

Supplementary information for: Coverage-dependent formic acid oxidation reaction kinetics determined by oscillating potentials

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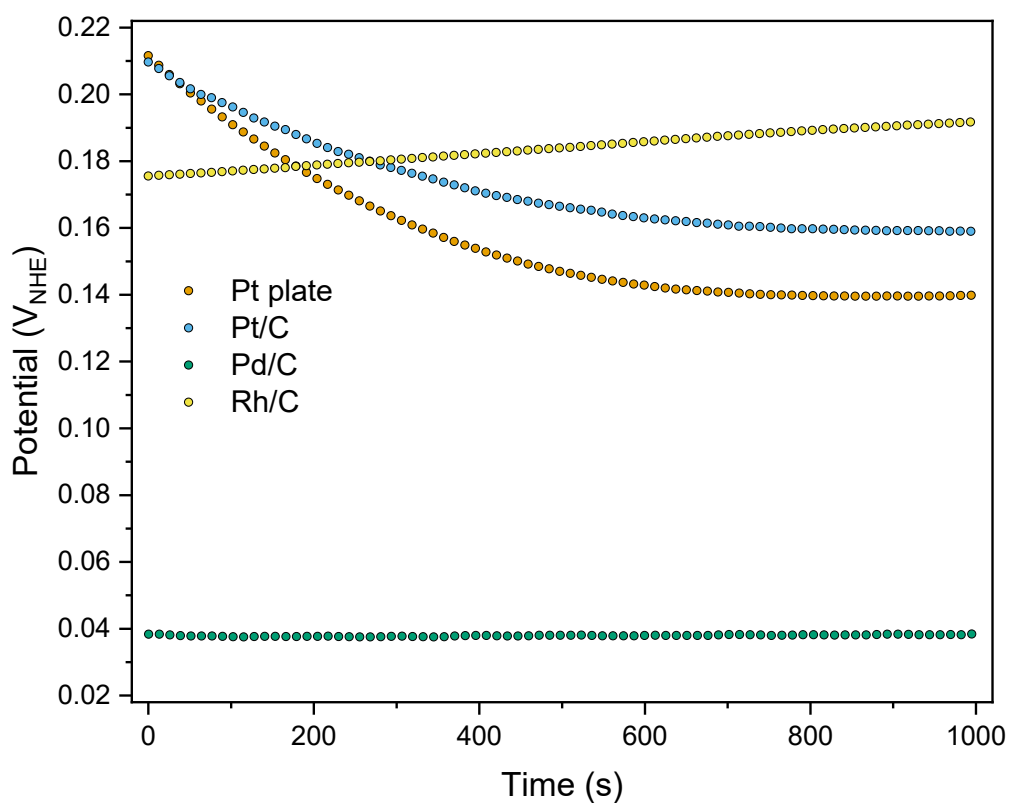


Figure S1. Open circuit potentials for all four electrodes in the 1000 s before starting the oscillating potential measurements. The final potential values have been employed as open circuit potentials. Conditions: 0.25 M sulfuric acid, 0.25 M FA, 35 mL min⁻¹ N₂, 800 rpm.

