Supporting Information

Assessing the Electron Transfer and Oxygen Mass Transfer of Oxygen Reduction Reaction Using a New Electrode Kinetic Equation

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This supporting information contains 16-page document, including programming of nonlinear fitting, experimental details in this work and references, supplementary figures and tables (9 figures, 9 tables), references and this cover page.

Nonlinear fitting method for the parameter estimation using Equation (4) (@nlinfit in Matlab)

```
%%%%%%%% define the function of Equation (S4) %%%%%%%%%%%%
function y = f_O2( para,x )
% n is electron transfer number;
% x is overpotential;
% y is output current of function;
% af is electron transfer coefficient;
% j0 is exchange current density;
% k_O2 is mass transfer limited coefficient;
af=para(1);
j0=para(2);
k_O2=para(3);
n=4;
f=38.279741;          %%%%% f = F/RT;
BV=j0*(exp(-af*f*x)-exp((n-af)*f*x));
y=BV./(1+j0*k_O2*exp(-af*f*x));
end

%%%%%%%% main script execute parameter estimation%%%%%%%%%%%%
%%%% polarization data should store in a Excel file such as xxx.xlsx %%%%%%
clear
x_exp=xlsread('E:\xxx.xlsx',1,'A2:A39');     %%% x_exp is the overpotential array of polarization curve (V);
y_exp=xlsread('E:\xxx.xlsx',1,'B2:B39');     %%% y_exp is the current density array of polarization curve (A/m2);
para0=[0.2,0.2,0.1];
[para,r,J,cov]=nlinfit(x_exp,y_exp,@f_O2,para0);
ci=nlparci(para,r,'jacobian',J);
x_1=0:-0.002:min(x_exp);
y_sim=f_O2(para,x_1);
display(para);                    %%% output the estimated parameter values;
display(ci);                      %%% output the 95% confidence intervals of parameters;
figure
plot(y_exp,x_exp,'ro', y_sim,x_1,'b-');          %%% plot the experimental polarization data and fitting curve;
```

The polarizations obtained from the references:

Polarizations obtained from Chen et al.[1] The polarizations were obtained from the Figure 3c in Chen et al. The measurements were conducted in O_2-saturated 0.1 M KOH using a prepared Fe/N/C catalyst with RDE measurements and a scan rate of 10 mV/s.

Polarizations obtained from Liang et al.[2] The polarizations were obtained from the Figure 2c in Liang et al. The measurements were conducted in O_2-saturated 0.1 M KOH using a prepared Co_3O_4/N-rmGO hybrid catalyst with RDE measurements and a scan rate of 5 mV/s.

Polarizations obtained from Lin et al.[3] The polarizations were obtained from the Figure S10 in the supporting information of Lin et al. The measurements were

conducted in O_2-saturated 0.1 M KOH using a prepared Fe/N/C-800 catalyst with RDE measurements and a scan rate of 10 mV/s.

Effect of the capacitive current on the measurement of LSV. As shown in Figure S1a and S1b, the LSVs gradually shift towards larger current as the scan rate increase. The scan rate has a significant effect for CC even when as low as 0.5 mV/s. The effect is much lower for RDE because the effect is negligible when scan rate is no more than 5 mV/s. In Figure S1c, it is demonstrated that the shift of LSV is due to the capacitive current resulting from the potential-scanning. In N_2-saturated solution, the measured currents only contain capacitive currents, and basically correspond to the shift of the LSVs measured in O_2-saturated solution in all the four scan-rate conditions.

In Figure S2, the measured LSVs using 0.5 mV/s for RDE are well consistent with the steady-state polarizations. However, the LSVs measured with the same method for CC are not fully consistent with the steady-state polarizations, especially in the limiting current range. As a result, the LSV curve measured using a low scan rate is an appropriate polarization form for RDE and RRDE. We suggest that the scan rate should be no more than 1 mV/s. The steady-state polarizations are suitable for the assembled electrode using porous templates, such as the CC, carbon felt, activated carbon, etc.

