Glycerol Oxidation Pairs with Carbon Monoxide Reduction for Low-Voltage Generation of C₂ and C₃ Product Streams

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ABSTRACT: Electrochemical carbon dioxide reduction to multicarbon products provides the storage of renewable energy in the form of chemical bonds, as well as a means to displace fossil sources of chemical feedstocks. However, the accompanying anodic oxygen evolution reaction (OER) reduces the energy efficiency of the process without providing a salable product. Replacing OER with alternative organic oxidation reactions (OORs) is an emerging strategy to reduce the full-cell potential and generate valuable products on both sides of the cell. We pursue carbon monoxide reduction that avoids carbonate formation and benefits from highly alkaline anode conditions favorable for OOR. This coelectrolysis strategy achieves a cathodic C₂⁺ product stream (71% FE) and an anodic C₃ product stream (75% FE) at 180 mA cm⁻² with a full-cell potential of 1.34 V. The integrated system reduces the CO-to-C₂H₄ energy requirement by 55% (to ∼72 GJ/ton_C₂H₄), halving the projected energy cost of ethylene production from CO₂.

Decarbonization of energy generation and chemical production motivates the conversion of renewably generated electrical energy into commodity fuels and chemicals. Electrocatalytic conversion of CO₂ to chemicals provides a means to store intermittent renewable energy and displace fossil-fuel-based chemical production.1

With a global annual production of 192 Mt in 2019,2 ethylene (C₂H₄) is the most in-demand multicarbon product accessible via the CO₂ reduction reaction (CO₂RR). C₂H₄ is currently produced through energy-intensive steam cracking of long-chain hydrocarbons which produce 2–3 tCO₂/tC₂H₄.3 CO₂ electrolyzers can produce C₂H₄ with high Faradaic efficiencies (FEs) of 70–80% and energy efficiencies (EES) over 30% at current densities greater than 100 mA cm⁻².4−7 However, this process does not currently compete with the incumbent thermochemical route in production costs and energy input.8 The conversion of CO₂ to C₂H₄ requires an electrical energy input of 196 GJ/tC₂H₄ (at today’s best with 80% FE, 30% EE), and this corresponds to $1340/tC₂H₄ in electricity cost alone (at $0.03/kWh). These values greatly exceed the energy value of C₂H₄ at 49.4 GJ/tC₂H₄ and therefore also its market price of ∼$800/tC₂H₄. Addressing these limitations will require innovation on both sides of the cell.

Present-day CO₂ electrolyzers employ the oxygen evolution reaction (OER) as the counter anodic half-reaction. On the basis of Gibbs free energy, up to 90% of input energy is consumed by OER in an idealized CO₂ electrolyzer.8 Our empirical analysis of voltage distribution in a membrane electrode assembly (MEA) electrolyzer indicated that sluggish OER kinetics accounts for 50% of the imposed overpotential to the cell.9 The value of the produced oxygen (∼$25/tO₂) is negligible and does not contribute to economic feasibility. Replacing OER with organic oxidation reactions (OORs) is an emerging strategy to lower the full-cell potential in CO₂ electrolyzers10–15 as well as electrochemical hydrogen generation16–18 and to produce valuable anodic products.19–21 Electrooxidation of organic biomass conforms with the principal process design rules of low feed cost, high product market price, and a market size suitable to be paired with CO₂RR.8,19 Glycerol is a low-cost byproduct of surfactant and biodiesel production from vegetable oils and waste fats22,23 and has been emphasized as a promising anode-side reactant for CO₂RR that could reduce the full-cell potential and provide value-added products. Lactic acid (or lactate in the conjugate base form) is a product of particular interest for the production
of biodegradable thermoplastic, poly(lactic acid), which accounts for 10% of current bioplastics. To realize the benefits of coelectrolysis of anode and cathode products, the reactions must be compatible within a single system—electrolyte, membrane, and temperature—at practical reaction rates (>100 mA cm$^{-2}$). To date anodic upgrading of glycerol has been limited to <10 mA cm$^{-2}$.

Here we find OOR to be incompatible with carbon dioxide reduction to ethylene in an MEA. On the cathode, hydrogen evolution dominates because of the loss of CO$_2$ reactant to carbonate. On the anode, OOR fails to compete with oxygen evolution beyond a moderate reaction rate because of the relative abundance of water. We pursue carbon monoxide reduction that benefits from highly alkaline anodic conditions and avoids CO$_2$ reactant loss to carbonate and associated losses. This approach motivates a two-step cascade with CO$_2$ to CO via established solid oxide technology, followed by CO to higher value products. The second step can also facilitate organic oxidation reactions such as glucose oxidation. We develop the coelectrolysis of CO and glycerol here to reduce the energy required for C$_2$ cathode products while producing a second stream of valuable C$_3$ products with large market size. To overcome the kinetic limitations to high-rate OOR, we develop a hierarchical hydrophilic nano-structured catalyst that accelerates the transfer of charge and hydrophilic organic reactants. As a result, we achieve high-rate OOR by feeding glycerol in 2.0 M KOH electrolyte into a standard CO$_2$RR MEA electrolyzer. Analysis of the cathodic gas products in the current density range of 20 to 300 mA cm$^{-2}$ (Figure S6) indicated hydrogen (H$_2$) to be the major product, with C$_2$H$_4$ FE not exceeding 15%. The dominance of HER at these alkaline conditions indicated a low CO$_2$ concentration at the catalyst surface—an artifact of severe CO$_2$ reactant loss to carbonate that is typical at high alkalinity in these systems.

