Electronic Supplementary Information

Direct Epoxidation of Propylene with Water at PtO$_x$ Anode Using a Solid-Polymer-Electrolyte Electrolysis Cell

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Preparation of electrocatalysts

PtO$_x$ electrocatalysts for anodes were synthesized through the reduction of PtO$_2$ or the oxidation of Pt black.

Reduction method: 150 mg of PtO$_2$ (FUJIFILM Wako Pure Chemical Corporation) powder was suspended in 20 mL of de-ionized water. An aqueous N$_2$H$_4$ solution containing y equiv. (y = 0.1−2.0, where 1.0 equiv. means N$_2$H$_4$/PtO$_2$ mole ratio = 1) was gradually added to the suspension at 323 K, and then stirred vigorously for 30 min. The solid sample was collected by vacuum filtration, followed by dried at 353 K for 2 h. The prepared catalysts are presented as PtO$_x$(N$_2$H$_4$) in the present study.

Oxidation method: Pt black was primarily prepared from H$_2$PtCl$_6$ reagent (FUJIFILM Wako Pure Chemical Corporation) *via* the liquid phase reduction process. Aqueous H$_2$PtCl$_6$ solution (Pt content: 300 mg as Pt) was added to 40 mL of ethanol to give *solution-A*. On the other hand, *solution-B* was prepared by dissolving 0.70 g of NaBH$_4$ (mole ratio of NaBH$_4$/Pt = 12) in ethanol with continuous stirring. *Solution-A* was gradually dropped into *solution-B* for 30 min while cooling by ice bath, and then thoroughly stirred for another 30 min. The obtained solid sample was collected by the vacuum filtration, followed by washed with de-ionized water repeatedly. The resulted powder (Pt black) was dried at 373 K under vacuum condition. Subsequently, Pt black powder set on a quartz glass reactor was calcined at specified temperature in 20% O$_2$/He stream at a flow rate of 100 mL min^{-1}. The obtained catalysts are presented as PtO$_x$(O$_2$).

Cathode catalyst of 50wt%Pt/C was synthesized by the conventional impregnation method. 150 mg of carbon black (Vulcan®XC-72, Cabot Corporation) was suspended in the required concentration of aqueous H$_2$PtCl$_6$ solution, and the solvent was thoroughly evaporated by heating at 353 K while vigorous stirring. The obtained precursor was reduced in 100% H$_2$ stream at 423 K for 1 h, followed by at 573 K for 2 h.

Fabrication of membrane-electrode-assembly (MEA)

An anode was prepared by the mixing method; 70 mg of the prepared anode catalyst powder was mixed with 1 mg of PTFE powder (Poly-tetra-fluoro-ethylene, F-102, DAIKIN Industries, Ltd.) as a binder using an agate mortar, and the resulted powder was rolled on a stainless-steel sheet kept at 393 K to form a round shape electrode with a diameter of 16 mm. Then, it was coupled with a sheet of carbon paper (φ16 mm, SIGRACET® GDL-25BC) by dropping Nafion® dispersion. On the other hand, the Pt/C cathode was prepared by casting catalyst ink on a sheet of carbon paper (φ16 mm, SIGRACET® GDL-25BC) to prepare the cathode (so called casting method). The catalyst ink was prepared from 10mg of 50wt%Pt/C catalyst, acetone, and Nafion® dispersion by ultrasonic irradiation. The mixing method was also applied to fabricate a cathode; the 50wt% Pt/C catalyst was mixed with PTFE powder and VGCF® (SHOWA DENKO K.K.) using an agate mortar, and then integrated with carbon paper by casting the Nafion® dispersion. It has been confirmed that the cathode preparation method (casting method or mixing method) did not affect the electro-oxidation of C_3H_6 at the anode. The both prepared electrodes were thoroughly evacuated to remove the organic solvents. The MEA was fabricated by hot-pressing the proton exchange membrane (Nafion® 117, DuPont) sandwiched between the anode and the cathode at 413 K with applying 59 MPa. Prior to use, Nafion® membrane was boiled in 3%H_2O_2 aqueous solution, ion-exchanged water, 1.0 M H_2SO_4 solution, and de-ionized water in turn to remove residues and exchange K^+ with H^+.

