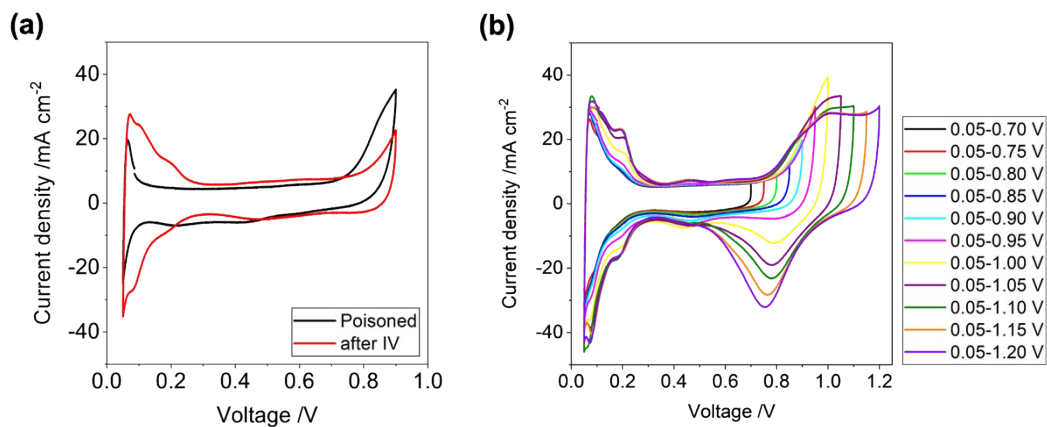
**Fig. S1** Experimental protocol of on-site catalyst poisoning with SO<sub>2</sub>, subsequent electrochemical recovery process, electrochemical analysis, and *operando* Pt  $L_{III}$ -edge XAFS and XAFS-CT measurements.



**Fig. S2** A schematic of the on-site  $\text{SO}_2$ -poisoning system and *operando* XAFS/XAFS-CT setup at the BL36XU station, SPring-8.<sup>S2</sup> The 200 ppm of  $\text{SO}_2$  in  $\text{N}_2$  gas was added to the humidified cathode gas ( $\text{N}_2$  or 20%  $\text{O}_2/\text{N}_2$ ) and 4 ppm–50 ppm of  $\text{SO}_2$  was supplied to the PEFC cathode. Residual  $\text{SO}_2$  at the cathode outlet was trapped by using a water trap.



**Fig. S3** (a) CV profiles after the catalyst poisoning with SO<sub>2</sub> under 20 %O<sub>2</sub>/N<sub>2</sub> or N<sub>2</sub> flow at the cathode. The estimated electrochemical active surface area (ECSA) of the Pt electrocatalyst was 8.3 m<sup>2</sup> g<sub>Pt</sub><sup>-1</sup> (20 %O<sub>2</sub>/N<sub>2</sub>) and 8.0 m<sup>2</sup> g<sub>Pt</sub><sup>-1</sup> (N<sub>2</sub>) after the catalyst poisoning treatment with SO<sub>2</sub>. (b) Chronoamperometry (CA) profiles during the SO<sub>2</sub>-poisoning treatments with 4 ppm (black square), 25 ppm (red circle), and 50 ppm (blue triangle) of SO<sub>2</sub> in 20% O<sub>2</sub>/N<sub>2</sub> at 0.4 V. Error ranges of poisoning with 4 ppm of SO<sub>2</sub> (black square) were estimated as the maximum deviation of 5 runs. (c) CV profiles after the catalyst poisoning with 4 ppm (black line), 25 ppm (red line), and 50 ppm (blue line) of SO<sub>2</sub> in 20% O<sub>2</sub>/N<sub>2</sub> at the cathode. (d) CA profiles during the SO<sub>2</sub>-poisoning treatment with 4 ppm of SO<sub>2</sub> in 20% O<sub>2</sub>/N<sub>2</sub> at 0.4 V for 4 h and 12 h.



