# SELECTIVE ELECTROCHEMICAL REDUCTION OF $CO_2$ TO HIGH VALUE CHEMICALS

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**Project Coordinator**: Dr. Brian Seger - DTU

## DELIVERABLE REPORT

| 2.1 – REPORT ON SITE DENSITY AND TOF OF BENCHMARK CATALYSTS | |
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| DISSEMINATION LEVEL | | |
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| **D** | *Demonstrator* | |
| **O** | *Other* | |

| SUMMARY | |
|---|---|
| **Keywords** | *Benchmarking, CO2 to CO, Active site density (SD), turnover frequency (TOF)* |
| **Abstract** | The metal-nitrogen functionalized carbon (M-N-C) is a promising alternative for electrochemical $CO_2$ reduction (ECO2R) to CO, and the metal-nitrogen (M-Nx) motif serves as the active site. In this WP, our target is to enhance CO evolution reactivity on novel M-N-C catalysts. Thus, in the catalyst development scenario, the intrinsic turnover frequency (TOF) and the extrinsic active site density (SD) are taken as the critical activity-relevant descriptors. In our WP, we select the M-Nx as the effective functional motif for ECO2R (holding promising TOF and selectivity) and improve its SD in our synthesized catalysts. An increased SD and the subsequently evolved CO activity could be achieved in our H-cell performance screening. |
| **Public abstract for confidential deliverables** | TOF and SD are two key descriptors in evaluating the single-site M-N-C catalysts for their ECO2R performance. In this WP, we improved the TOF and SD in our studied M-N-C candidates and deconvoluted their catalytic impacts. |

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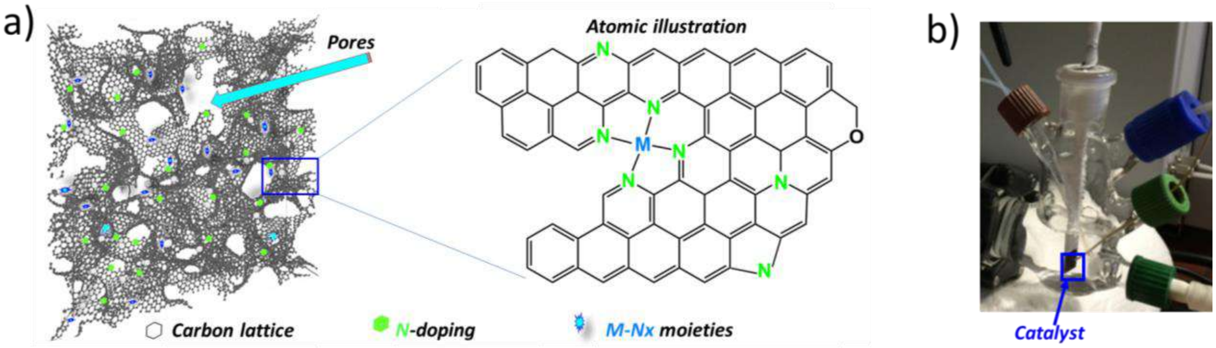
# SITE DENSITY AND TOF OF BENCHMARK CATALYSTS

## CONTENT

# 1 INTRODUCTION

The carbon-based M-N-C catalyst poses a non-noble alternative for electrochemical $CO_2$ reduction (ECO2R). The coordinative metal-nitrogen (M-Nx) motif is believed to be effective for this electrochemical conversion, yielding CO as the primary product. In this work package (WP2), TUB's task is to design, synthesize, and characterize the M-N-C candidates under DTU's theoretical guidance (D2.2), and the target is to scale up and evolve their ECO2R performance at the industrial relevant level. In this deliverable (D2.1), we report the experimental evaluation of our selected M-N-C catalysts benchmark for ECO2R to CO. A commercial Ag nanoparticle (D: 4~7 um, Alfa-Aesar, 011402) is deployed as the reference.



**Scheme 1.** a) Structural and atomic illustration of our studied M-N-C catalysts. b) Our H-cell for ECO2R performance screening.

The aspect of M-N-C material is the coordination of the metal single-site, nitrogen ligands, and the carbon sheet. Scheme 1a presents its structural and atomic illustrations. The graphene-like carbon-host provides the prominent architecture and charge transfer (inactive for ECO2R), whereas the embedded M-Nx moieties are catalytically responsible for ECO2R.[1] Thus, as our initial viewpoint, we propose the ECO2R performance relies on two crucial factors.

i) The intrinsic activity: the Turnover-Frequency (TOF) on one specific M-Nx site;
ii) The active sites amount: the Active-Site-Density (SD, sites amount per unit mass)

Thus, in this WP, we will experimentally pre-select the useful M-Nx sites for ECO2R, evaluate their TOF, and improve the SD using our synthesis protocols. To obtain the real reaction kinetic of our selected/synthesized catalysts by de-coupling mass transport limitations, we performed the ECO2R performance screening in regular liquid H-cell (shown Scheme 1b).