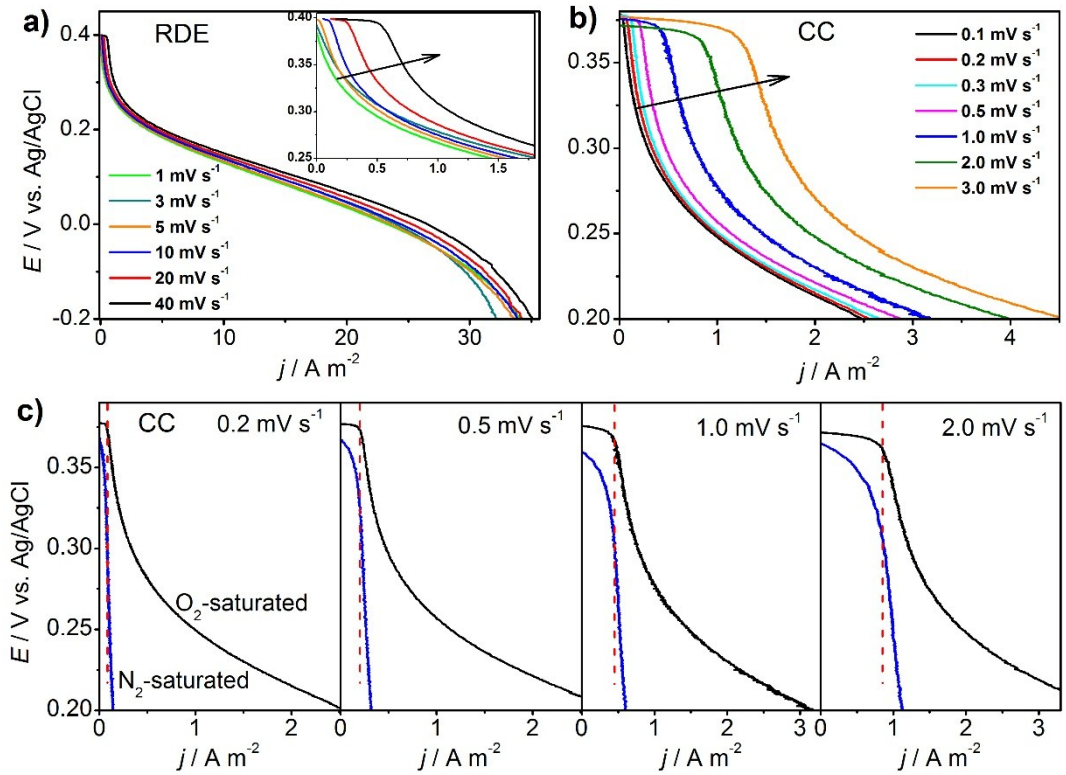

Figure S1. LSV curves recorded at various scan rates with PBS as the electrolyte: a) for RDE cathode, the inserted figure is an enlarged view, b) for CC cathode. c) comparisons between the LSVs of CC recorded in O_2-saturated and N_2-saturated solutions.

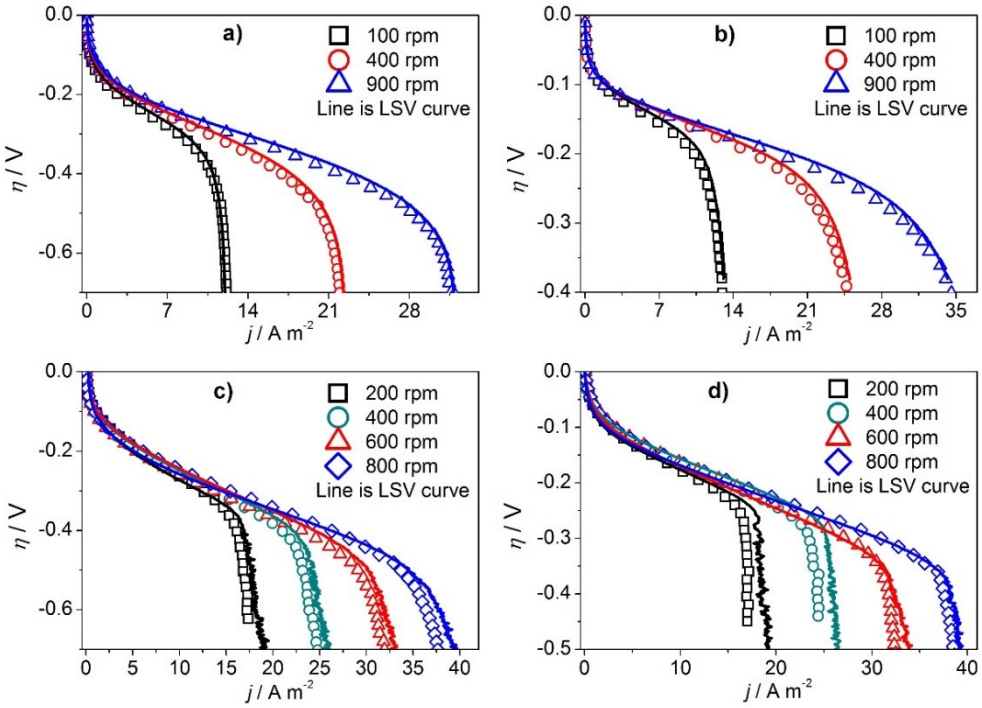

Figure S2. Comparison between the LSV curves recorded at 0.5 mV/s (solid line) and the steady-state polarization curves (discrete point) at different rotating or stirring rates: (a) for the RDE cathode in PBS; (b) for the RDE cathode in ABS; (c) for the CC cathode in PBS; (d) for the CC cathode in ABS.