**Fig. S4** (a) The comparison of CV profiles for the poisoned MEA by 4 ppm of SO<sub>2</sub> balanced with 20% O<sub>2</sub>/N<sub>2</sub> at 0.4 V for 4 h before and after the IV measurement. The supply of 20% O<sub>2</sub>/N<sub>2</sub> at the cathode and high open circuit voltage caused the partial recovery of the Pt electrocatalyst. (b) The set of CV profiles for the SO<sub>2</sub>-poisoned MEA by 4 ppm of SO<sub>2</sub> balanced with 20% O<sub>2</sub>/N<sub>2</sub> at 0.4 V for 4 h with different voltage sweep ranges from 0.05 V to 0.70–1.20 V.



**Table S1.** Examples of reported recovering protocols for SO<sub>2</sub> poisoning,

Sample setup	Cathode catalyst	Cell temp., Humidity	SO <sub>2</sub> poisoning conditions	Recovery conditions	Cathode gas during recovering	Recovery time	Recovery rate	ref
PEFC cell stack	Pt/NiG (N doped graphene)	70°C, 100%	100 ppm SO <sub>2</sub> /Air, 0.5 V, 900 s	OCV (1.6 V)	0.4 % O <sub>2</sub> /Air	15 min	100% (Power)	S5
PEFC single cell	Pt/C	70°C, 100%	25 ppm SO <sub>2</sub> /Air, 0.7 V, 5 h	CV scan (from 0.05 V to 0.75 V-1.4 V)	N <sub>2</sub>		98% (ECSA)	S6
RDE	Pt/C or Pt-poly	-	1mM SO <sub>2</sub> -0.1 M HClO <sub>4</sub> solution, 0.65 V	0.4 V-1.5 V	-	for each 5 sec, 3 cycle	94% (ECSA)	S7
PEFC single cell	Pt/C	60°C, 50%	1 ppm SO <sub>2</sub> /Air, 0.6 V, 3 h	CA 1.1 V, ①N <sub>2</sub> or ②Air ③CV 0.09-1.1 V, 800mV/sec, 15 cycles ④CV 0.09-1.1 V 20mV/sec, Air, 20 cycles ⑤0.0-1.2 A/cm <sup>2</sup> (0.4 V-0.6 V)	Air or N <sub>2</sub>	①2.4 min ②2.7 min ③3.0 min ④2.7 min ⑤4800 min	①99%(0.6 V), 92%(0.85V) ②92%, 73% ③99%, 98% ④92%, 73% ⑤91%, 72%	S8
PEFC single cell	Pt/C	80°C, 100%	Const. Current: 0.5 ppm SO <sub>2</sub> / Air, 1 A/m <sup>2</sup> , 45 h (R.H. 50%) Const. Voltage: 2 ppm SO <sub>2</sub> /N <sub>2</sub> 0.5-0.9V, 2h (RH100%)	I=1A/cm <sup>2</sup>	O <sub>2</sub>	2 h	100% (Power)	S9
PEFC single cell	Pt-Ru alloy	70°C, 100%	2.5 or 5 ppm SO <sub>2</sub> /Air, -0.7 V, 46 or 23 h	0.05-1.4 V CV 4 cycles (5mV/sec)	Air	24 h, CV4cycle	100% (Power)	S10
PEFC single cell	Pt/C	80°C, 50%	1, 2, 10 ppm SO <sub>2</sub> /Air, 0.6 A/cm <sup>2</sup> total dosage=160µmol	①CA=0.6A/cm <sup>2</sup> ②CV, 0.08-1.2 V 13 cycles, 0.08-1.5 V 3cycles	Air	60 h	①79.3%, 78.1%, 78.1%(1.2,10ppm SO <sub>2</sub> /Air) ②93%	S11
PEFC single cell	Pt/Vc	80°C, 100%	1 ppm SO <sub>2</sub> /Air, 0.5, 0.6, 0.7 V, 3 h	OCV, N <sub>2</sub>	N <sub>2</sub>	30 min.	-	S12

