Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information for

Insights into the Mechanism of Electrochemical Chloride Oxidation in Ethanol from X-ray Photoelectron Spectroscopy, Quiescent Solution Voltammetry, and Rotating Ring-Disk Electrodes

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Experimental Section

Materials and chemicals. Tetrabutylammonium chloride (Bu_4NCl, ≥97.0%, Sigma-Aldrich), tetrabutylammonium trifluoromethanesulfonate (Bu_4NOTf, >98.0%, Fisher), tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, ≥98.0%, TCI). These salts were separately purified in boiling ethanol three times and cooled in a 0°C freezer for recrystallization. Ethanol (200 proof, Fisher or Tax-Paid, Decon™ Labs) was distilled and stored over molecular sieves and sparged with argon. Acetonitrile (99.9%, Extra Dry AcroSeal™, Thermo Scientific Chemicals), chloroform-*d* (Cambridge Isotopes), and benzene (Sigma–Aldrich, ACS grade > 99.0%) were used as received. Ferrocene (98%, Sigma) is purified by sublimation at 120 ºC on a hot plate.

Electrochemical Reaction Conditions. All electrochemical measurements were carried out on a CHI760E electrochemical workstation (CH Instruments) if not specifically stated. All electrochemical data is plotted under IUPAC convention. Rotating ring-disk electrode measurements (RRDE) are carried out by RRDE-3A (ALS Japan) connected to the CHI760E. For all the RRDE measurements, a 3-electrode setup is used, where Ag wire is used as a pseudo reference electrode, Pt wire (Surepure Chemetals, 0.05 cm diameter, with 2 cm submerged, resulting with ~0.314 cm^2 surface area) is mounted to a piece of copper wire sealed in a glass tube and is used as the counter electrode. The working electrodes for RRDE analysis are also purchased from ALS Japan (013336, DRE-PGK Pt ring/GC disk replaceable electrode kit. The Pt ring and GC disk are polished separately, first with 0.3 micron alumina, then with 0.05 micron alumina on nylon polishing pads (Buehler). The GC disk is planar with a diameter of 4 mm. The disk is then surrounded with a ring of insulating Teflon (OD: 5mm; ID: 4mm) on the same vertical level, along with the Pt ring (OD: 7mm; ID: 5mm). The RRDE assembly, including its protective shell, has an overall diameter of 12 mm. The Ag wire reference electrodes were purchased from CH Instruments as well (CHI112P), but the glass frit attached is replaced with a more compact glass frit with plastic seals (Gamry, 955-00003). The solution in which the Ag wire is soaked is kept identical to the electrolyte in the cell. PTFE stir bars, when used, are purchased from Fisher with a length of 12.7 mm and a diameter of 3.2 mm. The single-compartment electrochemical cell specifically for RRDE measurements is also purchased from ALS Japan. All RRDE measurements are conducted on the CHI760E, where the disk electrode is always the *working electrode* with green wiring, and the ring electrode is always *secondary electrode* with yellow wiring. If not specified, the working electrode always performs oxidation and the secondary electrode always performs reduction. For subsequent RRDE measurements, a wait time of 300 s with rotation in effect is applied to ensure the thorough diffuse/decomposition of any generated intermediate in the previous run. To calibrate the pseudo reference electrode to ferrocene redox couple, the exact solution of interested is replicated but with an additional 10 mM ferrocene dissolved. Then with the same set of working/reference/counter electrodes as the RRDE measurement, a CV with a scan rate of 50 mV / s is carried out between 0 – 1 V to obtain the redox potentials of $Fc^{+/0}$ redox couple by calculating the average of both the oxidation and reduction peak potential. Note that during $Fc^{0/+}$ calibrations, the Pt ring is not connected to workstation and thus no current is recorded. All RRDE electrolyte solutions are prepared in volumetric glassware and each measurement, 50 mL of electrolyte is poured into the reaction cell. Solution deoxygenation is carried out by sparging the cell for 10 min with argon gas prior to recording the voltametric response. All voltammetry measurements are performed at room temperature with IR compensation applied in the CHI760E. Detailed information and photos of the electrochemical setup can be found in Figures S1-S4.

UV-Vis Spectroelectrochemical Analysis. The UV-Vis spectroelectrochemical measurement is carried out with a CHI1000C electrochemical workstation (CH instrument), Agilent Cary 5000 UV-Vis-NIR spectrophotometer and a custom-built spectroelectrochemical cell. For wavelength scan measurements, the measurement is carried out with a zero-baseline calibration in absorption mode, where zero is collected from atmosphere and baseline is collected from the identical electrolyte solution. The wavelength scan step size is 0.5 nm, and the range is 500 nm – 200 nm. A 3-electrode system similar to that described in the RRDE set-up is used, where the working electrode is a planar glassy carbon disk purchased from CH Instrument (CHI104P) with a diameter of 3.0 mm. For kinetic measurements, the measured wavelength is held at 237 nm while a linear sweep voltammetry measurement is run on the potentiostat. Following each measurement, the electrolyte post-electrolysis is replaced with fresh electrolyte. Detailed information and a photograph of the spectroelectrochemical setup is presented in Figure S4.

