# **Electronic Supplementary Information**

## An Extremely Low Pt Loading Cathode for a Highly Efficient Proton Exchange Membrane Water Electrolyzer

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### Supplemental text

#### **Experimental details**

#### Pt self-terminated electrodeposition on carbon paper

A deposition solution for Pt self-terminated electrodeposition (SED) consisted of 3 mM K<sub>2</sub>PtCl<sub>4</sub> and 0.5 M NaCl.<sup>41</sup> The solution pH was adjusted to 4.0 using dilute HCl.<sup>41</sup> A laboratory fabricated Teflon cell was used to configure a conventional three electrodes cell, containing carbon paper (CP, TGP-H-090, Toray) as working electrodes, Pt wire as counter electrodes, and saturated calomel electrodes (SCE) for reference electrodes. From the linear sweep voltammetry (LSV) analysis, the pulse potential was pre-determined for three consecutive ones with different times, e.g., 0.4 V<sub>SCE</sub> at 2 s, -0.9 V<sub>SCE</sub> at 10 s, and 0.4 V<sub>SCE</sub> at 3 s, which were controlled using a potentiostat (Autolab PGSTAT302F, Metrohm). Each Pt deposited CP was termed Pt#/CP where # was the number of deposition pulses.

#### Characterization

Surface morphology of electrodeposited Pt on carbon paper was imaged using field emission scanning electron microscope (FESEM, Sigma, Carl Zeiss). Several samples were analyzed elementally using energy dispersive X-ray spectroscopy (EDS, Thermo NORAN System 7) and X-ray photoelectron spectroscopy (XPS, Kratos, AXIS-His). For crystal structure investigation, X-ray diffraction (XRD, New D-8 Advance, Bruker-AXS) was used at a rate of 5°/min. In addition, the Pt loading mass after deposition was measured using inductively coupled plasma mass spectroscopy (ICPMS, Perkin-Elmer, ELAN 6100, Nexion 350D).

#### **Electrochemical measurement**

The hydrogen evolution reaction (HER) activity measurement for Pt electrodeposited with varying deposition pulse numbers was conducted in N<sub>2</sub>-purged 0.5 M H<sub>2</sub>SO<sub>4</sub> using cyclic voltammetry (CV) in the potential range of -0.2 to -0.8 V<sub>SCE</sub> at a scan rate of 50 mV/s. The recorded potential was converted to reversible hydrogen electrode (RHE). A solution resistance of 2.3  $\Omega$  between working and reference electrode was measured using electrochemical impedance spectroscopy (EIS, Wuhan CorrTest Instrument Co. Ltd.) at an amplitude of 10 mV in the range of 10<sup>5</sup> to 10<sup>-2</sup> Hz and used in iR-correction. After correcting the potential, the curves were fit with a Tafel line in the low current density region to determine the Tafel slope and exchange current density. These described experiments proceeded at room temperature and atmospheric pressure.

#### Single cell operation

For PEMWE single cell operation, the membrane electrode assembly (MEA) was prepared by sandwiching a Nafion membrane (212, Dupont Co.) between the anode and cathode. The cathode was prepared using Pt SED on CP as described previously, while the anode was fabricated from IrO<sub>2</sub> electrodeposition on carbon paper (IrO<sub>2</sub> loading mass: 0.10 mg/cm<sup>2</sup>).<sup>3</sup> As a reference, the Pt/C/CP cathode was prepared by spraying catalyst ink, Pt/C (46.5 wt%, TKK), Nafion ionomer (5 wt%, Dupont Co.), isopropanol, and deionized water at a weight ratio of 7:60:168:42. The Pt loading and Nafion content were controlled to 0.4 mg/cm<sup>2</sup> and 30 wt%, respectively. The active area of a single cell was fixed at 1.21 cm<sup>2</sup>. As a reactant, deionized water was preheated at 50°C and injected into the anode part of a single cell at a rate of 15 mL/min. The single cell test was carried out at 90°C using the potentiostatic method in the cell potential range between 1.35 and 2.00 V<sub>cell</sub> at an interval of 0.05 V. At each potential, the current was stabilized for 1 min and then the current-potential graph was obtained to represent the performance of the PEMWE single cell.

