

SUPPORTING INFORMATION: Resonance-Promoted Formic Acid Oxidation via Dynamic Electrocatalytic Modulation

Joshua Gopeesingh¹, M. Alexander Ardagh^{2,3}, Manish Shetty², Sean Burke¹,
Paul J. Dauenhauer^{2,3} and Omar A. Abdelrahman^{1,3*}

¹ Department of Chemical Engineering, University of Massachusetts Amherst, 686 N. Pleasant Street, Amherst, MA 01003.

² Department of Chemical Engineering and Materials Science, University of Minnesota, 420 Washington Ave SE, Minneapolis, MN 55455.

³ Catalysis Center for Energy Innovation, University of Delaware, 150 Academy Street, Newark, Delaware 19716, United States

*Corresponding Author: abdel@umass.edu

Section S1. Figure 1 volcano curve data

Catalyst	TOF (s ⁻¹) ^a	d-band center (eV) ^b
Ag	0.039	-4.3
Au	0.077	-3.56
Cu	32	-2.67
Pt	98	-2.25
Pd	16	-1.83
Co	0.003	-1.17
Ni	9.3	-1.29
Fe	0.022	-0.92
Rh	3.3	-1.73

a- Experimentally measured TOF at 523 K and 2000 ppm formic acid by Wachs et. al¹

b- Computationally calculated d-band center by Nørskov et. al²

Section S2. Electrochemical cell design. In order to ensure that the only observed catalytic activity was as a result of the Pt working electrode, it was required to ensure that all non-Pt materials in contact with the reactant solution were chemically inert. This promoted the design of custom cell fittings, which were machined at University of Massachusetts Amherst Physics machine shop. A 14-20 PTFE plug (Ace Glass Incorporated, 5846-44) was converted into an adapter that would accept a 10-32 male PEEK finger-tight fitting (IDEX, F-120X) for 1/16-inch OD tubing. One of these custom pieces was used for the inlet gas stream which was delivered via a 1/16-inch PEEK tube (Valco, TPK105-5M), this is shown in Figure S1. Another custom piece was used to hold the Pt working electrode; since the electrode was a 1/32-inch OD wire, a 1/16" OD PTFE sleeve (Gamry, 990-00402) with a 1/32-inch ID was placed over the wire to create a gas-tight seal with the 10-32 PEEK finger-tight fitting. This avoided the need for any additional electrical connections other than the Pt itself inside of the electrochemical cell, where alligator clips connected the external portion of the Pt wire to the potentiostat (Figure S2). The Pt coil counter electrode was housed within fritted glass isolation tube with a 14/20 port opening (Pine Research, RRP32), which allowed a compression seal adapter to provide a gas tight medium for the counter electrode (Ace Glass Incorporated, 8300-07).

