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Kristian Torbensen, Benjamin Boudy, Dorian Joulié, Niklas von Wolff, Marc Robert. Emergence of CO<sub>2</sub> electrolyzers including supported molecular catalysts. *Current Opinion in Electrochemistry*, 2020, 24, pp.49-55. <10.1016/j.coelec.2020.07.001>. <hal-03004869>

**HAL Id: hal-03004869**

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Submitted on 13 Nov 2020

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# Emergence of CO<sub>2</sub> electrolyzers including supported molecular catalysts

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## Abstract

With access to cheap, sustainable electricity, electrocatalysis is a promising technology for converting electric power into storable chemical fuels or value added chemical compounds. This has sparked the development of electrocatalysts that need to operate at high product selectivity and high energy efficiency. Electrocatalytic alcohol oxidation, oxygen activation, nitrogen and carbon dioxide reduction are examples of reactions with a huge industrial potential. Notably, electrocatalytic reduction of carbon dioxide has recently developed as a favourable pathway to convert this greenhouse gas into value added chemicals and fuels. Earth abundant metals stabilized by carbon/nitrogen macrocycle ligands are well-known efficient and selective catalysts for the electrochemical reduction of CO<sub>2</sub> in homogeneous conditions. Recently, such catalysts have also been used in supported conditions and implemented in flow cell electrolyzers, showing promising performances. This review provides a synopsis for the evolution of CO<sub>2</sub> electrolyzers employing molecular catalysts.

## Keywords

CO<sub>2</sub> catalysis, molecular catalysts, flow cells, electrolyzers.

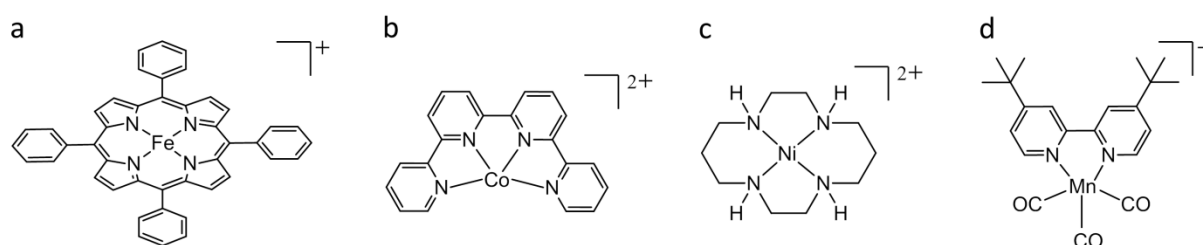
## Introduction

Emission of carbon dioxide (CO<sub>2</sub>) to an alarming atmospheric level has driven the search for materials capable of catalysing the CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR). Combined with renewable energy, the electrocatalytic conversion of CO<sub>2</sub> is an appealing method for storing energy in the form of carbon-based fuels (e.g. methane, methanol and ethanol),[1] or for generating commodity chemicals (e.g. carbon monoxide, formic acid, ethanol and ethylene).[2, 3] With power-to-X approach employing CO<sub>2</sub> electrolyzers, ideally situated at local emission sources,

such renewable energy driven CO<sub>2</sub> conversion will help mitigating CO<sub>2</sub> emission and in addition generate valuable chemical feedstocks. With more and more countries taxing CO<sub>2</sub> emission (currently the tax per emitted tonne of CO<sub>2</sub> is around 150 € in many EU countries, a number that will likely increase in the future),[4] there is a growing economic incentive for the industry and governments to invest in the development of CO<sub>2</sub> electrolyzer plants. However, environment friendly electro-materials with high efficiencies are a prerequisite. Regarding the efficiency criteria, there is a consensus that electrolyzers must operate at current density >200 mA cm<sup>-2</sup>, with the area measure referring to the geometric surface of the electrolyzer cathode.[5-7] Until recently, this value has only been approached with copper or precious metal catalysts such as silver and gold employed in gas diffusion CO<sub>2</sub> electrolyzers (see Table 1 for a summary of the state-of-the-art metrics). To reach higher performances, with respect to both current density and product selectivity, thorough mechanistic studies of the electrocatalytic CO<sub>2</sub>RR are necessary. However, metallic coatings and nanoparticles typically include different grain boundaries, crystal defects, oxygen derived species and various open facets exposed to the reacting CO<sub>2</sub>. [8, 9] To elucidate the structure-activity relationship of such complex surfaces, one must know in detail what are the active sites and the density of states responsible for the electrocatalytic CO<sub>2</sub>-to-product conversion. *Operando* characterization methods are developing fast, albeit a tedious task regarding the nanometric scale of the active sites combined with beam attenuation in the electrolyte solution in operating electrolyzers.[10, 11]

