Electronic Supplementary Information for

Modelling electrochemically-roughened porous platinum electrodes for water oxidation

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Experimental

Electrochemical roughening

A 2 mm diameter platinum disc electrode was polished to a mirror finish with progressively finer grades of alumina (Buehler), ending with 0.05-μm grade and finally rinsed with Milli-Q water. The electrodes were electrochemically cleaned in 0.5 M H_2SO_4 by cycling the electrodes between -0.2 and $+1.25$ V vs Ag|AgCl|sat'd KCl at 0.2 V s^{-1} until reproducible cyclic voltammograms were obtained. The cleaned electrode was electrochemically roughened using a repetitive square wave potential cycle. A square wave of frequency 1 kHz with lower and upper potentials of -0.4 and $+2.4$ V vs Ag|Ag_2SO_4|sat'd K_2SO_4 was applied to the electrode in 0.5 M H_2SO_4 for 3 min after which the potential was maintained at -0.4 V until oxides on the surface were completely reduced. The reference electrode was constructed with silver sulphate, rather than silver chloride to avoid possible oxidation of leaked chloride, which deleteriously affects oxide formation. The Ag|Ag_2SO_4 reference electrode was

calibrated against Ag|AgCl|sat KCl, which gave a voltage of +0.25 V in 0.5 M H_2SO_4 solution. All potentials reported herein are referenced to Ag|AgCl|sat KCl. After roughening, the electrode was again cleaned electrochemically in a fresh 0.5 M H_2SO_4 until reproducible cyclic voltammograms of platinum were obtained. The surface roughness (f_R) was calculated through the relationship:

$$f_R = \frac{Q_H}{\sigma_{H,ideal} A_{geom}}$$
(Eqn. S1)

where Q_H is the measured charge of hydrogen desorption and A_{geom} is the geometric area of the electrode. $\sigma_{H,ideal}$ is the surface density of charge associated with monolayer adsorption of hydrogen, which has been reported as 210 $\mu C\ cm^{-2}$. [1]

Central composite design

The effects of reduction potential (E_r), oxidation potential (E_o) and ORC duration (t_{OCR}) on surface roughness were investigated using a rotatable circumscribed central composite design. The factor levels in experimental design were given as coded values that are mapped onto a range of actual values

$$X_i = \frac{x_i - x_0}{\Delta x}$$
(Eqn. S2)

where X_i is a coded value of the factor. Accordingly, x_i is the value of the factor, x_0 is the value of the factor at the centre and Δx is the step change.

For the circumscribed central composite design , the selected factors were coded at 5 levels (-1.68, -1, 0, 1 and 1.68) (Table S1), and the range of real values was chosen based on preliminary experiments. This design included a total of $2^k + 2k + r$ runs, where k is the number of studied factors, 2^k are the points from the factorial experiments carried out at the corners of the cube, $2k$ are the points carried out on the axes at a distance of $\pm\alpha$ from the centre and r is the number of replicate experiments at the central point. For a three variable

central composite design, α value of 1.68 was used to ensure a rotatability of the design as calculated by Eqn S3.

$$\alpha = \pm \left(2^k\right)^{1/4}$$ (Eqn. S3)

Where k is the number of factors studied.

Table S1. The experimental range and levels of the variables in the CCD

Variable	code	Levels (α = 1.68)				
		Low		Centre	High	
		(-α)	(-1)	(0)	(+1)	(+α)
Reduction potential (V)	E_r	-0.32	-0.23	-0.15	-0.05	0.018
Oxidation potential (V)	E_o	2.23	2.40	2.65	2.90	3.07
ORC time (min)	t_{ORC}	7.91	12.00	18.00	24.00	28.09

In this study, fourteen experiments and six replications at the centre point were performed in random order. A second order polynomial model with interactions of order 2 (Eqn. S4) was used to model surface roughness [2] :

$$\begin{aligned} f_R &= \beta_0 + \beta_1 E_r + \beta_2 E_o + \beta_3 t_{OCR} + \beta_{11} E_r^2 + \beta_{22} E_o^2 \\ &+ \beta_{33} t_{OCR}^2 + \beta_{12} E_r E_o + \beta_{13} E_r t_{OCR} + \beta_{23} E_o t_{OCR} \end{aligned}$$ (Eqn. S4)

where β_0 is a constant and β_i, β_{ii}, β_{ij} (i = 1,2,3, j = 1,2,3) are the coefficients of the linear, quadratic and interaction effects, respectively. The three-way interaction was assumed to be zero.