Gas chromatography quantification of the 1,1-DEE product. This experiment is carried out to confirm the presence of the *one and only* direct ethanol oxidation reaction with the absence of chloride. This means the following anodic reaction is expected to happen: $\mathrm{EtOH} \rightarrow \mathrm{MeCHO} + 2\mathrm{H}^+ + 2\mathrm{e}^-$. This reaction will result in the detection of 1,1-diethoxyethane (DEE) as product by gas chromatography, guided by the following reaction: $\mathrm{MeCHO} + 2\mathrm{EtOH} \rightarrow \mathrm{DEE} + 2\mathrm{H_2O}$. However, if 4-electron (over)oxidation occured, one would expect to observe acetic acid and/or ethyl acetate. Constant potential coulometry (CPC) is applied to access the oxidation products. The CHI760E potentiostat and a 3-electrode setup is used in all CPC experiments, where a glassy carbon disk electrode (CHI104P, surface area: 0.07 cm^2) is used as the working electrode, and same reference/counter electrodes in the previous sessions are used. The electrochemical cell is a custom-made 2-compartment glass cell with a glass frit as the separator. The potential applied was held at 1.4 V vs $\mathrm{Fc}^{+/0}$. CPC electrolysis was carried out with constant stirring (600 rpm) until a significant quantity of charge is passed for accurate detection of products.

The GC sample is prepared by performing a 10-fold dilution of the post-CPC solution with EtOH. In the sample, 2 mM toluene is added as an internal standard. The GC measurement is then carried out with a ThermoFisher Trace 1310 gas chromatograph equipped with a capillary column and flame ionization detector (FID). During analysis, the column oven was warmed from 40 to 200 °C at a 10 °C min^{-1} ramp rate.

***ex-situ* X-ray Photoelectron Spectroscopy (XPS).** Spectra for experiments in which acetonitrile was used as the solvent were collected on a Kratos Axis Ultra and spectra for experiments in which ethanol was used as a solvent were collected on a Kratos Axis Supra+ both using a monochromatic Al source with a pass energy of 20 eV. The spectra were corrected for charging by referencing highest intensity C(1s) peak to 284.8 eV. All peaks were fitted in Casa XPS[1] with the Shirley-type background.

^{1}H-NMR spectroscopy was recorded on a Varian Vnmrs 700 MHz spectrometer using chloroform-d (Cambridge Isotopes) as the internal reference. The spectra were the average of 32 scans with a 25 second pulse delay and a 90° phase angle. The NMR sample consisted of 300 μL of sample solution and 300 μL of chloroform-d.

Figure S1. Custom-made CPC electrolysis cell for the quantification of direct ethanol oxidation reaction made from Pyrex glass. All 4 openings have an ID of 12 mm and an OD of 20 mm. All arms have a length of ~80 mm. The working (3 arms) and counter (1 arm) compartments are separated by a glass frit (pore size ~1 micron, diameter 8 mm, thickness 2 mm). The length of the cell is 80 mm. During the CPC measurement, 10 mL of solution is added to the working compartment, while sufficient electrolyte is added to the counter compartment to maintain the same solution height (~ 7 mL) to avoid liquid pressure across the frit. The glassy carbon disk working electrode is inserted to the cell through the middle opening, while the reference is placed in the left-most opening. The distance between the working and reference electrodes are purposedly held at 10 mm. The CPC experiments are conducted without IR compensation, and all reactions are carried out in an air-conditioned room held at 20º C.

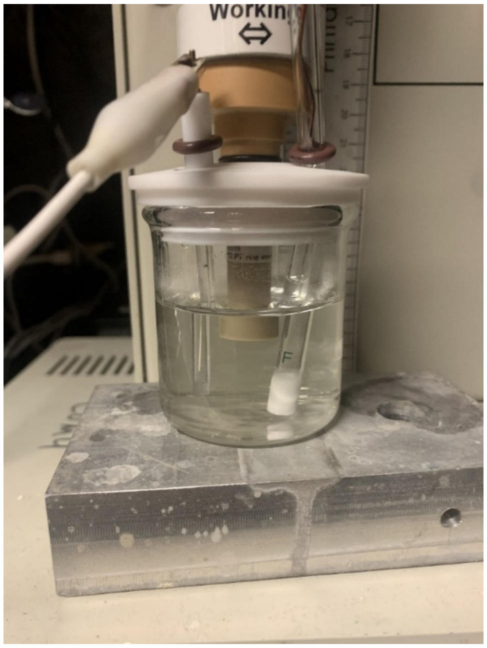

Figure S2. RRDE setup with CHI760E potentiostat and RRDE-3A from ALS Japan. The volume of electrolyte solution is always 50 mL Both the reference and the counter electrodes are separated from the bulk solution by fine glass frits.