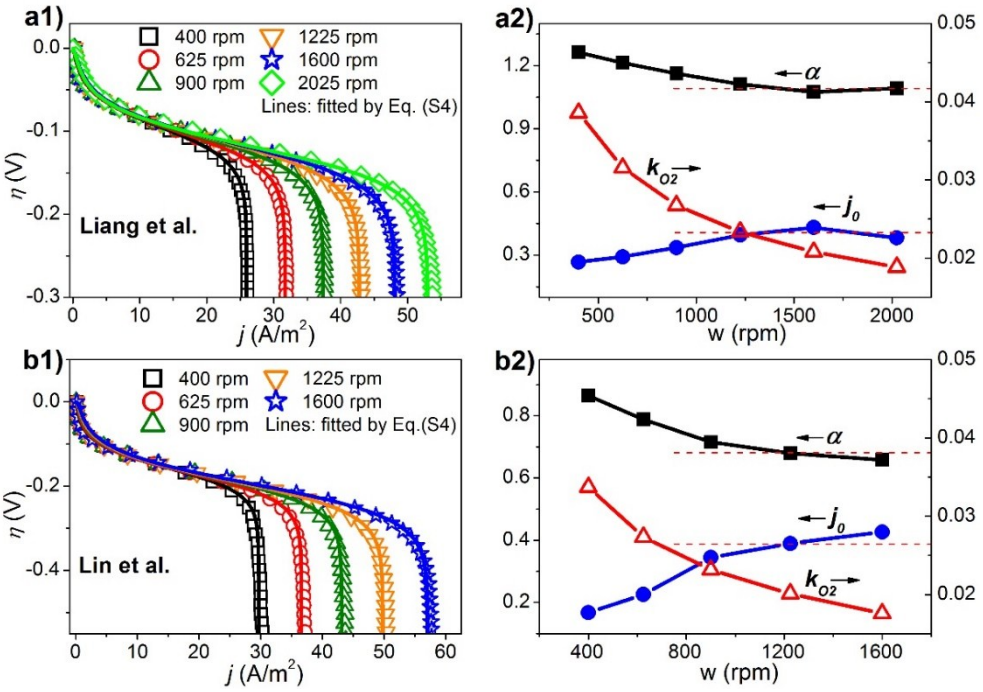

Figure S3. Nonlinear fitting results of the polarizations a1) obtained from Liang et al. measured in 0.1 M KOH with a scan rate of 5 mV/s and Co3O4/N-rmGO as catalyst, b1) obtained from Lin et al. measured in 0.1 M KOH with a scan rate of 10 mV/s and Fe-N/C-800 as catalyst. (a2, b2): the parameters obtained from the left figures, the steady value is marked by the red dashed line.

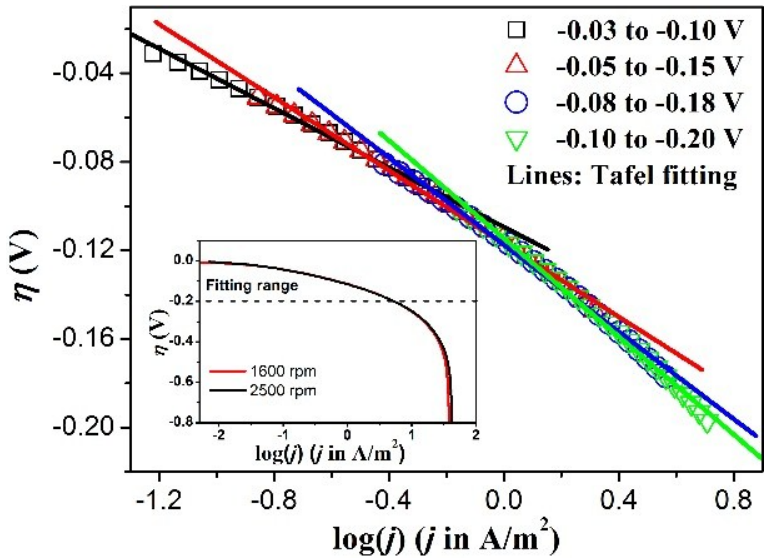

Figure S4. Tafel fitting of the polarizations measured from RDE in PBS at 2500 rpm, four fitting ranges are used; inserted figure is the Tafel plots at 1600 and 2500 rpm in full regime.

