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# Electrolysis of ethylene to ethylene glycol paired with acidic CO<sub>2</sub>-to-CO conversion

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Electrochemical conversion of CO<sub>2</sub> into CO, ethylene, and other valuable chemicals is a promising method for carbon capture and utilisation. However, when carried out in an alkaline or neutral media, (bi)carbonate formation leads to low atom efficiency in the electrocatalytic process. In contrast, acidic conditions enable >80% CO<sub>2</sub> utilization, but there is a need to lower full-cell voltage. In this work, we paired the acidic cathodic CO<sub>2</sub>-to-CO reaction with acidic anodic ethylene-to-ethylene glycol (C<sub>2</sub>H<sub>4</sub>-to-EG) conversion for the first time. For the selective oxidation of ethylene to EG, we employed a homogeneous redox mediator ruthenium–polyoxometalate (Ru–POM) with gold-modified electrodes for the first time to facilitate the redox cycle. This resulted in enhanced selectivity and stability, achieving a faradaic efficiency (FE) of 83% for EG. At the cathode, a porous nickel single-atom catalyst drives the conversion of CO<sub>2</sub> into CO in an acidic electrolyte with an FE of 97%. The paired system operates at a full-cell voltage of 3.1 V, compared to 3.3 V for a reference system using the oxygen evolution reaction. The demonstrated system offers a promising route for reducing carbon emissions with high atom efficiency.

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## Broader context

Electrochemical CO<sub>2</sub> conversion to CO, ethylene, and other valuable chemicals is a promising route to reduce carbon emissions. However, in alkaline or neutral media, over 85% of CO<sub>2</sub> is lost to carbonate formation, while acidic systems suffer from an inefficient and energy-intensive oxygen evolution reaction (OER) at the anode. Moreover, O<sub>2</sub> as a byproduct holds little economic value (~\$25 per ton), limiting overall viability. To address these challenges, we pair CO<sub>2</sub> reduction with ethylene oxidation to ethylene glycol (EG) using a Ru-based polyoxometalate (Ru–POM) redox mediator. This strategy upgrades ethylene—a key CO<sub>2</sub> reduction product—into EG, a high-value industrial chemical used in polyesters, resins, and antifreezing. Compared to the traditional EG production process, which emits ~1.6 tonnes of CO<sub>2</sub> per tonne of EG, this method offers a low-emission alternative. Our approach combines CO<sub>2</sub> utilization with value-added anodic chemistry, enhancing energy efficiency and economic potential. This work is relevant to researchers in electrocatalysis, green chemistry, and industrial decarbonization.

## 1. Introduction

Electrochemical CO<sub>2</sub> reduction (CO<sub>2</sub>R) to valuable chemicals such as CO, ethylene and ethanol is a promising means to reduce carbon intensity.<sup>1</sup> However, when conducted in an alkaline or neutral environment, a majority of CO<sub>2</sub> is lost to (bi)carbonate formation. To address this issue, acidic CO<sub>2</sub>R methods have been developed, enabling single-pass CO<sub>2</sub> conversion efficiency, which is the percentage of CO<sub>2</sub> converted relative to the total input, to exceed 80%.<sup>2–6</sup> These acidic systems typically require ~4 V to deliver 200 mA cm<sup>–2</sup> when paired with the kinetically limiting oxygen evolution reaction (OER) (Fig. 1a).<sup>7–9</sup>