Procedures and evaluation of electro-oxidation of C_3H_6

After dipping in de-ionized water for 5 min, the fabricated MEA (geometrical area: approx. 2.0 cm^2) was set at the center of glass-made divided electrolysis cell. The schematic diagram of the SPE-type electrolysis cell is presented in Figure S1. Anode potential was controlled by using a potentiostat (Ivium vertex, IVIUM TECHNOLOGIES) with a reference Ag/AgCl-electrode (KCl saturated) connecting to the Nafion® membrane through a KCl-salt bridge. In the present study, all the potentials are noted against the SHE scales unless otherwise specified. The anode chamber and cathode chamber were respectively filled with CH_2Cl_2 solution and de-ionized water, and then air in the both chambers were displaced by flowing He gas. 20min after switching the gas for the anode chamber to C_3H_6 (100% C_3H_6 gas was bubbled into CH_2Cl_2 solution at a flow rate of 15 mL/min unless otherwise specified), the potentiostatic electrolysis was started. Averaged current density (j) was calculated by eq.S1. Yields of propylene oxide (PO) and acetone produced in CH_2Cl_2 solution after the electrolysis for 120 min were determined by FID-GC (GC-8A, SHIMADZU) equipped with the PEG-20M packed column using 1-butanol as an external standard. Formation rates of PO and acetone were calculated by eq.S2. Formation rates of gaseous products (CO_2 and O_2) were quantified 15, 30, 60, 90, and 120 min after the reaction started by using TCD-GC (GC-8A, SHIMADZU) equipped with the Porapak-Q and the MS-5A packed columns, respectively. Then, yields of CO_2 and O_2 were calculated by using eq.S3. Faradic efficiency (FE) of anode products were respectively calculated in accordance with the following eq.S4. A steady H_2 evolution at the cathode was observed by using TCD-GC (GC-8A, SHIMADZU) equipped with an Activated carbon packed column.

eq.S1 Averaged current density (j) / mA cm^{-2}

= 1000 * (charged passed / C) / (electrolysis time / s)

eq.S2 Formation rate of X / μmol h^{-1}

= (yield of X / μmol) / (electrolysis time / h)

eq.S3 Yield of X / μmol

= (formation rate of X / μmol h^{-1}) * (reaction time / h)

eq.S4 Faradic efficiency (FE) of X / %

= 100 * (Yield of X / μmol) * N_X * F / (charged passed / C)

, where X, N_X, and F are name of products (PO, acetone, CO_2, or O_2), number of electrons passed for X production (eq.S5-S8), and faradic constant, respectively.

eq.S5 $C_3H_6 + H_2O \rightarrow C_3H_6O$ (PO) $+ 2H^+ + 2e^-$, E^0 = +0.74 V

eq.S6 $C_3H_6 + H_2O \rightarrow C_3H_6O$ (Acetone) $+ 2H^+ + 2e^-$, E^0 = +0.10 V

eq.S7 $C_3H_6 + 6H_2O \rightarrow 3CO_2 + 18H^+ + 18e^-$, E^0 = +0.10 V

eq.S8 $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$, E^0 = +1.23 V
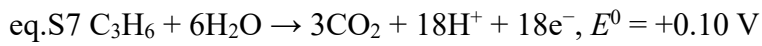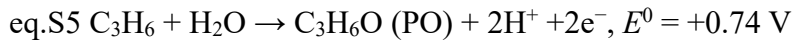
Characterization of anode electrocatalysts