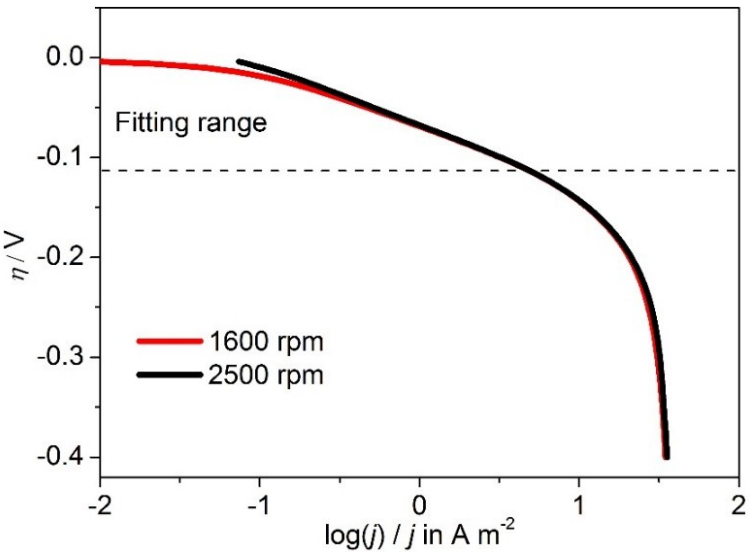

Figure S5. Tafel plots of the polarizations measure from the RDE in ABS at 1600 and 2500 rpm, the Tafel fitting range is marked in figure.

