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Selective Lactic Acid Synthesis via Ethylene Glycol Electrooxidation in Borate Buffer

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Buffer preparation

For pH 7-13 conditions, a borate-based buffer was prepared by mixing different amounts of 0.2 M $Na_2B_4O_7$ solution with 0.8 M H_3BO_3 solutions. Na_2SO_4 was added as a supporting electrolyte to equalize the concentration of Na^+ to maintain a similar ionic strength across all pH values. The pH 7-9 buffers were prepared as follows: a 0.8 M H_3BO_3 solution in >18 MΩcm water was adjusted to the desired pH with 0.2 M $Na_2B_4O_7$ solution, monitored by a pH electrode before Na_2SO_4 was added to ensure a final concentration of Na^+ of ~1 M. The pH 10-13 buffers were prepared as follows: a 0.2 M $Na_2B_4O_7$ solution in >18 MΩcm water was adjusted to the desired pH with 1 M NaOH solution, monitored by a pH electrode before Na_2SO_4 was added to ensure a final concentration of Na^+ of ~1 M. 1 M KOH was used as pH 14 electrolyte being aware that due to the activity coefficients the pH value is lower.

Electrochemical measurements

All electrochemical measurements were carried out in a three-electrode flow-through electrolyzer cell using a Gamry 1000 E potentiostat. A Ni foam (NF) substrate was used as the working electrode (WE) as well as the counter electrode (CE). The reference electrode (RE) was a Ag/AgCl/3 M KCl with a double junction filled with borate buffer. The WE and CE compartments were separated by a Fumatech Fumasep FAA-3-PK-130 membrane. Borate buffer at different pH was filled to the reservoirs and circulated to the cell as the electrolyte using a Perimax 12 peristaltic pump. Before carrying out each experiment, the NF catalyst was

activated in 1 M KOH at a constant potential of 1 V vs Ag/AgCl/3 M KCl for 5 mins. For OER measurement: Open circuit potential (100 s), galvanostatic impedance spectra (10000 Hz to 1 Hz, at 0 A), linear sweep voltammetry (potential range (1 to 2 V vs RHE, scan rate: 10 mVs^{-1}), for EGOR: identical measurement protocol as for the OER in the presence of 1 M ethylene glycol. All chronopotentiometry measurements were done at 5 $mAcm^{-2}$ for 1 h (18 C) or 3 h (54 C), until stated otherwise.

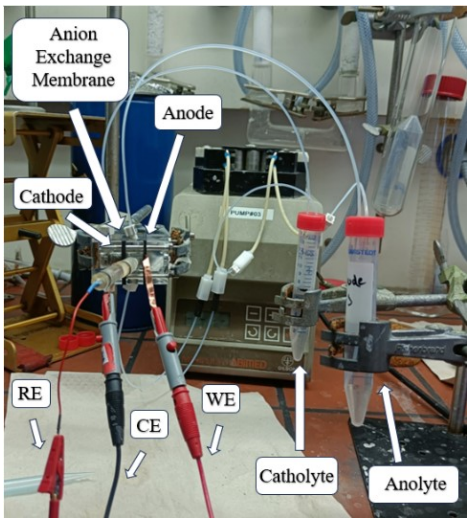

Fig. S1. Picture of the electrochemical setup used for ethylene glycol oxidation.

HPLC measurements

The liquid products were analyzed by high-performance liquid chromatography (HPLC, Dionex ICS-5000 ThermoFisher) with an ion-exclusion column of Aminex HPX-87H (Bio-Rad), a diode array detector at 220 nm, and a refractive index detector (RefractoMax520). The eluent was 4 mM H_2SO_4. The eluent flow rate was 0.6 mL min^{-1} and the column temperature was 70 °C. In the HPLC sample preparation process, each sample, collected at various time points (0 h, 1 h, 3 h,), was prepared by mixing 500 µl of the collected sample with an equal volume of water.

Determination of the number of electrons transferred to obtain various products formed during ethylene glycol electrooxidation.

The balanced reactions and the electron count for each product are summarized below. The number of electrons for each half-reaction is divided by the stoichiometric coefficient to give the number of electrons required to form one mole of product which was used further for FE calculation.