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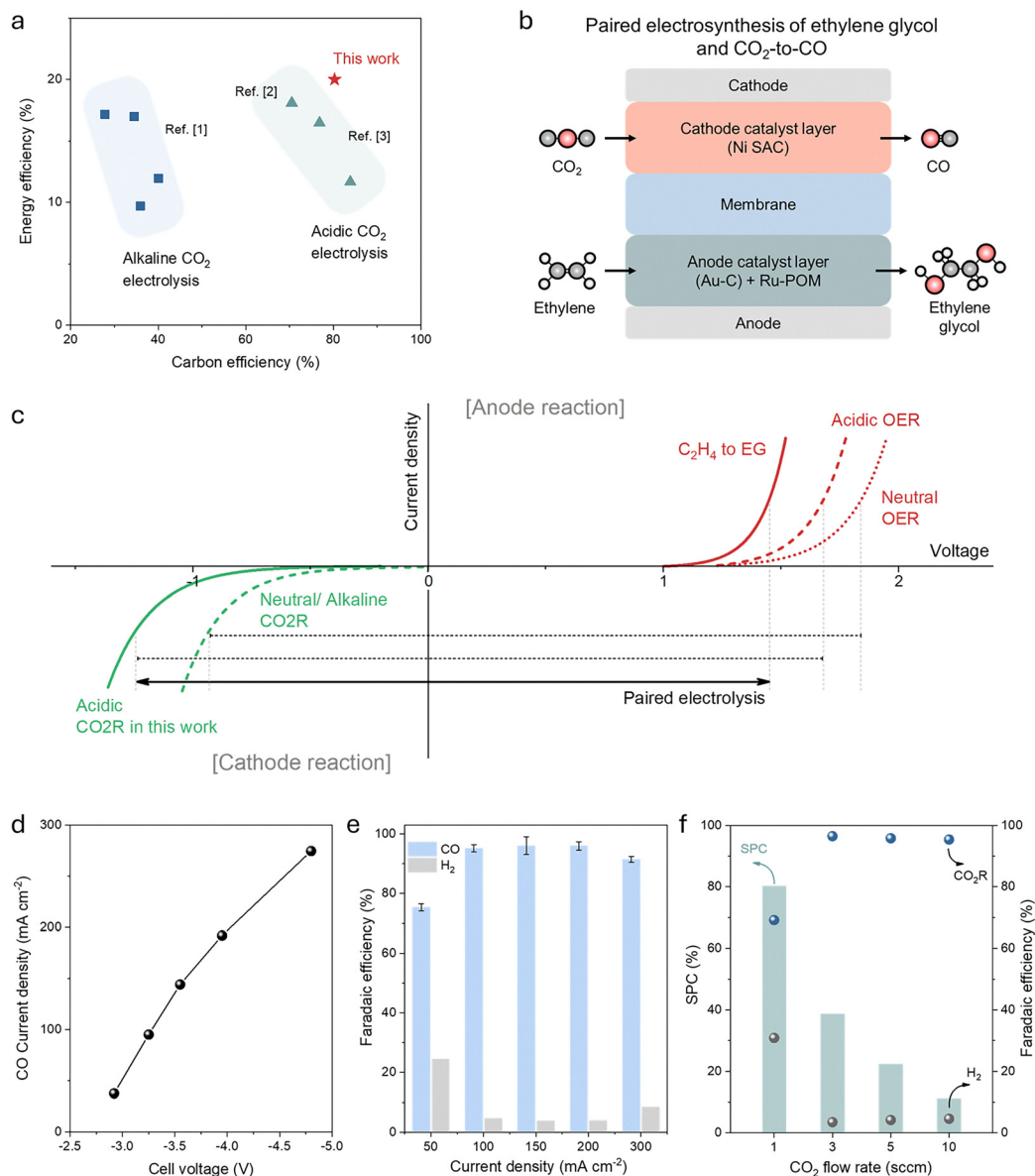
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**Fig. 1** (a) Energy efficiency vs carbon efficiency of alkaline (square) and acidic (triangle) CO<sub>2</sub>-to-CO conversions. Value achieved by this work is represented by the star symbol. (b) Schematic of the acidic CO<sub>2</sub>-to-CO conversion paired with ethylene-to-ethylene glycol electrolysis. (c) Qualitative performance comparisons of neutral and acidic reactions for unpaired and paired CO<sub>2</sub> to CO conversions. (d) Cell voltages required for acidic CO<sub>2</sub>-to-CO conversion (0.05 M H<sub>2</sub>SO<sub>4</sub> – 2.5 M KCl) at different current densities. (e) Faradaic efficiency for CO and H<sub>2</sub> on a nickel single-atom catalyst (NiSAC). (f) Single-pass CO<sub>2</sub> conversion SPC efficiency (left Y-axis) and FE (right Y-axis) as a function of CO<sub>2</sub> flow rates.