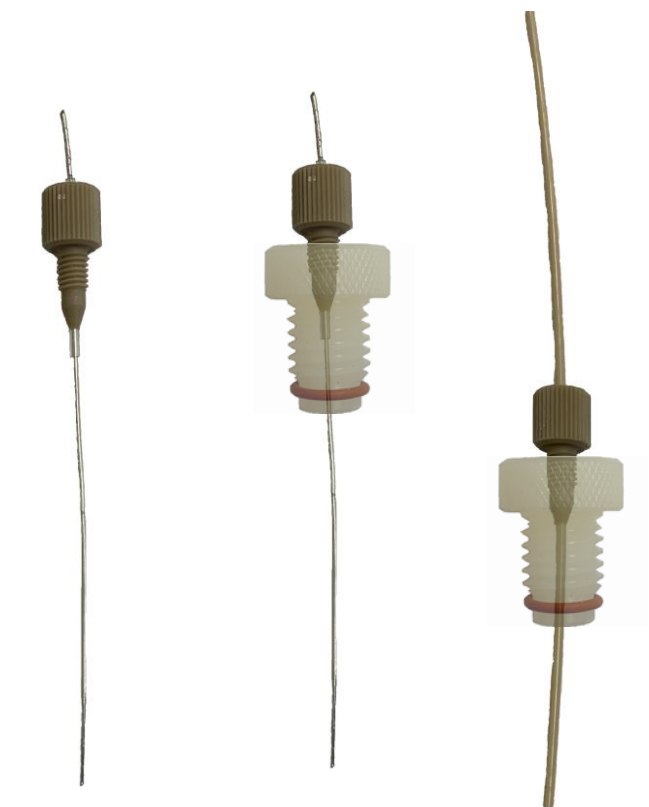


Figure S1. PEEK finger tight fitting for gas tight connections with working electrode and gas feed capillary tubing.

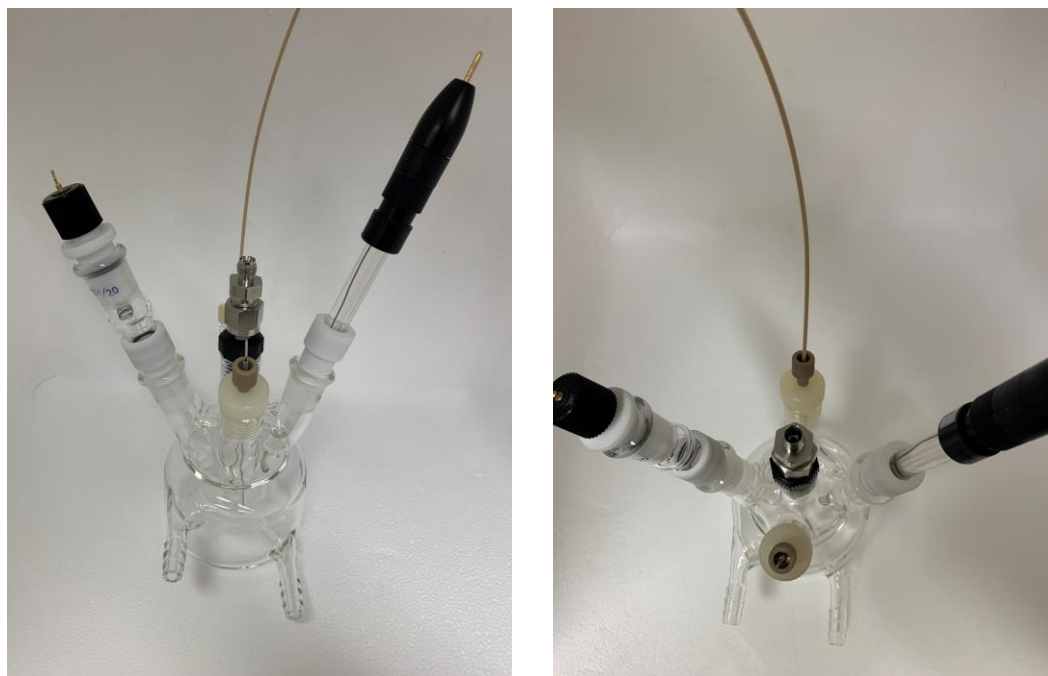


Figure S2. Fully assembled modified electrochemical cell

Section S3. Residence Time Distribution. The residence time of the electrochemical reactor system as a whole was measured via a residence time distribution (RTD) experiment, where an instantaneous step change from a pure nitrogen stream to one blended with CO₂ as a tracer gas was implemented. The switch was facilitated by an electronically actuated (VICI, ED26UWT) two-position six port valve (VICI, 26UWT). This allowed for a 35 sccm stream of N₂ to flow the electrochemical reactor, the effluent of which was blended with a 1.5 sccm stream of CO₂ (Bypass mode, **Figure S3A**) which subsequently passed to an online GC for chemical analysis. Once the CO₂ mole fraction (y_{CO_2}) was found to be stable, the same blended N₂/CO₂ stream was passed through the reactor via a switch in the six-port valve (Reactor mode, **Figure S3A**). The reactor effluent was then sampled every 3.4 minutes via gas chromatography until the mole fraction of CO₂ reached that of the reactor feed ($y_{\text{CO}_2}/y_{\text{CO}_2,0} = 1$, **Figure S3B**). Treating the electrochemical reactor system as a continuously stirred tank reactor (CSTR), the mole fraction of CO₂ can be quantitatively described as a function of time,