### Supporting information 2: EXAFS fitting analysis

*Operando* Pt  $L_{III}$ -edge XAFS data for three different states of the MEA (after the conditioning (fresh), after the catalyst poisoning with  $\text{SO}_2$ , and after the subsequent electrochemical recovery process) were analyzed. In this study, we used the 3-scattering shells of Pt-Pt, Pt-O, and Pt-S bonds. Although the obtained data satisfied the quality that allowed the fitting using 13 free parameters estimated by the Nyquist equation, to converge the curve fitting in a reasonable range, we fixed some parameters. All data were transformed into  $R$ -space ( $k = 3.0\text{--}13.5 \times 10 \text{ nm}^{-1}$ ) and fitted in  $R$ -space ( $R = 1.2\text{--}3.2 \times 10^{-1} \text{ nm}$ ).  $S_0^2$  value (0.94) was referred from our previous works.<sup>S4</sup>

In step 1, we first conducted the curve-fitting of the fresh MEA at 1.0 V, which presents the surface oxidation of the Pt surface, using 2-scattering shells of Pt-Pt and Pt-O bonds. Then, the estimated  $R$ ,  $\delta^2$ , and  $\Delta E_0$  of the Pt-O shell were fixed. The fresh MEA at 0.4 V was successfully fitted with negligible Pt-O contribution as shown in Table S2.

**Table S2.** The curve-fitting results of the  $k^3$ -weighted Pt  $L_{III}$ -edge EXAFS FTs of the Pt/C cathode catalyst in the fresh MEA at 1.0 V and 0.4 V using the 2-scattering shells of Pt-Pt and Pt-O bonds,

	Shell	CN	$R / 10^{-1} \text{ nm}$	$\sigma^2 / 10^{-5} \text{ nm}^2$	$\Delta E_0 / \text{eV}$	$R$ -factor %
1.0 V	Pt-Pt	$8.0 \pm 0.7$	$2.74 \pm 0.01$	$7.7 \pm 0.5$	$3.9 \pm 1.1$	0.59
	Pt-O	$0.9 \pm 0.3$	$1.98 \pm 0.02$	$2.8 \pm 2.1$	$6.5 \pm 4.0$	
0.4 V	Pt-Pt	$8.6 \pm 0.8$	$2.75 \pm 0.00$	$6.6 \pm 0.4$	$6.1 \pm 1.0$	0.85
	Pt-O	$0.1 \pm 0.2$	1.98	2.8	6.5	

The values with/without error indicate free/fixed parameters, respectively.

In step 2, the  $\text{SO}_2$ -poisoned MEA at 0.4 V was fitted by the 2-scattering shells of Pt-Pt and Pt-S bonds. Then, the  $\text{SO}_2$ -poisoned MEA at 1.0 V, which may include the oxidation of the Pt surface and residual S adsorbates, was fitted by the 3-scattering shells of Pt-Pt, Pt-O, and Pt-S bonds and fixing the estimated  $R$ ,  $\delta^2$ , and  $\Delta E_0$  of the Pt-O and Pt-S bonds. Finally, to confirm a negligible residual contribution from the Pt-O bond (within error) on the  $\text{SO}_2$ -poisoned MEA at 0.4 V, the curve fitting with the 3-scattering shells was performed (Table S3).

**Table S3.** The curve-fitting results of the  $k^3$ -weighted Pt  $L_{III}$ -edge EXAFS FTs of the Pt/C cathode catalyst in the  $SO_2$ -poisoned MEA at 1.0 V and 0.4 V using the 2 or 3-scattering shells of Pt-Pt, Pt-O, and Pt-S bonds,

	Shell	CN	$R / 10^{-1}$ nm	$\sigma^2 / 10^{-5}$ nm <sup>2</sup>	$\Delta E_0$ /eV	$R$ -factor %
0.4 V	Pt-Pt	8.6	2.74	6.9	3.3	1.77
	Pt-S	$0.6 \pm 0.5$	$2.29 \pm 0.06$	$8.0 \pm 6.8$	$7.3 \pm 10.4$	
1.0 V	Pt-Pt	$8.0 \pm 1.1$	$2.75 \pm 0.01$	$7.1 \pm 0.7$	$5.2 \pm 1.6$	1.56
	Pt-S	$0.2 \pm 0.3$	2.29	8.0	7.3	
	Pt-O	$0.6 \pm 0.2$	1.98	2.8	6.5	
0.4 V	Pt-Pt	$8.5 \pm 1.1$	$2.74 \pm 0.01$	$6.9 \pm 0.6$	$2.3 \pm 1.8$	1.63
	Pt-S	$0.6 \pm 0.3$	2.29	8.0	7.3	
	Pt-O	$0.1 \pm 0.3$	1.98	2.8	6.5	