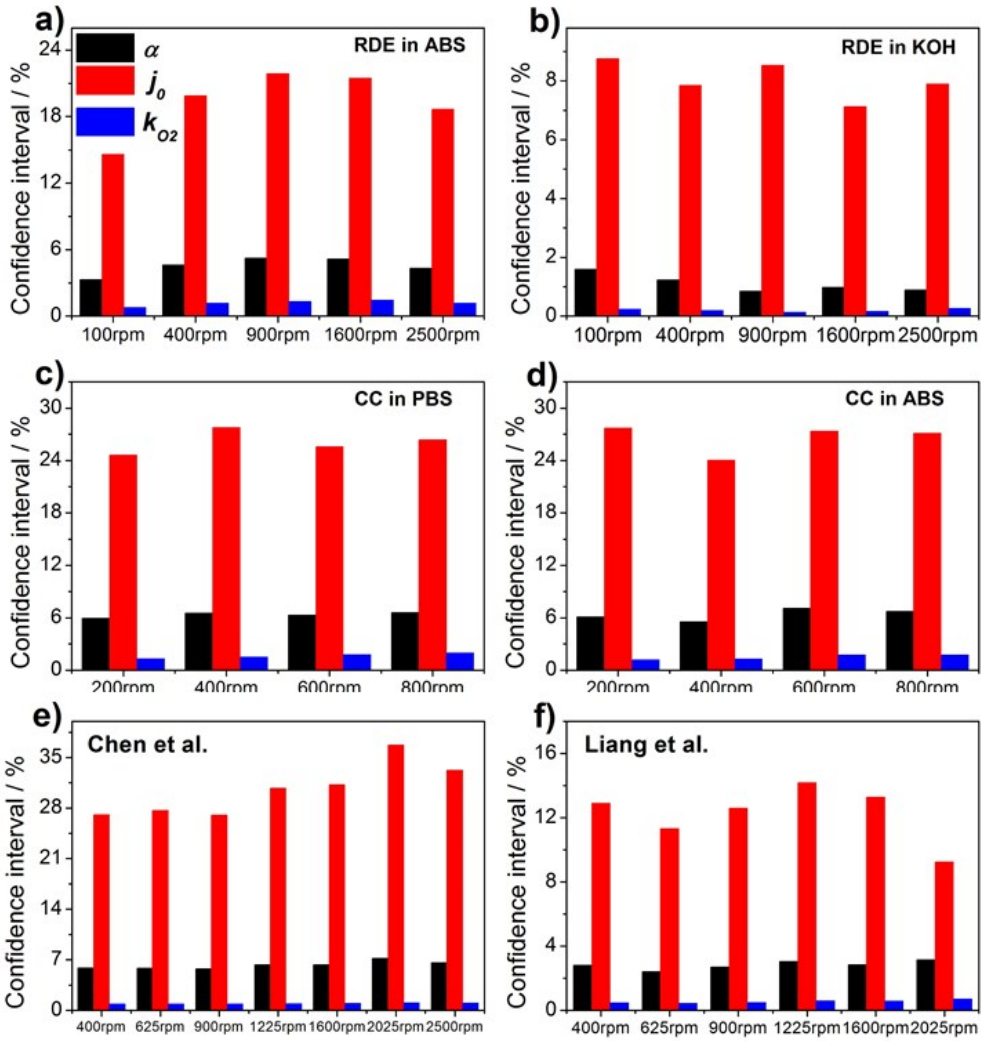

Figure S6. The 95% confidence intervals of the parameters estimated from the polarizations measured in this paper and obtained from references, the values are listed in Table S2-S7.

Uncertainty analysis of parameters. Nonlinear fitting method for parameter estimation is performed by minimizing the mean square error (MSE) which describe the derivations between predicted data and experimental data. MSE is calculated as below:

$$\mathrm{MSE} = \frac{1}{n-p}\sum_{i}^{n}(y_{i,predict} - y_{i,\exp})^2$$

where n is the number of experimental data, p is the number of parameter.

Uncertainty analysis of the parameter combination is performed by the contour plot of MSE calculated around the optimum of parameters. The change degree of parameter is uniformly expressed as percentages of variance (%) :

$$\text{Variance} = (P_i - P_{opt}) \times 100 / P_{opt}$$

The estimated parameters from RDE in PBS at 2500 rpm and CC in PBS at 800 rpm, are taking as the examples, and the results are shown in Figures 2b and S4, respectively.

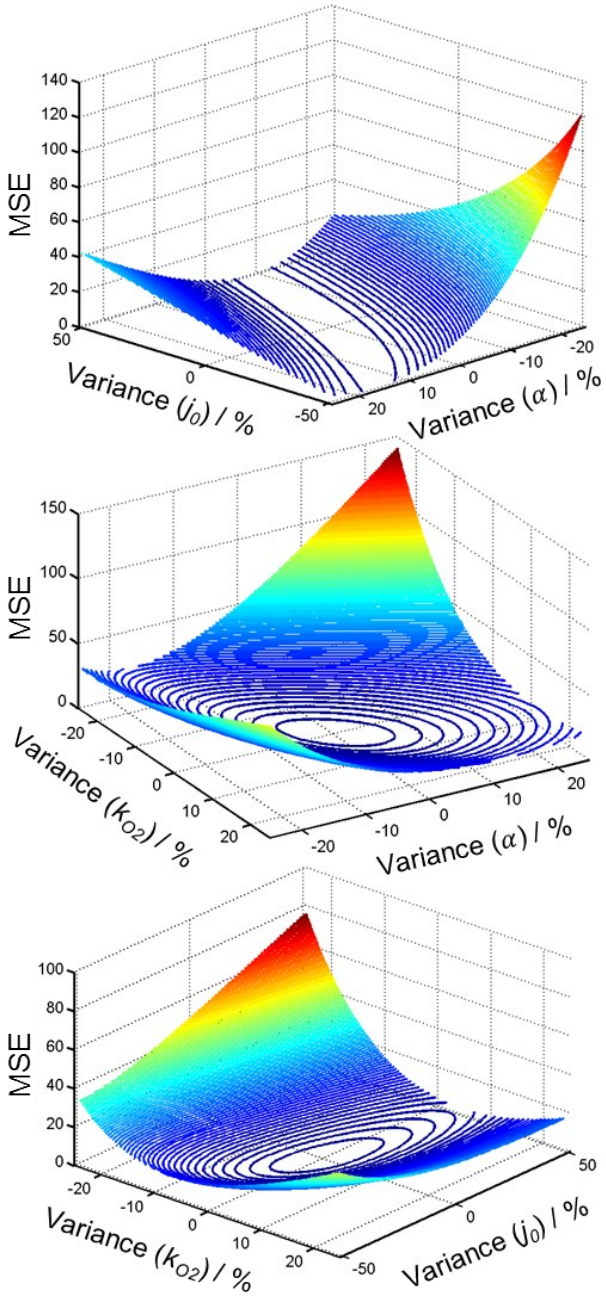

Figure S7. Uncertainty analysis of the parameters estimated from CC in PBS at 800rpm: Contour plots of mean square error (MSE) for parameter combinations of j_0 vs. α, k_{O2} vs. α and k_{O2} vs. j_0.