### Molecular catalysts provide well-defined and tunable reaction centres

When discrete molecules are employed as catalysts, mechanistic studies become more accessible. With activated molecules being all identical, catalytic activity would result in a characteristic response. Solution based spectro-electrochemical methods, cyclic voltammetry (CV) and preparative electrolysis have proven powerful tools for investigating



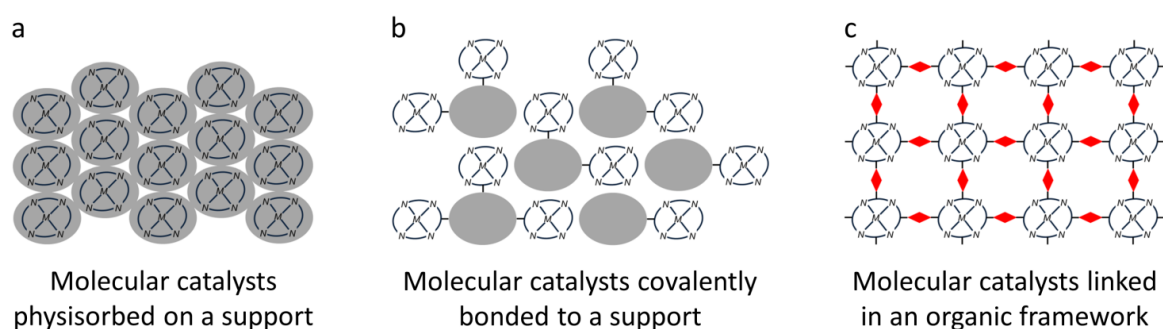
**Figure 1.** Selective electrocatalysts for the 2e<sup>-</sup> reduction of CO<sub>2</sub>. (a) Iron tetraphenyl porphyrin, (b) Cobalt quaterpyridine, (c) Nickel cyclam and (d) Manganese triscarbonyl di-*tert*-butyl bipyridine.

structure-activity relationship of various molecular catalysts in homogeneous conditions.[12-14] Using these relatively easy to implement electrochemical methods, catalytic Tafel plots relating the turnover frequency (TOF) to the applied overpotential can be obtained, providing a benchmark method for quantifying the catalytic activity and enabling comparison between different metal centres and ligand structures.[15] The most active molecular catalysts reported share a metal center coordinated to a tetradentate nitrogen-donor based ligand, such as porphyrins, phthalocyanines, polypyridines and cyclams, some examples being shown in Figure 1.[16-22] Further insight on homogenous electrocatalyzed CO<sub>2</sub>RR using molecular catalysts can be found in recent reviews.[2, 3, 23]

Albeit homogeneous conditions are appropriate for deciphering the intrinsic activity of molecular catalysts, there are several barriers toward high substrate-to-product conversion efficiency. Main limitations consist in catalyst and substrate mass transfer to the electrode, and catalyst solubility which constrains the choice of electrolyte solution (e.g. few catalysts are soluble in water). Immobilization of the catalyst onto a conductive material can help solving these issues.

