

## Supporting Information

# **Oxidative Degradation of Multi-Carbon Substrates by an Oxidic Cobalt Phosphate Catalyst**

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## Experimental Details

**Materials.**  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  99.999% was used as received from Strem. KOH, 88% and  $\text{KH}_2\text{PO}_4$ , 99.9% were reagent grade and used as received from Macron. All electrolyte solutions were prepared with type I water (EMD Millipore, 18.2 M $\Omega$  cm resistivity). Fluorine-oxide coated glass (FTO; TEC-7) was purchased as pre-cut 9"  $\times$  11" and 1 cm  $\times$  2.5 cm glass pieces from Hartford Glass. Unless stated otherwise, all experiments used FTO with 7  $\Omega$ /sq surface resistivity. Ethylene glycol ( $\geq$ 99% spectrophotometric grade), Kraft lignin, DMSO (reagent grade) and phenol (reagent grade) were purchased from Sigma Aldrich.  $\text{KNO}_3$  was ACS reagent grade and was purchased from VWR.  $^{13}\text{C}$ -Labeled ethylene glycol, 99%  $^{18}\text{O}$ -labeled  $\text{H}_2\text{O}$ , 99% and  $\text{D}_2\text{O}$ , 99.96% were purchased from Cambridge Isotopes. Argon (research grade) and CO (research grade) were purchased from Airgas.

**General electrochemical methods.** All electrochemical experiments were conducted using a CH Instruments 760C or 760D bipotentiostat, a BASi Ag/AgCl reference electrode, and a Pt-mesh counter electrode for steady state electrochemical measurements. Steady-state electrochemical experiments were performed using a three-electrode electrochemical cell with a porous glass frit separating the working and auxiliary compartments. All experiments were performed at room temperature ( $23 \pm 1$  °C). Unless stated otherwise, the electrolyte comprised 0.1 M potassium phosphate ( $\text{KP}_i$ ) electrolytes.

**Differential electrochemical mass spectrometry (DEMS) experimental setup.** DEMS experiments were conducted on a home-designed/assembled DEMS system that has a detection limit of  $\sim$ 0.1 nmol. The DEMS setup consists of two differentially pumped chambers (ionization chamber and analysis chamber) and a quadrupole mass spectrometer (PrismaPlus™ QMF 110, Pfeiffer-Vacuum). The ionization and analysis chambers are pumped to high vacuum by two Pfeiffer 65 L/s turbomolecular pumps backed by a Pfeiffer dry diaphragm pump, in order to avoid contamination by oil vapors. The PrismaPlus™ quadrupole mass spectrometer was connected to the analysis chamber and equipped with electron multiplier/faraday cup dual detecting units. The time constant of the mass spectrometer was in the millisecond regime. Mass spectrometric data was collected with Quadera software, with three selective channels recording  $m/z$  of 32, 34, and 36 in real time during the electrochemical CV experiments.

A dual thin layer flow electrochemical cell made of Kel-F was connected to the ionization chamber via an angle valve. The upper chamber, which houses the electrochemical reaction, is connected to the lower chamber, which is under high vacuum and in line with the mass spectrometer, by 6 capillaries. In the upper compartment, the working electrode is pressed against a  $\sim$ 100 mm thick Teflon gasket with an inner diameter of 6 mm. This leaves an exposed area of 0.28 cm $^2$  and results in an electrolyte volume of  $\sim$ 3  $\mu\text{L}$ . In the lower compartment, a porous Teflon membrane (Gore-Tex) supported on a stainless steel frit serves as the interface between the electrolyte and vacuum. It is pressed against a  $\sim$ 100

mm thick Teflon gasket with an inner diameter of 6 mm. The Gore-Tex Teflon membrane has a thickness of  $\sim 75 \mu\text{m}$ , a mean pore size of  $0.02 \mu\text{m}$  and a porosity of 50%. A leak-free Ag/AgCl reference electrode is connected at the inlet side of the flow cell by insertion into a capillary, and a Pt wire counter electrode is connected in a similar fashion at the outlet of the cell. Electrolyte (100 mM  $\text{KP}_i$ , 200 mM  $\text{KNO}_3$ ) was purged with argon for 1 h before being transferred to a syringe pump (Harvard Apparatus PHD 2000 Infusion). Electrolyte flow into the electrochemical cell was then controlled by the syringe pump, at 60 mL/hr, which ensures fast transport of the species formed at the electrode to the mass spectrometric compartment, where the volatile products were evaporated into the vacuum system of the DEMS through the porous Teflon membrane. CV experiments were performed using a CH Instruments 760C potentiostat.

