Modulating the mechanism of electrocatalytic CO\textsubscript{2} reduction by cobalt phthalocyanine through polymer coordination and encapsulation

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The selective and efficient electrochemical reduction of CO\textsubscript{2} to single products is crucial for solar fuels development. Encapsulating molecular catalysts such as cobalt phthalocyanine within coordination polymers such as poly-4-vinylpyridine leads to dramatically increased activity and selectivity for CO\textsubscript{2} reduction. In this study, we use a combination of kinetic isotope effect and proton inventory studies to explain the observed increase in activity and selectivity upon polymer encapsulation. We provide evidence that axial-coordination from the pyridyl moieties in poly-4-vinylpyridine to the cobalt phthalocyanine complex changes the rate-determining step in the CO\textsubscript{2} reduction mechanism accounting for the increased activity in the catalyst-polymer composite. Moreover, we show that proton delivery to cobalt centers within the polymer is controlled by a proton relay mechanism that inhibits competitive hydrogen evolution. These mechanistic findings provide design strategies for selective CO\textsubscript{2} reduction electrocatalysts and serve as a model for understanding the catalytic mechanism of related heterogeneous systems.
The selective electrochemical conversion of CO₂ to value-added products in the CO₂ reduction reaction (CO₂RR) offers a promising approach for recycling CO₂ into value-added products and the storage of intermittent energy sources as chemical fuels. State-of-the-art polycrystalline Cu catalysts produce useful products such as methanol, but do so non-selectively and form a variety of other gaseous and liquid products including H₂ from competitive H⁺ or water reduction. Materials such as planar polycrystalline Au⁹ and Ag foils and some metal-doped nitrogenated carbon materials (MNCs) with M-N₄ porphyrin-like active sites are more selective for CO₂ reduction to single C-containing products, primarily CO, but these systems still suffer from the competitive H₂ evolution reaction (HER). For instance, planar polycrystalline Ag catalysts selectively reduce CO₂ to CO with >90% Faradaic efficiency at −1.1 V vs RHE, but that selectivity drops to 60% Faradaic efficiency due to competitive H₂ evolution when the potential changes by 0.2 V in either direction. Similar potential-dependence on product distribution is seen for various MNC materials. Therefore, the discovery of systems that preferentially promote selective CO₂ reduction to single products with high activity while suppressing HER is critically important for the realization of selective electrochemical CO₂ reduction.

Our research approach is to encapsulate molecular catalysts within coordinating polymers to promote selective CO₂ reduction. By encapsulating the molecular catalysts within the coordinating polymers, we are able to not only control H⁺ and CO₂ delivery to the catalyst centers, but also tune catalytic activity through primary-, secondary-, and outer-coordination sphere effects. These polymer-catalyst composite systems are inspired by enzymatic systems such as NiFe carbon monoxide dehydrogenase and FeFe hydrogenase where fast catalytic activity and high product selectivity are achieved by carefully controlling the primary-, secondary-, and outer-coordination spheres of the enzyme's active site.

Our initial studies focused on encapsulating cobalt phthalocyanine (CoPc) within the coordinating polymer poly-4-vinylpyridine (P4VP)⁴⁻¹⁹. When adsorbed onto graphite electrodes without a polymer binder, CoPc by itself is a non-selective CO₂RR catalyst that shows only modest activity for CO₂ reduction to the Co center in the primary-coordination sphere increasing due to three synergistic effects: (1) axial-coordination of pyridyl residues in the polymer to the Co center in the primary-coordination sphere increasing the catalyst’s nucleophilicity for CO₂ binding, (2) H-bonding interactions in the secondary-coordination sphere that stabilize reactive CO₂ through intermediates, and (3) control of proton delivery through the pyridyl residues within the polymer as proton relays in the outer-coordination sphere (Fig. 1)⁴⁻¹⁹. We propose that axial coordination of pyridyl facilitates CO₂ coordination and thus changes the rate-determining step of CO₂RR by five-coordinate CoPc-P4VP systems to a step subsequent to CO₂ coordination. Therefore, the discovery of systems that preferentially promote selective CO₂ reduction to single products with high activity while suppressing HER is critically important for the realization of selective electrochemical CO₂ reduction.