### Supported molecular catalysts for the CO<sub>2</sub>RR, an emerging approach with remaining challenges

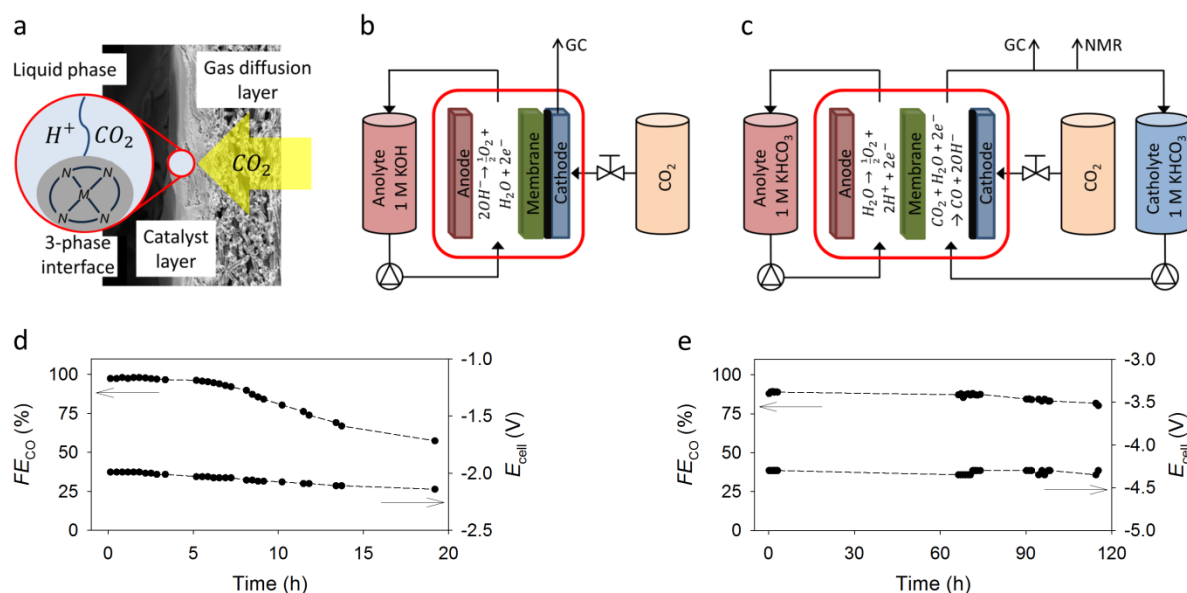
The main strategies for catalyst immobilization are outlined in Figure 2.[24] They include physical adsorption, chemical bonding and integration into 3-D frameworks. Physical adsorption occurs *via*  $\pi$ - $\pi$ , Van der Waals or electrostatic interactions between the molecular catalyst and the conductive support. With most reported molecular catalysts bearing conjugated organic ligands,  $\pi$ - $\pi$  interactions are advantageous for immobilization on conjugated and



**Figure 2.** Strategies for the immobilization of molecular catalysts on conductive supports. (a) Physisorption via catalyst-support interactions, (b) chemisorption via catalyst-support linkage and (c) integration of the catalyst in a conjugated organic framework.

conductive support materials such as carbon nanotubes,[18] graphene[25] and carbon black particles.[26] Direct chemical bonding (or covalent grafting) of the catalyst to the support has been investigated, such as phosphonate linkage to a metal oxide[27, 28] or via diazonium and amide chemistry.[29] Such approach was developed by Zhu et al.,[30] for grafting a Co protoporphyrin at carbon nanotubes through covalent linkage between the support and the cobalt atom of the complex. It led to a current density for CO<sub>2</sub> reduction in an H-cell close to the substrate mass transfer limiting value (*vide infra*). In comparison with homogeneous conditions, enhanced catalytic activity upon catalyst immobilization has been observed in some cases.[31]

Integration of the catalyst into metal organic frameworks is another strategy providing porous materials with electronically addressed well-defined catalytic centres, although conductivity of such materials remains an issue.[32-35] The above mentioned examples have been beneficial in establishing a better comprehension of the CO<sub>2</sub>RR in supported conditions and for the development of catalytic materials,[36] but mechanistic studies remain scarce and need to be vigorously developed. Additional difficulties toward this goal arise from the fact that only a fraction of the supported catalysts is active within films (the exact active surface concentration is not easily assessed). Moreover, the exact degree of electronic interaction between the molecules and the conductive support may vary from weak to strong coupling which may



**Figure 3.** (a) Schematic representation of the 3-phase (solid-liquid-gas) reaction interface in a gas diffusion electrode (GDE). (b) Sketch of a zero-gap electrolyzer without catholyte flow. (c) Sketch of an electrolyzer with both anolyte and catholyte flow. (d and e) Stability test of the cobalt phthalocyanine catalyst CoPc at constant current density of 50 mA cm<sup>-2</sup> in a zero-gap electrolyzer and in a flow cell electrolyzer, respectively.