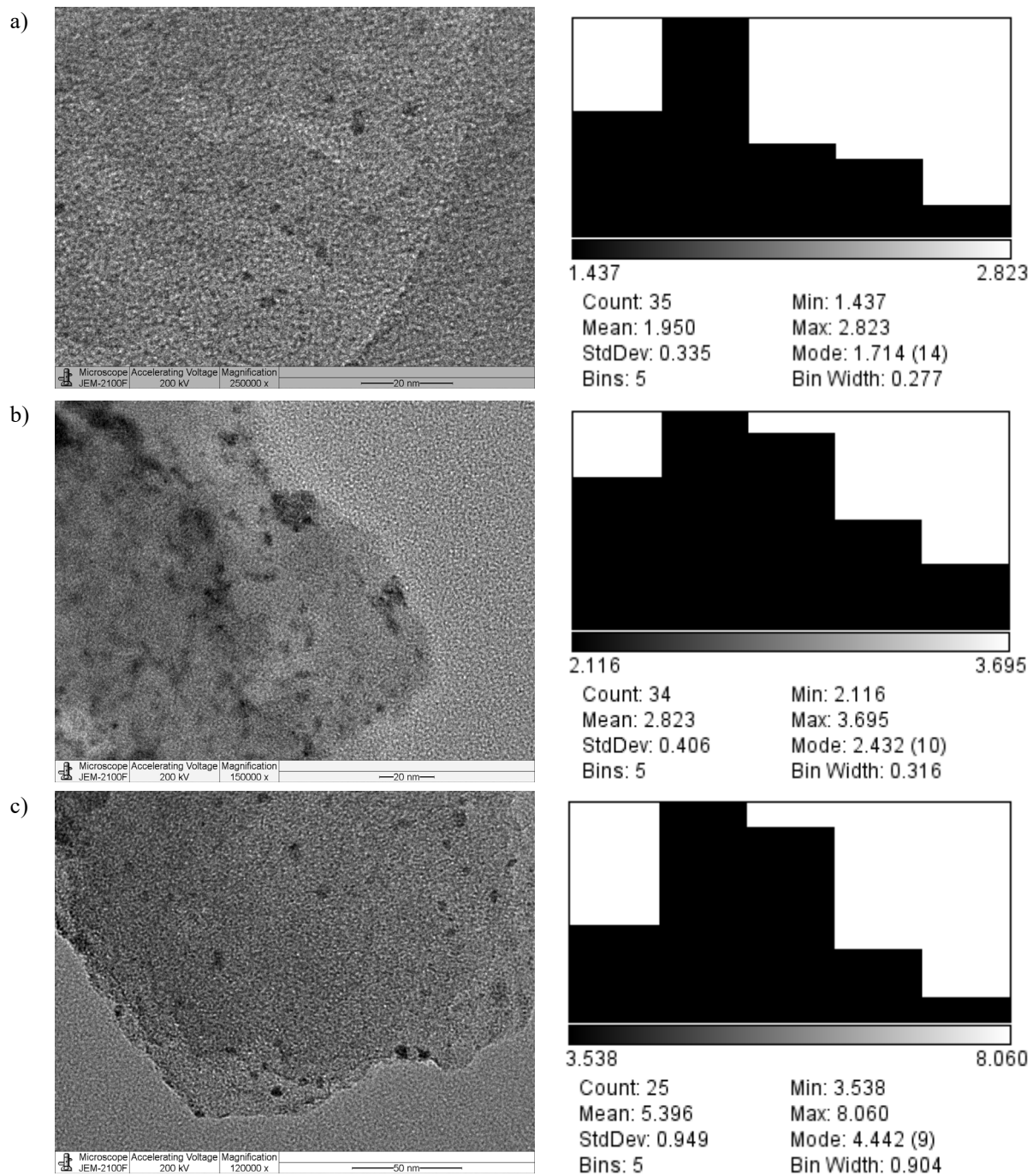


Figure S2. Selected TEM images and particle size distributions for a) Pt/C, b) Pd/C, and c) Rh/C. Means, standard deviations, minima, maxima, modes and bin widths are in nm.

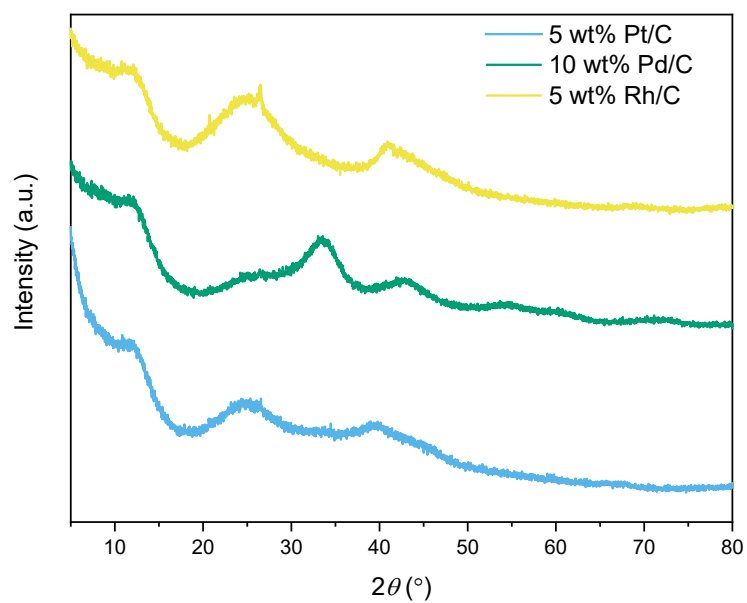


Figure S3. XRD pattern for the different commercial carbon-supported metal catalysts used in this study.

