Electrochemical Ethylene Oxide Synthesis from Ethanol

*Christine Lucky[1], Taobo Wang[1], and Marcel Schreier[1,2]**

[1] Department of Chemical and Biological Engineering, University of Wisconsin-Madison, Madison, Wisconsin 53706, United States

[2] Department of Chemistry, University of Wisconsin-Madison-Madison, Wisconsin 53706, United States

AUTHOR INFORMATION

Corresponding Author

* Prof. Marcel Schreier

Department of Chemical and Biological Engineering & Department of Chemistry

University of Wisconsin – Madison

1415 Engineering Drive, Madison, WI 53706

E-mail: mschreier2@wisc.edu

ABSTRACT

Ethylene oxide is a crucial precursor for chemical and plastic synthesis. Its production is carbon intensive, however, releasing 1.9 tons of CO_2 per ton of product. Reducing this footprint is possible if ethylene oxide is produced using *both* a renewable substrate *and* renewable energy. Here we pioneer a sustainable pathway to ethylene oxide via the electrochemical oxidation of ethanol to 2-chloroethanol and its subsequent alkaline cyclization in a single electrochemical cell, using chloride ions as catalysts. This approach is enabled by the electrochlorination of ethanol to 2-chloroethanol, which requires the activation of an inert C(sp^3)–H bond and is shown here for the first time. We investigate the branchpoints controlling the selectivity of this chlorination and show how they are influenced through the reaction conditions and electrode material engineering. Our method is generalizable to the production of other valuable chemicals and strengthens the foundation for sustainable chemical synthesis using renewable energy.

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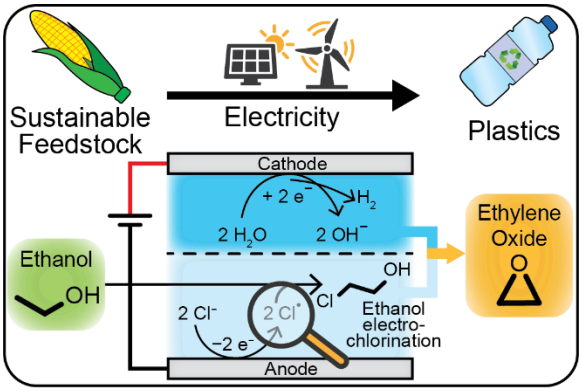


Ethylene oxide is central to the chemical industry, where it serves as a precursor for ethylene glycol, glycol ethers, epoxy resins, and numerous other bulk chemicals and plastics.[1,2] To date, ethylene oxide is manufactured through the direct oxidation of ethylene using O_2 as an oxygen source. This reaction occurs on supported silver catalysts at 200−260°C and 10−30 bar,[1] in a process that has a significant environmental impact due to its reliance on fossil energy. Not only are 0.9 tons of CO_2 emitted per ton of ethylene oxide produced,[3] but the substrate alkenes themselves have a substantial carbon footprint, as their synthesis releases a ton of CO_2 for every ton of alkene.[4]

These figures highlight that sustainable ethylene oxide production requires *both* the use of renewable energy as a driving force *and* a renewable substrate. Achieving this dual objective requires new reaction paradigms.

Using renewable electricity as the driving force in conjunction with a renewable substrate opens a net-zero emissions pathway for ethylene oxide synthesis.[5] Ethanol is an attractive substrate because, as one of the most abundant sustainably produced chemicals and a less costly alternative to ethylene, it holds the promise of a more sustainable and economical route to ethylene oxide.[5–9]

However, these advantages of synthesizing ethylene oxide from ethanol electrochemically have not yet been realized. Previous schemes rely on fossil energy to initially convert ethanol to ethylene before producing ethylene oxide from ethylene electrochemically.[10] This increases the energy demand while wasting the oxygen atom already present in the alcohol. A more direct route, which overcomes these shortcomings, is the chlorination of ethanol to chlorohydrin (2-chlorethanol), followed by an internal cyclization of the intermediate (Figure 1a). This approach uses chloride ions as a catalyst to increase the overall atom economy, while reducing the number

of intermediate reactions. When driven by renewable electricity, this route represents a sustainable pathway to ethylene oxide.

