Supporting Information

Thermochemical Aerobic Oxidation in Water Proceeds via Coupled Electrochemical Half-Reactions

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Index *Page*

Experimental Details

Chemicals and Materials. Perchloric acid ($HClO_4$, 99.999%), potassium hydroxide (KOH >99.9%, semiconductor grade), formic acid (HCOOH, >98%), methanol (CH_3OH, > 99%), ethanol (CH_3CH_2OH, >99.5%), and d_6-dimethyl sulfoxide (DMSO, >99%) were obtained from Sigma Aldrich and were used as received. 1-Propanol ($CH_3CH_2CH_2OH$, > 99%) was obtained from MACRON and was used as received. Deuterium oxide (D_2O, >99%) was obtained from Cambridge Isotope Laboratories and used as received. O_2 (Ultra High Purity, 99.9994%) and Ar (Ultra High Purity, 99.999%) were purchased from Airgas. 0.1M $HClO_4$ and 0.1M KOH solutions were prepared with reagent grade water (Millipore Type 1, 18 MΩ-cm resistivity). Ti wire, Au mesh (99.99%), and Pt mesh (99.99%) were obtained from Alfa Aesar. Leakless Ag/AgCl reference electrodes were purchased from eDAQ and stored in Millipore water between measurements. Nafion 117 (178 μm thick) was purchased from Ion Power Inc. and activated by established pretreatment procedures before its usage.[1] Briefly, Nafion membrane was heated at 70–80 ˚C, in 3% H_2O_2 and subsequently in 0.5 M H_2SO_4, for 30–60 min each, then stored in 0.5 M H_2SO_4 or water.

Gas Diffusion Electrode. Pre-fabricated Pt/C (60 wt%, 0.5 mg cm^{-2}), PtRu/C (60 wt%, 0.5 mg cm^{-2}, 1:1 in atomic ratio), Pd/C (60 wt%, 0.5 mg cm^{-2}), and Au/C (20 wt%, 0.3 mg cm^{-2}) gas diffusion electrodes (GDE) were obtained from the Fuel Cell Store. These electrodes consisted of a sandwich of the catalyst layer, microporous carbon layer (MPL), and gas diffusion layer (GDL). Each catalyst layer is composed of 60/20 wt% metal nanoparticles, 5–8 nm, supported on Vulcan XC-72. The MPL is composed of carbon black matrix and the GDL is consisted of carbon cloth. These pre-fabricated catalysts/electrodes were used as received without further modification.

Reaction Cell Design and General Reaction Conditions. The reaction cell was comprised of a hanging-strip GDE working electrode (~0.5 cm^2), a leakless Ag/AgCl electrode (eDAQ) reference electrode, and a high surface area Au-mesh counter electrode (99.99%, Alfa Aesar). The leakless Ag/AgCl electrode was stored in Millipore water between measurements and were periodically checked to ensure against potential drift. All experiments were conducted in an airtight H-cell separated by a pre-activated Nafion 117 membrane. The H-cell was cleaned rigorously with reagent grade water (Millipore Type 1, 18 MΩ-cm resistivity) prior to each experiment. Reaction solutions (0.1M $HClO_4$ or 0.1M KOH, 20.0 mL in total) were used for working (10.0 mL) and counter compartments (10.0 mL), and the working compartment was stirred by a magnetic stir bar (2×5 mm) at a constant rate of 700 rpm during all experiments unless otherwise noted. The desired gas (ultra-high purity Ar or O_2) was flowed into the working compartment of the reaction cell at a flow rate of 10, 20, or 50 sccm (cm^3 min^{-1}), using a series of mass-flow controllers (Alicat Scientific) affixed to each gas line. The reaction solution in the counter compartment was sparged continuously with N_2. An extra mass flow meter was placed downstream of the cell and comparison of its flow rate with the input flow was used to verify that the cell assembly was leak free during the reaction. All experiments were performed at ambient temperature (24 ± 1 ˚C).