Ethylene glycol ⟶ Glycolic acid

$C_2H_6O_2 + 4\ OH^- \longrightarrow C_2H_4O_3 + 3\ H_2O + 4\ e^-$ e^- count for Glycolic acid = 4 e^-

Ethylene glycol ⟶ Formic acid

$C_2H_6O_2 + 6\ OH^- \longrightarrow 2\ CH_2O_2 + 4\ H_2O + 6\ e^-$ e^- count for Glycolic acid = 3 e^-

Ethylene glycol ⟶ glycolaldehyde

$C_2H_6O_2 + 2\ OH^- \longrightarrow C_2H_4O_2 + 2\ H_2O + 2\ e^-$ e^- count for Glycolaldehyde = 2 e^-

Ethylene glycol ⟶ Formaldehyde

$C_2H_6O_2 + 2\ OH^- \longrightarrow 2\ CH_2O + 2\ H_2O + 2\ e^-$ e^- count for Formaldehyde = 1 e^-

Glycolaldehyde ⟶ Glyceraldehyde

$C_2H_4O_2 + CH_2O \longrightarrow C_3H_6O_3$ e^- count for Glyceraldehyde = 0 e^-

Glyceraldehyde ⟶ Glyceric acid

$C_3H_6O_3 + 2\ OH^- \longrightarrow C_3H_6O_4 + H_2O + 2\ e^-$ e^- count for Glyceric acid= 2 e^-

Lactic acid is formed by aldol condensation of glycolaldehyde and formaldehyde followed by a Cannizzaro reaction. Therefore, one mole of formaldehyde and one mole of glycolaldehyde are required to produce one mole of lactic acid. The total number of electrons required to produce one mole of formaldehyde and one mole of glycolaldehyde from the electrooxidation of ethylene glycol is 3. Therefore, three electrons are used for the FE calculation of lactic acid. One mole of glyceric acid is formed by aldol condensation of one mole of glycolaldehyde and one mole of formaldehyde followed by oxidation. So, the total number of electrons required to produce one mole of glyceric acid is 5.

Faradaic Efficiency Calculations

The Faradaic efficiencies (FE) for each product formed during ethylene glycol electrooxidation were calculated using the following formula:

$$FE(\%) = \frac{n.z.F}{Q} \times 100\ \%$$

where n is the moles of each product formed (determined by HPLCa), z is the number of electrons required to form that product, F is Faraday constant (96485 C mol^{-1}), and Q is the total charge passed.

The selectivity was calculated using the formula:

$$Selectivity\ (\%) = \frac{no.\ of\ mole\ of\ individual\ product}{total\ no.\ of\ moles\ of\ liquid\ products} \times 100\ \%$$

Electrochemistry data

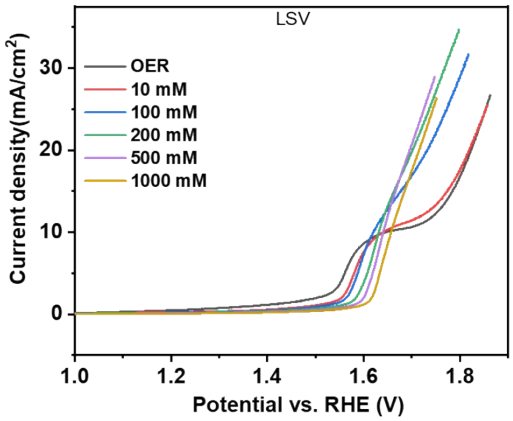

Fig. S2. LSVs over Ni foam in the absence and presence of different concentrations of ethylene glycol in borate buffer of pH 10 at a scan rate of 10 mVs^{-1}.