impact both the catalytic activity and mechanisms. Practical applications are also still limited. Due to the low solubility of CO<sub>2</sub> in aqueous media (~34 mM at 298 K and 1 atm.), semi-infinite boundary diffusive models predict a limiting current density of ~35 mA cm<sup>-2</sup> for CO<sub>2</sub> conversion at planar electrodes.[37]

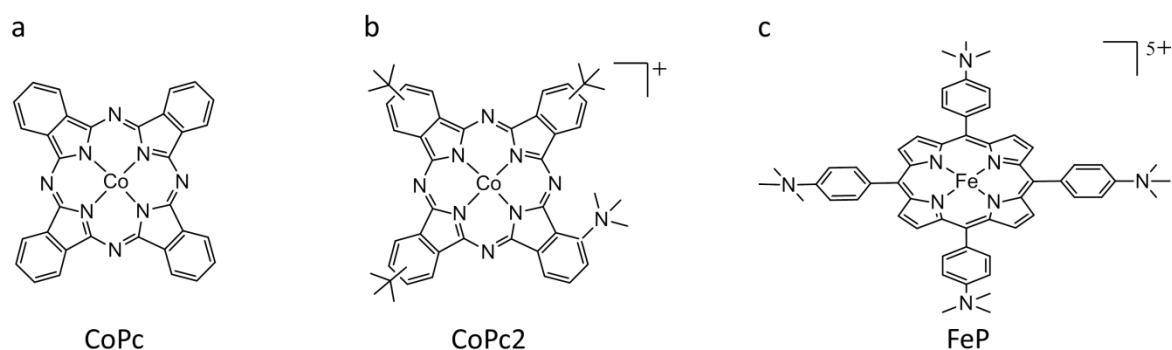
As mentioned in the introduction, electrolyzers mounted with vapour-fed gas diffusion electrodes (GDEs) and employing solid state precious metal catalysts are now reaching commercially relevant current densities for the CO<sub>2</sub>RR. Such performance was made possible by increased mass transfer in the gas phase combined with a high density of catalytic sites at the 3-phase interface in the GDE, as illustrated in Figure 3a. Taking inspiration from such design may provide a route for implementing molecular catalysts made of earth abundant elements in electrolyzers meeting commercial requirements.

### **Illustrative advances and opportunities in using supported molecular catalysts in CO<sub>2</sub> electrolyzers**

The use of molecular catalysts such as porphyrins and phthalocyanines at gas diffusion electrodes has been pioneered in the 80's and 90's, with current densities reaching a few tens of mA cm<sup>-2</sup>. [38-40] Implementation of commercially available cobalt phthalocyanine (CoPc, Figure 4a) in a zero-gap electrolyzer was recently reported (Figure 3b). [41] The GDE employed was manufactured by spray coating an ink comprising carbon black supported CoPc onto hydrophobic carbon paper, and subsequently deposited at an anion exchange membrane. With a constant flow of humidified CO<sub>2</sub> to the GDE, performances (Faradaic efficiency for CO (FE<sub>CO</sub>) and cell potential) were evaluated at current densities ranging from 25 to 200 mA cm<sup>-2</sup>. FE<sub>CO</sub> >95% was maintained at current densities up to 150 mA cm<sup>-2</sup>, for which the cell potential was 2.43 V (energy efficiency (EE) of 52%). At higher current densities, FE<sub>CO</sub> dropped rapidly, reaching 60% at 200 mA cm<sup>-2</sup>. Such decrease is likely a consequence of the generation of hydroxide ions within the GDE (*vide infra*). The stability of the CoPc catalyst in the zero-gap electrolyzer was investigated at a current density of 50 mA cm<sup>-2</sup>. As shown in Figure 3d, FE<sub>CO</sub> could be maintained above 90% for more than 8 hours, corresponding to >4.000 catalytic cycles (CCs) for each active site. Hereafter, the FE<sub>CO</sub> dropped quite rapidly. Hereafter, a gradual decrease reaching ~60% in the FE<sub>CO</sub> was observed. Lack of long term stability in this zero-gap configuration was mainly ascribed to the formation of potassium carbonate on the cathode flow plate, obstructing the free flow of CO<sub>2</sub> to the GDE. This precipitation occurs when potassium ions cross the membrane from the anodic side and react with the carbonate, the latter being formed in large amounts with increasing current density.[42] Initial performance could be