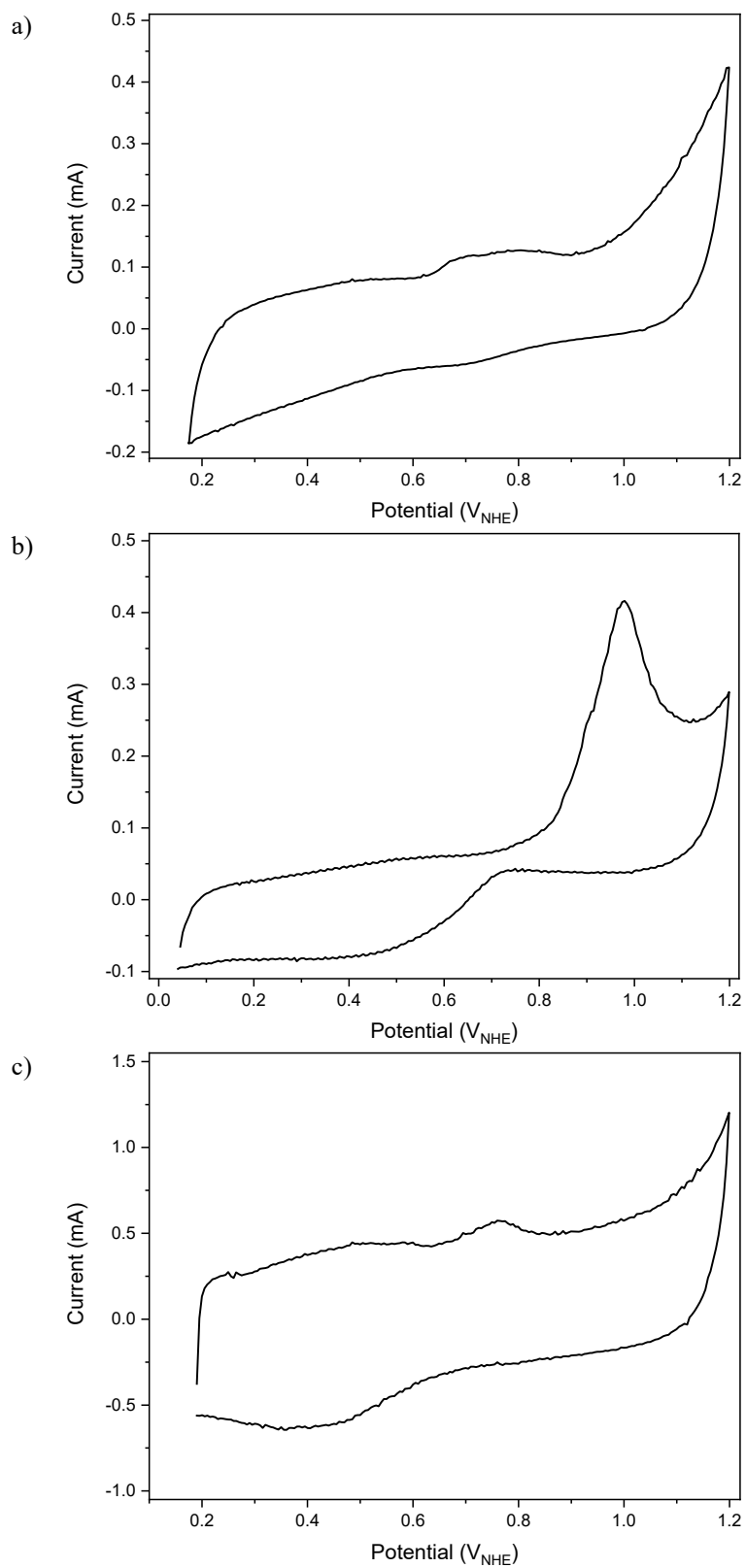


Figure S4. CV scans in 0.25 M H₂SO₄ obtained from CO stripping of a) Pt/C, b) Pd/C, and c) Rh/C. Scan rates were 10 mV s⁻¹.

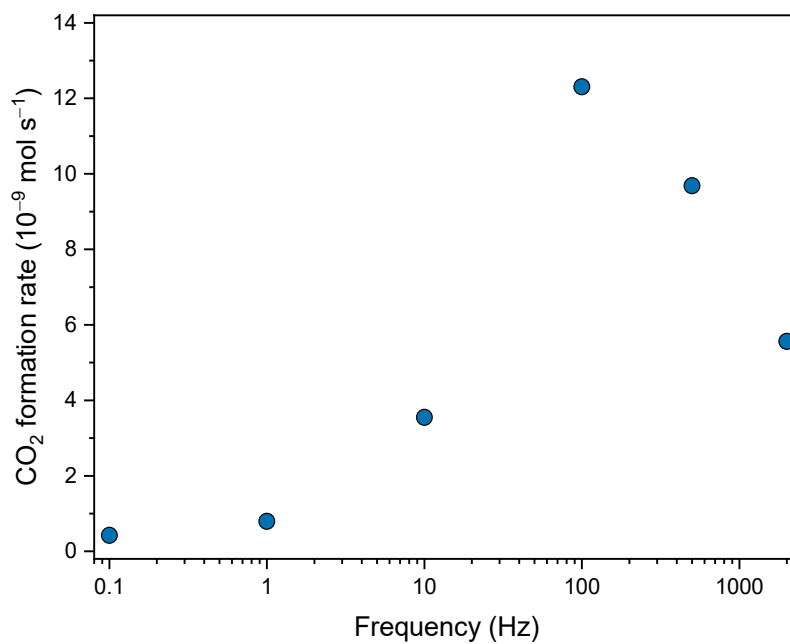


Figure S5. Dependence of CO₂ formation rate for Pt plate electrodes on the frequency of potential oscillations. Conditions: 0.25 M sulfuric acid, 0.25 M FA, 35 mL min⁻¹ N₂, 800 rpm.

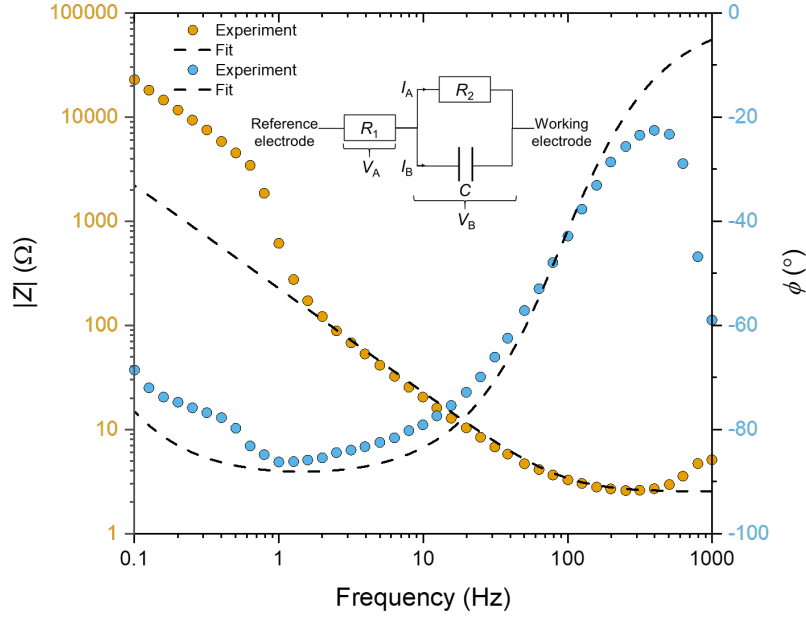


Figure S6. Electrochemical impedance spectroscopy. A Randles circuit (schematically shown here) was used for fitting the impedance of our electrochemical system between 0.1 Hz and 1000 Hz. R_1 is the bulk electrolyte resistance, R_2 the charge transfer resistance and C the double-layer capacitance at the interface between the electrode and the electrolyte. Conditions: 0.25 M sulfuric acid, 35 mL min⁻¹ N₂, 800 rpm.