Specific surface areas of the electrocatalysts were estimated from the N_2 adsorption isotherms at 77 K measured by using BELSORP-mini II (Microtrac BEL). Powder XRD patterns were collected using MiniFlex 600 (Rigaku) with Cu Kα characteristic X-ray source at a scan rate of 10.0 deg min^{-1}. Pt 4f XPS spectra were measured by using JPS-9010MC (JEOL) with Al Kα radiation (8 kV, 10 mA). Prior to measurements, the sample powder was mechanically mixed with graphite powder as a reference. The binding energy of obtained spectra were corrected by peak position of C 1s (284.485 eV), which was calibrated by Au $4f_{5/2}$ peak (84.0 eV) in advance. After a background removal, the Pt 4f region spectra were deconvoluted to three components; Pt(0), Pt(IV), and the other; it is regarded as Pt(II) in the present work. The peak top positions of the binding energy for Pt(0), Pt(II), and Pt(IV) were respectively defined to be 70.97, 72.37, 74.53 eV, and 74.29, 76.08, 77.82 eV for $4f_{7/2}$ and $4f_{5/2}$ levels, which were determined from the reference to spectra of Pt metal plate and PtO_2. XAFS measurements were performed at BL-9C beamline with the approval of High Energy Accelerator Research Organization (KEK, Japan, proposal No. 2019G629). Pt L3-edge spectra of the pelletized samples were recorded using a monochromatized X-ray in a transmission mode. The photon energy was calibrated at an inflection point of the reference spectrum of Pt metal foil (11564.0 eV). Higher harmonics was removed by detuning the parallelism of Si(111) double monochromater. The data reduction was executed using REX 2000 software (Rigaku). Linear combination fitting (LCF) analysis was performed for the normalized X-ray absorption near edge structure (XANES) spectra by using Pt foil and PtO_2 references. Amount of the released O_2 by the decomposition of PtO_x species was evaluated by temperature programmed desorption (TPD) method. 25 mg of samples, which were fabricated with varied conditions, were fixed on a quartz glass reactor, and then heated at a ramp rate of 5 K min^{-1} under He gas atmosphere with a flow rate of 40 mL min^{-1}. Outlet gas was analysed by online TCD-GC (GC-323, GL Science)