Decreasing the anolyte KOH concentration 20-fold (0.1 M KOH) suppressed hydrogen evolution in favor of CO production, without a significant improvement in C$_2$H$_4$ activity (Figure S8). However, the full-cell potential increased because of the higher anodic potentials. A similar product distribution was achieved in the control, CO$_2$RR-OER experiment with 0.1 M KOH anolyte (Figure S9). These results indicate the incompatibility of CO$_2$RR and alkaline OOR. The high anolyte pH required for OOR on the anode side results in extreme CO$_2$ reactant loss and low C$_2$ selectivity on the cathode side. Although high C$_2$ selectivity can be achieved in a flow-cell configuration under alkaline conditions, the loss of reactant CO$_2$ to carbonates results in unacceptably high operation costs. We conclude that the promise of glycerol oxidation cannot be realized in conventional CO$_2$RR systems.

Carbon monoxide reduction exhibits high C$_2$ product efficiency under highly alkaline conditions, offering compatibility with glycerol oxidation. Moreover, electrochemical conversion of the CO$_2$-to-CO step is maturing rapidly, with efficiencies greater than 90% now achieved at industrial scale. The effectiveness of the CO$_2$RR step is now limiting on the path of CO$_2$ conversion to multicarbon products.

Both OOR and OER configurations were tested in an MEA electrolyzer (Scheme 1a,b). CO was fed onto a similar copper-
coated GDL separated from the anode by an AEM. Glycerol was dissolved in the anolyte. The CORR-OOR cell provided 51% FE for C2H4 at 1.34 V (180 mA cm−2). The control case of CORR-OER provided 41% FE for C2H4 at 2.40 V (180 mA cm−2). We estimated the electrical energy input for production of one tonne of C2H4 by both approaches using the full cell voltages and Faradaic efficiency values obtained here through eqs 9−11 (Supporting Information). We found that C2H4 produced in the CORR-OER process would not be profitable based on the cost of input electricity alone (Scheme 1c). In addition, emissions associated with the electrical energy input would be 75% of the converted CO2 based on the current grid emission factor (GEF).8 With reduced energy demand, the grid electricity emissions are reduced to 33% of converted CO2 in the CORR-OOR case.

We explored C2H4 production in the CORR-OOR pair as a function of glycerol and KOH concentrations using a Pt/C catalyst loaded GDL. Figure S10 and S11 compare the gas product distribution at different glycerol and KOH concentrations, respectively. The partial current density of C2H4...
normalized by cell potential ($J_{C2H4}$/potential) at fixed current (120 mA cm$^{-2}$) provided a means of assessing performance as a function of KOH and glycerol concentrations (Figure S12). The system provided the highest C$_2$H$_4$ partial current density (37 mA cm$^{-2}$) at a low full-cell potential (1.25 V), with 4.0 M glycerol in 2.0 M KOH anolyte. However, practical application of COR-OOR will require still higher reaction rates. We sought to accelerate anode reaction kinetics by reducing mass and charge transfer resistances. With glycerol being hydrophilic, we envisioned an ideal OOR electrode to provide a hierarchical hydrophilic framework exposing the high surface area of active catalyst. A hydrophilic carbon cloth (CC) provided a three-dimensional substrate, and Pt catalyst was synthesized directly on the carbon cloth (see the Supporting Information for details). The synthesized Pt-CC electrode provides a dual-porous network comprising the CC substrate decorated with Pt nanoparticles smaller than 5 nm (Figures 1a and S13). While hydrophobic Pt/C-loaded GDL showed a sharp jump in full cell potential at 180 mA cm$^{-2}$ (Figure S10c), the Pt-CC electrode maintained a low potential up to 360 mA cm$^{-2}$. Considering the similar loading of Pt on both electrodes, the improved electrochemical performance is attributed to enhanced mass transport in the Pt-CC case. The hydrophilic macropores in the CC substrate enable mass transport through the electrode while the small Pt nanoparticles expose a large area of catalytic active sites with which to achieve high current density.

Transmission electron microscopy (TEM) analysis of the Pt-CC electrode indicates aggregates of nanoparticles smaller than 5 nm (Figures 1b and S14). Moreover, energy dispersive X-ray (EDX) mapping of the sample shows a uniform mixture of Pt and carbon (Figure 1c). A similar microporous structure was prepared for the cathode electrode by coating Cu nanoparticles (25 nm) on a hydrophobic GDL. Spherical Cu nanoparticles smaller than 50 nm can be seen in the TEM micrographs (Figure 1e,f) as well as EDX mapping (Figure 1g). TEM images shown in Figure S15 further confirm the uniform dispersion of ionomer on Cu nanoparticles. Ex situ X-ray photoelectron spectroscopy (XPS) indicates the presence of metallic Pt and Cu, at anode and cathode, respectively (Figure 1d,h).