In this work, we expand upon our previous studies of the CoPc-polymer systems to explicitly investigate the mechanistic implications of primary- and outer-coordination sphere effects on the CO₂ reduction activity by catalyst-polymer composites. To do this, we use a combination of kinetic isotope effect (KIE) measurements and proton inventory studies to determine both the involvement of protons in the rate-determining step of the catalytic mechanism and the mechanism of H⁺ transport through the polymer chain as we systematically alter the nature of the CoPc-polymer interactions. We observe a difference in the measured KIE for the four-coordinate CoPc systems (such as CoPc and CoPc-P2VP) compared to the five-coordinate systems (such as CoPc(py) and CoPc-P4VP) that is consistent with a change in the rate-determining step of the mechanism from CO₂ binding step to a subsequent protonation of the coordinated CO₂ intermediate. In addition, using proton inventory studies—a technique that is used in enzymology to study the kinetics of proton delivery to enzymatic active centers based on the attenuation of kinetic rates as a function of fractional solvent deuteration—we show that proton-transport to the Co active site in CoPc-P4VP and related systems is controlled by proton relays in the polymer rather than diffusion through the film. Thus, we provide direct experimental evidence that proton relays in the outer-coordination sphere of the catalyst in CoPc-P4VP play an important role in promoting selective catalytic activity as has been suggested for other synthetic molecular and enzymatic systems. We believe this work is among the first examples of extending proton inventory studies from traditional enzymological systems to electrocatalytic studies in synthetic molecular-based assemblies. Our studies help us to better understand the CO₂ reduction mechanism of polymer-encapsulated catalysts for comparison to related MNC and planar metal catalyst systems and more generally provides a strategy to probe fundamental catalytic mechanism of CO₂ reduction by molecular assemblies using KIE and proton inventory measurements.

**Results**

**Surface immobilized catalysts and catalyst-polymer systems.** To determine both the involvement of protons in the rate-determining step of the catalytic mechanism and the mechanism of H⁺...
transport through the polymer chain, we use a combination of KIE measurements and proton inventory studies on different catalytic systems as we systematically alter the nature of the CoPc-polymer interactions (Fig. 2). All catalysts and catalyst-polymer composite systems studied were surface-immobilized by drop-casting a catalyst film directly onto edge-plane graphite (EPG) disk electrodes and drying at 70 °C as described in the Supplementary Methods section in the Supplementary Information. For each system, plots of peak area as a function of scan rate for the non-catalytic $[\text{CoPc}]^+ / [\text{CoPc}]^-$ peak are linear (Supplementary Figs. 1–14) which is consistent with a surface-immobilized species. The Co loading of each system was calculated to be $2.19 \times 10^{-9} \text{ mol cm}^{-2}$ based on the deposition procedures and this was confirmed by dissolving the catalyst film from the surface into 1 M HNO$_3$ aqueous solution and then measuring the concentration in the resulting solution with ICP-MS (Supplementary Table 1).

**Proposed CO$_2$RR mechanisms by CoPc.** The exact mechanism for electrocatalytic CO$_2$ reduction by CoPc remains a point of discussion within the community. Based on previously reported experimental evidence, a proposed mechanism for CO$_2$ reduction by CoPc with the competitive HER pathway is shown in Fig. 3a. In the proposed mechanism, CoPc is first reduced to $[\text{CoPc}]^-$ followed by protonation of the complex (presumably on the Pc ring) to form $[\text{CoPcH}]^-$ and a second reduction to produce $[\text{CoPcH}_2]^-$ (Fig. 3a). Here, there is a branch in the mechanism where $[\text{CoPcH}_2]^-$ can either react with H$^+$ to evolve H$_2$ and regenerate the CoPc starting material in step (iv), or $[\text{CoPcH}_2]^-$ can react with CO$_2$ to form a CO$_2$ adduct in step (i) that, upon subsequent protonation in step (iii), generates CO$_2$. This mechanism is consistent with previous results for CoPc and CoPc-P4VP in phosphate solutions which show the onset of catalytic activity occurs at the second reduction event in the voltammogram. However, our recent electrochemical study of CoPc in DMSO solutions suggest that under conditions of low H$^+$ activity, a third reduction event is required for catalytic turnover of CO$_2$RR (see Supplementary Fig. 15). This is consistent with a previous spectroelectrochemical studies in organic systems under CO$_2$, which suggests that further reduction of the [CoPc-CO] adduct is required to release CO and re-enter the catalytic cycle at $[\text{CoPc}]^-$ (Fig. 3b). Alternatively, recent reports of CO$_2$ reduction by...
adsorbed CoPc in bicarbonate solutions have suggested that CO₂ coordination may occur at the 1 e− reduced species, and this pathway has been further supported by a recent Tafel analysis and DFT studies (Fig. 3c). Although we cannot distinguish between the three mechanisms, all support our postulate that promotion of CO₂ reduction over competitive H₂ evolution can be achieved by either (a) facilitating CO₂-coordination or (b) controlling H⁺ delivery to the active site to inhibit the competitive H₂ evolution pathway. In addition, all three pathways are consistent with our KIE and proton inventory studies discussed below. The mechanistic discussions in the manuscript will focus on the mechanism shown in Fig. 3a because it is the mechanism that has been proposed to operate under our reaction conditions.