and Q-MASS (OmniStar GSD320 O2, Pfeiffer Vacuum). Turn over number (TON) of Pt for the PO formation was estimated from PO yield (130.9 μmol for 4 h) and a number of surface Pt atoms (77.1 μmol, which was calculated using values of specific surface area of $PtO_x(O_2)$ catalyst (45.3 m^2 g^{-1}), surface density of Pt (2.43×10^{-5} mol cm^{-2}), and atomic weight of Pt (195 g $umol^{-1}$)).
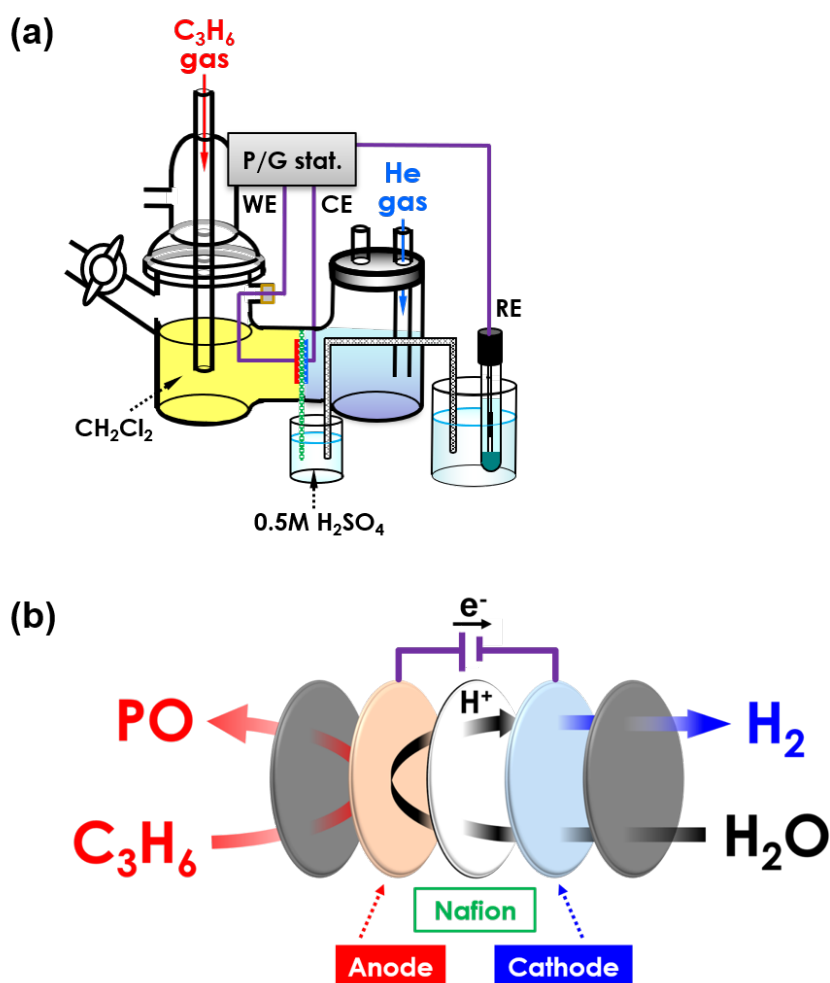
Figure S1 (a) Schematic diagram of the SPE electrolysis cell for the electro-oxidation of C_3H_6. (b) Conceptual illustration of the SPE electrolysis cell for the electro-oxidation of C_3H_6. Water in the cathode chamber is considered to be transferred to the anode through the electrolyte membrane, and then water should be oxidized at the anode. Active oxygen species formed by the incomplete oxidation of water is utilized to oxidize C_3H_6. The produced protons by the water activation are returned to the cathode *via* the electrolyte membrane, and then H_2 is evolved at the cathode by the reduction of protons.
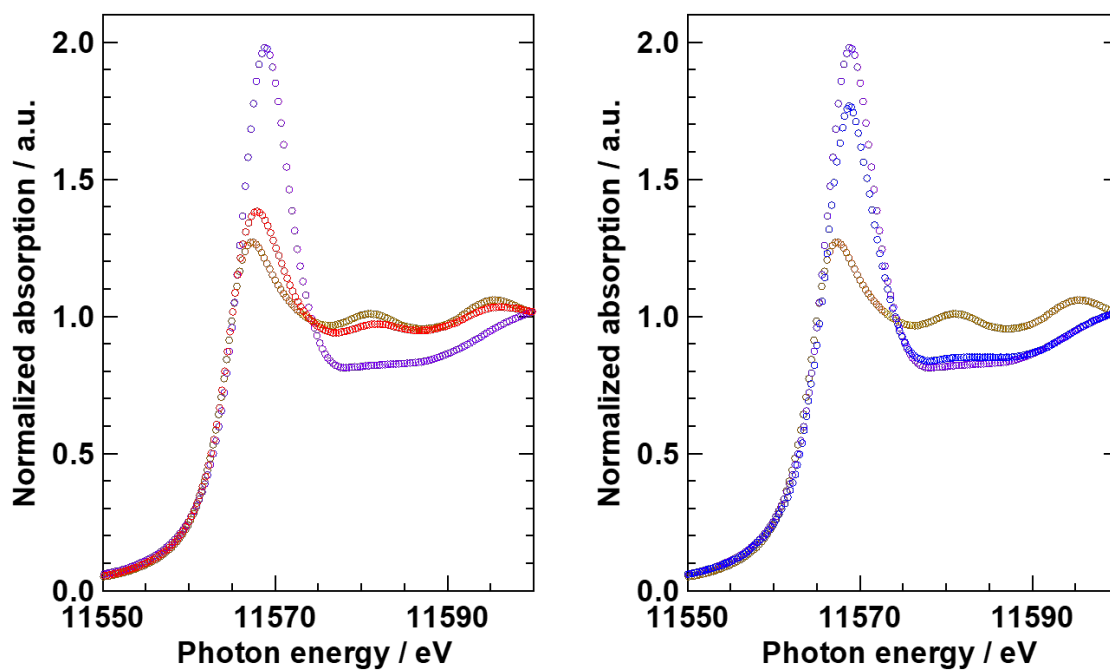
Figure S2　　　　Normalized Pt L_3-edge XANES spectra of PtO_x (O_2) (red), PtO_x (N_2H_4) (blue), Pt foil (brown), and PtO_2 (purple). These spectra were correctly normalized at the isosbestic point, and then used in the LCF analysis presented in Figure 1D. PtO_x (O_2) and PtO_x (N_2H_4) were prepared from Pt black by 20%O_2 treatment at 623 K and from PtO_2 by 0.4 eq. N_2H_4 treatment, respectively.