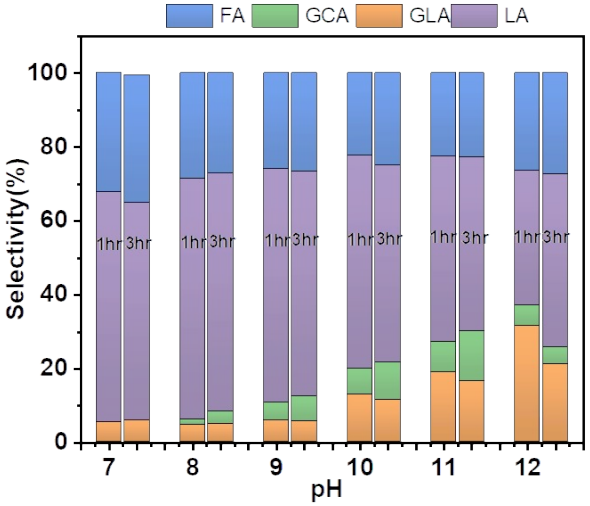

Fig. S3. EGOR product selectivity after 1 h and 3 h of electrolysis at a current density of 5 mA cm^{-2} in borate buffer solution of pH 10.

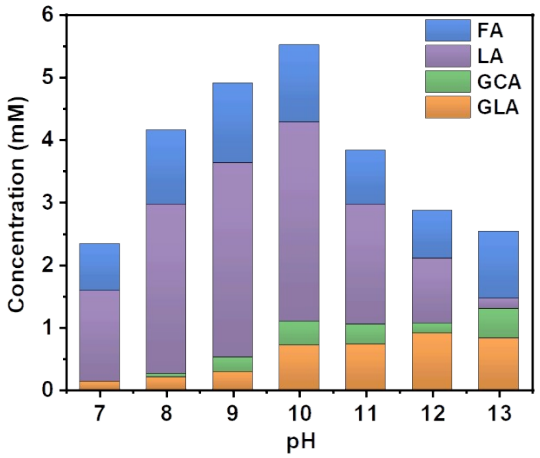

Fig. S4. Product distribution showing concentrations at various pH conditions after 1 h of electrolysis at a current density of 5 mA cm^{-2}.

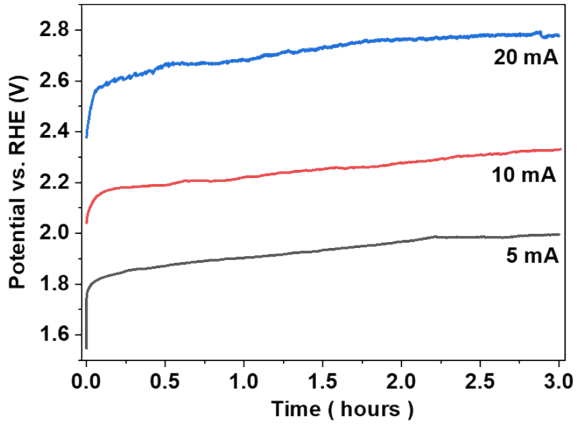

Fig. S5. Chronopotentiometry curves measured at different current densities in the presence of 1 M ethylene glycol in borate buffer of pH 10.

Raman spectroscopy was performed using a Lab-RAM HR Raman microscopy system (Horiba Jobin Yvon, HR550) equipped with a 532 nm laser as the excitation source, a water immersion objective (Olympus LUMFL, 60×, numerical aperture 1.0), a monochromator (1200 grooves mm^{-1} grating), and a Synapse CCD detector. Each spectrum is an average of two to five continuously acquired spectra with a collection time of 50 s each.

In-situ Fourier Transform Infrared (FTIR) measurements were conducted using a three-electrode setup. A NF electrode was integrated into a borehole electrode, serving as the working electrode (WE). A platinum mesh was employed as the counter electrode, and a leakless Ag/AgCl electrode served as reference electrode. The distance between the electrode and the internal reflection element (IRE) was precisely set at 20 µm. During the measurements, a constant current density of 5 mA cm^{-2} was applied. Spectra were acquired using a Bruker

Tensor 27 spectrometer with a commercial A530/P reflection unit. Each spectrum was recorded by accumulating 200 scans over 30 s.

Fig. S6. Electrodes used for collecting FTIR spectra.