Pairing CO<sub>2</sub>R with alternative electrochemical processes presents an opportunity to increase the total kg of CO<sub>2</sub> abated per kWh of electricity.<sup>7,10,11</sup> Since O<sub>2</sub> gas is abundant with limited economic value, it is desirable to develop alternative electrochemical processes to replace the OER to increase the overall reaction profit. The production of ethylene glycol (EG) from ethylene is of particular interest since it has an annual demand of 20 million tonnes.<sup>12–15</sup> Today, the production of EG follows a two-step thermocatalytic process: ethylene (C<sub>2</sub>H<sub>4</sub>) is first epoxidized to ethylene oxide (EO) under high pressure and temperature, followed by EO hydrolysis in the presence of a strong acid. This leads to ~1.6 tonnes of CO<sub>2</sub> per tonne of EG.<sup>16</sup>

Electrochemical production of EG from C<sub>2</sub>H<sub>4</sub> is a promising alternative that could potentially improve the overall profit of the full cell and reduce the carbon intensity if achieved efficiently under mild reaction conditions, in light of its high industrial value and carbon intensity. In addition, the low thermodynamic potential for ethylene oxidation (0.6 V vs. standard hydrogen electrode (SHE)) is expected to further reduce full cell voltage compared to the traditional OER process (1.23 V vs. SHE). Furthermore, a chemical loop is potentially built if C<sub>2</sub>H<sub>4</sub> is the main product generated from CO<sub>2</sub>R or electrochemical CO reduction (COR) after further improvement on product selectivity and efficiency in the near future.

Successful demonstration includes the use of electrochemically generated hypochlorous acid (HClO), but the possibility of producing chlorinated organics is undesirable. Additionally, the high thermodynamic potential for the Cl evolution reaction (1.36 V vs. SHE) actually causes a higher full cell voltage, motivating the search for other options.<sup>17–22</sup> To date, the performance of a direct one-step electrochemical C<sub>2</sub>H<sub>4</sub>-to-EG conversion has been limited to  $J_{\text{partial}} < 20 \text{ mA cm}^{-2}$ <sup>23</sup> and a faradaic efficiency (FE) of 60–90%.<sup>15,23,24</sup>

Here, we report a paired electrolysis system (Fig. 1b) that couples C<sub>2</sub>H<sub>4</sub>-to-EG conversion using a ruthenium–polyoxometalate (Ru–POM) redox mediator with an acidic CO<sub>2</sub>-to-CO conversion with a porous nickel single-atom catalyst (NiSAC). The Ru–POM redox selectively oxidizes the C<sub>2</sub>H<sub>4</sub>-to-EG conversion with a FE of 83%, while the CO<sub>2</sub>-to-CO conversion achieved a FE of 97%. The system operates at a full cell voltage of 3.1 V, compared with 3.3 V for acidic CO<sub>2</sub>R paired with an acidic OER (Fig. 1c). We also developed a gold-modified carbon felt electrode to accelerate the Ru–POM redox cycle, thereby increasing EG productivity while protecting the carbon substrate underneath during anodic oxidation.

## 2. Results and discussion

To facilitate acidic CO<sub>2</sub>-to-CO conversion, we developed NiSAC for the cathode, with atomically dispersed Ni sites serving as active centers for selective CO production from CO<sub>2</sub>. To maximize the number of electrochemically accessible Ni active sites, a porous structure based on ~50 nm-sized Zeolite imidazolate frameworks-8 (ZIF-8) was employed,<sup>25,26</sup> an approach that addresses the limited accessibility of inner micropores. High-resolution transmission electron microscopy (HR-TEM) images and energy dispersive spectroscopy mapping showed the uniform dispersion of Ni sites on the carbon support (Fig. S1). Results from X-ray absorption spectroscopy (XAS) revealed that the Ni atoms remain atomically dispersed, with no metallic nickel or nickel oxide-based nanoparticles on the NiSAC (Fig. S2). Results from X-ray photoelectron spectroscopy (XPS) showed pyridinic nitrogen peaks in the N 1s spectra, indicating strong Ni–N bonding which is evidence for the presence of Ni atoms (Fig. S3).