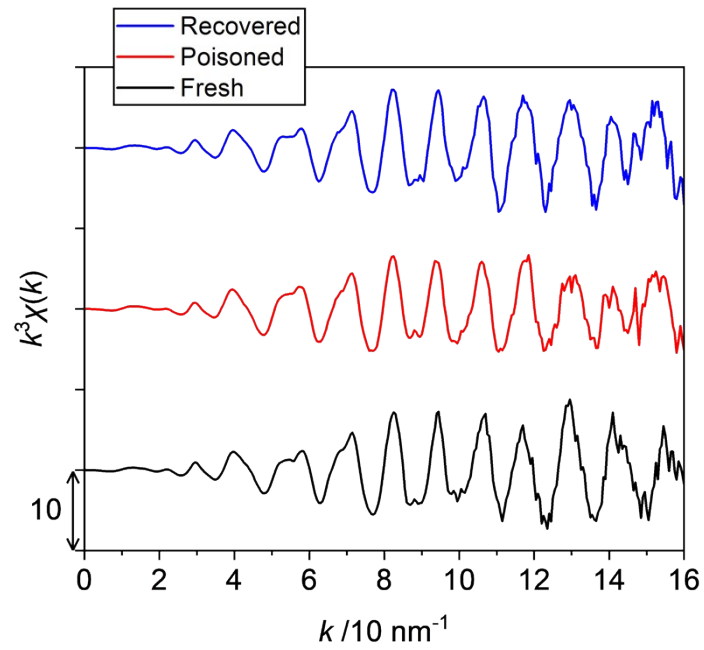
The values with/without error indicate free/fixed parameters, respectively.

In step 3, the electrochemically-recovered sample at 0.4 V was fitted by the 3-scattering shells of Pt-Pt, Pt-O, and Pt-S bonds. Then, the curve fitting of the recovered MEA at 1.0 V was conducted. Since the contribution of the Pt-S bond was found to be negligible on the recovered MEA, we added the fitting data with the 2-scattering shells of Pt-Pt and Pt-O bonds in Table S4.

**Table S4.** The curve-fitting results of the  $k^3$ -weighted Pt  $L_{III}$ -edge EXAFS FTs of the Pt/C cathode catalyst in the electrochemically-recovered MEA at 1.0 V and 0.4 V using the 2-scattering shells (Pt-Pt and Pt-O bonds) or the 3-scattering shells (Pt-Pt, Pt-O, and Pt-S bonds),