The Randles circuit consists of two resistors (bulk electrolyte resistance, R_1 and charge transfer resistance, R_2) and a capacitor (interfacial double-layer capacitance, C). R_2 is in parallel with C , while both of them are in series with R_1 . We used V_A and V_B to denote the potential differences across R_1 and the parallel branch of R_2 and C respectively. Letting I_A and I_B be the currents through R_2 and C respectively, the current response, $I_{\text{background}}(t)$, of a Randles circuit following a step increase in applied potential from open circuit to V at $t = 0$ was derived:

$$V_A = (I_A + I_B)R_1 \quad (\text{S1})$$

$$V_B = I_A R_2 = \frac{1}{C} \int I_B dt \quad (\text{S2})$$

$$V = V_A + V_B = (I_A + I_B)R_1 + I_A R_2 \Rightarrow I_A = \frac{V - I_B R_1}{R_1 + R_2} \quad (\text{S3})$$

Alternatively, we can also write

$$V = V_A + V_B = (I_A + I_B)R_1 + \frac{1}{C} \int I_B dt \quad (\text{S4})$$

Differentiating (S4) with respect to t ,

$$\frac{dV}{dt} = \left(\frac{dI_A}{dt} + \frac{dI_B}{dt} \right) R_1 + \frac{1}{C} I_B \quad (\text{S5})$$

Since $\frac{dV}{dt} = 0$ when $t > 0$ for a step change, combining (S3) and (S5) gave

$$\left[\frac{1}{R_1 + R_2} \left(\frac{dV}{dt} - R_1 \frac{dI_B}{dt} \right) + \frac{dI_B}{dt} \right] R_1 + \frac{1}{C} I_B = 0 \quad (\text{S6})$$

Using again $\frac{dV}{dt} = 0$ and after some rearrangement,

$$\frac{dI_B}{dt} = -\frac{1}{C} \frac{R_1 + R_2}{R_1 R_2} I_B \quad (\text{S7})$$

Integration of (S7) gave

$$I_B = I_{Bi} \exp\left(-\frac{1}{C} \frac{R_1+R_2}{R_1 R_2} t\right) \quad (\text{S8})$$

where I_{Bi} is the current through the capacitor at $t = 0^+$.

Now, using (S3),

$$I = I_A + I_B = \frac{1}{R_1+R_2} [V - R_1 I_{Bi} \exp\left(-\frac{1}{C} \frac{R_1+R_2}{R_1 R_2} t\right)] + I_{Bi} \exp\left(-\frac{1}{C} \frac{R_1+R_2}{R_1 R_2} t\right) \quad (\text{S9})$$

Simplifying gave

$$I_{\text{background}}(t) = \frac{V}{R_1+R_2} + \frac{R_2}{R_1+R_2} I_{Bi} \exp\left(-\frac{1}{C} \frac{R_1+R_2}{R_1 R_2} t\right) \quad (\text{S10})$$

The values of resistances and capacitance were obtained from fitting the EIS results in a dilute sulfuric acid electrolyte using the Randles circuit model: $R_1 = 2.525 \, \Omega$, $R_2 = 9.519 \times 10^3 \, \Omega$, $C = 7.06 \times 10^{-4} \, \text{F}$. Since R_2 was much greater than R_1 , the expression for $I_{\text{background}}(t)$ can be simplified to give

$$I_{\text{background}}(t) = I_{Bi} \exp\left(-\frac{t}{R_1 C}\right) \quad (\text{S11})$$

Physically, this implies that the current I_A through resistor R_2 is much smaller compared to the current through the capacitor, I_B . This is because the resistance, R_2 , was much larger in magnitude than the capacitor impedance, C . The electrochemical system effectively behaved like a simple RC series circuit with an exponentially decaying current response when subject to a step change in applied potential from an initial state of open circuit.

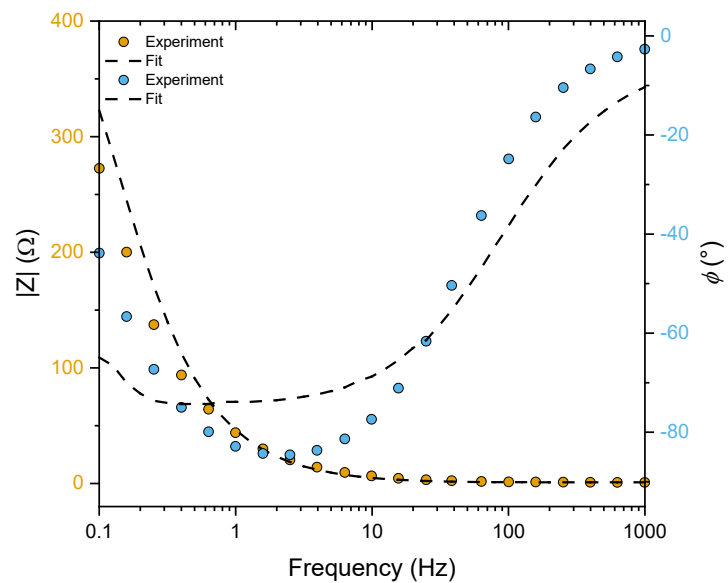


Figure S7. Electrochemical impedance spectroscopy. A Randles circuit was used for fitting the impedance of our electrochemical system between 0.1 Hz and 1000 Hz. R_1 is the bulk electrolyte resistance, R_2 the charge transfer resistance and C the double-layer capacitance at the interface between the electrode and the electrolyte. Conditions: 1.25 M sulfuric acid, 1.25 M FA, 35 mL min⁻¹ N₂, 800 rpm.