$$\frac{y_{\text{CO}_2}}{y_{\text{CO}_2,0}} = 1 - e^{-\frac{t}{\tau_r}} \quad (\text{S1})$$

where τ_r is the residence time of the reactor system, which is estimated by via minimizing a least squares minimization between Eq. X and the experimental data (Figure XB). Based on this approach, we estimate the residence time to be 4.2 mins. We therefore expect the reactor to reach >99% of a new steady state value after ~ 20 mins from when a step change occurs ($5\tau_r$).

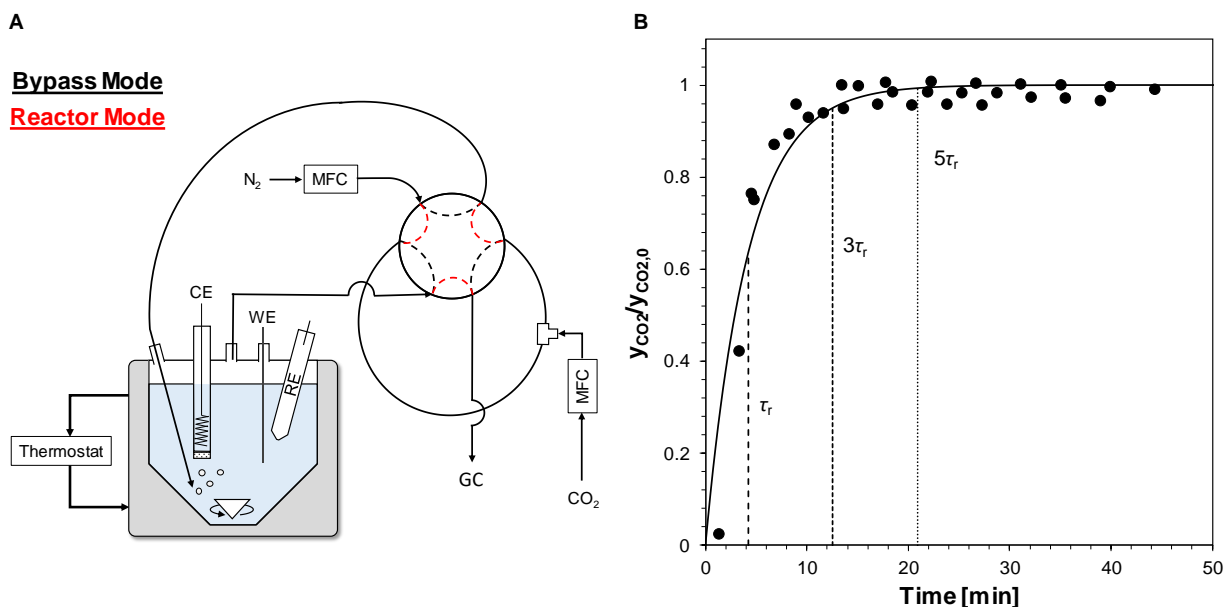


Figure S3. Residence time distribution measurement of electrochemical reactor. (A) Electrochemical reactor setup to create step change in CO₂ concentration by switching between bypass (black) and reactor (red) mode via a two position six-port valve. (B) Experimental (filled symbols) measurement of normalized effluent CO₂ mole fraction after a step change from pure nitrogen to a 4.1 mol% CO₂ feed to the electrochemical reactor. Theoretical prediction of normalized CO₂ mole fraction response indicated by solid line (Eq. S1, $\tau_r = 4.2$ min).