**Preparation of Co-OEC thin film for use in DEMS experiments.** A Co-OEC thin film electrocatalyst was prepared via an anodic electrodeposition process. A glassy carbon working electrode fabricated for use in the DEMS electrochemical cell (diameter 7.2 mm) was used as the substrate for deposition of Co-OEC films. Deposition was carried out in 0.1 M  $\text{KP}_i$  pH 7 electrolyte containing 1 mM  $\text{Co}^{2+}$ . A constant potential was held at 0.9 V (all potentials are referenced to Ag/AgCl unless noted otherwise) for a total of 35 mC/cm<sup>2</sup> charge passed.

**Preparation of <sup>18</sup>O-labeled CoP<sub>i</sub> thin film for use in DEMS experiments.** A CoP<sub>i</sub> thin film electrocatalyst was prepared via an anodic electrodeposition process. A glassy carbon working electrode fabricated for use in the DEMS electrochemical cell (diameter 7.2 mm) was immobilized upside-down and onto it was dropped a 0.12 mL droplet of 1 mM  $\text{Co}(\text{NO}_3)_2$  in 97%  $\text{H}_2^{18}\text{O}$ -labeled 100 mM  $\text{KP}_i$  buffer. A leak-free Ag/AgCl reference electrode (Warner Instruments) and a Pt wire counter electrode were suspended into the droplet and a constant potential was held at 0.9 V for a total of 35 mC/cm<sup>2</sup> charge passed. The electrode was rinsed quickly by dipping once into unlabeled de-ionized water for 1 s, and then immediately placed into the DEMS electrochemical cell.

**Preparation of CoP<sub>i</sub> thin film for use in gas quantification experiments.** A CoP<sub>i</sub> thin film electrocatalyst was prepared via an anodic electrodeposition process. A FTO-coated glass plate was used as the substrate for deposition of CoP<sub>i</sub> films. Kapton tape was applied to the plate such that a 1 cm<sup>2</sup> area was exposed to the deposition solution. Deposition was carried out in 0.1 M  $\text{KP}_i$  pH 7 electrolyte containing 0.5 mM  $\text{Co}^{2+}$ . A constant potential of 0.85 V was applied for a total of 15 mC charge passed.

**Gas phase product distribution ( $\text{CO}_2$ , CO,  $\text{O}_2$ ).** Unless otherwise noted, all electrolyses for product quantification experiments were performed at a constant potential of 1.0 V with a 15 mC/cm<sup>2</sup> CoP<sub>i</sub> film in solutions containing 500 mM ethylene glycol and 100 mM  $\text{KP}_i$  pH 7 electrolyte.  $\text{CO}_2$  production was quantified using an airtight glass cell and an Agilent 7890A injection GC. Prior to electrolysis, the cell headspace was purged with  $\text{N}_2$  for at least 1 hour to remove any atmospheric gases. Throughout electrolysis, 0.25 mL samples of the cell headspace were periodically extracted using an airtight syringe, and sampled to determine

the concentration of CO<sub>2</sub> in the cell. The cell was then backfilled with an equal volume of N<sub>2</sub> gas to avoid creating a pressure differential. The total amount of CO<sub>2</sub> produced was calculated using the following formula:

$$mol(\text{CO}_2)_{\text{Tot}} = \chi_{\text{CO}_2} * P_{\text{Tot}} * \left[ \left( \frac{V_{\text{HS}}}{RT} \right) + \left( V_{\text{Soln}} * (5.45) * \left( K_{\text{H, CO}_2} \right) \right) \right] \quad (\text{S1})$$

where  $\chi_{\text{CO}_2}$  is the measured concentration of CO<sub>2</sub> in the sample,  $V_{\text{HS}}$  and  $V_{\text{soln.}}$  are the volumes of the headspace and solution, respectively, in the working compartment of the cell,  $K_{\text{CO}_2}$  is the Henry's law constant for CO<sub>2</sub>, and 5.45 is a factor accounting for the speciation of CO<sub>2</sub> in water at pH 7.

The Faradaic efficiency of CO<sub>2</sub> production for each electrolysis was determined by plotting moles CO<sub>2</sub> produced vs. charge passed, and using the following equation,

$$FE_{\text{CO}_2} = nF * \left( \frac{d(mol(\text{CO}_2)_{\text{Tot}})}{dQ} \right) \quad (\text{S2})$$

where n is the number of moles of electrons required for the production of one mole of CO<sub>2</sub>.