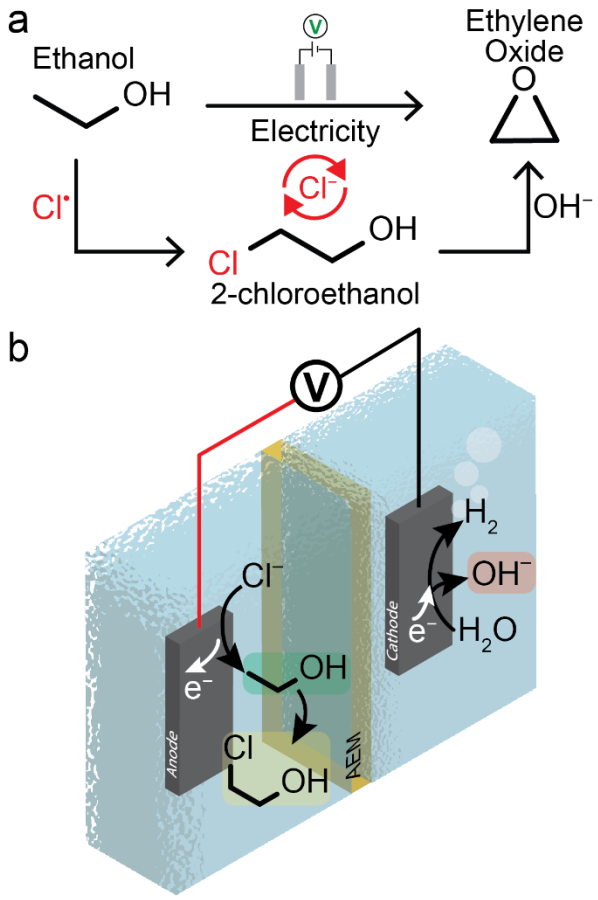


Figure 1. a) Schematic of the conversion of ethanol to ethylene oxide in an electrochemical cell using a two-step radical mediated process. b) Design of the electrochemical cell. Ethanol chlorination occurs at the anode (boron-doped diamond or tetrahedral amorphous carbon nitride) and hydrogen evolution occurs at the counter electrode (boron-doped diamond or platinum).

Prior examples have leveraged the cyclization of 2-chloroethanol to ethylene oxide, but rely on facile chlorination reactions. For instance, an electrochemical process that converts alkenes to epoxides using electricity and a metal halide electrolyte was patented in 1966.[11] This process forms a halohydrin from an electrochemically generated dihalogen and olefin. The subsequent

epoxidation reaction in an alkaline environment regenerates the halide ion and forms ethylene oxide.[12] Recently, this route has been demonstrated on a variety of materials and at current densities up to 1 A cm^{-2}.[12,13] However, all these routes to epoxides rely on the straightforward halogenation of $C(sp^2)=C(sp^2)$ double bonds in alkene substrates. Expanding the potential feedstocks to sustainable substrates such as ethanol, which do not contain C=C double bonds, requires the challenging activation of a saturated $C(sp^3)$–H bond. Applying a chlorohydrin-based strategy to synthesize ethylene oxide from ethanol thus hinges on the successful electrochemical chlorination of ethanol to 2-chloroethanol, a reaction which has not been demonstrated to date.

Indeed, the difficulty of activating the stable $C(sp^3)$–H bond in ethanol to produce the 2-chloroethanol intermediate has precluded this electrochemical valorization strategy. Prior investigations into the electrochlorination of ethanol did not produce chlorohydrin. Instead, in aqueous electrolytes trichloromethane and 2,2,2-trichloroethane-1,1-diol were formed in yields of >95%, while anhydrous electrochlorination led to chloroacetaldehyde.[14] These more highly substituted products rapidly react further under the strong driving forces needed for the initial halogenation. Similarly, the strong oxidative potentials required for chlorination on most electrocatalyst materials result in overoxidized products, including CO_2, in the complete oxidation of ethanol.[15] Recently, the selective chlorination of neat ethanol to ethyl hypochlorite via an indirect oxidation method using a glassy carbon working electrode has been reported.[16] However, this approach also did not produce 2-chloroethanol. These studies highlight the difficulty of selectively oxidizing ethanol to the desired chlorohydrin and the promise of halide mediated reaction pathways.

Avoiding overoxidation requires reaction pathways which suppress oxidation of ethanol at the electrode, while promoting its chlorination. This can be accomplished by electrochemically

generating chlorine radicals, while suppressing ethanol and water oxidation on the electrode surface. Chlorine radical species can subsequently abstract a hydrogen atom from ethanol, initiating its chlorination to 2-chloroethanol. This radical reaction has unfavorable thermodynamics, however, since production of 2-chloroethanol requires hydrogen abstraction at the β-carbon of ethanol. Yet, hydrogen abstraction from the α-carbon (forming 1-chloroethanol) is 7.6 kcal/mol more favorable and leads to acetic acid through the transient formation of acetaldehyde.[17,18] Thus controlling the activation of the more challenging β *vs* α $C(sp^3)$–H bond is central to the electrochemical synthesis of ethylene oxide through 2-chloroethanol.

In this work, we demonstrate how the use of so-called polarizable electrodes, combined with careful tuning of the reaction conditions allows for the first successful electrochemical chlorination of ethanol to 2-chloroethanol, which is subsequently converted to ethylene oxide by reaction with electrogenerated OH^- in a single electrochemical cell (Figure 1b). We show that the selectivity of ethanol chlorination controls ethylene oxide production and highlight how the chloride-mediated $C(sp^3)$–H activation can be tuned by the applied potential, reaction temperature, and electrode material.