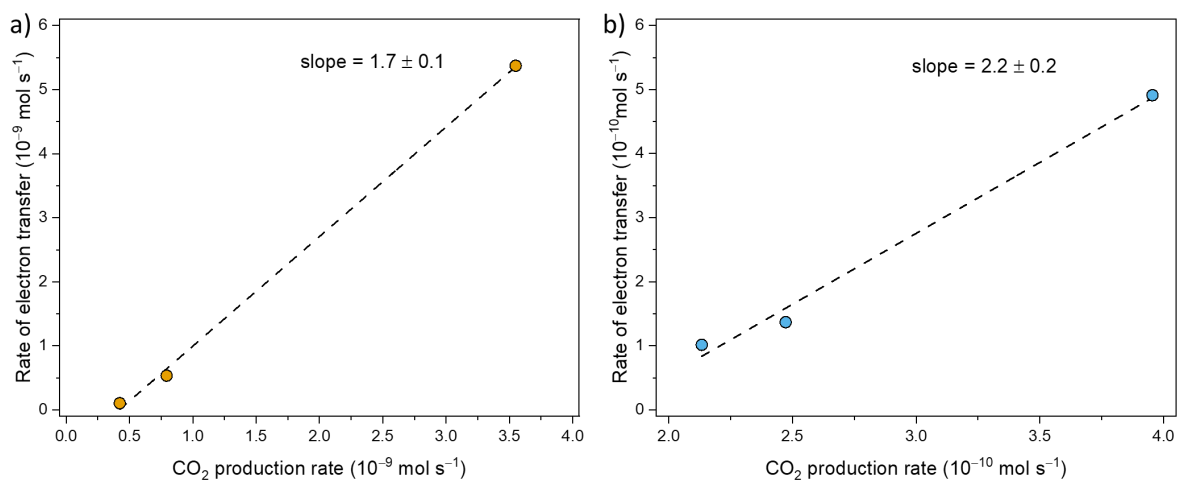


Figure S8. Correlation between the CO₂ production rate and the rate of the electron transfer for different a) dynamic, and b) static potentials on a Pt plate electrode. Conditions: 0.25 M sulfuric acid, 0.25 M FA, 35 mL min⁻¹ N₂, 800 rpm.

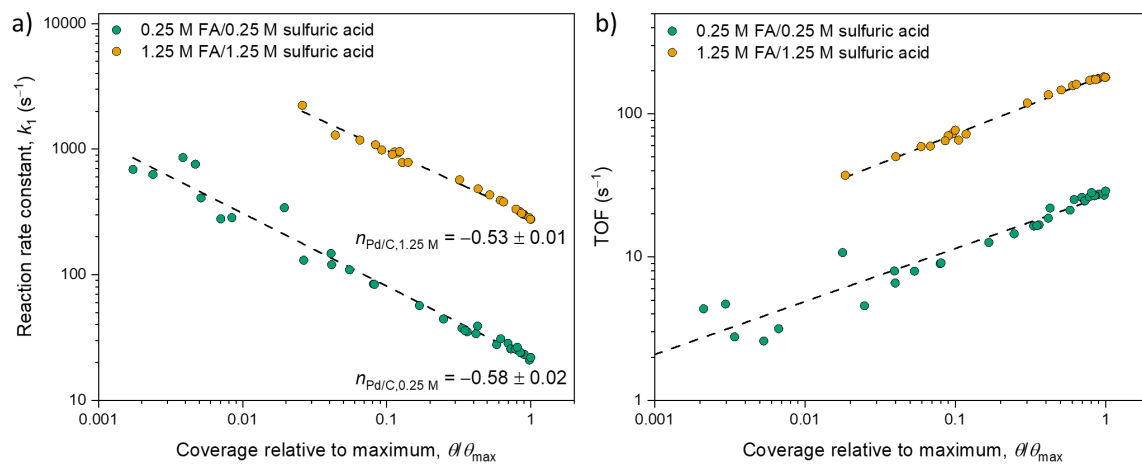


Figure S9. Dependences of reaction rate constant and turnover frequency of oxidative desorption of CO on relative surface coverage for Pd/C in two different electrolyte concentrations. Values of n for power law " $k_1 = a\theta^n$ " are shown in a).