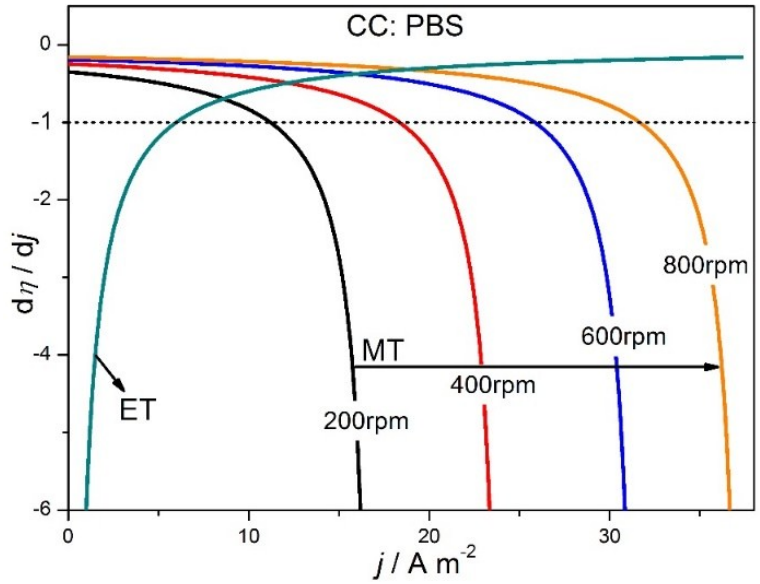

Figure S8. Derivative analysis of overpotential against j for CC in PBS, derivative of ET is calculated using α and j_0 obtained at 2500 rpm, derivatives of OMT are calculated in all the w conditions.

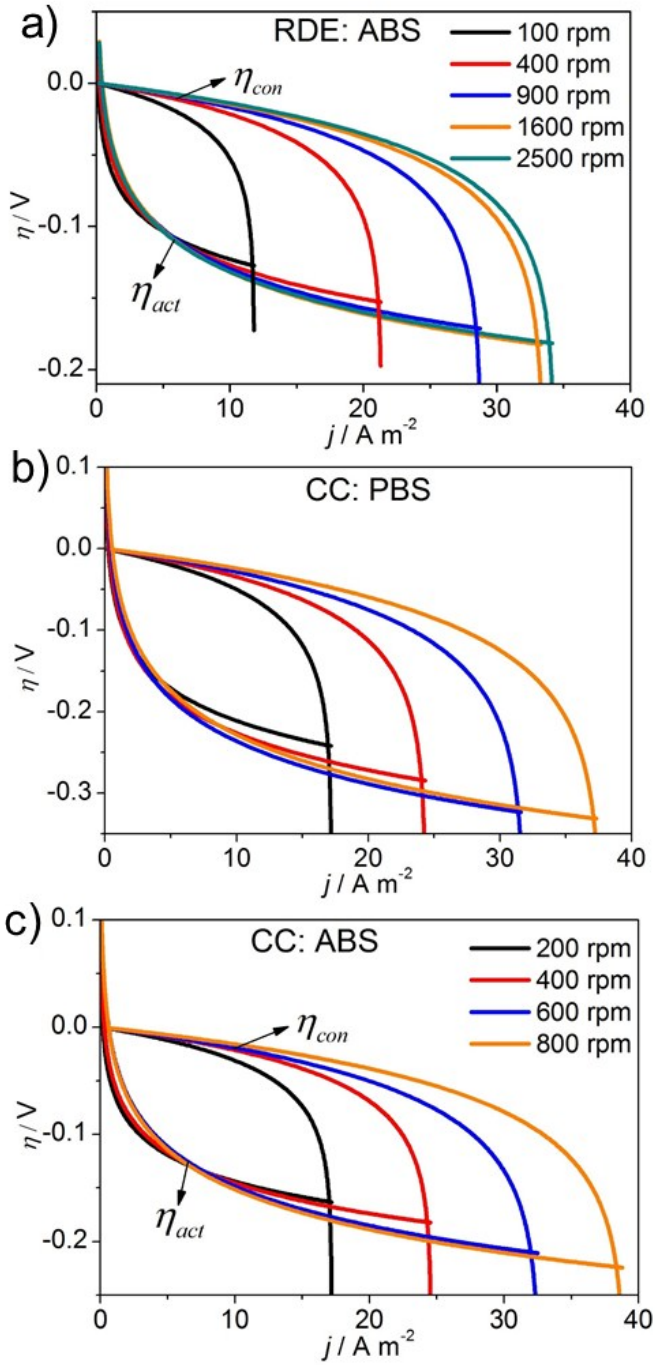

Figure S9. Activation overpotential (η_{act}) of ET and concentration overpotential (η_{con}) of OMT calculated from the estimated parameters of a) RDE in ABS, b) CC in PBS, c) CC in ABS.