regenerated after disassembling the electrolyzer and washing the precipitated salt, indicating that no molecular degradation of the catalyst had occurred. This was further confirmed by incorporating the GDE in a flow cell electrolyzer with a continuous flow of an electrolyte solution (0.5 M NaHCO<sub>3</sub>) between the GDE and the membrane (Figure 3c). In such a configuration, a FE<sub>CO</sub> above 80% was maintained for >100 hours at a current density of 50 mA cm<sup>-2</sup> (corresponding to ~16000 CCs), with no significant change of FE<sub>CO</sub> and cell potential (Figure 3e). In this configuration, hydroxide ions are continuously removed by the electrolyte solution. However, this type of electrolyzer runs at lower EEs, due to an increased ohmic cell resistance.

CV studies of a cobalt phthalocyanine bearing one trimethyl ammonium group and three *tert*-butyl groups appended on the phthalocyanine macrocycle (CoPc2, Figure 4b) showed an ~25% increase in the catalytic activity towards CO<sub>2</sub>-to-CO conversion compared to CoPc.[43] It was mainly ascribed to the through-space stabilizing effect on the Co(I)-CO<sub>2</sub><sup>-</sup> adduct exerted by the positive charge on the quaternary ammonium appended to the macrocycle, as previously reported for an iron porphyrin.[16] CoPc2 was incorporated at a GDE which was inserted in a flow cell configuration using 1 M KOH as electrolyte solution. With a catalyst amount of only 0.2 mg cm<sup>-2</sup>, a partial current density for CO (*j*<sub>CO</sub>) of 112 mA cm<sup>-2</sup> (with 96% selectivity and an overpotential (*E*<sub>electrode</sub> - *E*<sup>0</sup><sub>CO<sub>2</sub>/CO</sub>) of 610 mV) was maintained for 3 hours. Each catalyst site endured 29000 CCs providing a turn over frequency of 2.7 s<sup>-1</sup>. At an overpotential of 810 mV, a *j*<sub>CO</sub> of 165 mA cm<sup>-2</sup> was reached (selectivity of 94%), matching state-of-the-art Ag based catalysts so far reported with respect to both current density and CO selectivity. Stability test at a current density of 75 mA cm<sup>-2</sup> provided an average selectivity of 94% for more than 10 hours. Post-electrolysis examination of the GDE (Co K-edge XANES spectroscopy) showed no degradation of the catalyst.



**Figure 4.** (a) Cobalt phthalocyanine (CoPc), (b) substituted cobalt phthalocyanine (CoPc2), (c) substituted tetraphenyl iron porphyrin (FeP).

Employing a cyano substituted CoPc adsorbed on carbon nanotubes, deposited at a GDE and inserted in a flow cell, Lu et al.[44] obtained a  $j_{\text{CO}}$  of 31 mA cm<sup>-2</sup> with a  $\text{FE}_{\text{CO}}$  of 94% (560 mV overpotential). A maximum  $j_{\text{CO}}$  of 82 mA cm<sup>-2</sup> was reached, with a  $\text{FE}_{\text{CO}}$  of ~50%. Further increase in the total current density ( $j_{\text{total}}$ ) resulted in hydrogen production mainly. At  $\text{FE}_{\text{CO}}$  of ca. 90% and at a current density close to 40 mA cm<sup>-2</sup>, performances were maintained during 10h.