The production of CO and O<sub>2</sub> was quantified using an airtight electrochemical cell connected directly to a gas chromatograph. Throughout electrolysis, argon gas was flowed through the cell at a constant rate. The composition of the cell headspace was sampled every 15 min. O<sub>2</sub> was quantified using a TCD detector, while CO was quantified using a FID detector equipped with a methanizer. Faradaic efficiencies for each gas were calculated using the following equations,

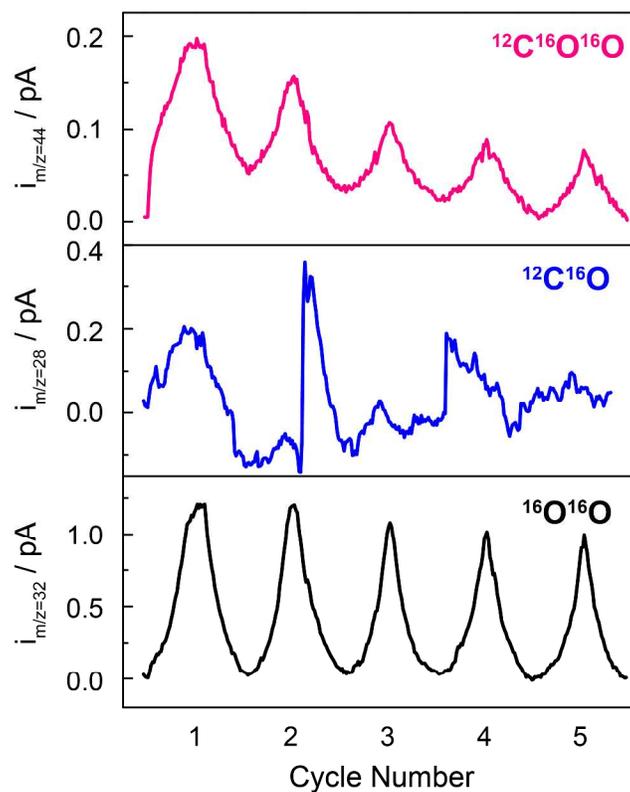
$$FE_{\text{O}_2} = v_{\text{Flow}} * [\text{O}_2]_{\text{Detected}} * \left( \frac{n_{\text{OER}} * F}{j_{\text{tot}}} \right) \quad (\text{S3})$$

$$FE_{\text{CO}} = v_{\text{Flow}} * [\text{CO}]_{\text{Detected}} * \left( \frac{n_{\text{CO}} * F}{j_{\text{tot}}} \right) \quad (\text{S4})$$

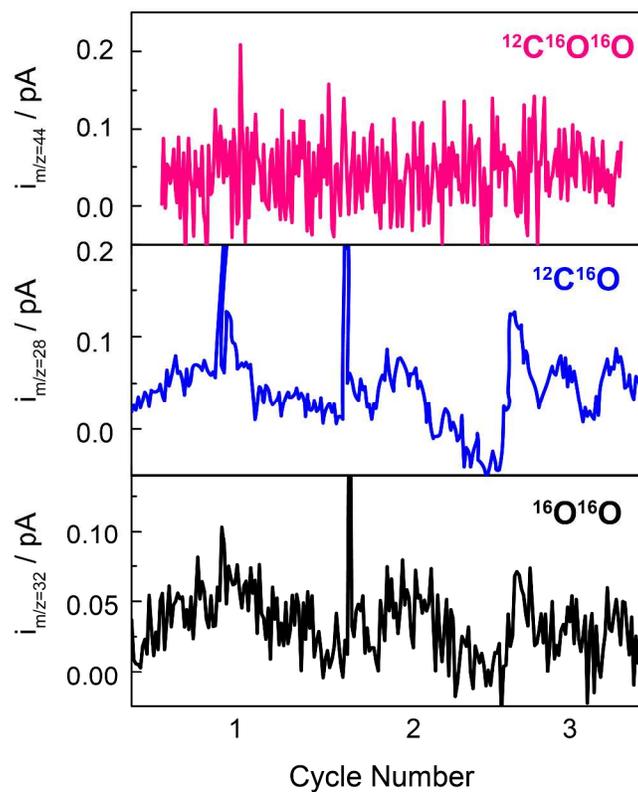
where  $v_{\text{flow}}$  denotes the flow rate of argon through the cell, and denotes the moles of electrons required to produce a mole of product.