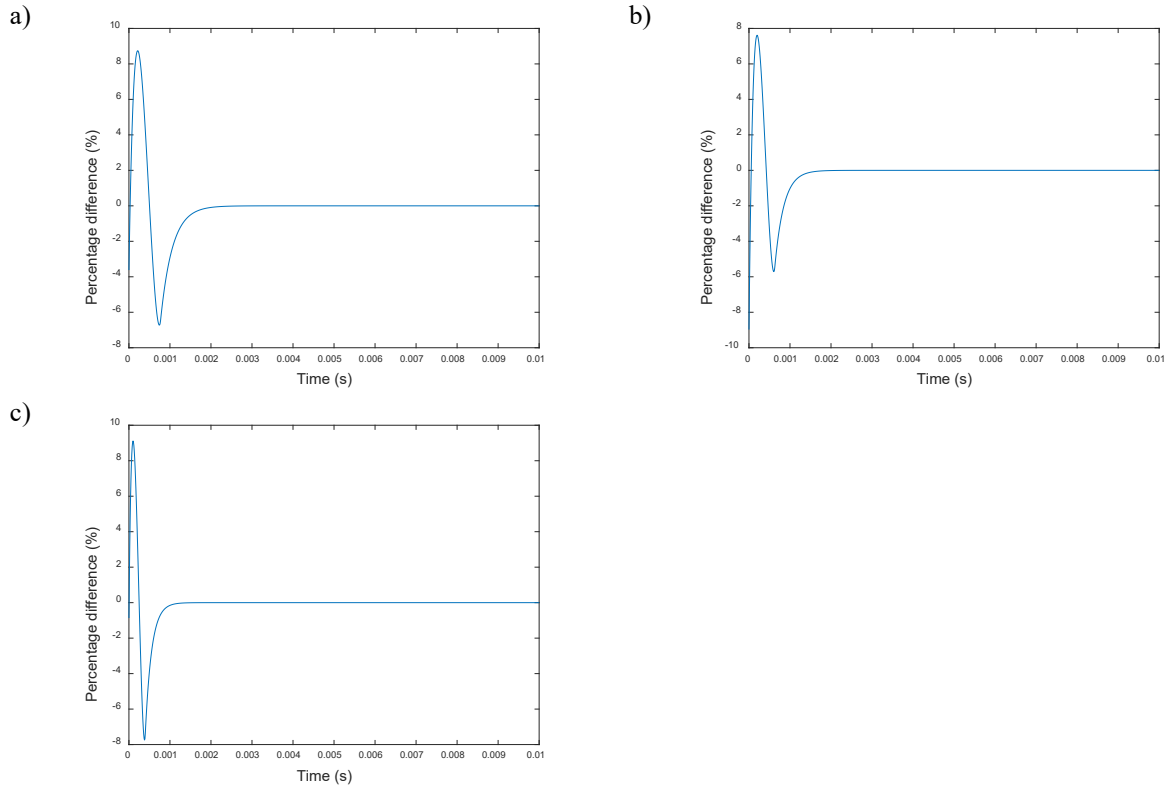


Figure S10. Percentage differences between values of I_{reaction} predicted by (7) and (S2) for Pt plate under applied square wave shaped oscillating potentials at 0.1 Hz for duty cycles a) 99%; b) 99.9%, and; c) 99.99%.

A model that allows the reaction rate constant to vary according to coverage is given by:

$$\text{TOF} = -\frac{d\theta}{dt} = a\theta^{n+1} \quad (\text{S12})$$

where a and n are model parameters with $-1 \leq n \leq 0$ and the apparent rate constant is equal to $a\theta^n$. Values of a and n can be obtained from **Figure 5a**.

The relationship between I_{reaction} and TOF in (5) holds, giving:

$$I_{\text{reaction}} = N_{\text{sites}} \times m \times F \times a\theta^{n+1} \quad (\text{S13})$$

(S12) was numerically solved and (S13) was then used to evaluate I_{reaction} for comparison with the model presented in (7). The differences between values of I_{reaction} predicted by both models were normalized by the current at $t = 0$ to obtain the percentage differences, which are shown in **Figure S10**. The percentage differences between the two models were always less than 10% over the range of duty cycles investigated, indicating that the simpler model presented in (7) was effective at modelling the rate of CO oxidative desorption.

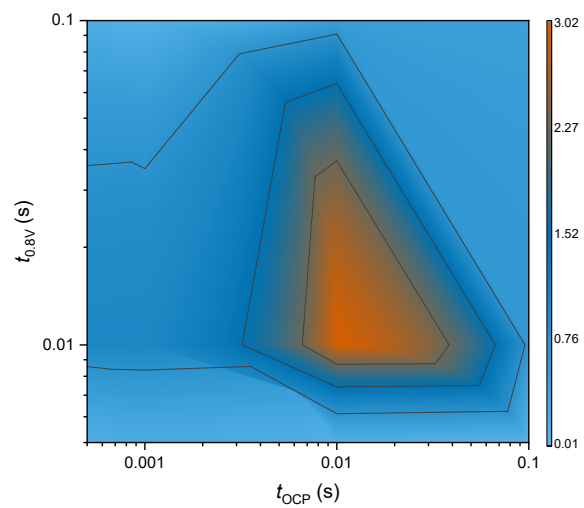


Figure S11. TOF dependence on t_{OCP} and $t_{0.8V}$ for Pd/C at 270 K. Reactions were conducted with varying frequencies and duty cycles to match the values for t_{OCP} and $t_{0.8V}$. TOF values are given in s^{-1} .

Table S1. Amount of sites on each electrode determined using various methods.

Electrode	Amount of sites (10^{-8} mol)		
	Dispersion	CO stripping	θ_{\max}^a
Pt/C	20.1	0.223	0.272
Pd/C	25.9	1.518	1.653
Rh/C	18.6	0.544	1.617

^a These values correspond to the maximum current integral observed for each electrode in **Figure 4**.

Table S2. Current response fitting parameters for the Pt plate electrode at different frequencies and duty cycles. Electrolyte: 0.25 M sulfuric acid, 0.25 M FA

f (Hz)	Duty cycle (%)	A_1 (A)	k_1 (s^{-1})	A_2 (A)	k_2 (s^{-1})	Initial TOF (s^{-1})	Current integral (10^{-6} C)
0.1	50	0.138762	2819.743	0.011331	53.84403	216.5581	49.21078489
0.1	90	0.176885	2862.047	0.011422	52.36006	276.0543	61.80350042
0.1	95	0.187054	2994.503	0.010637	50.86045	291.9248	62.46570444
0.1	97	0.176967	3158.497	0.010018	56.033	276.1827	56.02882087
0.1	99	0.171232	3475.471	0.009034	78.32756	267.2334	49.26885054
0.1	99.3	0.153753	3329.223	0.008487	82.34202	239.9546	46.18294366
0.1	99.5	0.155907	3699.045	0.008302	90.92416	243.3165	42.14804011
0.1	99.7	0.150636	3905.492	0.008311	113.7601	235.0889	38.57018642
0.1	99.9	0.13071	4517.597	0.007637	162.2786	203.9928	28.9336125
0.1	99.93	0.11731	4709.579	0.005829	129.366	183.0802	24.90891435
0.1	99.95	0.105153	4901.401	0.004978	124.7643	164.1064	21.45361897
0.1	99.97	0.08829	5592.647	0.004625	152.5048	137.7896	15.78681234
0.1	99.99	0.056971	6433.462	0.001839	58.31929	88.91182	8.855439891
0.1	99.993	0.044339	7062.827	0.001495	54.82302	69.19693	6.277743846
0.1	99.995	0.034422	7419.399	0.001079	39.58963	53.72101	4.639496454
1	90	0.156647	3317.704	0.009557	71.91848	244.4708	47.21552912
1	99	0.130065	4303.869	0.007083	145.8056	202.9849	30.22039443
1	99.9	0.059177	6510.673	0.001643	52.417	92.35485	9.089274758
10	90	0.14762	3880.222	0.007665	107.2432	230.3828	38.04424145
10	99	0.06888	6279.22	0.001875	50.36741	107.4979	10.96957641