Selective chloride oxidation for ethanol chlorination

The selective generation of chlorine radicals in aqueous solutions is challenging, because both oxygen evolution from water (E^0 = 1.23 V *vs* SHE) and the direct formation of Cl_2 gas (E^0 = 1.36 V *vs* SHE) are more thermodynamically favorable than chloride oxidation to $Cl^\bullet$ (E^0 = 2.43 V *vs* SHE).[19] Achieving $Cl^\bullet$ generation thus requires the use of so-called polarizable electrode materials, which display low activity for inner-sphere reactions. Boron-doped diamond (BDD) is among this class of materials and has been shown to suppress oxygen evolution and catalytic chlorine gas formation, while maintaining low overpotentials for outer-sphere reactions.[20] This

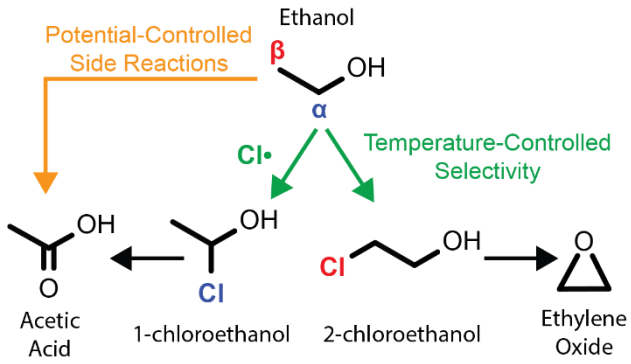
behavior was attributed to the limited adsorption of intermediates on diamond electrodes, which are believed to be necessary for catalytic water oxidation and catalytic Cl_2 generation, but not for chlorine radical formation.[20] Favorably, Cl$^{\bullet}$ is formed at lower potentials than $^{\bullet}$OH ($E^0 = 2.74$ V *vs* SHE), which is key to suppressing outer-sphere water oxidation and allowing for chlorine radical formation to take place.[21] Indeed, mechanistic studies suggest chlorine evolution occurs through a radical pathway on BDD electrodes at potentials below $^{\bullet}$OH formation, with the initial discharge to form Cl$^{\bullet}$ as the rate determining step.[21,22]

In our cyclic voltammetry measurements on BDD electrodes, chloride oxidation started at approximately 1.7 V *vs* Ag/AgCl in 0.5 M NaCl solutions of varying pH levels, in close agreement with literature values (Figure S1).[21] Importantly, chloride oxidation occurs at a lower potential than water oxidation in both acidic and neutral conditions (Figure S2), pointing to the ability of BDD electrodes oxidize chloride while avoiding reactions with water.

Steering the selectivity of ethanol chlorination

Leveraging the chemistry of BDD electrodes, we investigated their propensity to electrochemically chlorinate ethanol to form the key chlorohydrin intermediate. At ambient temperature, we exposed an aqueous chloride solution containing 100 mM ethanol to a BDD electrode at 2.05 V *vs* Ag/AgCl. This produced 2-chloroethanol demonstrating, for the first time, the electrochemical chlorination of ethanol to chlorohydrin (Figure S3). The formation of 2-chloroethanol takes place through an electrochemical route, likely from halogen radicals formed by the oxidation of chloride anions at the anode. While the reaction also produces chlorine gas, which is suggested to occur through the recombination of chlorine radicals,[22] light-driven radical formation plays no role in this system. Control experiments performed in the dark showed no decrease in 2-chloroethanol production (Figure S4). Furthermore, the presence of Cl_2 alone was

insufficient to produce chlorohydrin at room temperature. No reaction products were detected upon mixing with NaOCl or after bubbling Cl_2 gas through the cell for 4 hours at 25°C, suggesting that Cl_2, HOCl and ClO^-,[23] do not result in 2-chlorethanol generation (Figures S5 and S6). However, at higher temperatures some product formation was observed upon mixing with Cl_2. This is hypothesized to arise from small amounts of thermally-driven Cl_2 dissociation. Thus, we suggest that chlorohydrin generation takes place through an electrochemical pathway, likely involving chlorine radicals. As expected, NMR also indicated that acetic acid, the product of hydrogen abstraction at the α-carbon (Scheme 1), was present in the product mixture. The subsequent self-cyclization reaction to form ethylene oxide can only occur through the 2-chloroethanol intermediate formed from hydrogen abstraction at the β-carbon, highlighting the importance of controlling the site selectivity during ethanol chlorination.



Scheme 1. Schematic of the pathways involved in the conversion of ethanol to ethylene oxide. The parameters controlling the selectivity toward ethylene oxide and toward side products are indicated and the α and β positions of ethanol have been labelled.

To promote halogenation at the desired β-carbon, we investigated the role of temperature and applied potential in steering the selectivity of ethanol chlorination and studied the kinetics of the reaction. We started by investigating the temperature dependence at 2.05 V *vs* Ag/AgCl, which allowed reliable product quantification for all conditions. As shown in Figure 2a, the ratio of

2-chloroethanol to acetic acid increases with increasing temperature. This increase in selectivity is driven by a rising partial current toward 2-chloroethanol upon going from 25°C to 80°C (Figure 2b). These trends suggest that higher temperatures promote the production of the thermodynamically less favorable product. We explain this behavior on kinetic grounds. The activation energy for hydrogen abstraction at the β-carbon is 7.6 kcal/mol higher than at the α-carbon. Thus, at increased temperatures, more molecules can take the higher energy pathway to 2-chloroethanol, as highlighted by the ratio of the Arrhenius equations of two processes with different activation energies: $\frac{k_1}{k_2} = \frac{A_1}{A_2}\exp\left(\frac{1}{RT}\left(E_{a,2} - E_{a,1}\right)\right)$. Consequently, temperature serves as a handle to tune the selectivity of ethanol chlorination, because it controls the site of the first hydrogen abstraction from ethanol.

