Electrosynthesis

https://doi.org/10.1038/s41929-023-00989-2

Nexus molecule outputs pure ethylene glycol

Chuan Xia

Ethylene glycol is traditionally manufactured through energy-intensive thermocatalytic processes. Now, in a marked advance, a cascade catalytic system using electrochemically synthesized H_2O_2 for ethylene oxidation has been introduced. This strategy represents a benchmark for sustainable chemical manufacturing.

As a cornerstone of industrial chemicals, ethylene glycol serves multiple functions. Not only does it find extensive application as an antifreeze agent, but it is also a critical precursor in the production of a diverse range of products such as polyester fibres, films and resins[1]. The currently dominant approach to ethylene glycol synthesis is grounded in a two-step energy-intensive process (Fig. 1a) that incorporates the generation of ethylene oxide as an integral intermediate step[2]. However, this approach suffers from limited product selectivity owing to the overoxidation of ethylene. This, in turn, culminates in considerable carbon dioxide emissions. Progress in renewable energy has sparked evolutionary advances in electrified chemical manufacturing, establishing a promising route to sustainable production of ethylene glycol under ambient conditions[3,4]. Illustratively, the electrochemical oxidation of ethylene to ethylene glycol has been successfully realized through the use of a Pd-based electrocatalyst in an aqueous electrolyte, demonstrating an alternative for ethylene glycol production at ambient temperature and pressure[5]. Nevertheless, the direct electrochemical oxidation of ethylene encounters formidable hurdles, including a limited current density (~5 mA cm^{-2}), by-product formation (formic acid, acetaldehyde, glycolaldehyde), high catalyst cost, and overoxidation to form CO_2 at high overpotentials (Fig. 1b).

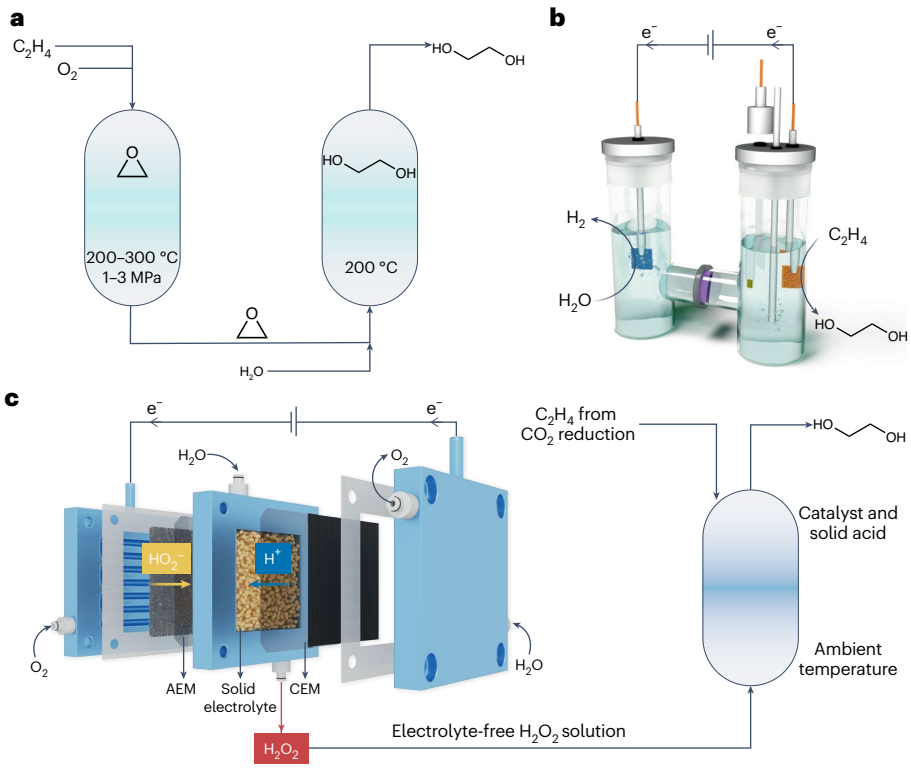

Fig. 1 | Different pathways for ethylene glycol production. a, The current industrial route, which suffers from high energy consumption and CO_2 emissions. **b**, Direct electrochemical oxidation of ethylene to ethylene-glycol can lower CO_2 emissions, but faces challenges such as low production rates due to the inevitable overoxidation of ethylene to CO_2 and other by-products at high current densities. **c**, The present cascade catalytic ethylene oxidation system. In this process, O_2 is first electrochemically converted into pure H_2O_2 solution. Subsequently, the H_2O_2 stream is introduced into a second reactor where it catalyses the direct oxidation of ethylene to pure ethylene glycol, with no other oxidation products observed. Notably, the entire process can be conducted at ambient temperature and pressure, and it only requires O_2, water and renewable electricity as feedstocks. AEM, anion exchange membrane; CEM, cation exchange membrane.