# 2 SCOPE

In D2.1, DTU predicted the ECO2R activity of M-N-C catalysts by taking into account the *CO2 and *COOH binding. Overall, the comprised metal single-site and relevant chemical/physic states (coordination environmental, spin state) play the dominant role in the intrinsic TOF. However, limited by the state-of synthesis strategies and characteristic methodologies, selectively preparing the M-N-C with well-defined fine-structure remains an enormous challenge.

To experimentally address and evaluate the intrinsic TOF and extrinsic SD of SELECT-CO2 M-N-C benchmark catalysts, we split our experimental work into two research thrusts:

1) Molecular M-Pc based catalysts;

The Pc family candidates possess a well-defined coordinative M-N structure. By substrating the molecular M-Pc on conductive CNT, a promising ECO2R performance could be reached. Moreover, we can accurately control the substrated M-Pc amount (SD) in this protocol; therefore, the relation between the intrinsic activity (TOF) and the transition metal single-sites could be mapped.

2) Solid pyrolyzed M-N-C catalysts upon the pre-selection in scenario 1);

As the takeaway of the scenario above, the M1-Pc- and M5-Pc- based catalysts are verified to be selective for CO evolution. Thereby, we perform our synthesis (involving structure formulation, pyrolysis, and acid-leaching) to build a porous structure, improving the SD in those as-synthesized catalysts. Furthermore, to address the extrinsic activity (SD per unit mass) of newly synthesized candidates, a combination of characteristic strategies, including Cryo-CO-chemisorption, $N_2$-physisorption (BET), X-ray photoelectron spectra (XPS), X-ray absorption spectra (XAS), etc., have been implemented.

# 3 DISCUSSION

## 3.1 Molecular M-Pc derived catalysts

In this scenario, we focus on M-Nx motifs and evaluate their relevant intrinsic activity (TOF). We deploy the M-Pc molecules as active sites. The typical cyclic motif lacks charge conductivity, thus performs negligible ECO2R. To overcome this shortage, additional conductive CNT was used as the substrate. The doping of M-Pc on CNT was mixed and stirred in a suspension for 24 hours. With this protocol, a 100% utilization of the molecular M-Pc could be expected.[2] In this section, M-Pc and CNT's mass ratio is kept constant in all synthesis protocols. Accordingly, the SD in this benchmark could be precisely held around 60 nmol/mg. The ECO2R performance was monitored in a typical liquid H-cell at low applied potential (from CO onset) to trace the true kinetics.

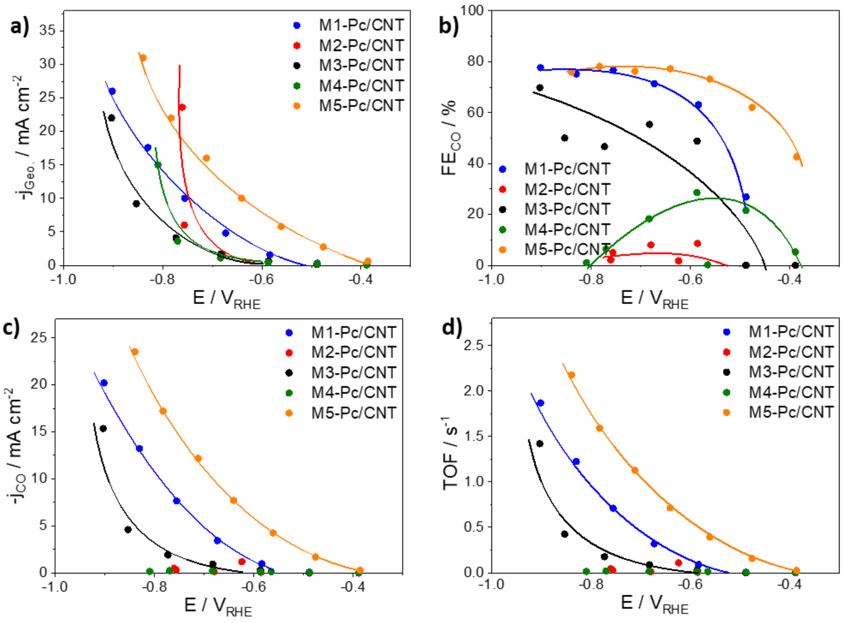


**Figure 1**. ECO2R performance of all M-Pc/CNT candidates characterized in liquid H-cell. a) Overall geometric current density, b) faradaic CO efficiency, c) CO evolution partial current density, and d) turnover frequency (TOF) on various M-Pc sites, as a function of applied IR-free potential.