Electrochemical Methods. All electrochemical experiments, including linear sweep voltammetry (LSV), cyclic voltammetry (CV), open circuit potential (OCP) measurements, and chronoamperometry (CA) were recorded using a Gamry REF 600 or REF 3000 potentiostat. For all LSVs provided in this work, a scan rate of 10 mV s^{-1} was used. Electrode potentials were converted to the reversible hydrogen electrode (E_{RHE}) scale using $E_{RHE} = E_{Ag/AgCl} + 0.20$ V + 0.06×pH. Data are plotted vs RHE unless otherwise noted. Potentials were corrected for uncompensated Ohmic loss (iR_u) *in situ* via positive feedback at 80% of the measured value. R_u was measured using the R_u test function in the Gamry Framework software. For the given cell configuration, R_u typically ranged from 5–10 Ω for all the electrolyte conditions.

Monitoring thermochemical Aerobic Oxidation at Open Circuit Potential (OCP) (Fig. 2, Fig. 3, Fig. 4, Fig. 5, Fig. 6, and Fig. S1). Using the general setup described above, thermochemical aerobic oxidation reactions were monitored in either 0.1 M $HClO_4$ (pH 1) or 0.1 M KOH (pH 13) while the OCP of catalysts (E_{cat}) were simultaneously recorded during the run. All potential values in this study were found to have a standard error of ±0.01 V obtained from 3 or more independent replicates.

The reaction solution (10.0 mL) in the working compartment was initially sparged for ~30 min with Ar gas at a flow rate of 20 or 50 sccm (cm^3 min^{-1}) to remove any dissolved O_2. The same solution in the counter compartment was sparged continuously with N_2. After complete removal of O_2, the electrode was cycled between 0.0 to 1.0 V vs RHE (20 mV s^{-1}) ~20 times to clean the catalyst surface. The substrate (formic acid, methanol, ethanol, or propanol) was then added to the working compartment of the reaction cell. The thermochemical oxidation reaction was initiated upon the introduction of O_2 into the working compartment at a continuous flow rate of 20 or 50 sccm (cm^3 min^{-1}). Over the entire course of the reaction, the OCP of catalyst (E_{cat}) was continuously monitored and its average value was reported in all cases examined. Using an in-line gas chromatograph (GC), gaseous products were analyzed simultaneously at 20 and 40 min (see below "**In-Line Gaseous Product Detection and Analysis**" section for details). At periodic intervals, aliquots (50.0 µL) of the reaction solutions were taken from the working compartment for ^{1}H NMR analysis to quantify liquid products (see below "**Quantification of Formate Production by ^{1}H NMR**" section for details). The specific TOF values provided are calculated using the mass loading of the metal catalyst (Pt, Pd, and Au) in contact with solution. After each reaction, the solution at the counter compartment was also checked by NMR to ensure against cross-over of liquid products from the working compartment. In all cases, no appreciable amount of product was found in the counter compartment. The pH of the solution was measured following each experiment and we observed no appreciable pH drift (< 0.05 pH units).

Monitoring Electrochemical Substrate Oxidation Reactions under Polarization (Fig. 2, Fig. 3, Fig. 4, Fig. 5, Fig. 6, and Fig. S1). Using the general setup described above, electrochemically-driven aerobic oxidation reactions were monitored in either 0.1 M $HClO_4$ (pH 1) or 0.1 M KOH (pH 13).

Prior to electrolysis, the reaction solution (10.0 mL) in the working compartment was sparged for ~30 min with Ar gas at a flow rate of 20 or 50 sccm (cm^3 min^{-1}) to remove any dissolved O_2. The same solution in the counter compartment was sparged continuously with N_2. After complete removal of O_2, the electrode was cycled between 0.0 to 1.0 V vs RHE (20 mV s^{-1}) for ~20 times to clean the catalyst surface. Substrate (formic acid, methanol, ethanol, or propanol) was then added to the working compartment of the reaction cell. With continuous flow of the gases to both compartments, the electrochemical oxidation reaction was initiated upon polarization of the catalyst electrode at E_{cat}. Using an in-line gas chromatograph (GC), gaseous products were analyzed simultaneously at 20 and 40 min (see below "**In-Line Gaseous Product Detection and Analysis**" section for details). At periodic intervals, aliquots (50.0 μL) of the reaction solutions were taken from the working compartment for ^{1}H NMR analysis to quantify the amount of liquid products (see below "**Quantification of Formate Production by ^{1}H NMR**" section for details). The specific TOF values provided are calculated using the mass loading of the metal catalyst (Pt, Pd, and Au) in contact with solution. After each reaction, the solution at the counter compartment was also checked by NMR to ensure against cross-over of liquid products from the working compartment. In all cases, no appreciable amount of product was found in the counter compartment. The pH of the solution was measured following each experiment and we observed no appreciable pH drift (< 0.05 pH units).