Supplementary Tables

The estimated parameters from the polarizations in this work and references at different *w* conditions are listed in Table S1-S8. The comparisons of the parameters obtained fromm nonlinear fitting and Tafel fitting are listed in Table S9. The summary of Tafel fitting results in references are listed in Table S10.

Table S1. Parameters with 95% confidence interval estimated from the nonlinear fitting at RDE in PBS (pH = 7).

w (rpm)	α	Confidence interval (%)	j_0 (A/m^2)	Confidence interval (%)	k_{O2} (m^{2}s/C)	Confidence interval (%)
100	0.548	2.31	0.106	11.1	0.0801	0.31
400	0.399	2.54	0.358	10.7	0.0416	0.44
900	0.368	2.42	0.404	10.4	0.0321	0.46
1600	0.340	2.19	0.496	9.3	0.0266	0.45
2500	0.337	2.04	0.507	8.8	0.0241	0.43

Table S2. Parameters with 95% confidence interval estimated from the nonlinear fitting at RDE in ABS (pH = 9).

w (rpm)	α	Confidence interval (%)	j_0 (A/m^2)	Confidence interval (%)	k_{O2} (m^{2}s/C)	Confidence interval (%)
100	0.932	3.31	0.125	14.6	0.0846	0.79
400	0.765	4.61	0.243	19.9	0.0468	1.16
900	0.659	5.25	0.381	21.9	0.0347	1.32
1600	0.623	5.18	0.431	21.5	0.0299	1.44
2500	0.644	4.35	0.389	18.7	0.0291	1.17

Table S3. Parameters with 95% confidence interval estimated from the nonlinear fitting at RDE in KOH.

w (rpm)	α	Confidence interval (%)	j_0 (A/m^2)	Confidence interval (%)	k_{O2} (m^{2}s/C)	Confidence interval (%)
100	0.944	1.60	0.050	8.8	0.0851	0.23
400	0.936	1.23	0.042	7.8	0.0406	0.19

900	0.904	0.85	0.047	7.5	0.0320	0.14
1600	0.896	0.98	0.046	8.1	0.0265	0.16
2500	0.893	0.90	0.045	7.9	0.0232	0.27

Table S4. Parameters with 95% confidence interval estimated from the nonlinear fitting at CC in PBS (pH = 7).

w (rpm)	α	Confidence interval (%)	j_0 (A/m^2)	Confidence interval (%)	k_{O2} (m^{2}s/C)	Confidence interval (%)
200	0.455	5.96	0.253	24.6	0.0582	1.32
400	0.399	6.55	0.315	27.8	0.0411	1.50
600	0.345	6.30	0.443	25.6	0.0314	1.78
800	0.334	6.60	0.541	26.4	0.0266	1.96

Table S5. Parameters with 95% confidence interval estimated from the nonlinear fitting at CC in ABS (pH = 9).

w (rpm)	α	Confidence interval (%)	j_0 (A/m^2)	Confidence interval (%)	k_{O2} (m^{2}s/C)	Confidence interval (%)
200	0.731	6.12	0.178	27.7	0.0582	1.18
400	0.636	5.56	0.290	24.0	0.0407	1.28
600	0.493	7.09	0.608	27.3	0.0307	1.73
800	0.486	6.75	0.597	27.1	0.0257	1.72

Table S6. Parameters with 95% confidence interval estimated from the nonlinear fitting for Chen et al.

w (rpm)	α	Confidence interval (%)	j_0 (A/m^2)	Confidence interval (%)	k_{O2} (m^{2}s/C)	Confidence interval (%)
400	1.476	5.91	0.321	27.1	0.0355	0.86
625	1.472	5.86	0.339	27.7	0.0278	0.86
900	1.433	5.79	0.415	27.0	0.0232	0.87

1225	1.458	6.32	0.389	30.7	0.0203	0.95
1600	1.460	6.33	0.406	31.2	0.0181	0.95
2025	1.513	7.21	0.378	36.7	0.0166	1.06
2500	1.465	6.62	0.442	33.2	0.0146	1.00