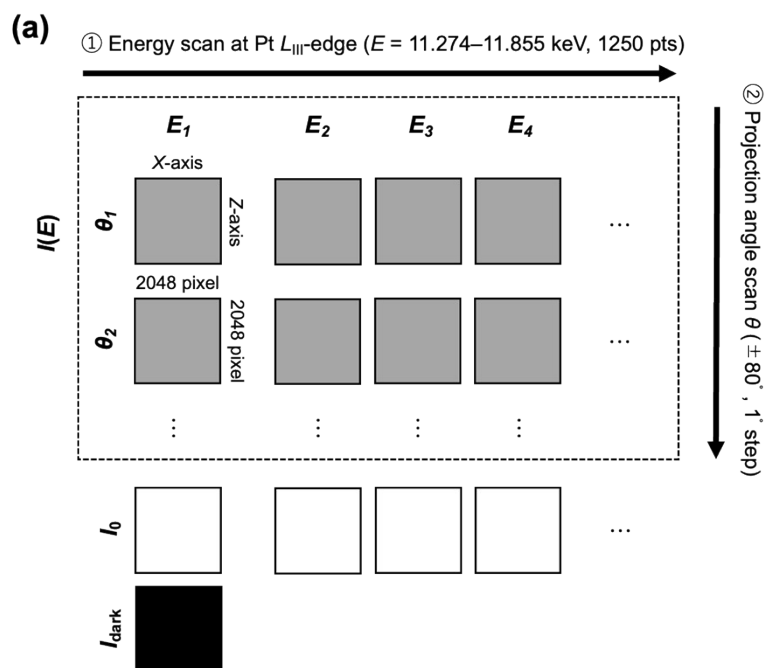
	Shell	CN	$R / 10^{-1}$ nm	$\sigma^2 / 10^{-5}$ nm <sup>2</sup>	$\Delta E_0$ /eV	$R$ -factor %
0.4 V	Pt-Pt	$9.1 \pm 0.9$	$2.75 \pm 0.00$	$6.6 \pm 0.5$	$4.4 \pm 1.1$	1.13
	Pt-S	$0.0 \pm 0.2$	2.29	8.0	7.3	
	Pt-O	$0.2 \pm 0.2$	1.98	2.8	6.5	
1.0 V	Pt-Pt	$8.5 \pm 0.6$	$2.75 \pm 0.00$	$7.6 \pm 0.3$	$4.1 \pm 0.9$	0.58
	Pt-S	$0.0 \pm 0.1$	2.29	8.0	7.3	
	Pt-O	$0.7 \pm 0.1$	1.98	2.8	6.5	
0.4 V	Pt-Pt	$9.0 \pm 0.9$	$2.75 \pm 0.00$	$6.6 \pm 0.5$	$4.3 \pm 1.1$	1.13
	Pt-O	$0.1 \pm 0.2$	1.98	2.8	6.5	
1.0 V	Pt-Pt	$8.5 \pm 0.6$	$2.75 \pm 0.00$	$7.5 \pm 0.3$	$4.0 \pm 0.8$	0.60
	Pt-O	$0.7 \pm 0.1$	1.98	2.8	6.5	

The values with/without error indicate free/fixed parameters, respectively.



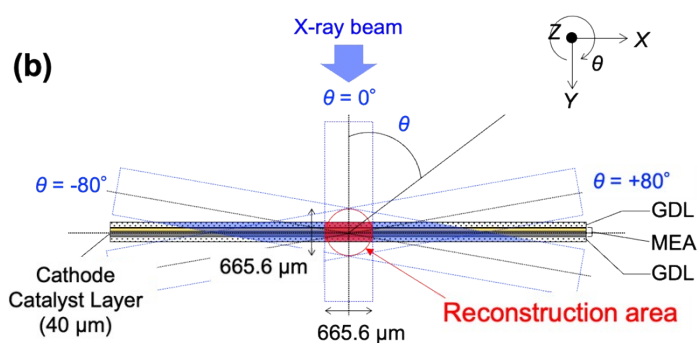
**Fig. S5** Pt  $L_{III}$ -edge  $k^3$ -weighted EXAFS oscillations of the Pt/C cathode electrocatalyst in the PEFC MEA measured at the cell voltage of 0.4 V. Black line: after the initial conditioning (fresh MEA). Red line: after the catalyst poisoning with  $\text{SO}_2$ . Blue line: after the subsequent recovery process.

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Dimensions of XAFS-CT data-set

- $I(XZ-E-\theta)$ : The X-ray transmission images (XZ) of a sample with energy ( $E$ ) and projection angle ( $\theta$ ) scans
- $I_0(XZ-E)$ : Images of incident X-ray intensity (XZ) with energy ( $E$ ) scan
- $I_{\text{dark}}(XZ)$ : Image of dark noise from sCMOS camera (XZ)



**Fig. S6** (a) The schematic of XAFS-CT measurement and the 2D images obtained by the energy ( $E$ ) scan and the projection angle scan ( $\theta$ ) of a sample. (b) The illustration of the X-ray irradiation area and the definition of  $\theta$ . The red circle means the reconstruction area of CT.