The ECO2R performance on those screened molecular M-Pc/CNT candidates is illustrated in Figure 1. Remarkably, the M1- and M5- functionalized candidates exhibit over 80% FECO at -0.6 $V_{RHE}$ and -0.8 $V_{RHE}$, respectively.

Furthermore, their absolute CO evolution activity as the TOF also greatly outperforms other metal functionalized moieties. In contrast, other candidates provide a CO selectivity below 50% or negligible current densities. Therefore, as a takeaway of this scenario, we demonstrate that M1-Nx and M5-Nx could serve as promising functionalities for ECO2R to CO.

## 3.2 Pyrolyzed M-N-C catalysts

As indicated in Section 3.1, the M1-Pc/CNT and M5-Pc/CNT with well-defined M-Nx motifs are promising for CO evolution. However, considering those planar molecules are immobilized on the CNT via pi-pi interactions, the SD and subsequential activity are limited by the substrate's surface area and the coverage, which is usually less than one monolayer. For this reason, the development of new M-N-C catalysts with increased practical SD is desired. In the WP activity to date, we selected the M1-Nx as the functional sites and improved the SD in our model catalysts.

In this scenario, we generated 4 types of pyrolyzed M1-N-C. Those are synthesized from ZIF, COF, MOF, and PANI-derived precursors. A pyrolysis protocol up to 800°C or 1000°C is conducted in a $N_2$ atmosphere for carbonization. After that, the samples are leached in acid to remove the exposed metal particles, leaving un-leachable coordinative single-site M1-Nx-C on the surface. We performed the TEM, BET, and XPS measurements to characterize the as-prepared catalysts. Here, the M1-Pc/CNT one is tested as the control. Their TEM images, BET surface area, pore distribution, and the surface atomic metal ratio (determined by XPS) are listed in Figure 2. It is clear that our synthesis protocol delivers a higher exposed surface area than the M1-Pc/CNT. Notably, the MOF- and COF-derived candidates could provide a mesoporous-rich structure, whereas the PANI-one shows the largest adsorption area.

In relation to the amount of M1 sites, the MOF and COF give a relatively higher M1 mole fraction on the surface, while the ZIF one shows the lowest. Unfortunately, using XPS to identify the metal site's chemical state is less likely. Our synthesis procedures involve multiple complicated steps at high-temperature and harsh alkaline/acidic conditions to their chemical states. This could formulate and cause various coordination types (M-Nx-C, x varies from 1 to 4). Using XAS to analyze the metal coordination environment is also challenging, as the possible O-, C- or N- ligands possess similar bond distances.[3]

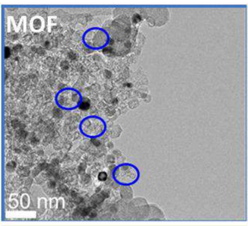
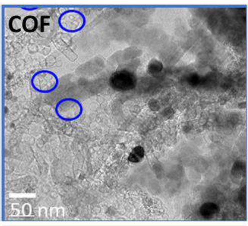
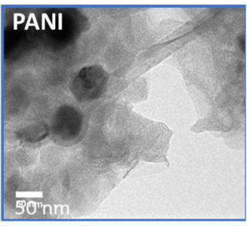
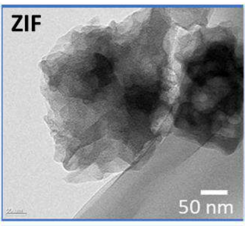
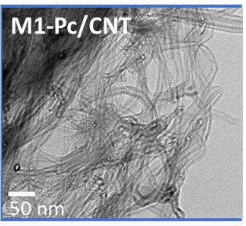
| **TEM** |  |  |  |  |  |
|---|---|---|---|---|---|
| **BET Area** | 219.3 $m^2 g^{-1}$ | 188.9 $m^2 g^{-1}$ | 414.3 $m^2 g^{-1}$ | 226.9 $m^2 g^{-1}$ | 85 $m^2 g^{-1}$ |
| **Pore Vol.** | 0.415 cc $g^{-1}$ | 0.489 cc $g^{-1}$ | 0.413 cc $g^{-1}$ | 0.216 cc $g^{-1}$ | 0.296 cc $g^{-1}$ |
| **$M1\%_{atom}$** | 0.82 % | 0.9 % | 0.38 % | 0.32 % | 0.55 % |

**Figure 2.** TEM images, BET $N_2$ adsorption area, pore-volume, and the catalyst surface's atomic metal ratio. Meso-pores are marked in MOF and COF ones.