**Liquid phase product distribution.** Liquid phase products were detected using <sup>1</sup>H and <sup>13</sup>C NMR, and quantified via <sup>1</sup>H NMR. For <sup>1</sup>H NMR quantification experiments, 15-20 mL of solution were electrolyzed at 1.0 V until between 10-20 C had been passed. Following electrolysis, NMR samples were prepared by combining 700 μL of electrolyte solution with 35 μL of a standard solution containing 49.835 mM Phenol and 8.064 mM DMSO in D<sub>2</sub>O. <sup>1</sup>H NMR spectra were obtained using an Agilent DD2 600 NMR, with a pre-saturation pulse applied at the chemical shift for H<sub>2</sub>O to improve signal to noise for product detection. Product peaks were then quantified by referencing weighted proton integrations to the afore-

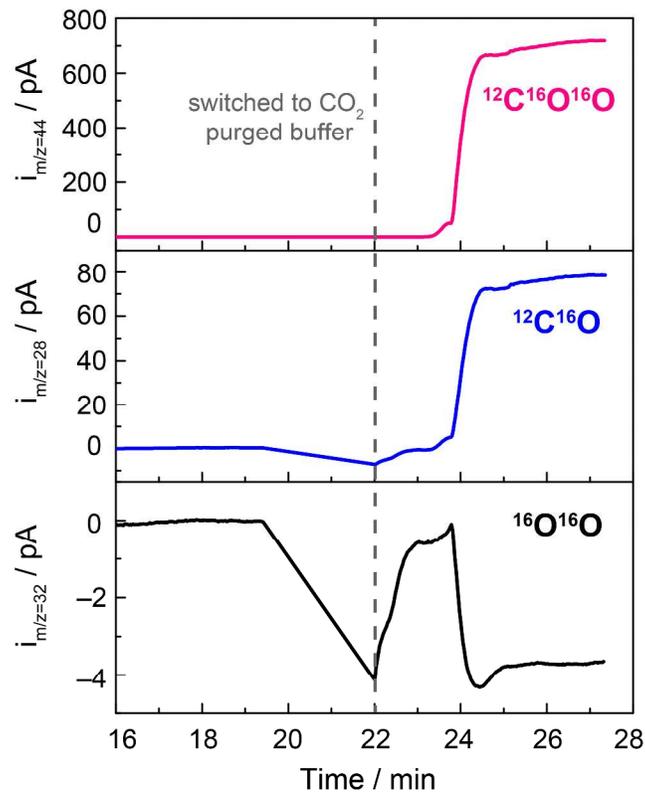
mentioned internal standards. Reported liquid phase product yields are the average of 4 separate experiments. A  $^{13}\text{C}$  NMR product spectrum was obtained by electrolyzing a solution containing 100 mM of fully  $^{13}\text{C}$ -labeled ethylene glycol and 100 mM  $\text{KP}_i$  pH 7 electrolyte at 1.0 V. Following electrolysis, the electrolyte solution was directly used for NMR analysis with a Varian I500 NMR.



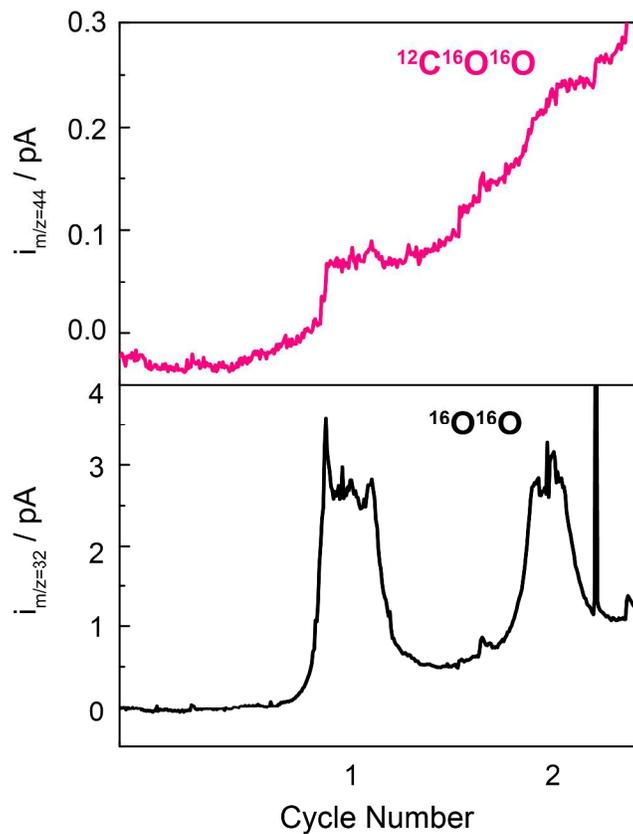
**Figure S1.** DEMS experimental data for CoP<sub>i</sub> operated in electrolyte containing 100 mM EG. Five consecutive CVs are scanned from 0.9 to 1.0 V vs. Ag/AgCl at 2 mV/s, while MS ion current is detected for mass channels  $m/z = 32, 28, 44$  (bottom to top).