**KIE studies.** KIE studies were conducted to investigate the influence of axial ligand coordination to CoPc on the CO₂RR mechanism. The magnitude of KIE is given by Eq. (1), where \( j_1 \) is the electrocatalytic current density measured in the protic solution and \( j_0 \) is the electrocatalytic current density measured in the deuterated solution:

\[
KIE = \frac{j_1}{j_0}
\]

Note that Eq. (1) assumes that the electrochemical reaction rate is directly proportional to the measured current density which is generally expected for a reaction occurring at a surface-immobilized species. However, Eq. (1) is valid for determining KIE only for systems in which the Faradaic efficiency, \( \varepsilon \), is the same for an electrocatalytic reaction conducted in protic and deuterated solvent. To confirm that the Faradaic efficiency for CO production does not change as the electrolyte is changed from a protic solution to a deuterated solution, we conducted 2-h controlled potential electrolyses (CPE) measurements in sealed protic solution and in pD 5 deuterated phosphate solution using 2-min rotating disk chronoamperometric (CA) step measurements at −1.25 V vs. SCE and a rotation rate of 1600 rpm (representative CA measurements for each system investigated are shown in Supplementary Figs. 17–27). The measured current densities and KIE values are reported in Fig. 4b, and all the KIE study results for CO₂RR are summarized in Table 1. Note that ICP-MS measurements show no difference in Co loading on samples measured pre-CA measurements and identically-prepared samples measured post-CA measurements (Supplementary Table 1). This suggests there is no loss of Co during the electrolyses.

In general, a KIE > 1 suggests that a proton transfer event is present in the rate-determining step of the mechanism, whereas a KIE = 1 suggests no involvement of a formal proton-transfer event in the rate-determining step. Thus, evaluation of the KIE for the adsorbed CoPc parent complex and our modified CoPc systems can provide information regarding the rate-determining step in the proposed electrocatalytic CO₂RR mechanism shown in Fig. 3a. To determine the KIE for our systems, we measured the electrocatalytic current for CO₂RR both in pH 5 phosphate solution and in pD 5 deuterated phosphate solution using 2-min rotating disk chronoamperometric (CA) step measurements at −1.25 V vs. SCE and a rotation rate of 1600 rpm (representative CA measurements for each system investigated are shown in Supplementary Figs. 17–27). The measured current densities and KIE values are reported in Fig. 4b, and all the KIE study results for CO₂RR are summarized in Table 1. Note that ICP-MS measurements show no difference in Co loading on samples measured pre-CA measurements and identically-prepared samples measured post-CA measurements (Supplementary Table 1). This suggests there is no loss of Co during the electrolyses.