On-Line Electrochemical Mass Spectrometry (Fig. 2c and Fig. S2.). The on-line electrochemical mass spectrometer used within this study was adapted from systems previously reported.[2,3] The reaction cell consisted of a quartz tube that was sealed against a Pt/C working electrode (0.45 cm^2), a miniature leakless Ag/AgCl electrode (eDAQ), and a high surface-area Pt-mesh counter electrode (99.95%, Alfa Aesar). Argon gas (Airgas, 99.999%) was flowed at 2 sccm (cm^3 min^{-1}) under the Pt/C GDE contacting the hydrophobic side and was routed into the differently pumped mass-spectrometer chamber ($<10^{-4}$ torr). The reaction solution (3.0 mL) was added to the reaction cell (0.1 M $HClO_4$) and was equilibrated (typically within 10 min), which was indicated by a constant OCP on a Gamry reference 3000 potentiostat. The electrode was cycled between 0.0 to 1.0 V vs RHE (50 mV s^{-1}) 30 times to reduce the native oxide layer on the surface of Pt and activate the electrode. Formic acid was then added to the cell (0.5 M) and was aspirated several times to form a homogenous solution. Thermochemical formic acid oxidation was initiated upon the introduction of O_2 (Airgas, 99.999%) at 2 cm^3 min^{-1} using a high-speed four-way actuated valve (Valco, Vici series). The relevant mass-to-charge (m/z) ratios for CO_2 (44), Ar (40), and O_2 (32) were recorded on a Pfeiffer HiQuad QMA 400 mass spectrometer in concert with the measurement of the OCP.

Quantification of Liquid Phase Products by ^{1}H NMR. The amount of liquid products (ethanal, acetic acid, propanal, and propionic acid) produced over time was quantified by 500 MHz ^{1}H NMR (Bruker). At given reaction times, aliquots (50.0 μL) of the reaction solutions were taken from the working compartment (see above) and each aliquot was added to 0.50 mL of D_2O which served as the ^{1}H NMR solvent. ^{1}H NMR spectra for each sample was recorded using DMSO as an

internal standard. The water peak was suppressed using the excitation sculpting “zgesgp” sequence. Delay time (d1) was set to 50 s to ensure complete relaxation.

In-Line Gaseous Product Detection and Analysis. Gaseous products were detected and measured using an in-line gas chromatograph (SRI Instruments, Multi-Gas Analyzer #3) equipped with a thermal conductivity detector, methanizer, and flame ionization detector in series following Molsieve 13x and Hayesep D columns. In this study, the sole detectable gaseous product was CO_2 in all cases. Electrodes were polarized, and GC traces were collected to allow for equilibration of the headspace and to ensure a steady state was achieved.

