

## ELECTROSYNTHESIS

## Towards the sustainable synthesis of ethylene glycol

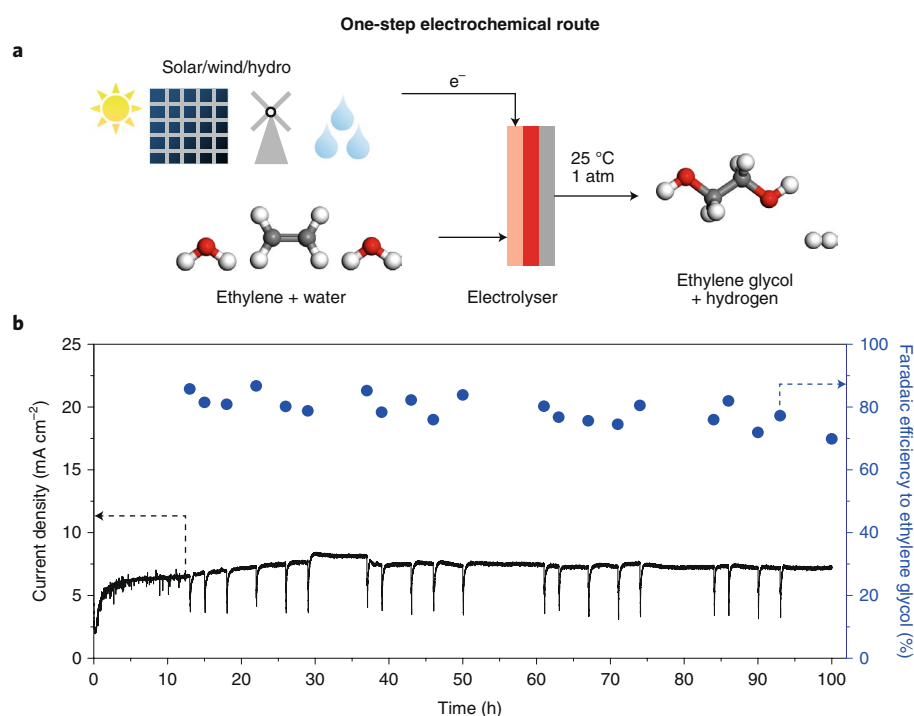
The electrochemical synthesis of high-value chemicals is still far from industrial application, mostly due to the lack of stable and efficient catalysts. Now evidence reveals that gaining a fundamental understanding of an electrochemical reaction can lead to faster development of optimal catalytic materials.

Marta C. Figueiredo

Research on the synthesis of chemicals by electrochemical techniques has increased considerably in recent years, attracting the attention of both academia and industry. The need to take serious measures to create a global independence of fossil fuel-based processes<sup>1</sup> and to lower global CO<sub>2</sub> emissions — as established in the Paris Agreement<sup>2</sup> — is particularly important regarding the synthesis of chemicals, as the chemical industry is one of the largest contributors to global greenhouse emissions. The use of electrochemical techniques offers several advantages<sup>3</sup> when compared with conventional approaches (mild temperatures, lower pressures and less waste), but the most important one is the direct use of renewable electricity to enable chemical bond formation. All of these factors, together with the rise of green electricity at lower prices in our grids, point towards a future where the use of electrochemistry for the synthesis of chemicals will not only be sustainable but also economically attractive.

Now, writing in *Nature Catalysis*, Edward Sargent and co-authors<sup>4</sup> make a step towards the development of new electrochemical processes for the synthesis of ethylene glycol (Fig. 1). Ethylene glycol is a valuable chemical that is used worldwide as an antifreeze and in the synthesis of polymers and solvents. By using a combination of electrochemical, operando characterization techniques and theoretical calculations, the researchers have developed a catalyst for the selective partial oxidation of ethylene to ethylene glycol with Faradaic efficiencies of ~80% for a period of 100 h, taking a major step towards the production of this important chemical by electrochemical means.