Oxygen evolution

The electrocatalytic OER activity of the roughened Pt was studied by linear sweep voltammetry in a three-electrode cell, with a Ag/AgCl (3 M KCl) reference electrode and a Pt wire counter electrode. The potentials obtained in this study were all calibrated to reversible hydrogen electrode reference (RHE) according to Eqn. S5 (ESI†) for comparison purposes.

$$E_{RHE} = E_{Ag/AgCl} + 0.197 + 0.059\,pH \qquad\qquad \text{(Eqn. S5)}$$

Steady state polarisation curves for oxygen evolution were recorded in 0.5 M H$_2$SO$_4$ at 5 mV s^{-1} scan rate. Electrochemical impedance spectroscopy (EIS) measurements were performed using a Solatron 1250 frequency response analyser. EIS spectra were acquired in 0.5 M H$_2$SO$_4$ at 1.6 V vs RHE with a ± 10 mV amplitude ac signal over a frequency range from 100 KHz – 0.1 Hz. The impedance data were modelled with ZSimpwin software

Table S2. 3-factor CDD matrix (coded values – see Table 3.1 for equivalent actual values) and the value of f_R.

Run	E_r	E_o	t_{ORC}	f_R
1	-1	-1	-1	338
2	-1	-1	+1	534
3	-1	+1	-1	541
4	-1	+1	+1	777
5	+1	-1	-1	425
6	+1	-1	+1	632
7	+1	+1	-1	393
8	+1	+1	+1	628
9	-1.68	0	0	424
10	+1.68	0	0	449
11	0	-1.68	0	520
12	0	+1.68	0	625
13	0	0	-1.68	395
14	0	0	+1.68	635
15	0	0	0	630
16	0	0	0	649
17	0	0	0	652
18	0	0	0	645
19	0	0	0	646
20	0	0	0	643

Table S3. Analysis of variance (ANOVA) for response surface quadratic model

Source	Degrees of freedom	Sum of squares	Mean square	F_{effect}	Prob F > F_{effect}
Model	9	253880.10	28208.90	24.50	<0.0001
E_r	1	342.89	342.89	0.30	0.5972
E_o	1	25212.87	25212.87	21.90	0.0009
t_{OCR}	1	119237.60	119237.60	103.58	<0.0001
$E_r E_o$	1	29080.28	29080.28	25.26	0.0005
$E_r t_{OCR}$	1	11.79	11.79	0.01	0.9214
$E_o t_{OCR}$	1	567.68	567.68	0.49	0.4986
E_r^2	1	63519.30	63519.30	55.18	<0.0001
E_o^2	1	4801.71	4801.71	4.17	0.06838
t_{OCR}^2	1	21309.88	21309.88	18.51	0.0016
Residual	10	11511.72	1151.17		

Table S4. Equivalent circuit parameters for smooth and roughened platinum catalysts according to the EIS spectra shown in figure Fig. 3c.

f_R	CPE (mF cm^{-2})	n	R_s (Ω cm^2)	R_e (Ω cm^2)	R_{ct} (Ω cm^2)
2 (smooth)	0.1	0.95	0.40	33.94	1040.3
124	11.5	0.92	0.38	0.20	5.7
268	25.3	0.91	0.42	0.11	2.7
455	44.6	0.92	0.41	0.02	1.6

Table S4 summarises the impedance parameters obtained by fitting the spectra using an equivalent circuit model represented by $R_s(R_e Q_1)(R_{ct} Q_{dl})$, in accordance with the predicted circuit for OER.[3] The R_s is the solution resistance; R_e is the electrode resistance, R_{ct} is the charge transfer resistance at the oxide/solution interface, which directly relates to the OER

activity. The capacitive element Q was treated as constant-phase-element (CPE), which is often used to model depressed semicircles due to heterogeneities and surface roughness.

Reference

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