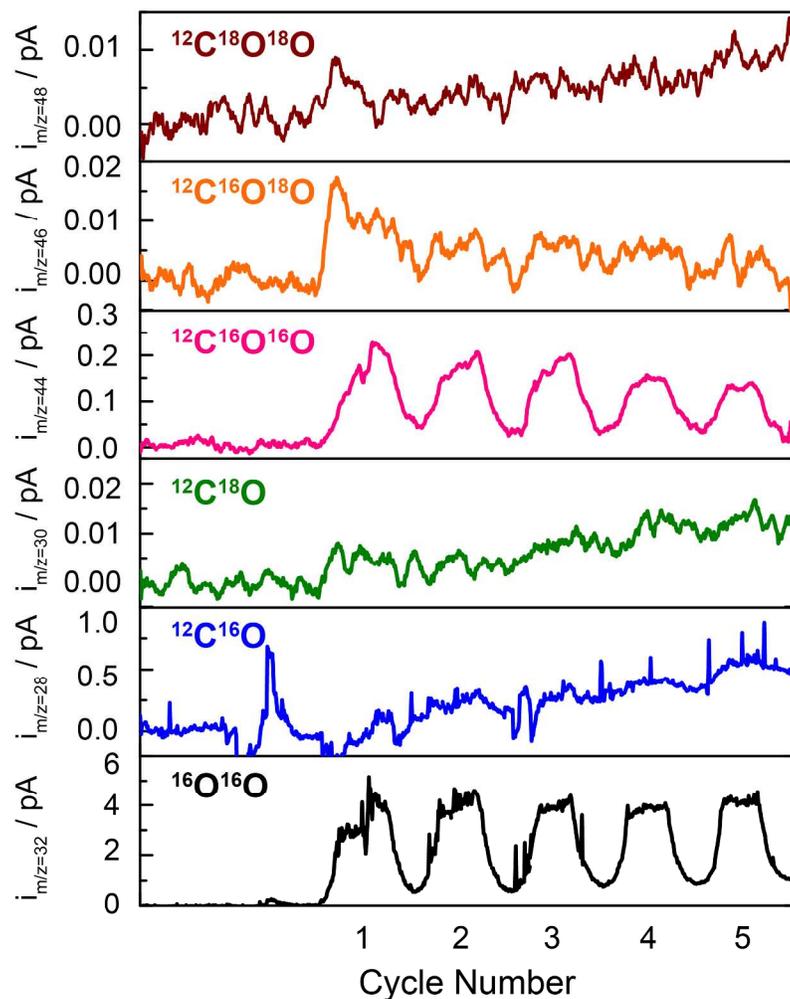
**Figure S2.** DEMS experimental data for a blank GC electrode operated in electrolyte containing 100 mM EG. Three consecutive CVs are scanned from 0.9 to 1.0 V vs. Ag/AgCl at 2 mV/s, while MS ion current is detected for mass channels  $m/z = 32, 28, 44$  (bottom to top).



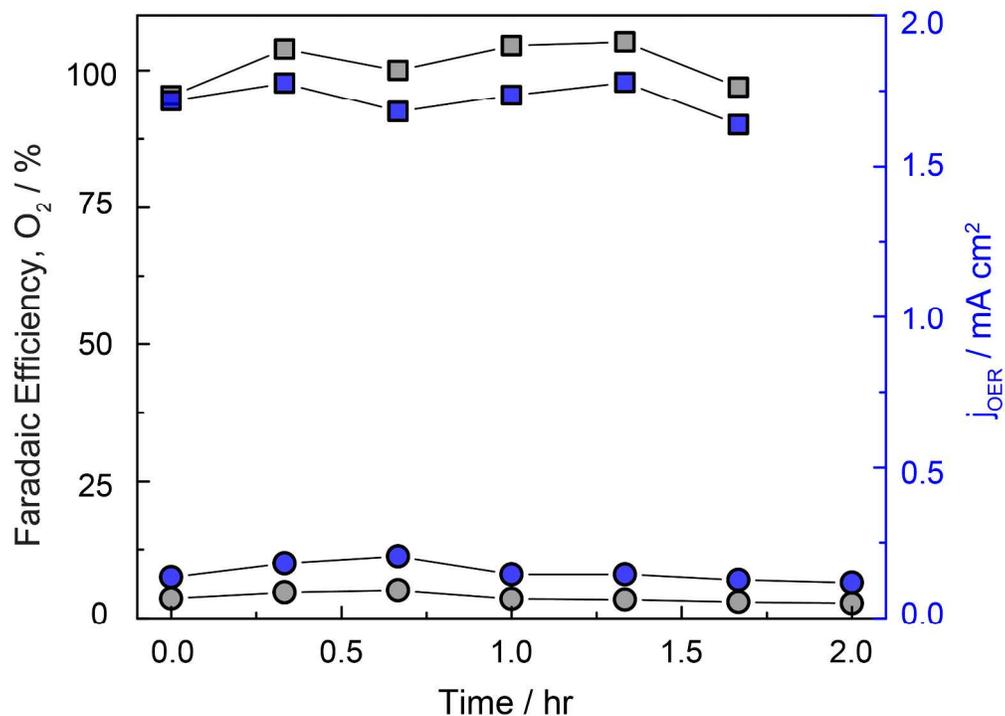
**Figure S3.** DEMS control experiment to test to what extent CO<sub>2</sub> fractionates to CO in the MS detector. Argon-sparged solution was flowed through the DEMS cell containing a blank GC electrode, and no potential was applied. The solution was switched to CO<sub>2</sub>-saturated electrolyte solution at  $t = 22$  min. MS ion current is detected for mass channels  $m/z = 32, 28, 44$  (bottom to top). Only ~10% of CO<sub>2</sub> fractionates to CO.