Supporting Figures

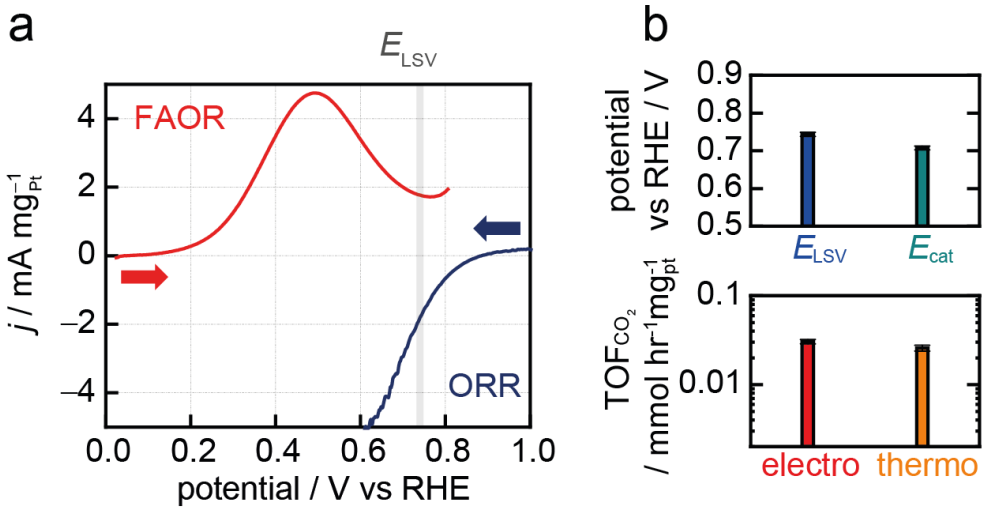

Fig. S1. (**a**) Linear sweep voltammograms (LSVs) of Pt mesh catalyzed formic acid oxidation reaction (FAOR, red) and oxygen reduction (ORR, blue) at pH 1 (0.1M $HClO_4$), scan rate: 10 mV s^{-1}. FAOR curve was collected with 0.5 M formic acid (FA) in the absence of O_2, whereas the ORR curve was collected without formic acid (FA) under 1 atm of O_2. The current equivalency point (E_{LSV}) is marked (vertical grey bar) on the figure. (**b, top**) Comparison of the expected catalyst potential, E_{LSV} (blue bar, 0.74 V) and the measured catalyst potential, E_{cat} (green bar, 0.71 V) during thermochemical formic acid oxidation. (**b, bottom**) Comparison of measured specific reaction rates during electrochemically-driven FAOR at E_{cat} (red bar, 0.030 ± 0.002 mmol $hr^{-1}mg^{-1}$) and thermochemical formic acid oxidation (orange bar, 0.026 ± 0.002 mmol $hr^{-1}mg^{-1}$). The recorded electrochemical currents in (a) are normalized by the Pt mass. Error bars indicate standard errors, obtained from 3 or more independent replicates.