#### **Overpotential analysis**

For overpotential analysis of a single cell, the EIS was conducted at 1.6 V<sub>cell</sub> and 90°C in a frequency range of 50 MHz to 10 mHz. The obtained ohmic resistance (R<sub>ohm</sub>) was used to calculate the ohmic overpotential ( $\eta_{ohm} = iR_{ohm}$ ) and iR-corrected cell voltage ( $E_{iR-free} = V - iR_{ohm}$ ). After fitting to determine the Tafel slope and exchange current density, the kinetic overpotential ( $\eta_{kin}$ ) was derived from the Tafel equation. The mass transfer overpotential ( $\eta_{mass}$ ) was assumed to be the remaining source of the voltage loss, and obtained using the following equation:  $\eta_{mass} = E - E_0$ 

 $-\eta_{kin} - \eta_{kohm}$ .

Electrode	Number of deposition pulse	Mass of Pt (µg/cm²)	Overpotential @ -10 mA cm <sup>-2</sup> (mV)	Tafel slope (mV/dec)	Exchange current density (mA/cm²)	Mass activity* (A/mg <sub>pt</sub> )
Pt1/CP	1	N/A	305	78	0.014	N/A
Pt3/CP	3	N/A	230	52	0.056	N/A
Pt5/CP	5	N/A	209	48	0.081	N/A
Pt10/CP	10	0.03	160	47	0.145	-45.6
Pt20/CP	20	0.15	122	47	0.191	-11.4
Pt100/CP	100	1.55	72	41	0.240	-2.43
Pt300/CP	300	21	45	36	0.562	-0.77
Pt500/CP	500	271	42	36	0.646	-0.07

### Table S1. Summary of cathodes and their catalytic activity

\*Mass activity at -0.05  $\mathrm{V}_{\mathrm{RHE}}$ 

References	Cathode (mg/cm <sup>2</sup> )	Membrane	Anode (mg/cm²)	Т (°С)	j @ 1.6 V <sub>cell</sub> (A/cm <sup>2</sup> )	j @ 1.9 V <sub>cell</sub> (A/cm <sup>2</sup> )
This study	Pt10/CP (<0.00003)	Nafion 212	IrO <sub>2</sub> (0.1)	90		0.11
This study	Pt20/CP (0.00015)	Nafion 212	IrO <sub>2</sub> (0.1)	90	0.005	0.38
This study	Pt100/CP (0.00155)	Nafion 212	IrO <sub>2</sub> (0.1)	90	0.42	1.81
This study	Pt300/CP (0.021)	Nafion 212	IrO <sub>2</sub> (0.1)	90	0.58	2.55
This study	Pt500/CP (0.271)	Nafion 212	IrO <sub>2</sub> (0.1)	90	0.60	2.55
[3]	Pt/C (0.4)	Nafion 112	IrO <sub>2</sub> (0.1)	90	1.01	2.24
[4]	Pt/C (0.25)	Nafion115CS	IrO <sub>2</sub> (0.71)	80	0.55	1.85
[5]	Pt (0.5)	Nafion 117	IrO <sub>x</sub> (0.5)	80	0.76	-
[6]	Pt/C (1.0)	Nation 212	IrO <sub>2</sub> /NPG (0.086)	80	0.92	-
[7]	Pt/C (0.4)	Nation 212	Ir ND/ATO (1.0)	80	0.69	1.92
[8]	Pt/C (0.4)	Nafion212CS	Ir <sub>0.7</sub> Ru <sub>0.3</sub> O <sub>2</sub> (1.0)	80	0.56	-
[9]	Pt/C (0.5)	Nafion 1035	IrO <sub>2</sub> (1.5)	80	0.68	1.74
[10]	Pt/C (1.0)	Nation 212	IrO <sub>x</sub> -Ir (1.0)	80	0.71	-
[11]	Pt/C (0.5)	Nafion 115	IrOx (1.5)	90	0.80	2.80
[12]	Pt/C (0.5)	Nafion 115	IrO <sub>2</sub> (1.6)	80	0.40	1.68
[13]	Pt/C (0.4)	Nafion 115	IrO <sub>2</sub> (2.0)	80	0.75	-
[14]	Pt (1.0)	Nafion 112	Ir (1.5)	80	0.60	2.11
[15]	Pt/C (0.5)	Nafion 112	IrO <sub>2</sub> (3.0)	80	0.87	-
[16]	Pt/C (0.5)	Nafion 212	IrO <sub>2</sub> (3.0)	80	1.32	-
[17]	Pt (3.0)	Nafion 115	IrRuO <sub>x</sub> (3.0)	80	1.36	-

Table S2. Summary of PEMWE operating conditions and performance described in the literature



Fig. S1 Current transient for a Pt SED on CP using the first 20 deposition pulses.



Fig. S2 Elemental mapping of (a) Bare CP, (b) Pt1/CP and (c) Pt5/CP.



Fig. S3 XRD patterns for bare CP and Pt#/CP.