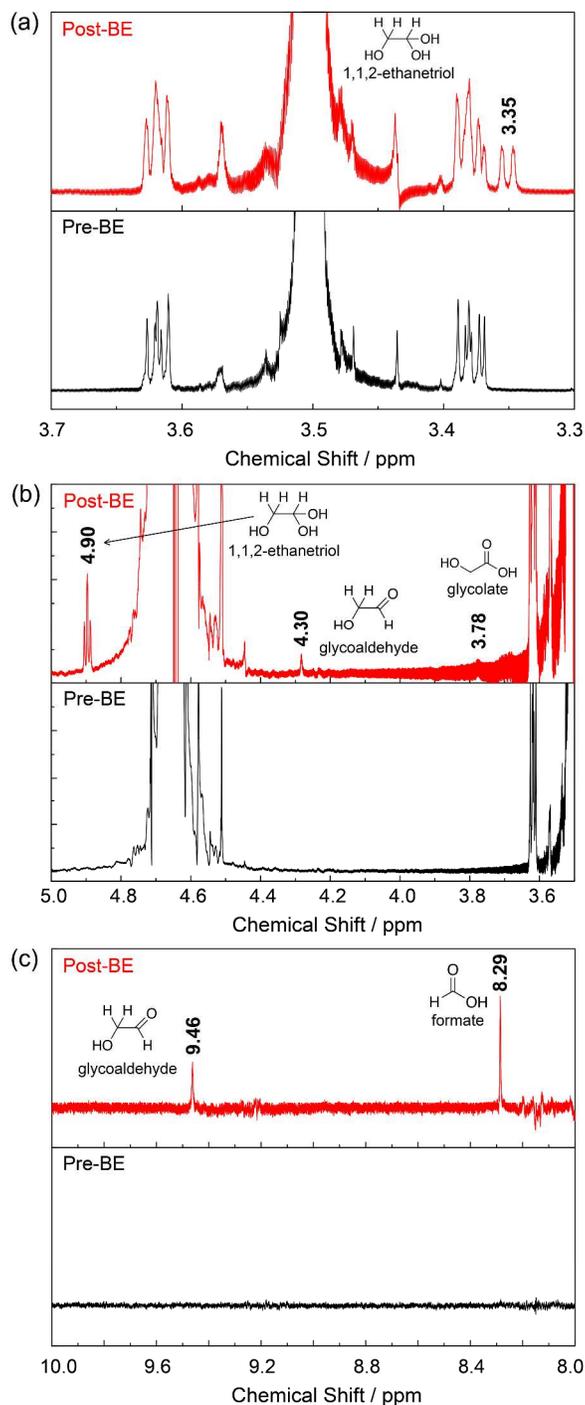
**Figure S4.** DEMS control experiment to test whether CO is oxidized to CO<sub>2</sub> on CoP<sub>i</sub>. A CO-saturated electrolyte solution was flowed over a CoP<sub>i</sub> electrode, and two consecutive CVs are scanned from 0.8 to 1.0 V vs. Ag/AgCl at 2 mV/s, while MS ion current is detected for mass channels  $m/z = 32$  and 44 (bottom to top).