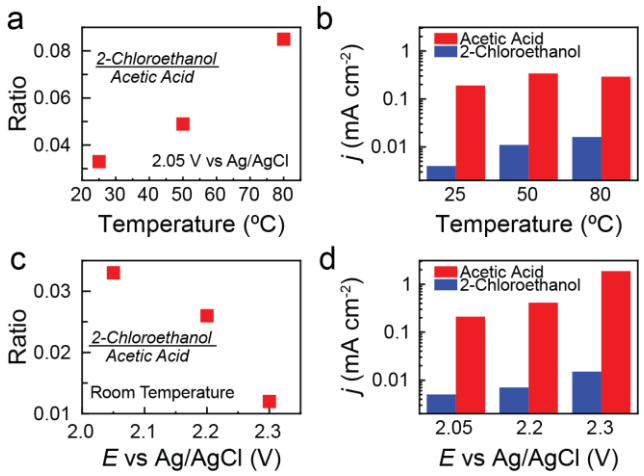


Figure 2. a) The ratio of 2-chloroethanol to acetic acid and b) partial current density toward each product after applying 2.05 V *vs* Ag/AgCl to 0.5 M NaCl and 100 mM ethanol at various temperatures. c) Ratio of 2-chloroethanol to acetic acid and d) current density toward each product following room temperature electrolysis of 0.5 M NaCl and 100 mM ethanol at varying potentials. The data shown is the average for three replicates at each condition. Statistical data is shown in Figure S11 and S12.

The temperature-dependence described above indicates that hydrogen abstraction from ethanol controls the kinetics of 2-chloroethanol formation. Further evidence for this finding emerges from measurements of the production rate of 2-chloroethanol under varying ethanol concentrations. At room temperature, the production rate of 2-chloroethanol increased with increasing ethanol concentrations (Figure S7). However, the ratio of 2-chloroethanol to acetic acid remained constant within experimental error. This suggests that once chlorine radicals are formed electrochemically, the thermodynamic cost of hydrogen abstraction from the α or β-carbon of ethanol dominates the reaction outcome. Operating at higher temperatures thus allows us to mitigate the difference in energy barriers and abstract a hydrogen at the β position, resulting in 2-chloroethanol.

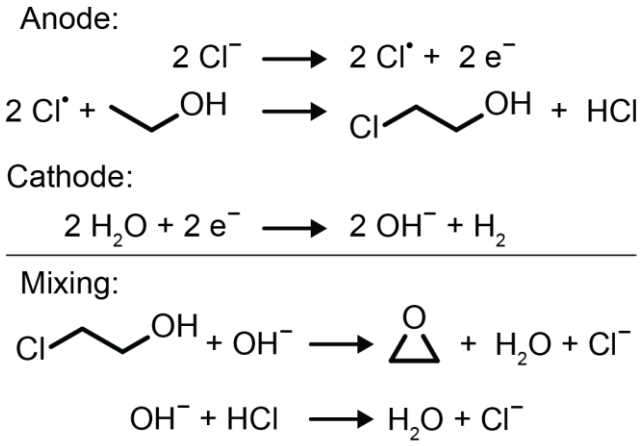
The applied potential also governs the selectivity of electrochemical ethanol chlorination. To characterize this behavior, we conducted potentiostatic experiments between 2.05 and 2.3 V *vs* Ag/AgCl at ambient temperature. The ratio of 2-chloroethanol to acetic acid was highest at lower driving forces (Figure 2c). This is due to an increase in acetic acid production at more oxidative potentials, which is accompanied by only a minor increase in 2-chloroethanol (Figure 2d). We attribute this to direct ethanol oxidation at the electrode surface. Indeed, we found that on BDD electrodes, the direct electrochemical oxidation of ethanol in the absence of Cl^- takes place at potentials between the onset of chloride and water oxidation (Figure S8 and S9).[20,24] This reaction produces acetic acid as the sole product (Figure S8). At more positive potentials the oxidation of ethanol competes with chloride oxidation, lowering the selectivity to the desired 2-chloroethanol intermediate. While the oxidation of bromide at lower potentials was considered as an alternative pathway to avoid direct ethanol oxidation, experiments showed no selectivity to the necessary 2-bromoethanol intermediate (Figure S10). We attribute this to the lower enthalpy of reaction for

bromination, which increases the selectivity to the thermodynamically favored hydrogen abstraction at the α-carbon according to the Hammond postulate.[25]

Electrochemically-induced epoxidation of 2-chloroethanol to ethylene oxide

Ethylene oxide can be produced from 2-chloroethanol through reaction with electrochemically formed hydroxide anions, in a process that regenerates the chloride ion used for 2-chloroethanol synthesis (Figure 1a).[18] This internal cyclization occurs in aqueous solutions at pH above 8 with high conversion.[12,18] In our case, the direct conversion of electrogenerated 2-chloroethanol to ethylene oxide in the anolyte is undesirable since further oxidation of the ethylene oxide is likely. Fortunately, this conversion is inhibited by the acidic conditions used to selectively oxidize chloride at the anode.

Electrochemical systems spatially separate oxidative and reductive reactions. We exploit this fact to generate ethylene oxide outside of the oxidizing environment of the anode. This is possible because the reaction stoichiometry dictates that for each molecule of 2-chloroethanol formed at the anode, two molecules of NaOH are formed at the cathode (Scheme 2).



