

Selective Electrocatalytic CO₂ Reduction to Synthetic Fuels using
Membrane-Controlled Proton Transport

Christopher J. Barile, Department of Chemistry, University of Nevada, Reno

Over the last year, our laboratory has designed new electrode architectures for CO₂ reduction that regulate proton transfer to catalysts. These electrodes consist of molecular catalysts covalently bound to an electrode and covered by a hydrophobic lipid membrane. We control the proton transfer rates to the embedded catalysts by incorporating proton carriers such as alkyl boronates and phosphates in the membrane. By tuning the rate of proton transfer to molecular electrocatalysts, we alter catalyst selectivity, an issue at the forefront of CO₂ reduction research.

To test our electrode architecture, we used catalysts based on coordination complexes of 3,5-diaminotriazole, which are active for both CO₂ reduction and O₂ reduction, the latter of which is a model reaction that is easier to interrogate due to a fewer number of possible products (Fig. 1). An azide-terminated self-assembled monolayer (SAM) was first assembled on a Au electrode. Using azide-alkyne click chemistry, a diaminotriazole-based ligand with a metal center (Cu for the case of O₂ reduction) was then covalently attached to the SAM. By changing the length of the alkyl linker in the SAM, the rate of electron transfer can be quantitatively modulated. After attachment, the catalysts were covered by a lipid monolayer with various amounts of proton carrier. The structures of these electrodes were assessed using atomic force microscopy, X-ray photoelectron spectroscopy, cyclic voltammetry, and electrochemical impedance spectroscopy.¹ These characterization techniques also revealed that the structures of the electrode architectures do not differ significantly before and after electrocatalysis, indicating that the electrode platforms are stable during catalysis. In work published in *Angewandte Chemie*,² we showed that the selectivity of the O₂ reduction catalyst can be improved such that it produces <1% H₂O₂ and O₂⁻, two partially reduced oxygen species (PROS) that are undesirable for most applications. By comparison, the catalyst without the lipid layer produces ~14% PROS. When modified with a lipid layer without a proton carrier, the catalyst produces a large amount of PROS

(>40%, leftmost points in Fig. 2). The hydrophobic lipid layer impedes proton transfer to the catalyst, resulting in primarily the production of O₂⁻, a proton-free product. In contrast without a lipid layer, a competition exists between O-O bond cleavage to produce H₂O and fast proton abstraction to yield H₂O₂. Finally, in the cases where proton transfer is regulated with the addition of various amounts of proton carrier in the lipid layer, the amount of PROS decreases to <1% (Fig. 2), likely because the side reaction of fast proton abstract is impeded by the relatively slower proton transfer kinetics. These sets of experiments were performed with SAMs of two different alkyl chain lengths (C5 and C11) to interrogate the effect of electron transfer kinetics on catalyst overpotential and selectivity along with proton transfer kinetics. Through a series of cyclic voltammetry experiments, the C11 SAM was found to exhibit ~30 times slower electron transfer than the C5 SAM

($1.2 \pm 0.2 \text{ s}^{-1}$ versus $39 \pm 3 \text{ s}^{-1}$). Taken together, these results demonstrate that controlling proton transfer to molecular electrocatalysts can improve their selectivity.

Having established the merit of membrane-modified electrodes for dictating product selectivity, we next evaluated the performance and selectivity of a Ag diaminotriazole catalyst for CO₂ reduction using an analogous electrode platform. Since thiol-based SAMs are not stable under the highly reducing conditions needed to conduct CO₂ reduction, we instead formed SAMs by oxidatively coupling primary amine-terminated catalysts on glassy carbon

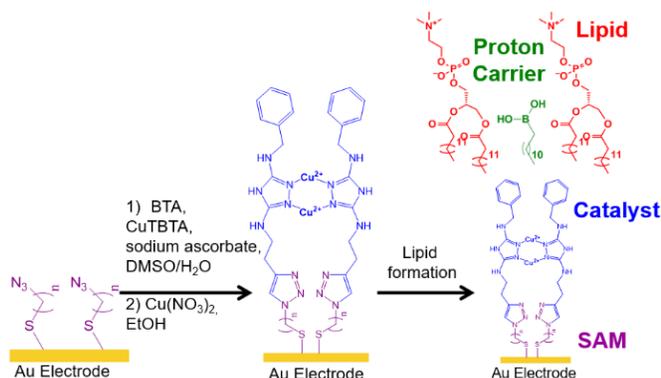


Fig. 1: Schematic of the formation of an electrode architecture that allows for the control of proton and electron transfer to a catalyst.