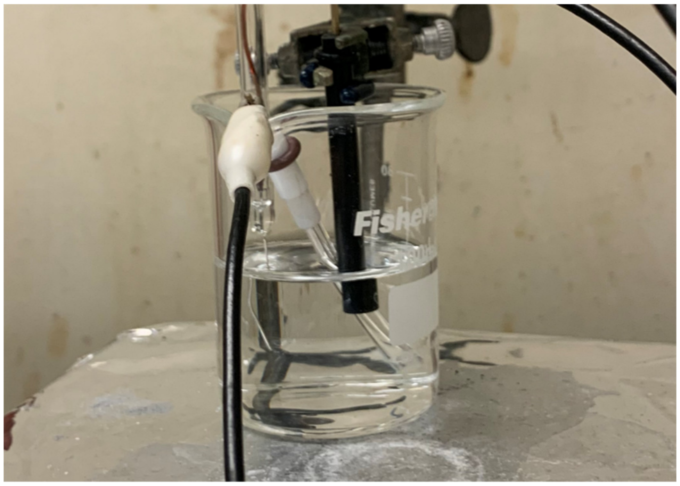

Figure S3. Cottrell measurement setup with CHI760E potentiostat. The volume of electrolyte solution is always 50 mL. The large volume of solution is designed to ensure a fully diffusion-controlled case with no effect from the shape or dimensions of the beaker.

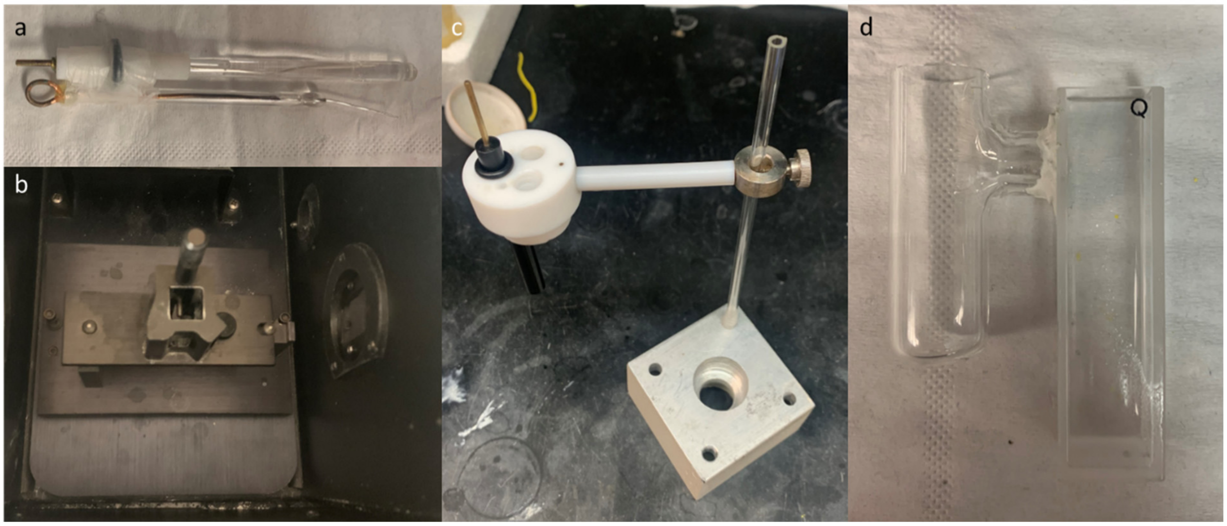

Figure S4. Custom spectroelectrochemical setup. (a) Assembly of the reference and counter electrodes used in the quartz cell (d).

(b) Inside of Agilent Cary 5000 UV-Vis-NIR spectrophotometer's absorption measurement chamber. The quartz cell (d) was placed in the square hole.

(c) The working electrode holder from CH Instrument with a simple stand that is able to place in (b). The glassy carbon working electrode inserted in the Teflon holder.

(d) Custom-made spectroelectrochemical cell. The quartz cuvette was sawed from a 4 mm diameter hole where a glass tube is attached to allow the placement of the other 2 electrodes, while the glassy carbon working electrode is placed in the quartz compartment. The junction was sealed with epoxy.