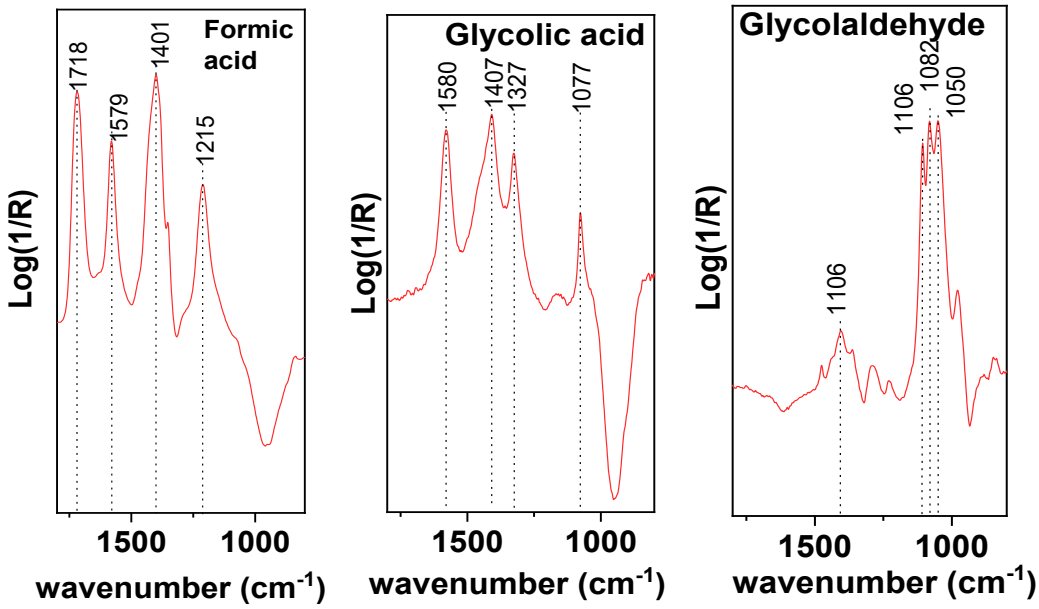

Fig. S7. Standard FTIR spectra of formic acid (FA), glycolic acid (GCA), and glycolaldehyde measured in borate buffer of pH 10.

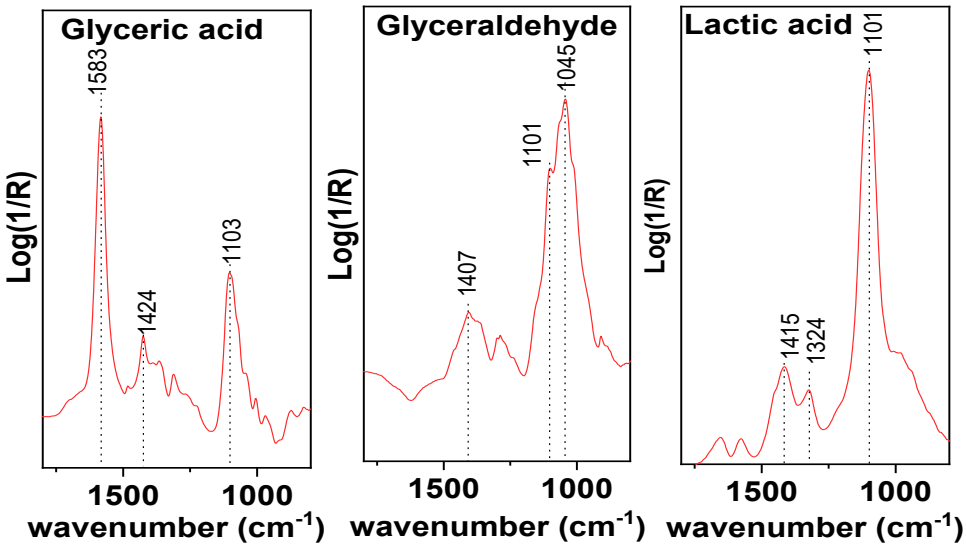

Fig. S8. Standard FTIR spectra of glyceric acid (GLA), glyceraldehyde, and lactic acid (LA) measured in borate buffer of pH 10.