**Table 1.** Metrics for state-of-the-art CO<sub>2</sub>-to-CO metal and supported molecular catalysts.

Catalyst/ support	Main product and partial current density (mA cm <sup>-2</sup> )	FE (%)	E (V vs RHE)	Electrolyte	Ref.
Ag/PTFE <sup>a</sup> grid	CO/150	90	-0.7	1 M KOH	[47]
Au/MWCNT <sup>b</sup>	CO/158	85	-0.55	2 M KOH	[48]
Cu/CP <sup>c</sup>	C <sub>2</sub> H <sub>4</sub> /473	63	-0.67	3.5 M KOH <sup>d</sup>	[49]
Ni SA/CF <sup>e</sup>	CO/308	88	-1.0	0.5 M KHCO <sub>3</sub>	[50]
CoPc2/CNP <sup>f</sup>	CO/165	94	-0.92	1 M KOH	[43]
FeP/CNP <sup>f</sup>	CO/152	98	-0.59	1 M KOH	[45]

<sup>a</sup> Polytetrafluoroethylene. <sup>b</sup> Multi-walled carbon nanotubes. <sup>c</sup> Carbon paper. <sup>d</sup> Includes 5 M KI.

<sup>e</sup> Single atom catalysts at carbon fiber. <sup>f</sup> Carbon nanoparticles.

In addition to tuning the catalyst structure, various parameters have been shown to influence cell performance. Using a substituted iron porphyrin (FeP, Figure 4c) based GDE, the cell temperature ( $T_{\text{cell}}$ ) played a significant role on the catalytic performance.[45] At neutral pH (CO<sub>2</sub> saturated 0.5 M NaHCO<sub>3</sub> electrolyte solution), a 39% current density increase was obtained by increasing  $T_{\text{cell}}$  from 24 to 40 °C without compromising the CO selectivity. At 40 °C, a current density of 50 mA cm<sup>-2</sup> was maintained for 3 hours with an average CO selectivity as high as 98.6%. In addition, the overpotential was lowered by 300 mV compared to that needed to achieve the same current density at 24 °C, illustrating the positive impact of such moderate temperature increase. As it has been shown for solid metal based catalysts,[46] the electrolyte cation size has a significant impact on the electrochemical CO<sub>2</sub>RR. Larger cations such as Cs<sup>+</sup> induce a higher surface charge density at the cathode and favour the CO<sub>2</sub>RR with stronger CO<sub>2</sub> affinity for the electrode surface. The same effect was observed for FeP immobilized on a carbon support in a flow cell with various bicarbonate species. At a fixed current density of 50 mA cm<sup>-2</sup>, a significant lowering of the overpotential (and hence an increased energy efficiency) was observed with increasing cation size in the order Cs<sup>+</sup> > K<sup>+</sup> > Na<sup>+</sup> as well as concomitant increase of selectivity. In alkaline conditions (1 M KOH), this



catalyst displayed promising metrics. At 470 mV overpotential, a current density of 155 mA cm<sup>-2</sup> was obtained with a CO selectivity >98%, better than noble metal catalysts performances.[47] At 50 mA cm<sup>-2</sup>, a remarkably low overpotential of 120 mV was maintained over 3 hours, with 99.8% CO selectivity and 57% EE, with only hydrogen as a trace by-product.

## Conclusions

Molecular catalysts implemented in CO<sub>2</sub> electrolyzers have shown promising performances, comparable to those of solid state precious metals. Their unexpected ability to maintain high selectivity at high rates for CO<sub>2</sub>-to-CO conversion opens new perspectives, although several aspects need to be addressed in order to meet industrial demands, in particular regarding long term stability at high current densities. Mechanistic studies so as to understand the exact catalytic mechanisms and degradation pathways are, in combination with engineering efforts to overcome cathode blockage, key to improve electrolyzer performances. Furthermore, turnover frequencies so far obtained in flow cells are still several orders of magnitude lower than the values reported for the same catalysts in homogeneous conditions. Better control and understanding of catalyst insertion and dispersion within GDEs is a pre-requisite to increase performances, since it may lead to optimization of both electronic addressability and substrate interaction at the catalytic sites. Reported results for the CO<sub>2</sub>-to-CO conversion will hopefully stimulate the development of improved CO<sub>2</sub> electrolyzers involving molecular catalysts, not only for CO production but also to get more reduced products such as methanol and methane, as well as C<sub>2</sub> and C<sub>2+</sub> species.

## Acknowledgement

Partial financial support from Air Liquide and from the Institut Universitaire de France (IUF) are gratefully acknowledged.

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