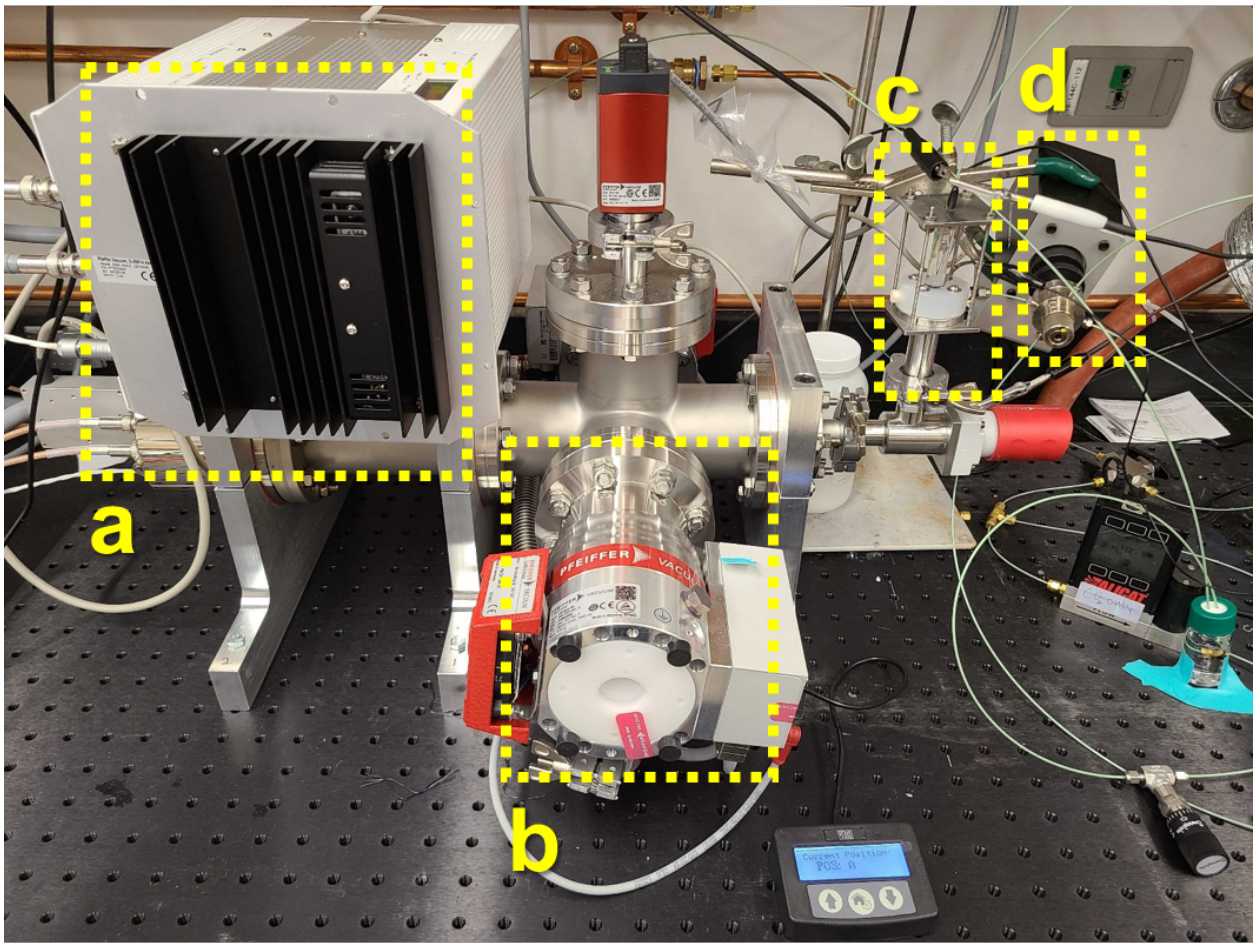

Fig. S2. The on-line mass spectrometry setup comprised of (**a**) mass spectrometer (Pfeiffer HiQuad QMA 400), (**b**) vacuum pump (Pfeiffer), (**c**) electrochemical cell, and (**d**) high-speed four-way actuated valve (Valco, Vici series).