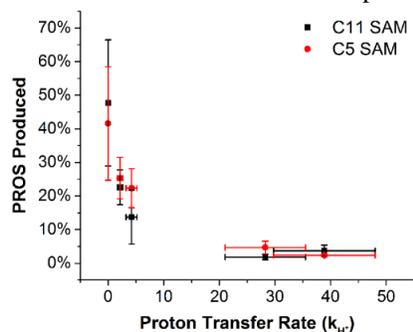


Fig. 2: Amount of PROS produced by an O₂ reduction catalyst as a function of membrane-controlled proton transfer rate.

electrodes.³ Through a series of control experiments, we first demonstrated that the Ag in Ag diaminotriazole catalysts formed in this manner is responsible for the elicited CO₂ reduction. Fig. 3 shows that the voltammetric response of the catalyst changes significantly when it is incorporated in the various membrane environments. Importantly, the products that are generated also correspondingly vary (Fig. 4). For instance, burying the catalyst inside a lipid decreases the Faradaic efficiency of H₂ production from ~71 to ~56%. The lower quantity of H₂ produced is attributed to the hydrophobic nature of the lipid, which diminishes the proton transfer rate to the catalyst. With a slower proton transfer rate, the catalyst has more time to bind and reduce CO₂ to either CO or HCOOH. The catalyst preferentially reduces CO₂ to CO (~32%) over HCOOH (~12%). Water is formed along with CO, but not with HCOOH. The preference for CO formation may be due to the favorable expulsion of water out of the hydrophobic lipid, which shifts the reaction equilibria toward producing CO. The product selectively is further modulated when a proton carrier is incorporated in the lipid with the Faradaic efficiency for H₂ increasing from ~56 to ~77%. The proton carrier increases proton transfer kinetics to the catalyst, which favors the production of H₂. The proton carrier also dramatically increases the ratio of CO to HCOOH generated while almost completely eliminating HCOOH formation.

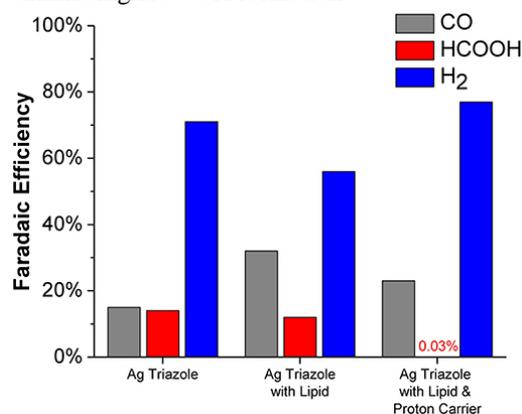


Fig. 4: Faradaic efficiencies for CO (gray), HCOOH (red), and H₂ (blue) production from the CO₂ catalyst (left) with lipid (middle) and DBA proton carrier (right) obtained at -1.75 V vs. Ag/AgCl.

catalysts³ and is now in graduate school in a chemistry-related field. Two graduate students and a post-doctoral scholar also worked on this project although their salaries were funded through other sources. The grant has been instrumental in propelling my independent career as a young scientist in two important ways. First, it has provided me with the budgetary freedom to hire a post-doctoral scholar early in my career, thus increasing my scientific productivity. Second, the projects supported have resulted in important preliminary and published findings that have allowed me to apply for larger grants from federal institutions.

References:

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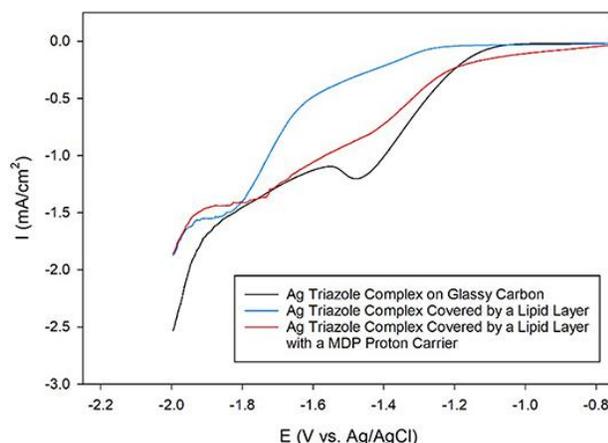


Fig. 3: Linear sweep voltammograms of a CO₂ reduction catalyst (black line) covered by a lipid membrane (blue line) with a proton carrier (red line).

In as of yet unpublished work, we have also synthesized an array of metal porphyrins that are compatible with the membrane-modified architectures described here. We are in the midst of assessing the selectivity and overpotential of these catalysts as a function of proton and electron transfer rate as well as the identity of the metal center. Our preliminary results indicate that the proton transfer rate has a dramatic effect on the selectivity of CO₂ electrocatalysis. Additionally, these molecular porphyrin catalysts possess lower overpotentials than the Ag triazole catalysts previously described, making them better candidates for incorporation in practical CO₂ reduction devices. We have also devised new strategies to increase the durability of these CO₂ reduction catalysts by altering the electrode-catalyst linking chemistry.

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An undergraduate (S. Supakul) directly supported by this grant published a first author paper studying the effect of proton permeable membranes on carbon-supported CO₂ reduction