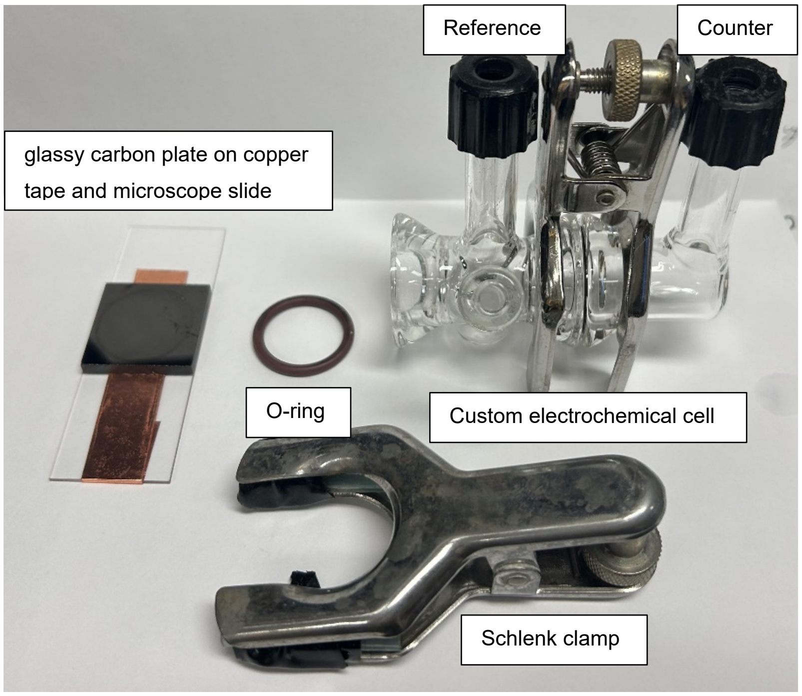

Figure S5. Custom electrochemical cell for XPS. Glassy (Vitreous) Carbon plates (25 mm × 25 mm × 3.0 mm) were purchased from MSE PRO SU6010. The plates were cleaned by sonication in acetone, ethanol and water for 30 minutes each and left to dry in the vacuum oven overnight (12 hours). The plate is connected to copper electrical tape (3M) on top of a Fisherbrand microscope slide. The #15 Schlenk clamp and O-ring is then used to seal the plate onto the cell. The cell itself (2 cm × 2 cm × 7.5 cm (cylindrical)) is custom made by Mr. Roy Wentz from Schlenk tube (#15, 2 cm internal diameter) the size of the O-ring dictates the electrode area with 3.14 cm^2 exposed to the solution. The reference electrode is placed in the first black caped vertical glass tube from the left and is 1.5 cm away from the working electrode. The counter platinum electrode is placed in the black capped vertical glass tube furthest from the left and is 6 cm away from the working electrode. 20 mL of solution is used for all experiments using this cell. The Ag wire reference electrodes were purchased from CH Instruments (CHI112P), but the frit is replaced with a glass frit with plastic seals (Gamry, 955-00003). The solution in which the Ag wire is soaked is kept identical to the electrolyte in the cell. Pt wire (Surepure Chemetals, 0.05 cm diameter, with 2 cm submerged, resulting with ~0.314 cm2 surface area) is mounted to a piece of copper wire sealed in a glass tube and is used as the counter electrode.

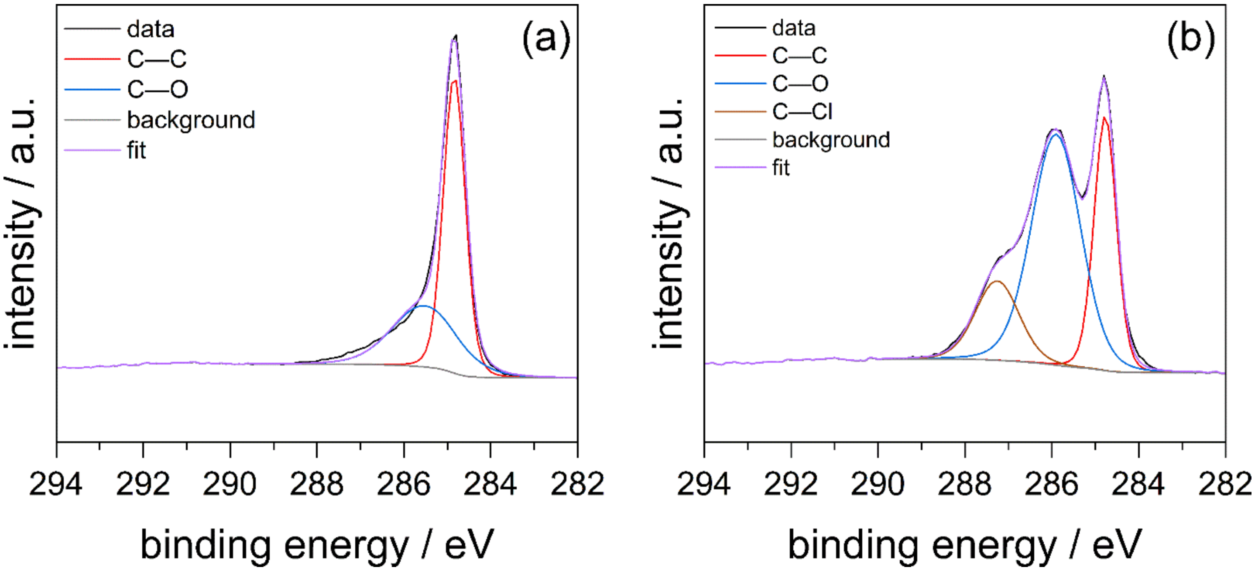

Figure S6. Carbon 1s XPS recorded on GC a) after soaking, and b) after polarizing a 10 mM Bu$_4$NCl solution in acetonitrile solvent with 500 mM Bu$_4$NPF$_6$ supporting electrolyte.