Table S1   Summary of characterization results and PO formation activities for Pt black, $PtO_x(O_2)$, PtO_2, and $PtO_x(N_2H_4)$ anode catalysts. [1] determined by linear combination fitting of XANES spectra using Pt metal and PtO_2 as references. [2] estimated by temperature programmed desorption method. [3] calculated by using the value of surface composition evaluated by the XPS analysis. PO production activities were evaluated by the potentiostatic electrolysis at +1.60 V (SHE) anode potential for 2 h. $PtO_x(O_2)$ and $PtO_x(N_2H_4)$ were prepared from Pt black by 20%O_2 treatment at 623 K and from PtO_2 by 0.4 eq. N_2H_4 treatment, respectively.

Catalyst	Oxidation state (bulk)		Surface composition / %			Oxidation state (surface) [3]	Yield(PO) / μmol	FE(PO) / %
	XANES [1]	TPD [2]	Pt(0)	Pt(II)	Pt(IV)			
Pt black	0.31	0.23	89	5.5	5.7	0.34	8.7	2.1
$PtO_x(O_2)$	0.48	0.55	61	26	13	1.03	74	7.4
PtO_2	-	-	0	16	84	3.68	8.3	35
$PtO_x(N_2H_4)$	2.96	-	64	18	18	1.08	68	14

Table S2   Summary of XAFS analysis for $PtO_x(O_2)$ and $PtO_x(N_2H_4)$ anode catalysts. Curve fitting of FT-EXAFS spectra was performed for the peaks in the R space. The phase shift and backscattering amplitude functions for the specified bonds were extracted from the crystal structure using the FEFF8.5L (A. L. Ankudinov, B. Ravel, J. J. Rehr, S. D. Conradson, Phys. Rev. B 1998, 58, 7565). $PtO_x (O_2)$ and $PtO_x (N_2H_4)$ were prepared from Pt black by 20%O_2 treatment at 623 K and from PtO_2 by 0.4 eq. N_2H_4 treatment, respectively.

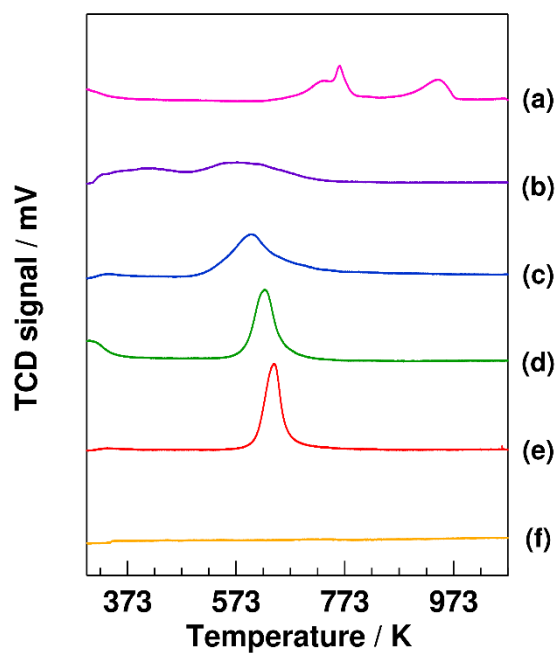| samples	LCF of XANES			Curve fitting of FT-EXAFS				
	Pt foil / %	PtO_2 / %	Average oxidation state (bulk)	Atom	N	R / Å	dE / eV	DW
$PtO_x(O_2)$	82	18	0.48	O	0.2	1.98	9.93	0.080
				Pt	4.2	2.75	7.43	0.017
$PtO_x(N_2H_4)$	26	74	2.96	O	1.9	2.01	8.82	0.052

Figure S3   Temperature programmed desorption profiles of (a) PtO_2, (b) Pt black(20%O_2, 298 K), (c) Pt black(20%O_2, 473 K), (d) Pt black(20%O_2, 573 K), (e) Pt black(20%O_2, 623 K), and (f) Pt black(20%O_2, 773 K).