Scheme 2. Schematic reactions occurring at the anode and cathode that allow the synthesis of ethylene oxide and regeneration of chloride upon mixing the anolyte and catholyte.

This is the result of water reduction which leaves behind OH^- ions while generating hydrogen. Consequently, in our experiments, mixing the anolyte and catholyte resulted in a solution with pH 11.5. The alkaline pH develops because the oxidation of chloride at the anode does not consume the hydroxide ions generated at the cathode. We found the mixed electrolyte environment alkaline enough for the quantitative transformation of 2-chloroethanol to ethylene oxide to occur (Figure 3). The epoxidation reaction took place for electrolytes with an initial pH value between 7 and 9 (Table S1), with the selectivity to 2-chloroethanol and ethylene oxide remaining similar across all starting pH values.

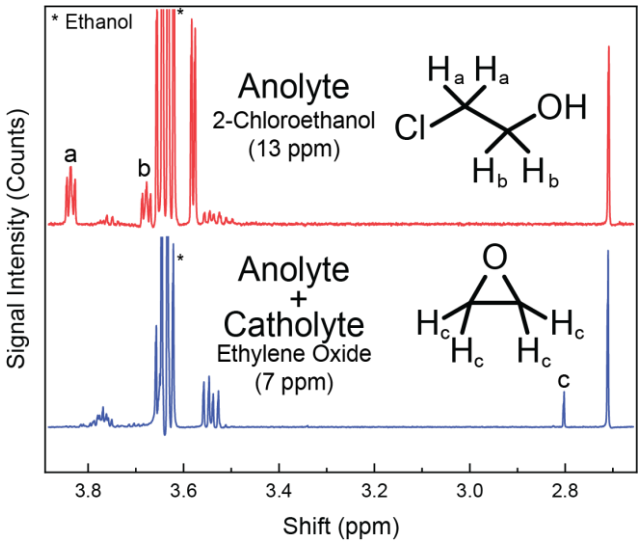


Figure 3. Proton NMR spectra of 2-chloroethanol in the anolyte being converted to ethylene oxide upon mixing with the catholyte. Spectra referenced to DMSO at 2.71 ppm. Ethanol peaks are clipped to show intermediate and product peaks.

Electrochemical epoxidation of ethanol to ethylene oxide in a continuous flow cell

Leveraging our ability to electrochemically synthesize 2-chloroethanol, we demonstrate the continuous conversion of ethanol to ethylene oxide in an integrated flow cell, capable of simultaneously chlorinating ethanol and transforming 2-chloroethanol to ethylene oxide. BDD

electrodes were used as both anode and cathode, with an anion exchange membrane separating the two compartments as shown in Figure 4 and Figure S13. The outlet of both compartments were