The parent four-coordinate CoPc system shows no KIE in our studies which is consistent with a rate-determining CO₂-coordination step (Fig. 3a, step (i)). In the case of CoPc-P2VP, the CoPc complex is immobilized within a non-coordinating P2VP polymer and again, there is no observed KIE. In contrast, the five-coordinate CoPc(py) system shows a KIE = 3.1, suggesting a rate-determining proton transfer step in the mechanism (Fig. 3a, step (ii)). When the five-coordinate CoPc(py) is immobilized within P2VP to form CoPc(py)-P2VP, we observe a KIE = 2.0 compared to the CoPc(py). Likewise, when CoPc is immobilized within the coordinating polymer P4VP to form CoPc-P4VP, the observed KIE = 2.1. The results with CoPc-P4VP and CoPc(py)-P2VP suggest that the polyvinylpyridine polymers are moderating the extent of KIE for the five-coordinate CoPc systems with axially-ligated pyridyls. To confirm that this moderation of the KIE is specifically due to the polyvinylpyridine and not a general effect with any polymer, we measured the KIE of CoPc and CoPc(py) immobilized within polystyrene (PS) where we expect no primary-, secondary-, or outer-coordination sphere effects within the polymer. In this case, CoPc-PS shows no KIE, and CoPc(py)-PS has KIE = 3.2, which is nearly identical to that of CoPc(py) without an encapsulating polymer. Based on the larger KIE for CoPc(py) compared to that of CoPc-P4VP and
CoPc(py)-P2VP, we hypothesize that the pyridyls in the polymer act as a proton relay controlling proton delivery to the CoPc active sites, and these sites have a weak inverse isotope effect (KIE < 1) that, in aggregate, moderates the overall KIE for CoPc-P4VP and CoPc(py)-P2VP compared to CoPc(py). Note that additional KIE measurements for HER for the catalysts studied in this work were also measured, and these results are summarized in Supplementary Table 4.

To confirm the five-coordinate nature of the CoPc in CoPc (py), CoPc-P4VP, CoPc(py)-P2VP, CoPc(py)-PS, and CoPc(py)-P2VP, we conducted UV–Vis spectroscopy studies of drop-cast films to characterize the coordination environment (see Supplementary Information for more details). As shown in Supplementary Fig. 28, the Q band of CoPc in PS and P2VP near 669 nm is red shifted to 674 nm in UV–Vis absorption spectrum of CoPc in P4VP, and CoPc(py) in PS and P2VP films. Similarly, red shifted Q bands are also exhibited in the UV–Vis spectra of solutions of CoPc(py) as prepared for deposition and solutions of independently synthesized CoPc(py) by about 5 nm compared to that of CoPc (Supplementary Fig. 29). These red shifts are consistent with the observation that the Q bands of metalloporphyrin-like complexes red shift when there are electron-donating ligands coordinated axially with the central metal ions. Thus, the UV–Vis spectrum suggests that CoPc exists as a five-coordinate complex in CoPc-P4VP, CoPc(py)-PS, CoPc(py)-P2VP samples, and CoPc(py) solutions, which is consistent with axial coordination of pyridyl groups to the CoPc in these systems.

Recent studies have suggested that CoPc aggregation occurs when CoPc is adsorbed to carbon surfaces at high loadings and that this aggregation limits the number of exposed active sites and, therefore, the measured per-CoPc TOFs. To explore whether aggregation influences the results of our mechanistic studies, we explored the loading dependence on CO2RR activity by CoPc both physisorbed onto EPG and within the P4VP films over four orders of magnitude of loading between 2.19 × 10⁻¹¹ mol cm⁻² and 2.19 × 10⁻⁷ mol cm⁻² (results are summarized in Supplementary Figs. 30–32). We observe a decrease in TOF for CO2RR with increasing CoPc loading consistent with previous aggregation studies. However, importantly the KIE results are statistically equivalent at every loading suggesting that aggregation does not change the rate-determining step in the catalytic mechanism (see Supplementary Table 5).

To confirm that the observed increased activity for CoPc(py) and CoPc-P4VP compared to the parent CoPc system is not due to electrocatalytic CO2 reduction by free pyridine in solution or the polymer pyridyl groups, we conducted several control experiments. We have previously conducted CPE experiments with CoPc-modified carbon electrodes in CO2-saturated pH 5 phosphate solutions containing 0.05 mM dissolved pyridine and saw no significant change in the CO2RR activity and Faradaic efficiency compared to analogous studies with no dissolved pyridine present. In addition, we have previously shown that CPE experiments conducted with EPG electrodes coated with P4VP (with no CoPc) showed negligible CO2RR activity. In this work we have conducted additional CPE experiments with bare EPG electrodes in CO2-saturated pH 5 phosphate solutions containing 0.05 mM dissolved pyridine and see negligible activity for CO2RR (Supplementary Table 6). Based on the results of these control experiments, we conclude that the enhanced current we observe in the CoPc(py) and CoPc-P4VP systems is not due to direct electrocatalytic CO2 reduction by free pyridine and/or the pyridyl moieties in the P4VP polymer.