### Supporting information 3: XAFS-CT analysis

The detailed procedure of XAFS-CT analysis was explained in our previous paper.<sup>S13</sup> The calculation of imaging data was processed via 5 steps as follows by using a custom-made GPGPU program on a commercial GPU board (ex. GeForce RTX3080, NVIDIA) within 6 h per each data.

In step 1, the set of X-ray transmission images of a sample ( $I(E)$ ) measured at different projection angles, an X-ray intensity image ( $I_0(E)$ ), and a dark signal image of the sCMOS camera ( $I_{\text{dark}}$ ) was converted to X-ray absorption coefficient ( $\mu t$ ) image by using the Beer's law (eq. S1).

$$\mu t = -\ln \frac{I(E) - I_{\text{dark}}}{I_0(E) - I_{\text{dark}}} \dots \text{(eq. S1)}$$

In step 2, the converted  $\mu t$  image has a 4D-matrix ( $XZ-E-\theta$ ) with the set of 2D-projection images ( $X'Z'$ ) along the energy scan ( $E$ ) and the projection angle scan ( $\theta$ ). XAFS spectra ( $\mu t$  against  $E$ ) were obtained for each pixel ( $XZ$ ) at each  $\theta$ . The obtained XAFS spectra for the original binning size (1 pixel  $\times$  1 pixel) were noisy and the spatial binning of the 2D image was processed. For this study, we used the binning size of 4 pixels  $\times$  4 pixels (1.3  $\mu\text{m}$   $\times$  1.3  $\mu\text{m}$ ) for further analysis. After the binning process of the raw data, the data size was reduced to 6.25% of the original data and around 40 million spectra remained for the next fitting analysis.

In step 3, the X-ray energy of the obtained Pt  $L_{\text{III}}$ -edge XANES spectra was calibrated using a XAFS spectrum of Pt foil as a reference. The maximum point of the 1st differential XANES spectrum was determined as the Pt  $L_{\text{III}}$  absorption edge ( $E_0 = 11.559$  keV). Then, the XANES spectra were fitted with the following equation (eq. S2),

$$\mu t = \{a_0 + a_1(E - E_0)\} + \frac{b_1 \left\{ \frac{\pi}{2} + \arctan\left(\frac{E - b_2}{b_3}\right) \right\}}{\pi} + \frac{c_1}{|E - c_2|_2}$$

where  $b_2$ ,  $b_3$ ,  $c_2$ , and  $c_3$  were fixed constants (determined by curve-fitting analysis) and  $a_0$ ,  $a_1$ ,  $b_1$ , and  $c_1$  were free-fitting parameters.  $a_0$ ,  $b_1$ , and  $c_1$  relate to the signal before the Pt  $L_{\text{III}}$ -edge (morphology), the Pt  $L_{\text{III}}$ -edge jump height (Pt density), and the Pt  $L_{\text{III}}$ -edge white-line height (the oxidation state of Pt), respectively. The fitting range was 11.400-12.000 keV.

In step 4, the 3D matrices of the analyzed XAFS parameters ( $XZ-\theta$ ; the  $XZ$  images along  $\theta$  axis) were resliced to the  $X\theta$  cross-section with  $Z$  axis to obtain their sinogram images ( $X\theta-Z$ ).

In step 5, the obtained sinogram for each analyzed XAFS parameter ( $a_0$ ,  $b_1$ , and  $c_1$ ) was individually reconstructed into real space coordinates ( $XYZ$ ) by an angle-limited CT calculation using the ordered-subset expectation maximization (OS-EM) method. Considering the calculation cost and quality, the numbers of calculation repetition and subset size were set to 20 cycles and 16 divisions, respectively. In this study, the MEA sample used for the XAFS-CT measurement was larger than the size of the field-of-view in the XAFS-CT measurement, and we used a filter for correcting the signals from the outside of the reconstruction area to reduce artifacts in a reconstructed image.<sup>S1</sup> The variation of X-ray absorption at the different projection angles of the MEA sample was also calibrated by the inversed-trigonometric function.<sup>S1</sup>