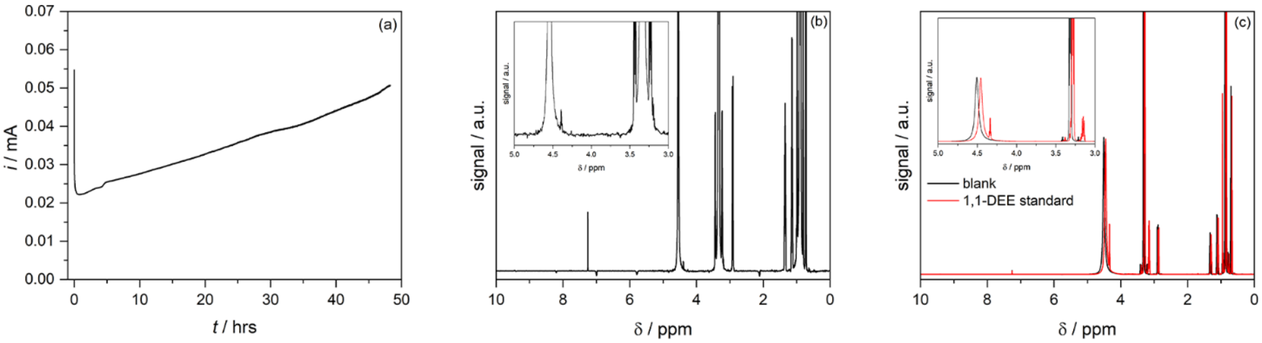

Figure S7. (a) CPC *i* - *t* curve glassy carbon electrode held at 1.0 V vs Fc$^{+/0}$ with 5 mM Bu$_4$NCl and 100 mM Bu$_4$NOTf supporting electrolyte. The total charge passed was 19.291 C. (b) post-CPC ^{1}H-NMR (Varian Vnmrs 700 MHz) spectrum. Chemical shifts: chloroform (7.26, 1H). tetrabutylammonium trifluoromethanesulfonate (3.21, 8H, m; 1.58, 8H, m; 1.37, 8H, m; 0.94, 12H, t). EtOH (3.60, 2H, q; 3.15, 1H; 1.14, 3H, t). DEE (4.61, 1H, q;3.43, 4H, m).**Error! Bookmark not defined.** A quartet appears at 4.3 ppm slightly obscured by the peak associated with water at 4.5 ppm. This was slightly (0.3 ppm) different than the literature and so we collected a 1,1-DEE standard ^{1}H-NMR (c) a quartet can be observed at 4.3 ppm as well as a multiplet at 3.1 ppm. This multiplet is obscured by the ethanol peak at 3.31 in the post CPC ^{1}H-NMR. The appearance of the small quartet demonstrates that 1,1-DEE is formed in small amounts at 1.0 V vs Fc$^{+/0}$.

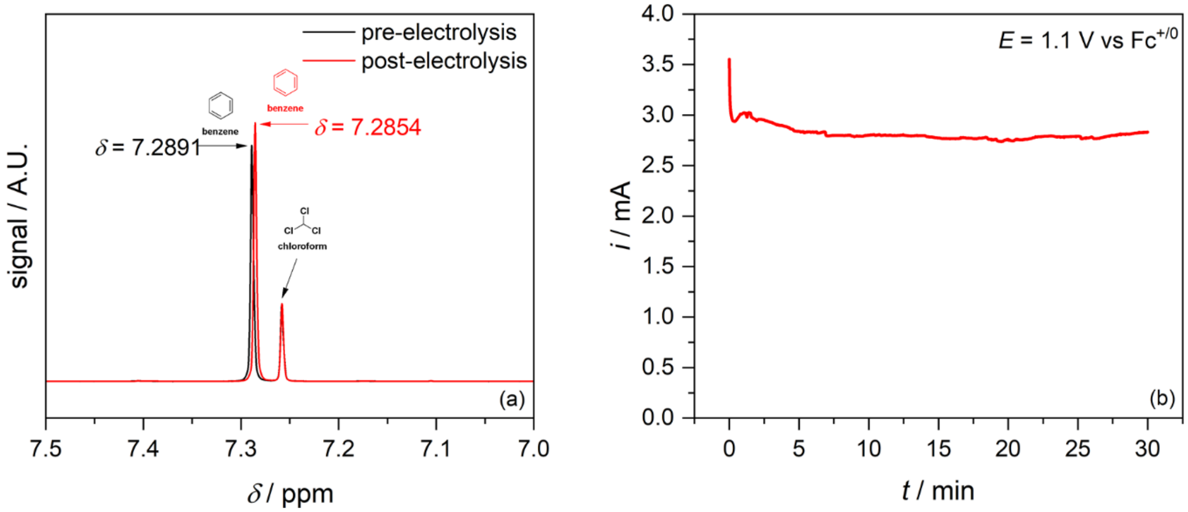

Figure S8. ^{1}H-NMR was collected on a Varian 700 MHz NMR (a) To test for chlorine radical, benzene was used as a radical trap since it reacts to form chlorobenzene,[2] which shows a peat at δ = 7.43 ppm.[3] This test is negative. The experiment begins with a 30-minute controlled potential chronoamperometry experiment (b) with 20 mM benzene, 10 mM Bu_4NCl, and 200 mM Bu_4NOTf supporting electrolyte in neat ethanol where 1.1 V vs $Fc^{+/0}$ was applied. 100 µL of solution was diluted 10-fold with deuterated chloroform and Figure S17 was collected before (red) and after (black) electrolysis. The peaks were normalized to the chloroform solvent peak. The slight increase in the peak size is likely due to variance in solution transfer. The slight decrease (0.0037 ppm) in chemical shift from 7.2891 ppm to 7.2854 ppm is likely the result of changes in the sample matrix. The concentration of both water and 1,1-diethoxyethane increase as the reaction proceeds.