Using the hierarchical hydrophilic anode, the CORR-OOR system could achieve current densities up to 360 mA cm$^{-2}$ without transitioning to OER. The attained OOR current density on the synthesized anode is 3-fold higher than that of a commercial Pt/C electrode (also see Figure S10). The highest C$_2$H$_4$ FE (51%) was achieved at 180 mA cm$^{-2}$ for CORR-OOR—a notable increase compared with the CORR-OER control case C$_2$H$_4$ FE (41%) (Figure 2a,b). The increased C$_2$H$_4$ FE is attributed to the enhanced kinetics of OOR compared to OER, with the OOR anode providing rapid OH$^-$ consumption and thereby accelerating the transport of OH$^-$ from the cathode. Ethanol and propanol were also detected, accounting for ~20% of the cathodic FE (Figure 2c). The remaining FEs are attributed to formate and acetate that migrated to the anode side (formate and acetate were detected in excess of these levels in the anolyte; the cumulative composition is reported in the anodic stream).

The full-cell potentials of CORR coupled with OER and OOR are compared in Figure S16. The CORR-OOR system realized over 1.0 V reduction in full-cell potential compared with CORR-OER, over the whole current density range, corresponding to a 47% reduction in cell voltage. The reduced full-cell potential decreases the required energy input for C$_2$H$_4$ synthesis from 161 GJ/tC$_2$H$_4$ in CORR-OER (Supporting Information) to 72 GJ/tC$_2$H$_4$ in the CORR-OOR process. As the most energy-intensive step in the tandem process, this improvement in CORR corresponds to a net energy input reduction approaching 50% for the full CO$_2$-to-C$_2$H$_4$ cascade.

To further assess the effect of OOR kinetics on the cell performance, we modeled the system as a one-dimensional
The CORR-OOR system exhibited a stable conversion catalyzed dehydration followed by intermolecular Cannizzaro alkaline conditions, glyceraldehyde may also undergo base-size of millions of tonnes. With a high value (1.58 (lactate in the conjugate base form) is the most viable product, increased production of OH− ions at the cathode along with faster consumption of OH− ions at the anode. The mass transport of OH− ions through the MEA limits the C2H4 partial current density, resulting in reduced C2H4 FE at current densities greater than 180 mA cm−2.

The anode side OOR products were analyzed using proton nuclear magnetic resonance (1H NMR) spectroscopy (Figure 3a). The CORR-OOR system exhibited a stable conversion efficiency during 50 h of continuous operation at 100 mA cm−2 (Figure 3b). Oxidation of glycerol on the Pt-CC electrode resulted in formation of more than 70% C3 products at 120 and 180 mA cm−2 with lactate (30–34%) and glyceraldehyde (40–41%) as the major products. Glycolate, acetate, and formate were also detected as C–C cleavage products at lower concentrations. Each product is an upgrade from glycerol input, with individual values ranging from 3- to 8-fold that of the glycerol input (Table S2). The developed CORR-OOR in this study offers a viable alternative for electrochemical synthesis of C2H4 that advances both economical profitability and carbon neutrality. CORR eliminated CO2 loss to carbonate formation which consumes the majority of energy input in CO2 electroreduction. Pairing CORR with glycerol oxidation using an alkaline anolyte enabled a synergistic effect between cathodic and anodic reactions, producing C2, products with more than 71% FE at the cathode. A hierarchical anode structure with nanoporous catalytic reaction sites enabled C3 products with 75% selectivity at the anode under industrially relevant current density of 180 mA cm−2. Replacing sluggish OER with glycerol oxidation reduced the full-cell potential by over 1 V, with an associated 49% reduction in energy required for the overall CO2-to-CO and CO-to-C2H4 process. The increasing global biofuel production is expected to provide a steady supply of low-cost glycerol while the growing demand for biodegradable polymers expands the market for renewable generated lactic acid. More generally, the dual C2 and C3 product outputs demonstrated here provide a model for paired reactions and a whole-cell approach to the efficient electroproduction of chemicals.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.1c01639.

Experimental data, electrochemical and microscopy data, SEM micrographs, gas and liquid analysis results, and Faradaic efficiency calculations (PDF)

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Author Contributions
D.S. and E.S. supervised the project. H.Y., D.S., and A.O. conceived the idea and designed the experiments. H.Y. carried out the experiments, collected and analyzed the data, and wrote the manuscript. A.O. aided with electrochemical measurements and analytical characterizations. T.A. performed the COMSOL modeling. All authors discussed the results and contributed to manuscript editing.

Notes
The authors declare no competing financial interest.

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