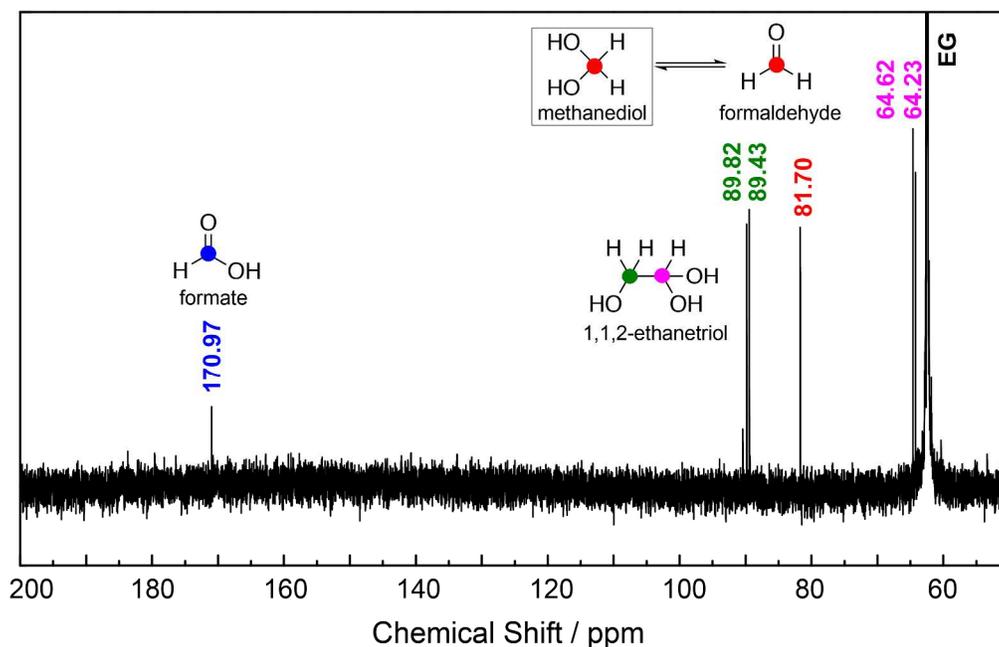
**Figure S5.** DEMS experimental data for  $^{18}\text{O}$ -CoP<sub>i</sub> operated in electrolyte containing 100 mM EG. Five consecutive CVs are scanned from 0.9 to 1.0 V vs. Ag/AgCl at 2 mV/s beginning at  $t = 5$  min, while MS ion current is detected for mass channels  $m/z = 32, 28, 30, 44, 46,$  and  $48$  (bottom to top).