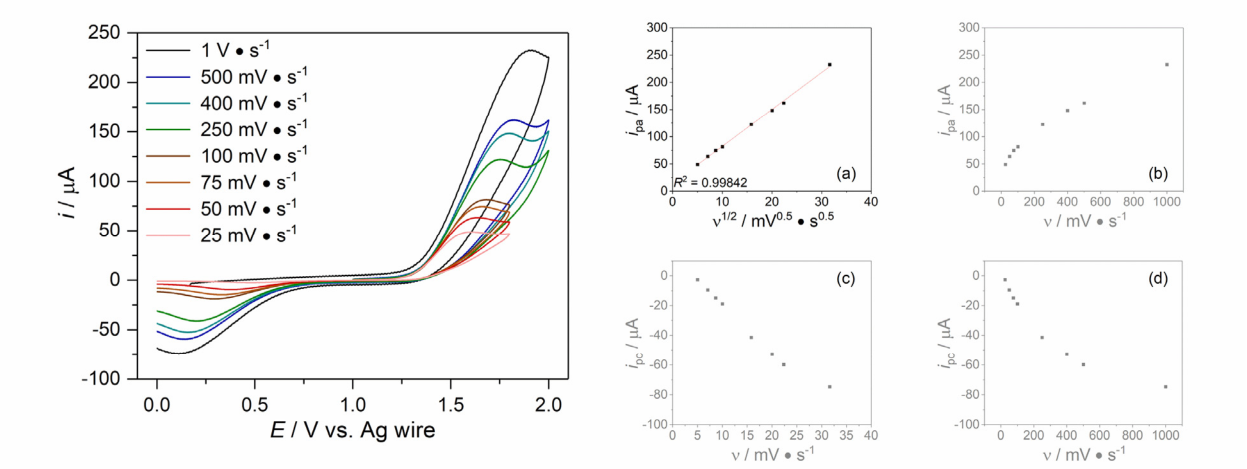

Figure S9. Variable scan-rate CV and peak current – scan rate analysis study for 10 mM Bu_4NCl and 90 mM Bu_4NOTf in ethanol. The working electrode is a glassy carbon disk. Left: CV curves. Right: Relationship of peak currents from the CV traces and either the square root of scan rate or scan rate.[4] Note that due to the spontaneous degradation of EtOCl, the species responsible for the cathodic current, measured cathodic currents are lower than what should be expected for either case. This mismatch is more significant for slower scan rates.

For a freely diffusing electroactive species, the peak current is given by the Randles-Sevcik equation:

$$i_p = (2.69 \times 10^5) n^{3/2} A D_{Cl}^{1/2} C_{Cl}^{*} \nu^{1/2}$$

For an adsorbed electroactive species, the peak current is described by:

$$i_p = \frac{n^2 F^2}{4RT} \nu A \Gamma^{*}$$

See ref. 4 in the ESI file for further discussion on peak-shape analysis.

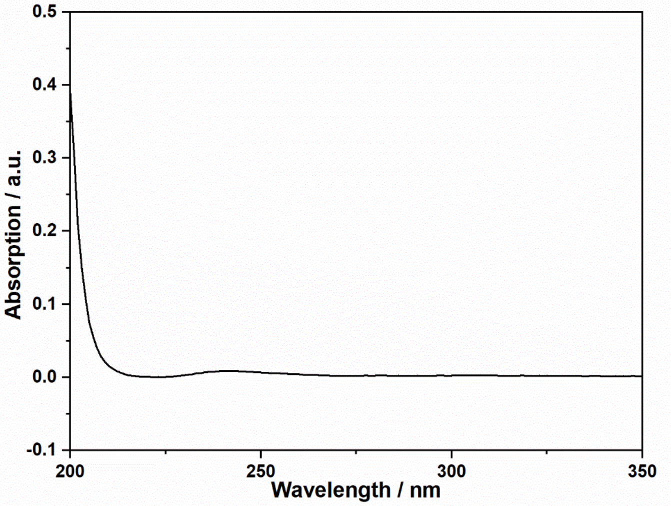

Figure S10. UV-vis absorption spectrum of 100 mM Bu_4NCl with ethanol as the background.