Table S3　　　Reproducibility in the potentiostatic electro-epoxidation of C_3H_6 at +1.60 V (SHE) for 2 h using $PtO_x(O_2)$ anode catalyst prepared by 20%O_2 treatment at 623 K. Reaction temperature: 298 K. C_3H_6 flow rate: 15 mL min^{-1} ($p(C_3H_6)$ = 1.0)). Geometric area of the electrodes: 2 cm^2.

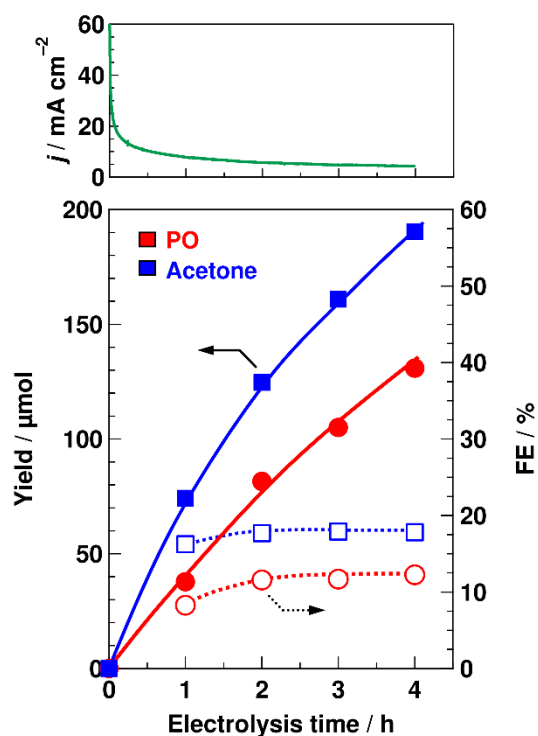| No.	j / mA cm^{-2}	Formation rate of PO / μmol h^{-1} cm^{-2}	Faradic efficiency / %			
			PO	Acetone	CO$_2$	O$_2$
1	13.4	37.1	7.4	11.6	24.1	3.3
2	12.2	41.6	9.1	13.9	18.2	0.4
3	12.5	33.6	7.2	12.3	24.2	1.2
4	12.5	35.6	7.6	18.5	24.9	0.9
5	14.2	48.9	9.2	13.2	20.0	5.6

Figure S4   Time courses of j, products yield (●, ■), and faradic efficiency (○, □) in the potentiostatic electro-epoxidation of C_3H_6 at +1.60 V (SHE) for 4 h using $PtO_x(O_2)$ anode catalyst prepared by 20%O_2 treatment at 623 K. Reaction temperature: 298 K. C_3H_6 flow rate: 15 mL min^{-1} ($p(C_3H_6) = 1.0$)). Geometric area of the electrodes: 2 cm^2.

Table S4   List of reported works for the epoxidation of C_3H_6. Although conversion rate of C_3H_6 and selectivity for PO are insufficient than previously reported superior catalytic system, further development in electro-epoxidation of C_3H_6 is strongly expected by considering advantage such as (1) PO production can proceed at room temperature, and (2) easy handling due to applying non-mixtured feeding gas (co-presence of O_2 is unnecessary).

Catalyst	C_3H_6 conversion / %	PO selectivity / %	Reactor type	C_3H_6 concentration in feed gas / %	Reaction temperature /K	Note	Ref
K-promoted Ag/CaCO$_3$	~6	15.2	Micro reactor	20	483		1
Au-Ba/Ti-TUD	1~2	93	Flow	10	423		2
Au/TS-1	8.3	84	Flow	10	473		3
Ag-Cu/BaCO$_3$	3.6	55.1	Flow	10	473		4
SnO$_2$-CuO-NaCl/SiO$_2$	0.95	58	Micro reactor	1	473-573		5
Ag/WO$_3$	~16	83	Pressured	4	523		6
Rb/V$_2$O$_5$-SiO$_2$	1.6	30.7	Flow	20	323	Photocatalysis	7
PtOx	0.4	7.4	Flow	100	298	Electrolysis	This work

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