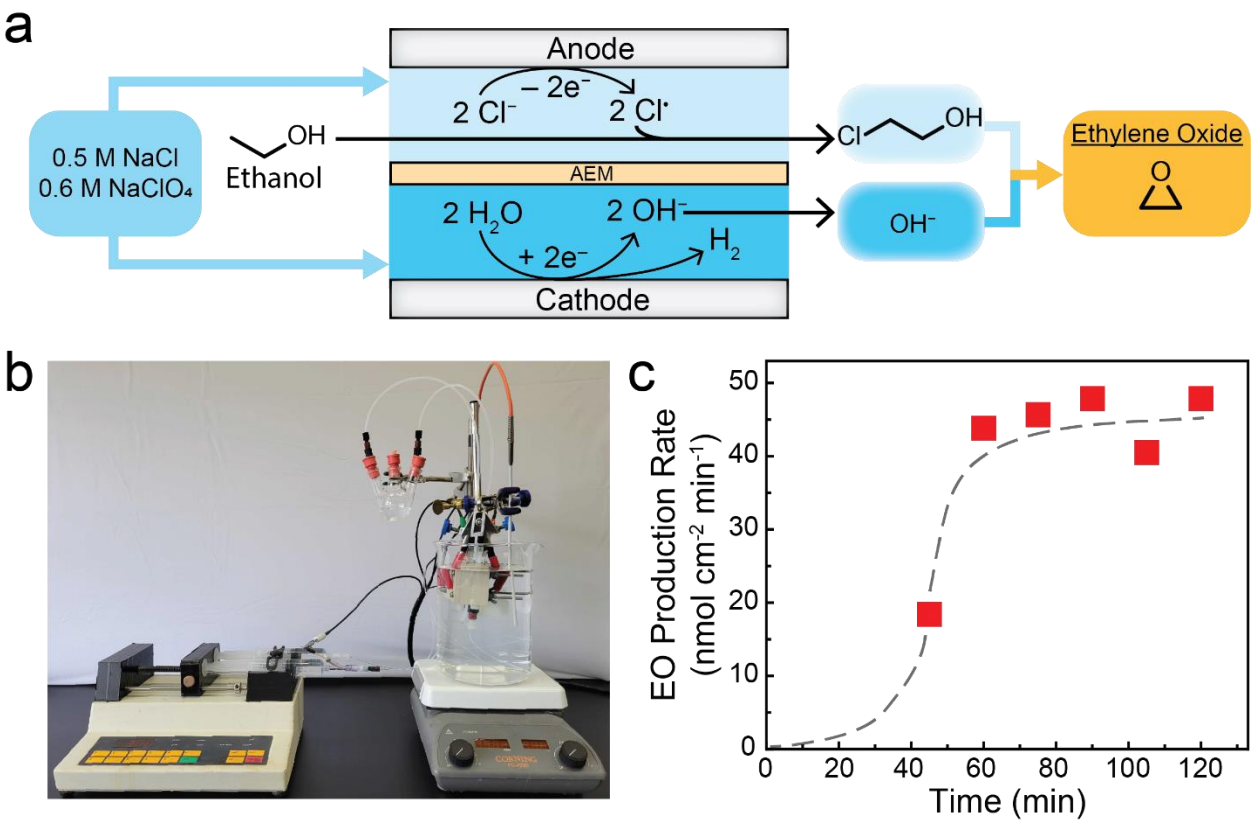


Figure 4. a) Schematic of the electrochemical ethanol-to-ethylene oxide integrated cell design. b) Photograph of the flow cell used in the integrated experiments. A more detailed picture of the experimental set up is available in Figure S18. c) The production rate of ethylene oxide in the integrated flow cell during a 2-hour experiment as measured by the concentration of the mixed anolyte and catholyte effluent. The dashed line serves as a guide to the eye. The shape of the curve is due to the follow dynamics of the system (see SI).

combined and the product concentrations were periodically analyzed. When operating the flow cell using a feed containing 100 mM ethanol as substrate at 80°C for 2 hours, we observed a steady-state Faradaic efficiency of 1% toward ethylene oxide and 31% when adding acetate production

(Figures S14-17). The IR-corrected voltage efficiency for the transformation of ethanol to ethylene oxide reached 32% when using a BDD working electrode and platinum counter electrode. The ethylene oxide production rate remained constant upon reaching steady-state conditions until the reaction was stopped at 2 hours, demonstrating the capability of our integrated electrochemical approach to sustainably produce ethylene oxide from ethanol over extended amounts of time.

Impact of anode material on chlorination selectivity

Our findings indicate that the conversion of ethanol to ethylene oxide is controlled by 2-chloroethanol formation at the anode with the subsequent cyclization being facile. A key challenge to selectively producing 2-chloroethanol is the competition between chloride oxidation and direct ethanol oxidation at the anode. Improving 2-chloroethanol selectivity thus requires increasing the difference between the onset potentials for chloride and ethanol oxidation. To fulfill this need, we investigated tetrahedral amorphous carbon nitride (ta-C:N) as an anode material, which has been reported to display a wider solvent window and higher catalytic activity for chloride oxidation than BDD.[26,27] Indeed, ta-C:N electrodes feature a substantially lower onset potential for chloride oxidation compared to BDD, resulting in a 180 mV larger window between the onset potentials of chloride and ethanol oxidation (Figure 5a). This allows chlorination to be carried out at decreased driving forces. As seen in Figure 5b, operating at 1.7 V *vs* Ag/AgCl strongly increased the ratio of 2-chloroethanol to acetic acid production from 0.09 to 0.19, pointing to an important role of the electrode material in electrochlorination reactions. We indeed observed that this increased 2-chloroethanol selectivity is a result of a substantially decreased production of acetic acid on ta-C:N (Table S3). The reduction in operating potential on ta-C:N also increased the IR-corrected voltage efficiency of the complete reaction to 42%.

Chlorine and oxygen production account for the current density not resulting from reaction of ethanol (Table S3). Notably, Cl_2 was generated with a faradaic efficiency of 68% on ta-C:N electrodes, with O_2 generation only reaching 6%. These findings suggest that the rate of ethanol chlorination is in competition with the recombination of chlorine radicals to form Cl_2. This observation, combined with the good stability exhibited by our system (Figure S19), suggests that improvements in reactor design and process engineering, which promote the reaction of chlorine species with ethanol by increasing the supply of ethanol to the electrode surface, hold the potential to dramatically improve the performance metrics.

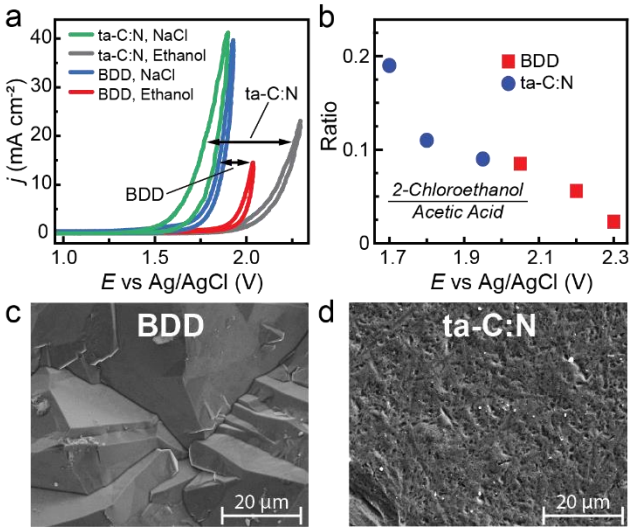


Figure 5. a) Comparison of the onset potential of chlorine oxidation and direct ethanol oxidation on ta-C:N and BDD electrodes. b) The ratio of 2-chloroethanol to acetic acid after electrolysis of a 0.5 M NaCl, 0.6 M $NaClO_4$, 0.1 M $HClO_4$ electrolyte containing 100 mM ethanol at 80° C on ta-C:N and BDD electrodes. c,d) SEM image of BDD and ta-C:N respectively following electrolysis.