Section S4. Gas Chromatograph Calibration. To accurately quantify the rate of CO₂ formation under reaction conditions, the FID/Jet analyzer detector was calibrated using different known concentrations of CO₂ in N₂. Briefly, the flow rate of CO₂ and N₂ was controlled via two independent mass flow controllers (Brooks Instruments, 5850) to generate the desired mole fraction of CO₂. The distinct flow rates were confirmed using a soap bubble flow meter. Three different mole fractions were then analyzed via gas chromatography to measure the relevant CO₂ calibration factor (**Figure S4**).

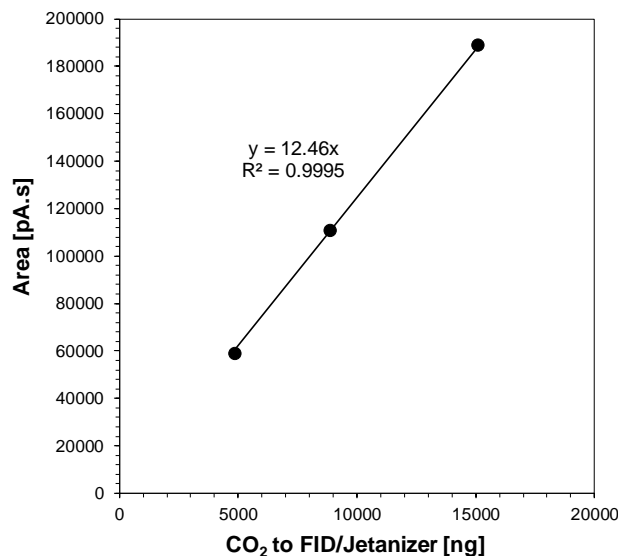


Figure S4. Gas chromatograph FID/Jet analyzer response area to ng of CO₂ sent to the detector.

Section S5. Initial Rate Measurement. To be able to accurately account for deactivation as a function of time on stream, it was necessary to first establish an accurate initial rate. This was estimated at 0.8 V NHE, measuring the rate of reaction every four minutes for approximately one hour. The rates with time on stream were then fit to a first order deactivation model,

$$\frac{da}{dt} = -k_d a \quad (\text{S2})$$

$$\ln r(t) = \ln(r_0) + e^{-k_d t} \quad (\text{S3})$$

where a is the activity defined as the ratio of the rate($r(t)$) and the initial rate at zero time on stream (r_0), k_d is the deactivation rate constant. Through this procedure, the initial rate at zero time on stream over a fresh catalyst could be estimated. Repeated measurements of the initial rate at 0.8 V NHE revealed a reproducible average of 22.8 ± 2.8 nmol CO₂ min⁻¹ over seven repeated regeneration /measurement cycles (**Figure S5**).

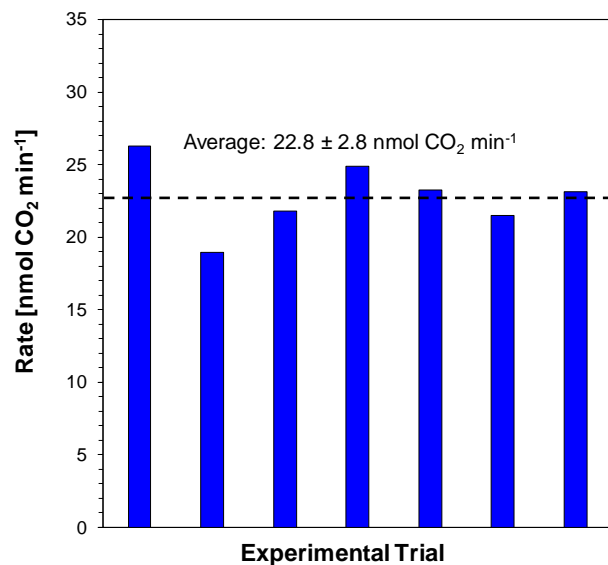


Figure S5. Initial rate estimates at 0.8 V NHE after thermal reduction of Pt wire at 673 K in H₂. Initial rates were estimated from time on stream rate measurements using a first order deactivation model. 0.25 M HCOOH, 0.25 M H₂SO₄ at 295 K. Average error estimated at 95% confidence interval.