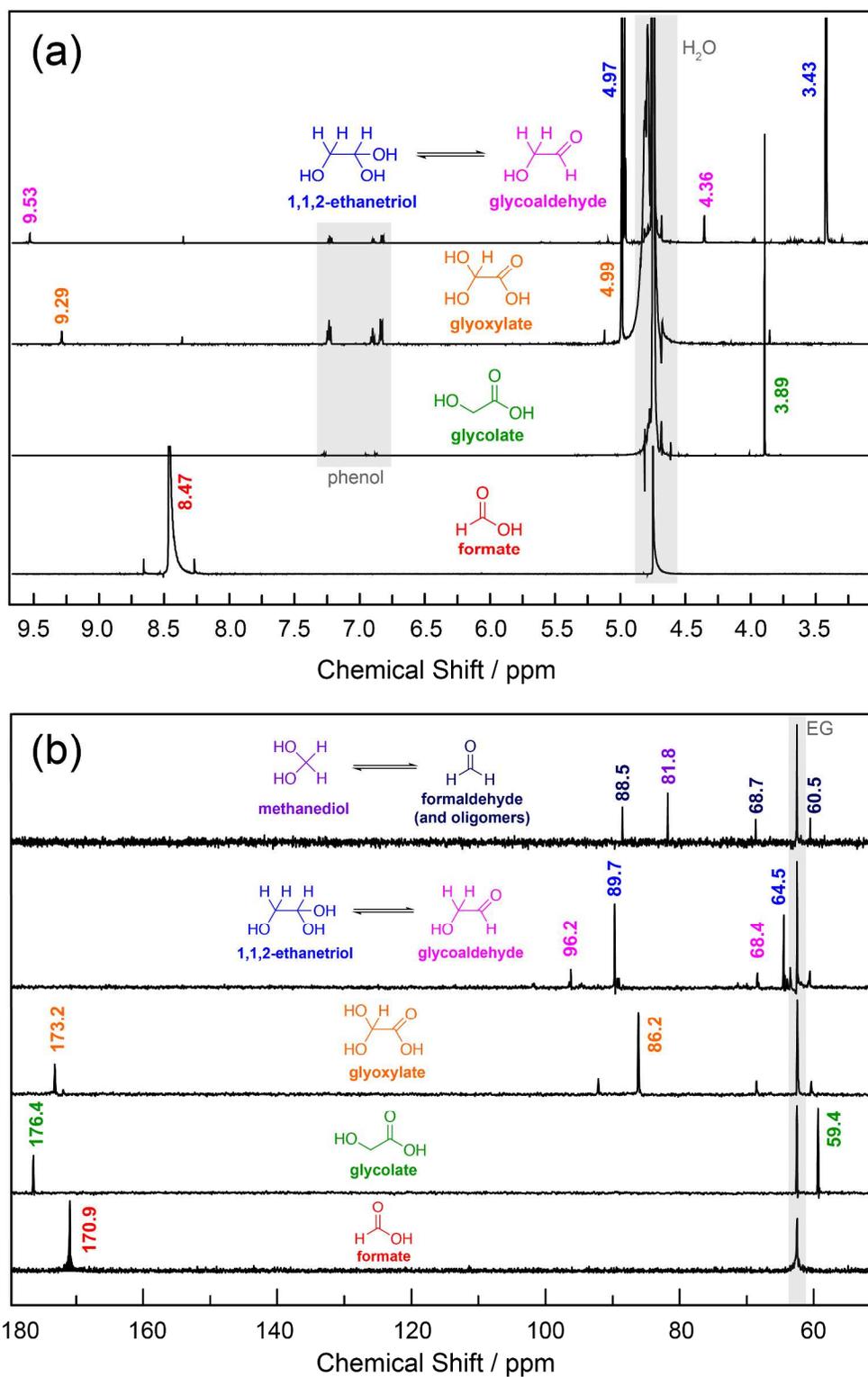
**Figure S6.** Flow GC experiment for 15 mC/cm<sup>2</sup> CoP<sub>i</sub> film at 1.1 V vs. Ag/AgCl in electrolyte containing 100 mM KP<sub>i</sub> at pH 7, and either 0 mM EG (squares) or 500 mM EG (circles). O<sub>2</sub> Faradaic efficiency data is given in grey, and absolute oxygen current density is given in blue. In the system containing EG, both O<sub>2</sub> Faradaic efficiency and absolute OER current density are suppressed compared to a system in which EG is absent.



**Figure S7.** Representative  $^1\text{H}$  NMR spectrum for  $15\text{ mC/cm}^2$   $\text{CoP}_i$  film operated at 1.0 V in electrolyte containing 100 mM  $\text{KP}_i$  at pH 7, and 500 mM EG (Red). NMR spectrum of pre-electrolysis solution is given for reference (Black). We note that there is a small peak at 4.82 assignable to methanediol, but this peak is not quantifiable due to overlap with solvent peak.



**Figure S8.**  $^{13}\text{C}$  NMR of 100 mM  $^{13}\text{C}$ -labeled EG, 100 mM  $\text{KP}_i$  pH 7 solution electrolyzed at 1.0 V with a  $15 \text{ mC}/\text{cm}^2$   $\text{CoP}_i$  film. Carbons are color-coded to match their corresponding NMR peaks. The peak at 81.70 ppm corresponds to methanediol, which is the hydrated form of formaldehyde. Methanediol was not quantified as an intermediate product, because it is not observed in the  $^1\text{H}$  NMR spectra due to overlap with the water solvent peak region near 4.7 ppm. The doublets at  $\sim 89$  ppm and  $\sim 64$  ppm correspond to the two carbons in 1,1,2-ethanetriol. The splitting at each of these peaks is a result of  $^{13}\text{C}$ - $^{13}\text{C}$  coupling due to the fully  $^{13}\text{C}$ -labeled starting material used.



**Figure S9.** Control NMRs for on-pathway intermediates. (a)  $^1\text{H}$  NMR; (b)  $^{13}\text{C}$  NMR. All NMRs were taken in 100 mM  $\text{KPi}$  pH 7 buffer solution.

**Table S1.** CO<sub>2</sub> Faradaic efficiency for on-pathway intermediates. All experiments were performed with 15 mC/cm<sup>2</sup> CoP<sub>i</sub> film held at 1.0 V in a solution containing 100 mM substrate, 100 mM KP<sub>i</sub>, pH 7. Intermediates further along in the reaction pathway generate CO<sub>2</sub> at a higher Faradaic efficiency.

Intermediate	# e <sup>-</sup> to intermediate	CO <sub>2</sub> Faradaic Efficiency (%)
1,1,2-Ethanetriol	2	11.9 ± 2.1
Glycolate	4	30.5 ± 9.8
Glyoxylate	6	60.1 ± 2.3