Ethylene oxide can be sustainably produced from ethanol through the electrochemical generation of 2-chloroethanol, followed by its alkaline transformation to ethylene oxide. Due to the nearly quantitative conversion of 2-chloroethanol to ethylene oxide, the product distribution is

defined by the chlorination selectivity, which is promoted at higher temperatures and low potentials in a manner consistent with a mechanism governed by an initial hydrogen atom transfer from ethanol. Based on these findings, we designed an integrated flow cell, capable of continuously transforming ethanol to ethylene oxide. This demonstrates the unique ability of electrochemical approaches to disrupt traditional pathways in platform chemical synthesis by opening the door to sustainably sourced feedstocks. The fundamental insights provided herein indicate that further reactor engineering and material optimization may significantly improve the rates and selectivity, akin to fields like CO reduction, which transitioned from μA cm^{-2} [28] to A cm^{-2} [29,30] through extensive optimization. In addition, our approach is generalizable to a broad array of bulk chemicals through the variation of the anodic reaction. We therefore expect our findings to play an important role in building the foundation for sustainable chemical synthesis technologies of the future.

ASSOCIATED CONTENT

Detailed experiment methods, electrode characterization, and additional results and data

AUTHOR INFORMATION

Prof. Marcel Schreier

Department of Chemical and Biological Engineering & Department of Chemistry

University of Wisconsin – Madison

1415 Engineering Drive, Madison, WI 53706

E-mail: mschreier2@wisc.edu

https://www.engineered-interfaces.org

Twitter: @MarcelSchreier2

Notes

A patent application has been filed based on this work.

ACKNOWLEDGMENT

We thank Logan Murphy for help with experiments, Hsiang-Sheng Chen for obtaining SEM images, and George Huber for helpful discussions. The Bruker AVANCE 600 NMR spectrometer was supported by NIH grant S10 OD012245. The authors acknowledge use of facilities and instrumentation at the UW-Madison Wisconsin Centers for Nanoscale Technology partially supported by the NSF through the University of Wisconsin Materials Research Science and Engineering Center (DMR-1720415). This material is based upon work supported by the National Science Foundation Graduate Research Fellowship Program under Grant No. DGE-1747503. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the National Science Foundation. Support was also provided by the Graduate School and the Office of the Vice Chancellor for Research and Graduate Education at the University of Wisconsin-Madison with funding from the Wisconsin Alumni Research Foundation. The authors also acknowledge support from the University of Wisconsin-Madison and the Wisconsin Alumni Research Foundation.

REFERENCES

(1) Zimmermann, H.; Walzl, R. *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA, 2000.

(2) Ausfelder, F.; Bazzanella, A.; VanBracki, H.; Wilde, R.; Beckmann, C.; Mills, R.; Rightor, E.; Tam, C.; Trudeau, N.; Botschek, P. *Technology Roadmap - Energy and GHG Reductions in the Chemical Industry via Catalytic Processes.*; 2013.

(3) Boulamanti A; Moya JA. *Energy Efficiency and GHG Emissions: Prospective Scenarios for the Chemical and Petrochemical Industry*; 2017.

(4) Ding, D.; Zhang, Y.; Wu, W.; Chen, D.; Liu, M.; He, T. A Novel Low-Thermal-Budget Approach for the Co-Production of Ethylene and Hydrogen via the Electrochemical Non-Oxidative Deprotonation of Ethane. *Energy and Environ. Sci.* **2018**, *11* (7), 1710–1716.

(5) Mohsenzadeh, A.; Zamani, A.; Taherzadeh, M. J. Bioethylene Production from Ethanol: A Review and Techno-Economical Evaluation. *ChemBioEng Reviews* **2017**, *4* (2), 75–91.

(6) Sun, J.; Wang, Y. Recent Advances in Catalytic Conversion of Ethanol to Chemicals. *ACS Catal.* **2014**, *4* (4), 1078–1090.

(7) Ripamonti, D.; Tripodi, A.; Conte, F.; Robbiano, A.; Ramis, G.; Rossetti, I. Feasibility Study and Process Design of a Direct Route from Bioethanol to Ethylene Oxide. *J. Environ. Chem. Eng.* **2021**, *9* (5), 105969.

(8) Lippits, M. J.; Nieuwenhuys, B. E. Direct Conversion of Ethanol into Ethylene Oxide on Gold-Based Catalysts: Effect of CeO_x and Li_2O Addition on the Selectivity. *J. Catal.* **2010**, *274* (2), 142–149.

(9) Lippits, M. J.; Nieuwenhuys, B. E. Direct Conversion of Ethanol into Ethylene Oxide on Copper and Silver Nanoparticles: Effect of Addition of CeO_x and Li_2O. *Catal. Today* **2010**, *154* (1–2), 127–132.

(10) Coupard, V.; Plennevaux, T. Method for Producing Ethylene Oxide from a Thermally Integrated Ethanol Stream. US 9,353,074 B2, 2016.

(11) Leduc, J. A. M. Electrochemical Process for the Production of Organic Oxides. 3,288,692, 1966.