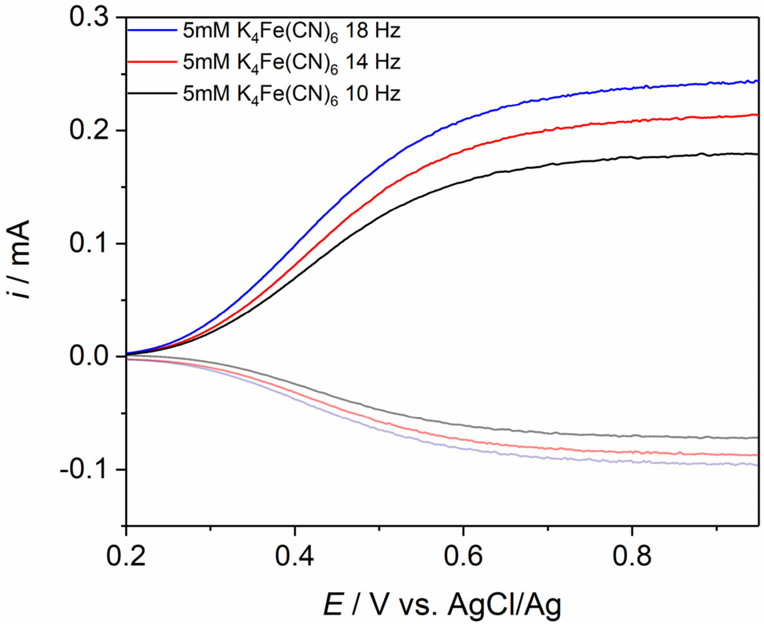

Figure S11. Collection efficiency measurement with the RRDE setup. RRDE LSV with Pt-ring and GC-disk in 100 mM Na_2SO_4, aqueous solution with 5 mM $K_4Fe(CN)_6$ dissolved. The Scan rate = 20 mV/s, E_{ring} = 0.1 V vs Ag/AgCl reference. The counter electrode is Pt wire. The experiment is conducted in a 3-compartment cell with no purging gas. Starting potential is OCP, scan direction is positive. At 0.9 V vs. Ag/AgCl, the corresponding collection efficiency: 10 Hz, 40.06%; 14 Hz, 40.60%; 18 Hz, 38.95%. The collection efficiency is determined from averaging these values, and it agrees with the manufacturer-provided theoretical value based on the dimensions and structure of the RRDE. [5]

$$N = \left|\left(\frac{i_{ring}}{i_{disk}}\right)\left(\frac{n_{ring}}{n_{disk}}\right)\right| \times 100\% \quad (4)$$

where n corresponds to the number of electrons transferred at the disk and at the ring (both equal to 1 for $[Fe(CN)_6]^{3-/4-}$) and *i* corresponds to the mass-transport limiting current. The measured collection efficiency is like other reports and agrees with theoretical value of 42.4%, reflecting the reliability of our RRDE setup.

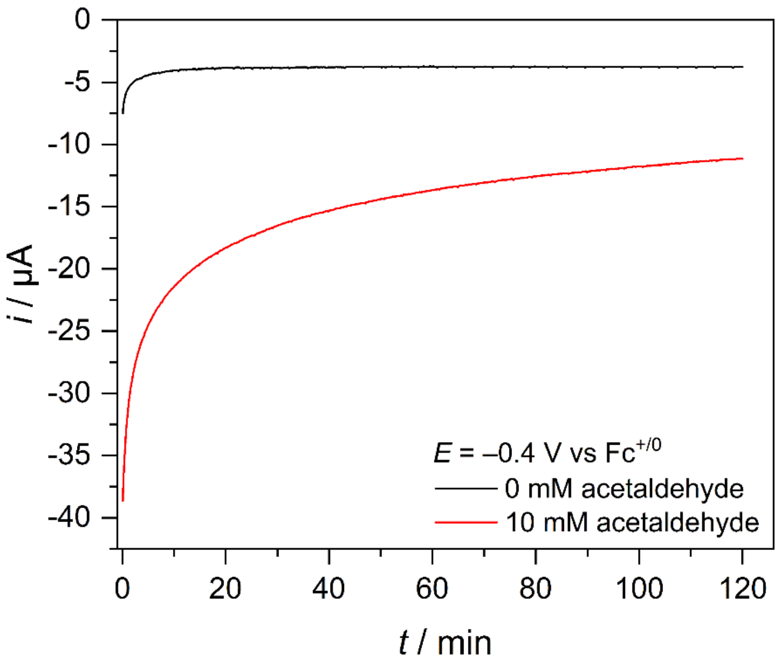

Figure S12. CPC trace showing acetaldehyde reduction at –0.4 V vs. $Fc^{+/0}$ in ethanol with 100 mM Bu_4NOTf supporting electrolyte.