In step 6, the reconstructed 3D image was processed by calculating  $c_1/b_1$  to estimate the

normalized XANES white-line height. The normalized XANES white-line height has a linear correlation to the Pt valence state, and the Pt valence state was calculated using equation S3, which was obtained by the analysis of three standard samples (Pt foil (0), Pt(acac)<sub>2</sub> (II), and PtO<sub>2</sub> (IV)).<sup>S1</sup>

$$Pt\ valence = \frac{c_1/b_1 - 0.51}{b_1}$$

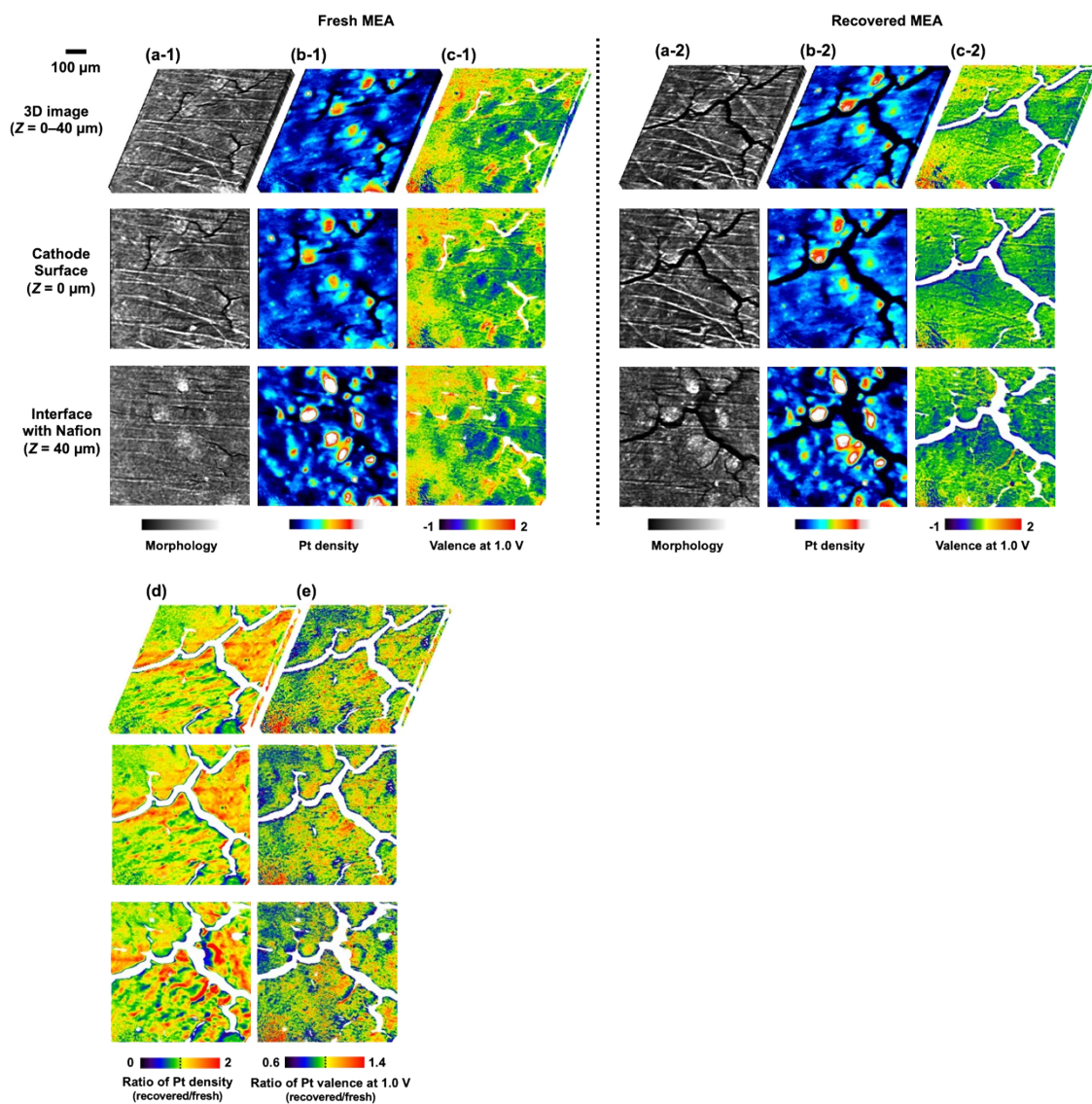
In step 7, the color contrast of the images was determined as follows. The data range of the Pt density images was 0 – 21, and the color scale of the Pt density image in Fig. 4 (b) was set as 1.2 – 13 to display the distribution of the Pt catalyst clearly. Parts whose values were higher than 13 were colored in white and parts whose values were less than 1.2 were colored in black. The Pt density values in the latter parts with too small Pt density were converted to NaN. These parts were presented by white in the Pt valence image in Fig. 4 (c).