Table S7. Parameters with 95% confidence interval estimated from the nonlinear fitting for Liang et al.

w (rpm)	α	Confidence interval (%)	j_0 (A/m^2)	Confidence interval (%)	k_{O2} (m^{2}s/C)	Confidence interval (%)
400	1.263	2.82	0.268	12.9	0.0386	0.47
625	1.213	2.42	0.292	11.3	0.0315	0.43
900	1.162	2.69	0.336	12.6	0.0268	0.50
1225	1.111	3.06	0.396	14.2	0.0234	0.59
1600	1.075	2.85	0.431	13.3	0.0208	0.58
2025	1.092	3.16	0.382	9.2	0.0189	0.71

Table S8. Parameters with 95% confidence interval estimated from the nonlinear fitting for Lin et al.

w (rpm)	α	Confidence interval (%)	j_0 (A/m^2)	Confidence interval (%)	k_{O2} (m^{2}s/C)	Confidence interval (%)
400	0.865	2.68	0.167	13.9	0.0337	0.42
625	0.788	2.69	0.226	13.6	0.0273	0.45
900	0.715	2.68	0.344	13.9	0.0232	0.45
1225	0.679	2.79	0.389	13.4	0.0201	0.54
1600	0.658	2.93	0.427	13.3	0.0176	0.55

Table S9. Review of the parameter values estimated from Tafel fitting in references.

Materials	α	Tafel slope (mV/dec)	j_0 (A/m^2)	Electrolyte	Polarizations	Ref.
Co–N/C	0.64	\	8.6×10^{-6}	0.5 M H_2SO_4	LSV: 5 mV/s	4
Activated carbon	\	\	0.76-1.58	0.05 M PBS	LSV: 1 mV/s	5
Pt/C	\	\	0.89			
Fe/N/C	0.90, 0.91[a]	66, 65	1.1×10^{-6}, 4.6×10^{-7}	0.5 M H_2SO_4	Mass-transfer corrected by K-L equation	6
Pt/C	0.77[a]	77	Low range: 3.9×10^{-4}			
	0.35[a]	167	High range: 0.39			
Fe/N/C	0.92[a]	64	Low range: 5.14×10^{-4}	0.5 M H_2SO_4	Staircase voltammetry	7
	0.42[a]	141	High range: 8.67			
Pt/C	0.98[a]	60	Low range: 1.41×10^{-3}			
	0.29[a]	202	High range: 36.3			
Cu/AC	\	\	10.3	0.05 M PBS	LSV: 0.1 mV/s	8
Flower-like Co_3O_4	\	\	2.46	0.1 M PBS	LSV: 1 mV/s	9
Fe/N/C	0.98, 0.97[a]	60, 61	3.7×10^{-2}, 1.8×10^{-2}	0.5 M H_2SO_4	LSV: 5 mV/s	10
Nanoporous Ni-Pt	0.49[a]	Low range: 120	\	0.1 M $HClO_4$	Steady-state polarization	11
	0.98[a]	Low range: 60	\			
$Co_{0.5}Mo_{0.5}O_yN_z$	0.83[a]	71	\	0.1 M KOH	LSV: 10 mV/s	12
Pt/C	0.68[a]	87	\			
Pt/C, Pt-Sn/C, Pt-Ni/C, Pt-Sn-Ni/C	0.66-0.54[a]	Low range: 90-110	Low range: 1.2×10^{-2}–5.6×10^{-2}	0.1 M $HClO_4$	Mass-transfer corrected by K-L equation	13
	0.41-0.28[a]	High range: 143-213	High range: 0.29 – 3.0			
Fe/N/C	1.00[a]	59	\	0.1 M KOH	LSV: 10 mV/s	14
Pt/C	0.95[a]	62	\			

N-O-S-C_8-900	1.48 [a]	40	\	0.1 M KOH	LSV: 10 mV/s	15
N-O-S-CB-900	0.88 [a]	67	\			
rGO/(Ni_2^+/THPP /Co_2^+/THPP)$_8$	1.18 [a]	50	\	0.1 M KOH	LSV: 5 mV/s	16
Ir/C	0.68 [a]	87	\			
Co_3S_4–S/G-800	1.41 [a]	42	\	0.1 M KOH	LSV: 5 mV/s	17
Pt/C	0.73 [a]	81	\			

[a]Only Tafel slope is given in reference, and the value of α is calculated from Tafel slope in this communication.

References

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