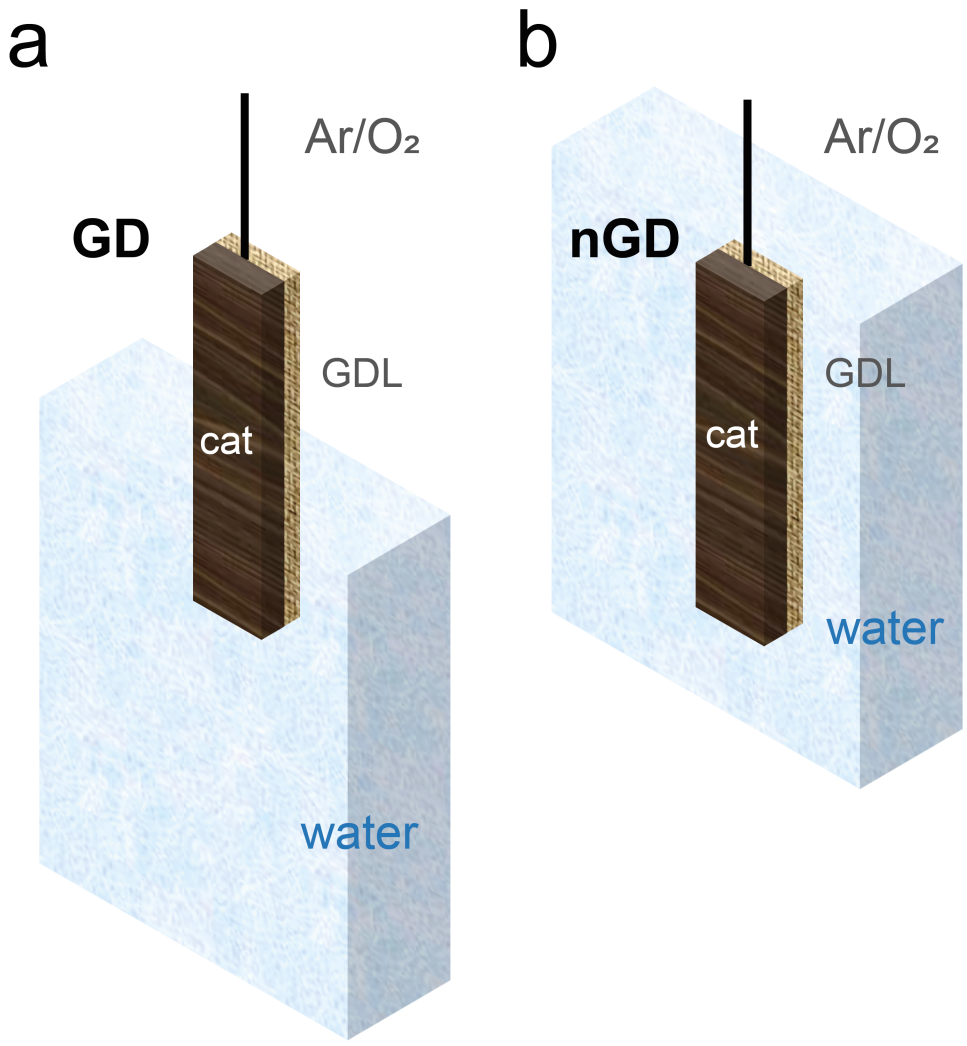

Fig. S3. Schematic illustrations of the hanging-strip working electrodes employed for (**a**) GD and (**b**) nGD reaction modes. For the nGD reaction mode, the catalyst layers were submerged entirely within the aqueous solution, thereby diminishing the direct O_2 flux to the catalyst film (cat) via gas diffusion layers (GDL).

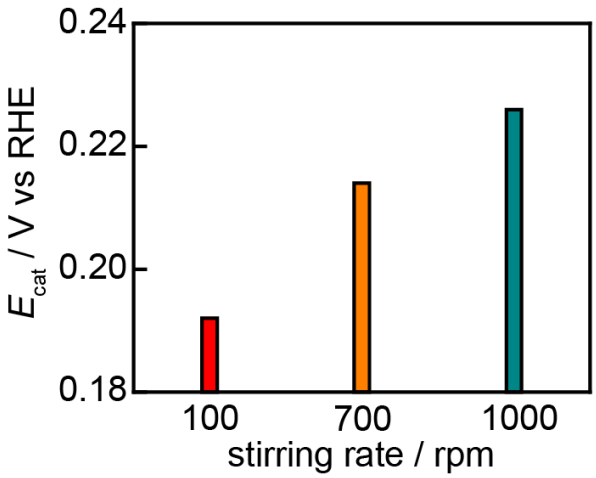

Fig. S4. Catalyst potentials, E_{cat}, monitored during thermochemical oxidation of formic acid (0.5 M) as a function of a stirring rate (100, 700, and 1000 rpm) under the nGD reaction mode.

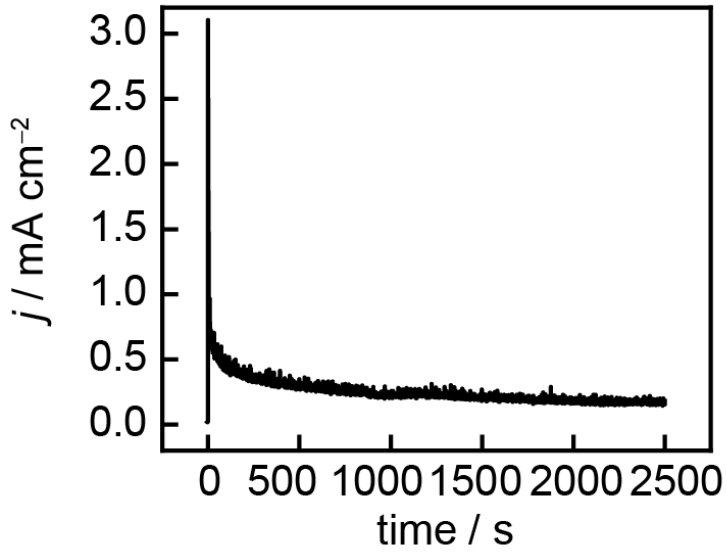

Fig. S5. Chronoamperometry trace of electrochemically-driven formic acid oxidation on Au/C measured at E_{cat} (0.67 V vs RHE).

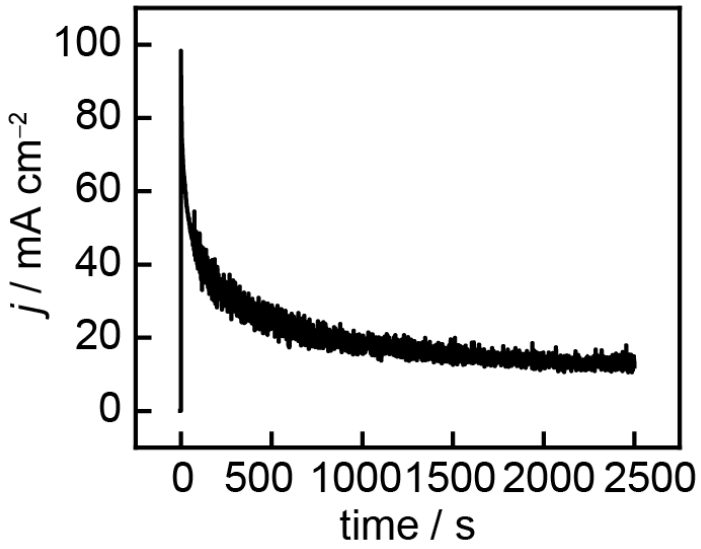

Fig. S6. Chronoamperometry trace of electrochemically-driven formic acid oxidation on Pd/C measured at E_{cat} (0.74 V vs RHE).