Table S3. Current response fitting parameters for the Pt/C electrode at different frequencies and duty cycles. Electrolyte: 0.25 M sulfuric acid, 0.25 M FA

f (Hz)	Duty cycle (%)	A_1 (A)	k_1 (s^{-1})	A_2 (A)	k_2 (s^{-1})	Initial TOF (s^{-1})	Current integral (10^{-5} C)
0.1	50	0.119716	215.8344	0.113598	20.7662	278.1570204	55.46659847
0.1	90	0.115804	232.9366	0.116765	25.0644	269.0675899	49.7148151
0.1	95	0.118611	236.5858	0.114833	27.51988	275.5895815	50.13445439
0.1	97	0.11678	240.0902	0.111373	29.27351	271.3353005	48.64005278
0.1	99	0.112699	238.3404	0.100035	35.2299	261.8532029	47.28489169
0.1	99.3	0.110914	236.7992	0.095247	38.11727	257.7058017	46.83884067
0.1	99.5	0.108457	275.8698	0.097634	43.73444	251.997026	39.31456071
0.1	99.7	0.104721	268.4546	0.083127	47.83706	243.3165269	39.00883054
0.1	99.9	0.094993	312.8179	0.05554	62.86002	220.7137712	30.36686839
0.1	99.93	0.090961	334.8474	0.046172	68.49765	211.3443659	27.16476647
0.1	99.95	0.08769	323.4283	0.033578	67.68549	203.7457181	27.11269628
0.1	99.97	0.073731	392.2823	0.022887	70.61461	171.3117395	18.79535559
0.1	99.99	0.04291	704.985	0.015735	101.6271	99.70090906	6.08669293
0.1	99.993	0.036478	621.2854	0.005941	60.52975	84.75466271	5.871304567
0.1	99.995	0.027769	652.2406	0.003874	49.22928	64.52148882	4.257539588
1	90	0.115085	237.032	0.100052	34.61883	267.397012	48.55251612
1	99	0.099051	298.7741	0.055183	62.60043	230.142429	33.15247205
1	99.9	0.043158	686.1187	0.014973	97.41214	100.2764934	6.290165244
10	90	0.108549	256.5113	0.046051	49.3935	252.2107856	42.31743396
10	99	0.048356	538.6917	0.009293	62.65432	112.3539116	8.976563032
0.1	80	0.113171	220.7701	0.10877	22.6755	262.9497162	51.26188942
0.1	70	0.113666	223.7442	0.110566	22.29614	264.1004535	50.80185914
0.1	60	0.117618	219.788	0.109723	21.54734	273.2835198	53.51452033
0.1	50	0.11505	226.0595	0.112129	21.86767	267.315089	50.89357322

Table S4. Current response fitting parameters for the Pd/C electrode at different frequencies and duty cycles. Electrolyte: 0.25 M sulfuric acid, 0.25 M FA

f (Hz)	Duty cycle (%)	A_1 (A)	k_1 (s^{-1})	A_2 (A)	k_2 (s^{-1})	Initial TOF (s^{-1})	Current integral (10^{-6} C)
0.1	50	0.076641	28.48158	0.140348	4.405596	26.12511025	2690.883381
0.1	90	0.072135	25.66421	0.137077	4.839989	24.58930234	2810.730038
0.1	95	0.062318	27.73708	0.139698	5.549914	21.24279665	2246.734629
0.1	97	0.054765	33.9467	0.129254	6.107408	18.66804953	1613.252445
0.1	99	0.049235	35.13057	0.081619	7.346102	16.78322798	1401.493779
0.1	99.3	0.04839	37.45162	0.064616	7.717332	16.49523031	1292.077944
0.1	99.5	0.042635	44.42635	0.05478	8.384015	14.53332167	959.6770457
0.1	99.7	0.037093	56.83882	0.040786	9.219338	12.64423723	652.6020752
0.1	99.9	0.026399	84.34399	0.016119	9.802814	8.999000409	312.9976163
0.1	99.93	0.023373	109.4267	0.012513	10.14526	7.967277744	213.5931917
0.1	99.95	0.01931	120.2029	0.009211	10.33255	6.582229744	160.6419884
0.1	99.97	0.013407	130.5364	0.005578	9.454127	4.570126641	102.7063734
0.1	99.99	0.008129	409.2025	0.002611	10.05187	2.770920475	19.86491409
0.1	99.993	0.005796	629.5633	0.001653	8.61801	1.97559212	9.205741697
0.1	99.995	0.004628	690.2186	0.000993	5.119894	1.577510508	6.704810748
1	90	0.048608	35.87895	0.083779	7.322321	16.56929193	1354.768484
1	99	0.026678	83.92816	0.016071	9.615119	9.094067412	317.87132
1	99.9	0.009265	284.8178	0.002116	8.036675	3.158271708	32.52994253
10	90	0.023435	147.5462	0.031775	11.7499	7.988405154	158.8299106
10	99	0.007605	278.8618	0.004001	13.48384	2.592496759	27.27282428
0.1	80	0.079195	20.91311	0.13207	4.506854	26.99585976	3786.862229
0.1	70	0.078933	25.04838	0.13842	4.552717	26.90639147	3151.205473
0.1	60	0.072548	25.67771	0.142134	4.586424	24.73014326	2825.343529
0.1	50	0.08085	23.09908	0.132486	4.326822	27.55993448	3500.132457

