

CO₂-to-CH₃OH Cascade Electroreduction: Molecular Catalyst Can Do It

Chengyu Liu^a, Junming Shao,^a Dorian Joulié,^a Marc Robert^{a,b}

^a Université Paris Cité, Laboratoire d'Electrochimie Moléculaire, CNRS, F-75006 Paris, France.

^b Institut Universitaire de France (IUF), F-75005 Paris, France.

Methanol is a high value-added alcohol widely used in industry. [1] Converting greenhouse-gas CO₂ into fuels using electricity is a promising solution to store renewable energies at very large scale. [2] Molecular electrocatalysis plays a significant role in CO₂-to-methanol conversion since molecular catalysts have controllable and well-defined active sites, generally resulting in better selectivity than solid materials. [3] However, electroreducing CO₂ beyond 2 electrons with a molecular catalyst remains a high challenge.

Recently, we have shown that cobalt phthalocyanine (CoPc) is highly active for CO₂-to-CO electro-conversion with a Faradaic Efficiency (FE) > 90%. [2] We have also discovered that using CO as a substrate instead of CO₂ led to the production of methanol when using the same CoPc catalyst. [4,5]. It opens the way to a cascade, efficient process with production of CO first and then its reduction into methanol. We have achieved a FE of 97% for CO₂-to-CO production with a current density of 600 mA/cm² in a flow cell. The system maintained a FE higher than 90% for more than 45 min with 500 mA/cm² current density and over 10 h at 200 mA/cm². Furthermore, we have successfully obtained a FE of 31% with 90 mA/cm² total current density for CO-to-methanol conversion, an excellent starting point toward high performances. Our recent results will be discussed. In particular, the reasons why CO₂ mainly produces CO, while CO itself could be transformed in CH₃OH will be uncovered.

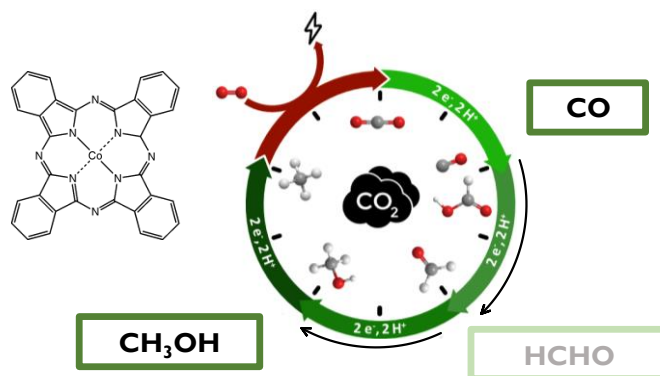


FIGURE: CASCADE CO₂ AND CO ELECTROREDUCTION TO METHANOL WITH A COBALT PHTHALOCYANINE CATALYST.

REFERENCES

1. Wu, Y.; Jiang, Z.; Lu, X.; Liang, Y.; Wang, H. *Nature* **2019**, 575, 639.
2. Wang, M.; Torbensen, K.; Salvatore, D.; Ren, S.; Joulié, D.; Dumoulin, F.; Mendoza, D.; Lassalle-Kaiser, B.; Işci, U.; Berlinguette, C. P.; Robert, M. *Nat. Commun.* **2019**, 10, 3602.
3. Ren, S.; Joulié, D.; Salvatore, D.; Torbensen, K.; Wang, M.; Robert, M.; Berlinguette, C. P. *Science*, **2019**, 365, 367.
4. Boutin, E.; Wang, M.; Lin, J. C.; Mesnage, M.; Mendoza, D.; Lassalle-Kaiser, B.; Hahn, C.; Jaramillo, T. F.; Robert, M. *Angew. Chem. Int. Ed.* **2019**, 58, 16172.
5. Boutin, E.; Merakeb, L.; Salamé, A.; Chatterjee, T.; Robert, M. *Chem. Eur. J.* **2022**, e202200697.