The researchers start by exploring the electrochemical oxidation of ethylene on palladium-based catalysts, such as palladium supported on carbon (Pd/C) and nanostructured palladium with a dendritic morphology (Pd/DNT). Pd/DNT shows



**Fig. 1 | Electrochemical synthesis of ethylene glycol.** **a**, A scheme of the pathway from renewable energy to ethylene glycol. **b**, The current density profile versus time (black line) and Faradaic efficiency towards ethylene glycol (blue circles) are shown for the 100-h continuous operation of the electrolyser at 1.1 V versus Ag/AgCl with PdAu/DNT. Credit: adapted with permission from ref. <sup>4</sup>, Springer Nature Ltd.

the best results and selectively generates ethylene glycol with a Faradaic efficiency of up to ~60% after a certain activation time, where the efficiency increases over time. A sequence of well-defined characterization and operando experiments, such as Raman spectroscopy, X-ray absorption spectroscopy, X-ray photoelectron spectroscopy and extended X-ray absorption fine structure were performed on a series of catalysts with different morphologies to determine the activation process and the origin of the higher activity. Interestingly,

the researchers observe that Pd/DNT and palladium oxide (PdO•H<sub>2</sub>O) both present high selectivity for ethylene glycol and an activation period despite their very different morphologies. The results suggest that intermediates such as \*OH probably promote ethylene glycol formation when compared with other possible products and catalysts such as Pd/DNT and PdO•H<sub>2</sub>O, show higher coverages and more favourable OH binding energies. The higher coverage of \*OH might be related to the dynamic surface reconstruction, which leads to an

evolution in time of the \*OH binding energy. The researchers also use density functional theory to explore a reaction mechanism in which lattice OH in PdO serves as a direct reaction intermediate for the formation of ethylene glycol, together with the possibility of using metallic dopants to optimize the \*OH binding energy towards improving the selectivity further. From the computational screening of ten different metals, gold was identified as the most promising dopant by not only showing desirable OH adsorptions, but also because it favours ethylene glycol desorption from the surface. Motivated by these findings, the researchers synthesize and test gold-doped palladium catalysts with different compositions. A remarkable gold-doped palladium catalyst (3.2 at% Au) showing ~80% Faradaic efficiency was obtained with this approach. Moreover, this catalyst kept its selectivity for a period of 100 h with no substantial loss of performance, mass or composition change during this prolonged period of operation.

Overall, this work demonstrates that the combination of electrochemical experimental techniques and surface characterization with well-defined theoretical calculations leads to fast

advances on the development of catalysts for synthesis reactions. The authors were able to use this approach to optimize the catalyst surface to hydroxyl binding energies that are favourable to the partial oxidation of ethylene. In fact, this type of methodology has been used for many years for reactions related to energy; for example, the hydrogen evolution or oxygen reduction reactions<sup>5</sup>. However, they are not so frequently used for electrosynthesis reactions, as normally they involve more complex molecules, many reaction intermediates and a wider variety of products. Moreover, electrochemistry and electrocatalysis research has been more focused on energy conversion reactions than synthesis reactions; for example, the oxidation of ethylene has been investigated already for more than half of a century on metal electrodes such as palladium, iridium, gold and rhodium<sup>6</sup>. Yet, the motivation for that study was the full conversion of ethylene to CO<sub>2</sub> for electrochemical energy conversion.

It becomes clear that more efforts will be needed to understand and optimize electrochemical reactions to produce high-value chemicals. Nevertheless, we should bear in mind that low-cost materials should

be used (expensive noble metals should be replaced by more abundant and economical catalysts) and the reactions should also be optimized in relevant conditions to make electrochemical solutions attractive to industrial processes, particularly to achieve the high current densities required at the industrial level. By understanding the reaction mechanisms, identifying active sites and further developing highly active catalysts, we will be one step closer to making electrochemistry a sustainable technology for chemical production. □

**Marta C. Figueiredo**

*Laboratory of Inorganic Materials and Catalysis, Eindhoven University of Technology, Eindhoven, the Netherlands.*

*e-mail: m.c.costa.figueiredo@tue.nl*

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#### References

1. Chu, S. & Majumdar, A. *Nature* **488**, 294–303 (2012).
2. Horowitz, C. A. *Int. Leg. Mater.* **55**, 740–755 (2016).
3. Mçhle, S. et al. *Angew. Chem. Int. Ed.* **57**, 6018–6041 (2018).
4. Lum, Y. et al. *Nat. Catal.* <https://doi.org/10.1038/s41929-019-0386-4> (2020).
5. Chen, Y. et al. *Nat. Commun.* **9**, 5422 (2018).
6. Dahms, H. & Bockris, J. O. J. *Electrochem. Soc.* **111**, 728–736 (1964).