Section S6. Cyclic Voltammetry. In order to investigate the state of the platinum working electrode during formic acid electro-oxidation, cyclic voltammetry scans were performed within the range of 0 to 1.2 V NHE (**Figure S6**). Using a scan rate of 500 mV s⁻¹ at a step size of 2 mV, scans were performed until there was no discernable difference between the ‘current vs potential’ profiles of consecutive scans.

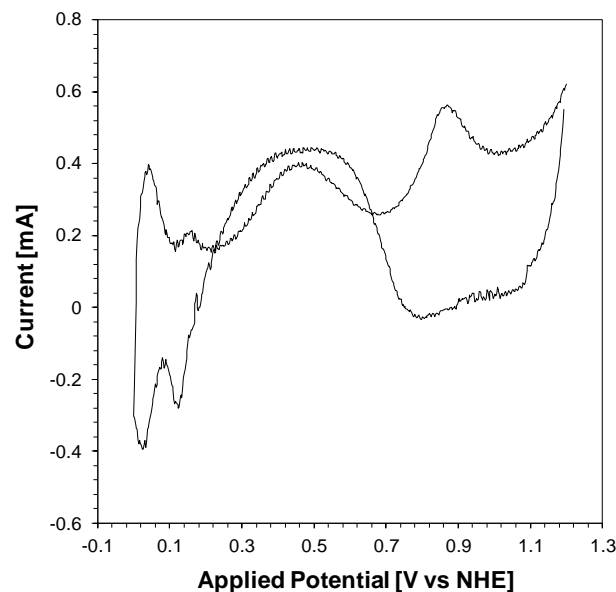


Figure S6. Cyclic voltammetry measurement between 0 and 1.2 V NHE with 0.25M formic acid and 0.25M sulfuric acid.

Section S7. Open Circuit Potential.

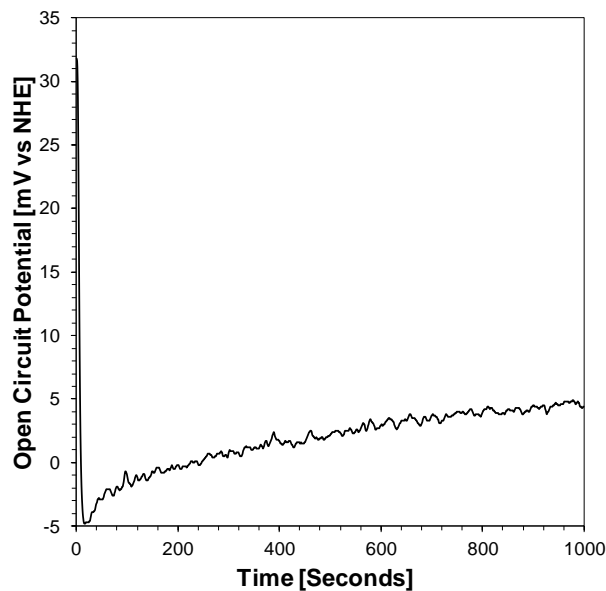


Figure S7. Open circuit potential measurement of with 0.25M formic acid and 0.25M sulfuric acid.

References

1. Tang, Y.; Roberts, C. A.; Perkins, R. T.; Wachs, I. E., Revisiting formic acid decomposition on metallic powder catalysts: Exploding the HCOOH decomposition volcano curve. *Surface Science* **2016**, *650*, 103-110.
2. Ruban, A.; Hammer, B.; Stoltze, P.; Skriver, H. L.; Nørskov, J. K., Surface electronic structure and reactivity of transition and noble metals1Communication presented at the First Francqui Colloquium, Brussels, 19–20 February 1996.1. *Journal of Molecular Catalysis A: Chemical* **1997**, *115* (3), 421-429.