(12) Chung, M.; Jin, K.; Zeng, J. S.; Manthiram, K. Mechanism of Chlorine-Mediated Electrochemical Ethylene Oxidation in Saline Water. *ACS Catal.* **2020**, *10*, 14015–14023.

(13) Leow, W. R.; Lum, Y.; Ozden, A.; Wang, Y.; Nam, D.-H.; Chen, B.; Wicks, J.; Zhuang, T.-T.; Li, F.; Sinton, D.; Sargent, E. H. Chloride-Mediated Selective Electrosynthesis of Ethylene and Propylene Oxides at High Current Density. *Science* **2020**, *368* (6496), 1228–1233.

(14) Lyalin, B. V.; Petrosyan, V. A. Electrochemical Halogenation of Organic Compounds. *Russ. J. Electrochem.* **2013**, *49* (6), 497–529.

(15) Sulaiman, J. E.; Zhu, S.; Xing, Z.; Chang, Q.; Shao, M. Pt–Ni Octahedra as Electrocatalysts for the Ethanol Electro-Oxidation Reaction. *ACS Catal.* **2017**, *7*, 5134–5141.

(16) Li, S.; Bartlett, B. M. Selective Chloride-Mediated Neat Ethanol Oxidation to 1,1-Diethoxyethane via an Electrochemically Generated Ethyl Hypochlorite Intermediate. *J. Am. Chem. Soc.* **2021**, *143* (39), 15907–15911.

(17) Oliver, B. G.; Carey, J. H. Photochemical Production of Chlorinated Organics in Aqueous Solutions Containing Chlorine. *Environ. Sci. and Technol.* **1977**, *11* (9), 893–895.

(18) Sun, H.; Bozzelli, J. W. Structures, Intramolecular Rotation Barriers, and Thermochemical Properties: Ethanol, a-Monoethanols, Dichloroethanols, and Corresponding Radicals Derived from H Atom Loss. *J. Phys. Chem. A* **2001**, *105* (41), 9543–9552.

(19) Armstronga, D. A.; Huie, R. E.; Lymar, S.; Koppenol, W. H.; Merényi, G.; Neta, P.; Stanbury, D. M.; Steenken, S.; Wardman, P. Standard Electrode Potentials Involving Radicals in Aqueous Solution: Inorganic Radicals. *Bioinorg React. Mech.* **2013**, *9* (1–4), 59–61.

(20) Garcia-Segura, S.; Vieira Dos Santos, E.; Martínez-Huitle, C. A. Role of sp^3/sp^2 Ratio on the Electrocatalytic Properties of Boron-Doped Diamond Electrodes: A Mini Review. *Electrochem. Commun*. **2015**, *59*, 52–55.

(21) Mostafa, E.; Reinsberg, P.; Garcia-Segura, S.; Baltruschat, H. Chlorine Species Evolution during Electrochlorination on Boron-Doped Diamond Anodes: In-Situ Electrogeneration of Cl_2, Cl_2O and ClO_2. *Electrochim. Acta* **2018**, *281*, 831–840.

(22) Ferro, S.; Battisti, A. De; Duo, I.; Comninellis, C.; Haenni, W.; Perret, A. Chlorine Evolution at Highly Boron-Doped Diamond Electrodes. *J. Electrochem. Soc.* **2000**, *147* (7), 2614–2619.

(23) Dionigi, F.; Reier, T.; Pawolek, Z.; Gliech, M.; Strasser, P. Design Criteria, Operating Conditions, and Nickel–Iron Hydroxide Catalyst Materials for Selective Seawater Electrolysis. *ChemSusChem* **2016**, *9* (9), 962–972.

(24) Macpherson, J. V. A Practical Guide to Using Boron Doped Diamond in Electrochemical Research. *Phys. Chem. Chem. Phys.* **2015**, *17*, 2935.

(25) Klein, D. R. *Organic Chemistry*, Second.; John Wiley & Sons, Inc: Hoboken, NJ, 2015.

(26) Yoo, K.; Miller, B.; Kalish, R.; Shi, X. Electrodes of Nitrogen-Incorporated Tetrahedral Amorphous Carbon A Novel Thin-Film Electrocatalytic Material with Diamond-like Stability. *Electrochem. and Solid-State Lett.* **1999**, *2* (5), 233–235.

(27) Yang, X.; Haubold, L.; Devivo, G.; Swain, G. M. Electroanalytical Performance of Nitrogen-Containing Tetrahedral Amorphous Carbon Thin-Film Electrodes. *Anal. Chem.* **2012**, *84*, 6240–6248.

(28) Li, C. W.; Ciston, J.; Kanan, M. W. Electroreduction of Carbon Monoxide to Liquid Fuel on Oxide-Derived Nanocrystalline Copper. *Nature* **2014**, *508* (7497), 504–507.

(29) Ripatti, D. S.; Veltman, T. R.; Kanan, M. W. Carbon Monoxide Gas Diffusion Electrolysis That Produces Concentrated C2 Products with High Single-Pass Conversion. *Joule* **2019**, *3* (1), 240–256.

(30) Jouny, M.; Luc, W.; Jiao, F. High-Rate Electroreduction of Carbon Monoxide to Multi-Carbon Products. *Nat. Catl.* **2018**, *1* (10), 748–755.