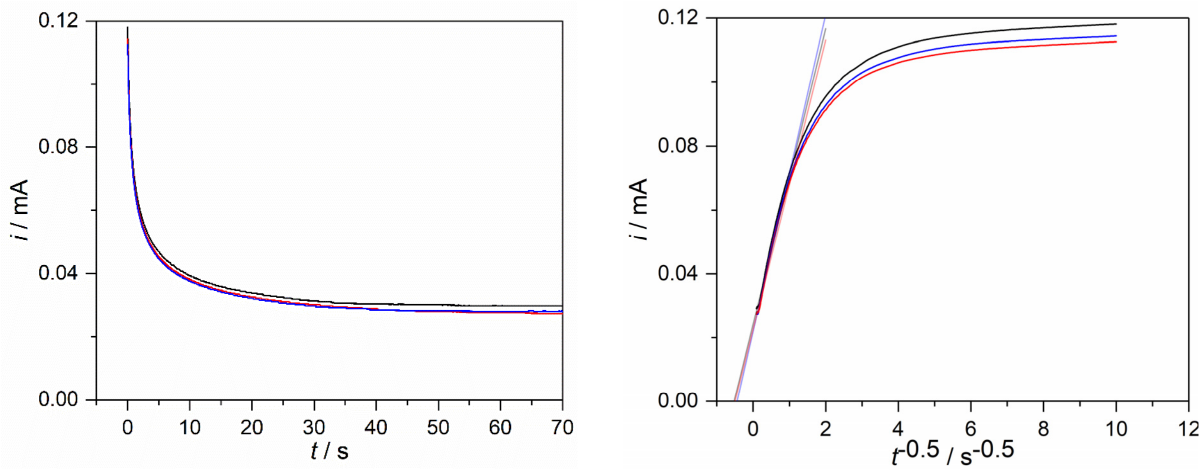

Figure S13. Cottrell experiments collected in a quiescent (no stirring) solution to measure the diffusion coefficient of Cl^- in ethanol. Electrolyte: 100 mM Bu_4NOTf, 5 mM Bu_4NCl. Electrodes: Glassy carbon disk (working), Ag wire (reference), Pt wire (counter). Data are recorded in triplicate and the numeric results are averaged. Left: replicates of CPC at 2 V vs. Ag wire. Right: i vs $t^{-0.5}$ plot, guided by $i = \frac{nFAC^{0}_{Cl^-}\sqrt{D_{Cl}}}{\sqrt{\pi t}}$ [ref 6]. The average slope is 4.701×10^{-5} mA · $s^{0.5}$, which gives an average D_{Cl} of 1.522×10^{-6} cm^2/s.

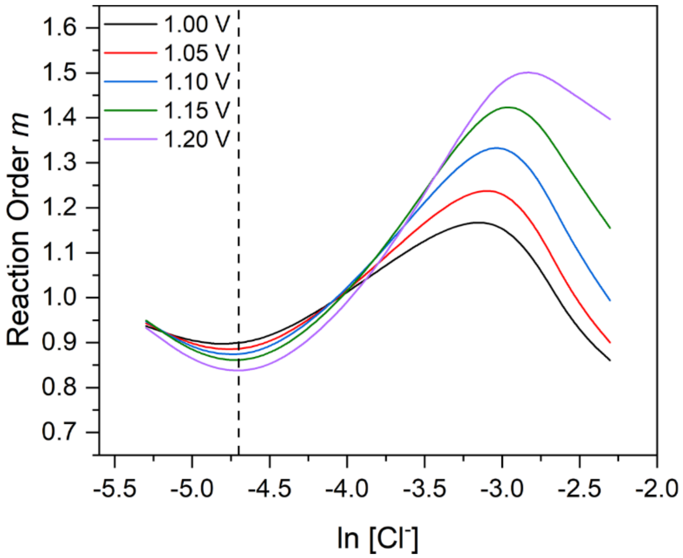

Figure S14. Estimate of apparent reaction order regarding the concentration of chloride. RRDE experiments at 2400 rpm rotation rate have been carried out for varied concentrations of chloride. m is obtained with the following equation[7]:

$$m = \left(\frac{\partial \ln(i)}{\partial \ln\left(c(Cl^-)\right)}\right)$$

Where i corresponds to the measured disk current. The vertical line in the figure represents the estimated reaction order with minimal interference from mass transport. Such reaction order values are used with the i_k calculated from K-L analysis, where ideal mass transport is assumed. Numerical values can be found on page S24.

Table S1 Values of k_f at varying potentials.

E / V vs $Fc^{+/0}$	k_f / 10^{-4} cm•s^{-1} 5 mM Bu_4NCl	Reaction order m in Cl^-
1.00	2.4277	0.902
1.05	3.15226	0.895
1.10	3.92309	0.884
1.15	4.80097	0.863
1.20	5.89176	0.839

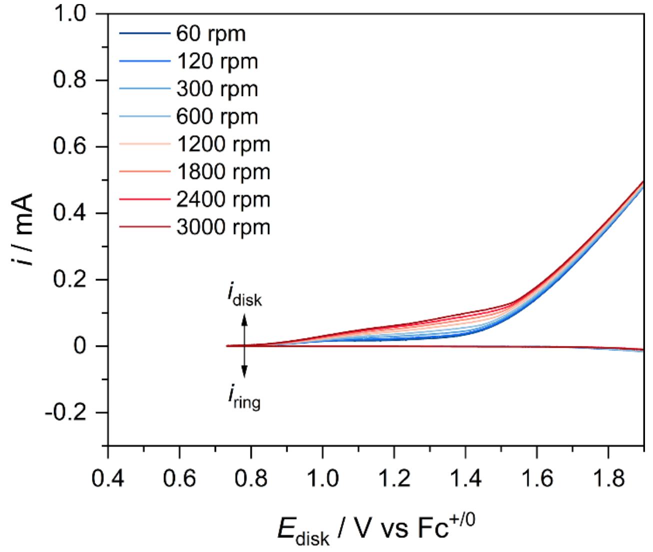

Figure S15. RRDE LSV (i - E_{disk}) with a GC-disk and Pt-ring in 100 mM Bu_4NOTf electrolyte in EtOH solvent. The scan rate is 20 mV/s and E_{ring} is poised at –0.4 V vs. Fc$^{+/0}$. The cell is sparged with argon prior to recording the data. Assuming the current is the reaction rate in ethanol solvent, the kinetically-limited rate constant is 10^{-13} cm/s.

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