Now, writing in *Nature Catalysis*[6], Lei Wang and colleagues describe a cascade catalytic approach that demonstrates remarkable selectivity (~100%) and productivity in the conversion of CO_2-derived C_2H_4 to ethylene glycol. This strategy capitalizes on the use of electrochemically generated pure H_2O_2 as a nexus oxidant (Fig. 1c). In this work, the cascade ethylene glycol production was initially demonstrated in an H-type reactor, in which titanium silicalite-1 (TS-1) particles were simply dispersed in the cathode chamber with a continuous supply of O_2 and ethylene. By using carboxyl-functionalized carbon nanotubes as the electrocatalyst for the $2e^-$ oxygen reduction reaction, H_2O_2 was produced as the desired oxidant, resulting in a maximum ethylene glycol production rate of 0.23 mmol h^{-1}. Furthermore, they uncovered the pivotal role of the acidic electrolyte in the cascade ethylene glycol production process. Specifically, although the electrochemical H_2O_2 production rates remained similar across all three types of electrolytes (0.1 M H_2SO_4, 0.1 M K_2SO_4 and 0.1 M KOH), significant ethylene glycol production was observed exclusively in the acidic electrolyte. It was revealed that the high proton concentration in the acidic electrolyte aids the transformation of the ethylene oxidation intermediate into ethylene glycol. Additionally, the absence of alkali ions in the acidic electrolyte effectively prevents catalyst poisoning in TS-1 (ref. 7).

Wang et al. then conducted a methodical inquiry into the kinetics associated with the production and consumption of H_2O_2. Interestingly, despite the consistently high Faradaic efficiency of H_2O_2 — which reaches approximately 90% across the entire range of current densities investigated — there is an observed reduction in the overall electron-to-ethylene-glycol efficiency (ETE) as the total current density increases. Through a series of control experiments, they concluded that the decrease in ETE resulted from two factors: electrochemical over-reduction of H_2O_2 to H_2O and the self-decomposition of H_2O_2 catalysed by TS-1. To overcome these challenges, the authors proposed a modified system that incorporates a solid-acid electrolyte[8]. This innovative approach not only tackles the constrained mass transport in the H-type reactor, but also addresses the onerous and costly tasks of downstream product separation and purification from the H_2SO_4 electrolyte. Initially, when directly integrating an H_2O_2 production solid-electrolyte reactor with an ethylene oxidation reactor, it was observed that the output consisted primarily of ethylene oxide, rather than ethylene glycol. To solve this issue, a highly acidic solid electrolyte, serving a similar function to H_2SO_4, was included as a co-catalyst to enhance the efficiency of ethylene glycol production on the ethylene oxidation reactor. Under optimized conditions, this cascade reactor achieved a rate of 2.4 mmol h^{-1} for ethylene glycol production with an overall electronic efficiency of approximately 70%. By using amine-functionalized carbon nanotubes as the electrocatalyst, the production rate of ethylene glycol was further improved to around 5.3 mmol h^{-1}. The authors further demonstrated the capability of generating highly concentrated ethylene glycol solution (up to approximately 0.5 M) using a 4 cm^2 electrolyser. They have engineered a highly advanced three-compartment electrolyser that excels at ethylene oxidation, functioning effectively at both the anode and cathode. The key innovation lies in the replacement of the traditional anodic water oxidation reaction with a chloride oxidation reaction. This configuration leads to the generation of hypochlorous acid in the anode, a highly effective oxidizing agent that plays a crucial role in converting ethylene into ethylene oxide.

Finally, the researchers successfully demonstrated the production of ethylene glycol from CO_2 via a cascade catalytic system that seamlessly integrates electrocatalysis and thermocatalysis. Based on this, they conducted a preliminary techno-economic analysis and underscored the economic viability of the proposed ethylene glycol production process, with an estimated production cost of US$1,031 t^{-1}, compared with the current market price of about US$1,400 t^{-1}. The two primary cost components are electricity and separation, so this outcome becomes particularly favourable when the process uses renewable electricity sources at their currently low but attainable prices. Additionally, achieving products with high concentration is desirable as the separation cost is closely tied to the concentration of the final product.

Moving forward, by using the complementary strengths of electrocatalysis and thermocatalysis, such a cascade catalytic strategy holds great promise for more sustainable and efficient chemical transformations. Furthermore, the cascade concept could be extended to various catalytic systems, such as photocatalysis, biocatalysis and enzyme catalysis. Although promising, there are potential limitations associated with such a strategy. For instance, the inclusion of additional processes can lead to increased operational and capital costs. Additionally, when integrating decoupled systems, there may be compromises in production rates, energy efficiency and other factors. To address these challenges, a participatory design approach might be beneficial, where all the components will be considered during the system design and optimization, with immediate feedback from systems to guide component-level designs.

Chuan Xia [1,2] ✉

[1]Yangtze Delta Region Institute (Huzhou), University of Electronic Science and Technology of China, Huzhou, PR China. [2]School of Materials and Energy, University of Electronic Science and Technology of China, Chengdu, PR China.

✉e-mail: chuan.xia@uestc.edu.cn

Published online: 25 July 2023

References

1. Yue, H., Zhao, Y., Ma, X. & Gong, J. *Chem. Soc. Rev.* **41**, 4218–4244 (2012).
2. Rebsdat, S. & Mayer, D. Ethylene glycol. In *Ullmann's Encyclopedia of Industrial Chemistry* (Wiley, 2000).
3. De Luna, P. et al. *Science* **364**, eaav3506 (2019).
4. Seh, Z. W. et al. *Science* **355**, eaad4998 (2017).
5. Lum, Y. et al. *Nat. Catal.* **3**, 14–22 (2020).
6. Fan, L. et al. *Nat. Catal.* https://doi.org/10.1038/s41929-023-00977-6 (2023).
7. Ko, M. et al. *Nat. Catal.* **5**, 37–44 (2022).
8. Xia, C., Xia, Y., Zhu, P., Fan, L. & Wang, H. *Science* **366**, 226–231 (2019).

Competing interests

The author declares no competing interests.