The ECO2R performance on our 4 candidates is screened in a liquid H-cell, presented in Figure 3 a and b. A maximum $FE_{CO}$ is achieved around -0.7 $V_{RHE}$ in all candidates. Notably, the MOF- and COF- derived candidates could reach over 90% CO faradaic efficiency, followed by the PANI- one and the M1-Pc/CNT reference. The ZIF-one, to some degree, delivers only 60% $FE_{CO}$. In terms of absolute CO evolution activity, all M1-N-C catalysts provide better CO activity than the commercial AgNPs with the same catalyst loading. Remarkably, the MOF shows the highest CO partial currents in the entire potential window. By contrast, the ZIF and the reference M1-Pc/CNT provide lower but elevating CO activity along with a rising overpotential.

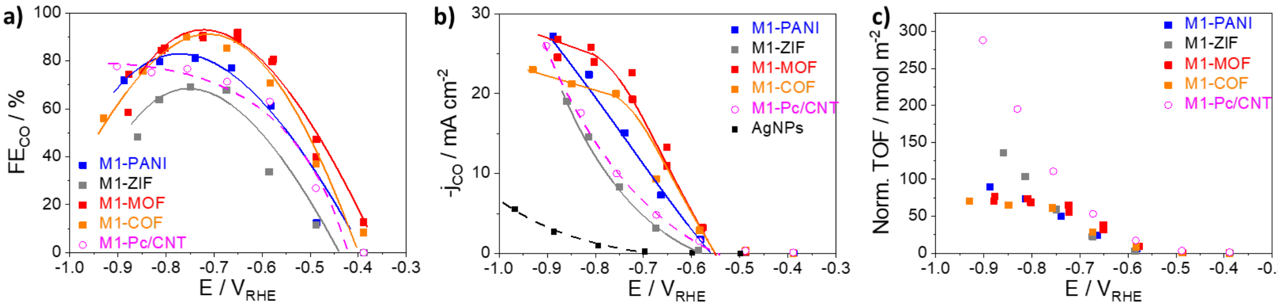


**Figure 3** a-b) ECO2R performance of all our studied M1-N-C catalysts in liquid H-cell. a) Faradaic CO efficiency, and b) CO evolution partial current density as a function of applied IR-free potential. c) "Turnover frequency (TOF)" of CO formation normalized by BET surface area and M1 atomic metal ratio.

It is well known that the M1-Nx moieties on the catalyst surface are responsible for CO formation.[4] To understand the TOF, it is primarily necessary to address the active motifs in our catalysts. The Cryo CO adsorption is a typical methodology to quantify the single M-Nx site. However, this strategy is based on the *CO chemisorption; thus, it is not available for the weak *CO-binding M1-Nx moieties.[5] Besides, using ICP-OES indicates both exposed active M1-Nx motif and underneath inactive M1 species. The in-bulk encapsulated M1 particles should also be considered, as they cannot be entirely removed in acid-leaching procedures. All these give enormous obstacles in accurately quantifying the useful catalytic active site.

Considering all issues mentioned above, we make two speculations to achieve a proposed SD in our context.
i) The overall surface area (determined by BET) is responsible for the electrochemical double layer;
ii) the M1-Nx sites (analyzed by XPS) are homogeneously distributed on the surface, and 100% participate in the ECO2R.

We could calculate the SD upon the BET-surface-area and the XPS-derived atomic metal ratio, namely, SD = BET * M1%. In Figure 3 c, we normalize the CO activity with this SD for a "quasi TOF" value. The "quasi TOF" of PANI, COF, MOF, and ZIF merge in the kinetic region (-0.5 $V_{RHE}$ to -0.7 $V_{RHE}$), implying that M1-Nx active moieties exhibit comparable TOF. Meanwhile, we could propose that MOF's superior absolute CO evolution activity could be addressed to its high SD.

## 4 CONCLUSIONS AND FUTURE WORK

We uncovered M1-N-C and M5-N-C as highly selective molecular and solid-state motifs for the electroreduction of $CO_2$ to CO. Increasing the SD was an effective strategy to improve catalytic activity (per unit mass).

In the present synthesis, controlling the active site fine-structure and their number has remained challenging. Also, the identification and quantification of those active sites remain difficult. Further systematic, iterative, and combined work, including synthesis, characterization, and performance screening, will be required to achieve this.

Moreover, the intrinsic ECO2R performance, namely, the TOF and selectivity, were also highly contingent on the catalysts' pores distribution. TUB will collaborate with EPFL, DTU, TUD, and DeNora, to address the in-depth mechanisms.

## 5 REFERENCES

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## 6 APPENDIX