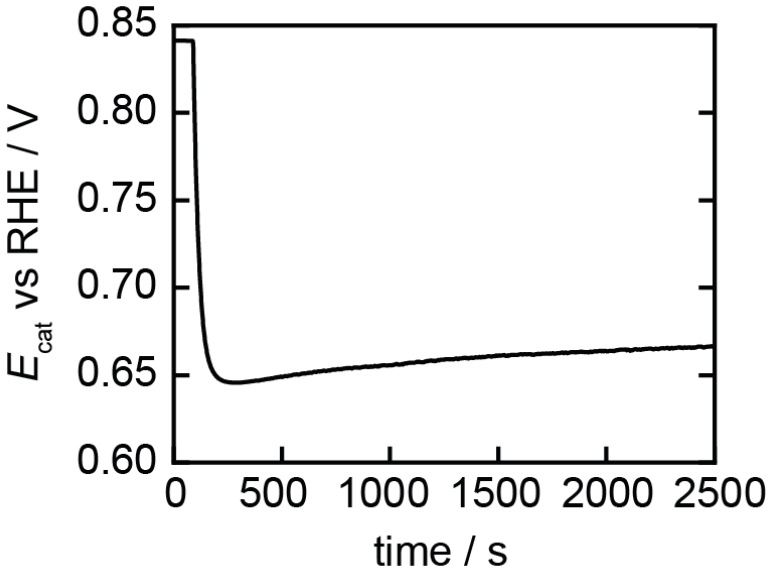

Fig. S7. Open circuit potential (OCP) trace of Au/C during thermochemical oxidation of formic acid (0.5 M) at pH 1 (0.1 M $HClO_4$).

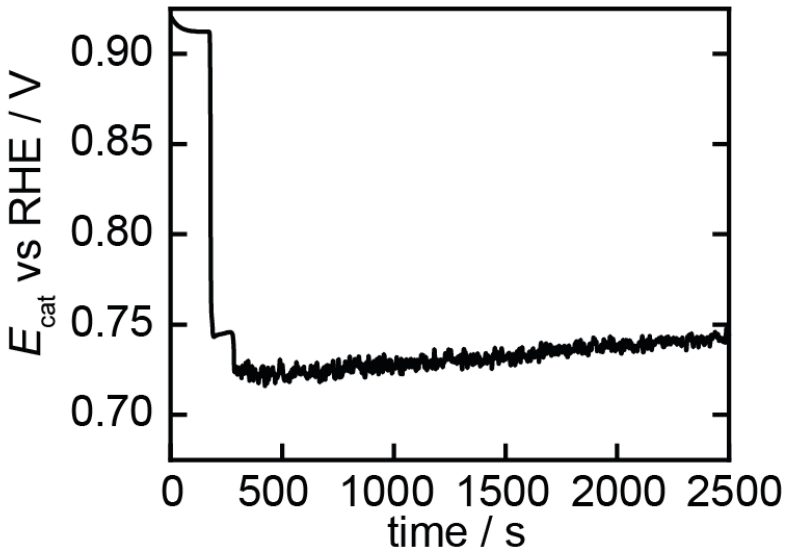

Fig. S8. Open circuit potential (OCP) trace of Pd/C during thermochemical oxidation of formic acid (0.5 M) at pH 1 (0.1 M $HClO_4$).

References

[1] Kim, R. S.; Surendranath, Y. *ACS Cent. Sci*. **2019**, *5*, 1179-1186.

[2] Rus, E. D.; Wang, H.; Wang, D.; Abruña, H. D. *J. Phys. Chem*. C **2011**, *115*, 13293-13302.

[3] Zeng, R.; Yang. Y.; Shen. T.; Wang. H.; Xiong, Y.; Zhu, J.; Wang, D.; Abruña, H. D. *ACS Catalysis* **2020**, *10*, 770-776.