The images of the ratio of Pt density and the ratio of Pt valence at 1.0 V were calculated as,  
the image of the ratio of Pt density

:= the Pt density image of the recovered MEA / that of the fresh MEA

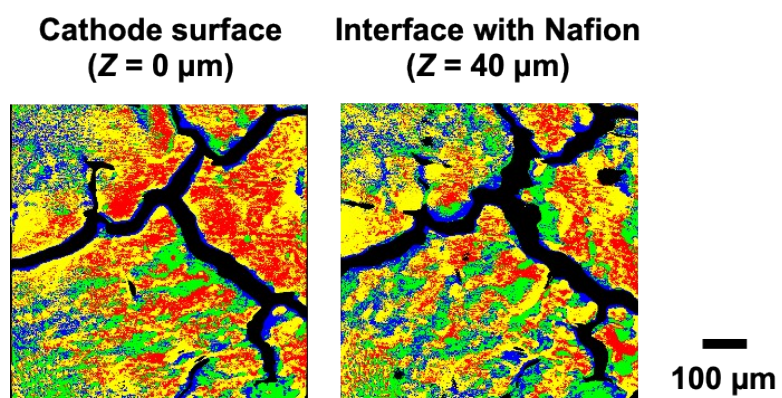
the image of the ratio of Pt valence at 1.0 V

:= the Pt valence image at 1.0 V of the recovered MEA / that of the fresh MEA.



**Fig. S7** 3D images ( $Z = 0\text{--}40\ \mu\text{m}$ ) and cross-sectional images at the surface of the cathode catalyst layer ( $Z = 0\ \mu\text{m}$ ) and the interface with the Nafion membrane ( $Z = 40\ \mu\text{m}$ ). (a) Morphology, (b) Pt density, (c) Pt valence at 1.0 V for the MEA (1) after the initial conditioning (fresh) and (2) after the catalyst poisoning with  $\text{SO}_2$  and the subsequent recovery process. (c) The ratio of the Pt density calculated by (b-2)/(b-1). (d) The ratio of the Pt valence at 1.0 V was calculated by (c-2)/(c-1).





**Fig. S8** Spatial cross-sectional maps of the Pt species at the surface of the cathode catalyst layer ( $Z = 0 \mu\text{m}$ ) and the interface with the Nafion membrane ( $Z = 40 \mu\text{m}$ ) categorized by the four quadrants in the kernel plot of Fig. 5 (c) (i; red, ii; green, iii; blue, and iv; yellow).

***Supporting reference list***

S1) ref. 34 in the manuscript.

S2) T. Uruga, M. Tada, O. Sekizawa, Y. Takagi, T. Yokoyama, Y. Iwasawa, *Chem. Rec.*, 2019, **19**, 1444.

S3) ref. 22 in the manuscript.

S4) ref. 27 in the manuscript.

S5) B. Kakati, A. Unnikrishnanm N. Rajalakshmi, R. Jafri, K. Dhathathreyan, A. Kucernak, *Int. J. Hydrog. Energy*, 2016, **41**, 5598.

S6) ref. 21 in the manuscript.

S7) ref. 11 in the manuscript.

S8) ref. 22 in the manuscript.

S9) Y. Nagahara, S. Sugawara, K. Shinohara, *J Power Sources*, 2008, **182**, 422.

S10) ref. 9 in the manuscript.

S11) ref. 20 in the manuscript.

S12) ref. 3 in the manuscript.

S13) ref. 28 in the manuscript.