We then evaluated acidic CO<sub>2</sub>R performance in a flow-cell electrolyzer with a buffered acidic electrolyte composed of 2.5 M KCl in 0.05 M H<sub>2</sub>SO<sub>4</sub> as the catholyte and 0.05 M H<sub>2</sub>SO<sub>4</sub> as the anolyte. For the optimization of the acidic CO<sub>2</sub>R performance, the cathodic CO<sub>2</sub>R was paired with an acidic OER half-reaction using an IrO<sub>x</sub>–Ti mesh anode. The current density was varied from 50 to 300 mA cm<sup>–2</sup> in a slim flow cell, and the applied full cell voltage was also varied from 2.9 to 4.8 V (Fig. 1d). The NiSAC electrode produced CO with a FE of 97% at 100 mA cm<sup>–2</sup> (Fig. 1e). The catalytic performance of NiSAC was consistent regardless of catalyst loading (from 0.6 to 2.3 mg cm<sup>–2</sup>), maintaining a CO FE of over 95% (Fig. S4). We found that increasing the pH from 0.3 to 1.0 or even 1.7 promoted the CO FE from <60% to 97% (Fig. S5). Therefore, for subsequent experiments, a pH of 1.0 was chosen for the catholyte which was

composed of 2.5 M KCl + 0.05 M H<sub>2</sub>SO<sub>4</sub>, where KCl offers cation effects to trigger CO<sub>2</sub> reduction.

Acidic electrolytes minimize carbonate formation, thus enabling increased carbon utilization compared to neutral and alkaline solutions (Fig. 1c). In principle, lowering the pH of the anolyte facilitates proton transport and addresses salt formation. However, the lower anolyte pH also decreases CO<sub>2</sub>R FE due to the faster proton transport that leads to HER. We sought to balance CO<sub>2</sub>R performance and salt formation at 100 mA cm<sup>–2</sup> via the use of 0.05 M H<sub>2</sub>SO<sub>4</sub>. Under the optimized condition, this limited salt formation and retained CO FE at above 90%. Completely avoiding salt formation is an important area for future work.

Lowering the CO<sub>2</sub> flow rate from 10 to 1 standard cubic centimeters per minute (sccm) enabled us to increase the single-pass CO<sub>2</sub> conversion (SPC) to CO from 11% to 80% at 100 mA cm<sup>–2</sup> (Fig. 1f). This is higher than that in alkaline and neutral CO<sub>2</sub>-to-CO electrolyzers, which are typically limited to < ~50%.<sup>6,27–29</sup>

We also studied the stability of NiSAC (Fig. S6). During an extended electrolysis at 100 mA cm<sup>–2</sup>, the system maintained an FE to CO of 97% over 16 h, with a slight potential shift from –3.3 to –3.5 V. Results from scanning electron microscopy (SEM) and XPS of the NiSAC after 16 h of electrolysis showed negligible changes in the electrode surface morphology (Fig. S7) and composition (Fig. S3).

For the anode development, we considered both direct (Fig. 2a) and mediated (Fig. 2b) ethylene oxidation. In each case, the competing reaction is water oxidation to O<sub>2</sub>. In direct oxidation, the goal must be to transfer the reactive oxygen intermediates associated with water oxidation – (\*OH, \*O, and \*OOH) – over to C<sub>2</sub>H<sub>4</sub> before these intermediates are fully oxidized to O<sub>2</sub>. In this case, electrooxidation is initiated by electron transfer at the catalyst surface. The thermodynamic potential for the ethylene oxidation (0.6 V vs. SHE) is much lower than that for OER (1.23 V vs. SHE). However, the actual ethylene oxidation process requires surface oxygen intermediates from water oxidation, and the slow kinetics of ethylene oxidation leads to a much higher overpotential than OER under a similar current density.<sup>15,23</sup>

Under the redox-mediated approach, the Ru–POM strategy (Fig. S8) was developed whereby Ru–POM was oxidized to an electron-deficient species, Ru–POM\*, by the anode. This, in turn, oxidized C<sub>2</sub>H<sub>4</sub>-to-EG with the recovery of Ru–POM (Fig. 2b).<sup>30–33</sup> The redox of POM also has a lower thermodynamic oxidation potential than the water oxidation,<sup>34</sup> as well as a faster kinetics than both ethylene oxidation and OER, which could decrease the actual full cell operating potential.

With OER as the competing reaction, it can be inferred that the catalyst with a high OER activity might result in a low FE for EG production. Therefore, we posited that the catalyst with a weaker O binding than the Pt group metals, with a higher redox potential than that of Ru–POM, can facilitate the oxidation of Ru–POM. To best protect the anode for Ru–POM oxidation in an acidic electrolyte, we herein designed a Au-modified carbon felt (Au/C) for the low activity of Au in OER. Compared to other anode materials such as bare carbon felt, Au-modified C-400,