Table S5. Current response fitting parameters for the Rh/C electrode at different frequencies and duty cycles. Electrolyte: 0.25 M sulfuric acid, 0.25 M FA

f (Hz)	Duty cycle (%)	A_1 (A)	k_1 (s^{-1})	A_2 (A)	k_2 (s^{-1})	Initial TOF (s^{-1})	Current integral (10^{-5} C)
0.1	50	0.082161	25.31705	0.193972	3.548389	78.25491532	324.5299153
0.1	90	0.070385	28.02113	0.194557	3.976963	67.03811198	251.1841971
0.1	95	0.060102	35.64727	0.186455	4.454779	57.24470194	168.6029611
0.1	97	0.053747	34.53767	0.161391	4.854947	51.19116272	155.6174127
0.1	99	0.048931	40.37596	0.095497	5.939615	46.60441033	121.1882115
0.1	99.3	0.049302	37.59204	0.073944	6.193629	46.95809113	131.1507248
0.1	99.5	0.048868	37.0378	0.057556	6.368089	46.54427637	131.9402384
0.1	99.7	0.042706	49.89378	0.039544	6.808035	40.67528511	85.59342365
0.1	99.9	0.028388	90.74854	0.017303	7.774246	27.03824027	31.28203371
0.1	99.93	0.023556	91.6802	0.012021	7.486692	22.43628035	25.69398754
0.1	99.95	0.021656	109.933	0.008823	7.295634	20.62602621	19.69898374
0.1	99.97	0.016547	162.7384	0.005992	7.422046	15.75991459	10.16763756
0.1	99.99	0.006185	104.0159	0.001708	4.029645	5.891152966	5.946433546
0.1	99.993	0.003666	88.41578	0.001045	3.38029	3.491919755	4.146585839
0.1	99.995	0.006672	403.6555	0.000968	3.147616	6.355231133	1.653014781
1	90	0.053016	35.20279	0.094152	5.668288	50.49482373	150.6003427
1	99	0.02789	78.65257	0.016257	7.29345	26.56379732	35.45957022
1	99.9	0.006355	111.2294	0.001745	4.399548	6.052710508	5.713293459
10	90	0.024251	147.2136	0.038008	9.610625	23.09806544	16.47340012
10	99	0.009897	665.633	0.004998	10.87458	9.426771784	1.486908797
0.1	80	0.076774	26.30316	0.195127	3.715183	73.12349871	291.8805886
0.1	70	0.077301	28.78752	0.198068	3.665003	73.62517448	268.5210258
0.1	60	0.085356	26.56344	0.194126	3.565595	81.29732831	321.3277044
0.1	50	0.078704	25.52082	0.196467	3.56204	74.96173498	308.3906854

Table S6. Current response fitting parameters for the Pd/C electrode at different frequencies and duty cycles. Electrolyte: 1.25 M sulfuric acid, 1.25 M FA

f (Hz)	Duty cycle (%)	A_1 (A)	k_1 (s^{-1})	A_2 (A)	k_2 (s^{-1})	Initial TOF (s^{-1})	Current integral (10^{-6} C)
0.1	50	0.516777	301.8175	0.115926	42.71394	176.1579839	1712.217084
0.1	90	0.513075	305.1276	0.125039	48.4566	174.8960776	1681.509807
0.1	95	0.511143	319.9127	0.139308	55.40717	174.2374088	1597.757102
0.1	97	0.503287	333.207	0.151833	61.44429	171.5594392	1510.432861
0.1	99	0.461852	392.8999	0.205772	84.75174	157.4351612	1175.49468
0.1	99.3	0.430313	433.2633	0.239503	97.30482	146.6843919	993.1913797
0.1	99.5	0.398737	483.4238	0.276334	112.1221	135.9205734	824.817925
0.1	99.7	0.349229	570.6392	0.323116	134.185	119.0446823	611.9970517
0.1	99.9	0.213013	933.4584	0.400468	202.3512	72.61155085	228.1979068
0.1	99.93	0.173339	1083.792	0.397946	231.3789	59.0875065	159.9375561
0.1	99.95	0.147328	1182.21	0.381142	260.9134	50.22078272	124.6205421
0.1	99.97	0.192263	782.6746	0.252086	270.2424	65.53822584	245.6486205
0.1	99.99	0.17431	986.4792	0.116505	335.879	59.41857113	176.6994309
0.1	99.993	0.111049	2236.14	0.112264	448.0171	37.85411392	49.66095629
0.1	99.995	0.109138	1296.53	0.057855	381.6197	37.20264645	84.1767621
1	90	0.471338	380.3623	0.198673	81.93409	160.6686731	1239.180591
1	99	0.206384	951.4937	0.402205	199.6308	70.35173314	216.9051041
1	99.9	0.190207	909.2511	0.098733	313.1745	64.83727828	209.1904507
10	90	0.225662	956.8116	0.407512	196.2942	76.92337534	235.8483198
10	99	0.211959	786.1505	0.065722	256.3037	72.25220829	269.6164132
0.1	80	0.530779	284.7207	0.108087	41.79761	180.9310797	1864.211094
0.1	70	0.509017	308.5083	0.132835	48.98669	173.5127082	1649.929025
0.1	60	0.52721	275.8358	0.100743	38.32711	179.7143151	1911.318144
0.1	50	0.52673	276.7784	0.100955	38.29135	179.5506425	1903.074015