**Proton inventory studies.** Although we invoke the existence of proton relays to help explain trends in catalyst selectivity and activity in the CoPc-P4VP and related systems, traditional KIE measurements are not sufficient to definitively argue for their existence. To provide further support for the existence of proton relays within our catalyst-polymer systems we have conducted electrochemical proton inventory studies. The proton inventory method is a technique that is used in enzymology to study the kinetics of proton delivery to enzymatic active centers in which the attenuation of a kinetic rate is measured as a function of the fractional concentration of D2O in a mixed D2O–H2O solvent. The method is particularly useful for resolving the number of exchangeable hydrogenic sites that contribute to the
catalytic rate within a system. The dependence of the rate attenuation on fractional deuteration of the electrolyte can be expressed with a modified Gross-Butler equation (Eq. (2)).

\[ j_n = j_0 (1 - n + n\phi)Z^n \]  
\[ n = \frac{[D_2O]}{[D_2O] + [H_2O]} \]

Here \( j_n \) is the measured current density at a given fractional deuteration concentration \( n \) (Eq. (3)), \( j_0 \) is the measured current density in solutions with only protic electrolyte present, \( \phi \) is the isotopic fractionation parameter which is related to the propensity for a hydrogenic site in the rate-determining step of the reaction to interact with \( D^+ \) compared to water, and \( Z \) is a parameter related to the aggregate isotope effect from multiple equivalent hydrogenic sites, called \( Z \)-sites, with individual weak isotope effects (see Supplementary Information for an explanation of Eq. (2)).

For all the systems investigated, the electrocatalytic current for \( \text{CO}_2 \) reduction by \( \text{CoPc-PS} \) results in a non-linear dome-shaped response as shown in Fig. 5a, and a fit of this curve to equation (2) results in \( \phi = 0.3 \) and \( Z > 1 \). Note that \( \phi \) represents the isotopic fractionation factor of the hydrogenic site involved in step (iii) in Fig. 3a, and \( \phi = 0.3 \) is a typical fractionation factor for transition-state hydrogen bridges corresponding to hydrogen transfer reactions of small molecules.

These results are consistent with a normal isotope effect at a single hydrogenic site in the rate-determining step at the active site coupled with an aggregate inverse-isotope effect from the \( Z \)-sites (pyridyl sites on the polymer). Note that a weak inverse-isotope effect is a somewhat common phenomena for \( H^+ \) exchange reactions at weak bases such as pyridine. The results of the \( \text{CoPc-P4VP} \) proton inventory studies support our hypothesis that proton delivery to the active site is controlled by a polymer-based proton relay mechanism. Note that in our analysis we do not take into account contributions to the overall isotope effect from the expected H-bonding interactions between the P4VP polymer and reactive \( \text{CO}_2 \) intermediates (i.e., secondary-coordination sphere effects). This is because weak H-bonds tend to have negligible isotope effects with \( \phi \sim 1 \) and therefore do not typically contribute significantly to the overall isotope effect.

In contrast to \( \text{CoPc-P4VP} \), the activity of \( \text{CoPc(py)} \) shows a linear attenuation with increasing \( n \) confirming that without the encapsulating polymer only one hydrogenic site (the hydrogenic site involved in step (iii) in Fig. 3a) is involved in the rate-determining step of the catalytic mechanism and there is no.
Z-effect (i.e., \( Z = 1 \)). This is also consistent with the larger observed KIE = 3.1 for CoPc(py) compared to KIE = 2.1 for CoPc-P4VP, where the overall KIE is modulated by the inverse-isotope effects of the Z-sites. Note that CoPc(py)-P2VP with axially-coordinated pyridyls (Fig. 5a) shows a response nearly identical to that of CoPc-P4VP with identical values of \( \phi \) and \( Z \) (Table 1). Both the parent CoPc system (Fig. 5a) and the CoPc-P2VP system (Fig. 5a) show no attenuation of activity in the proton inventory studies as expected from our KIE measurements and consistent with a rate-limiting step (i) (Fig. 3a) in the catalytic cycle for the parent system.

In order to confirm that the KIE originates from the proton channel along the partially protonated pyridyl residues rather than the mass transport of protons through the polymer membrane, proton inventory studies for CoPc and CoPc(py) encapsulated in PS were performed. CoPc-PS (Fig. 5b) shows identical behavior to that of CoPc (Fig. 5a), and CoPc(py)-PS (Fig. 5b) shows identical behavior to that of CoPc(py) (Fig. 5a) for proton inventory studies. This suggests that the dome-shaped responses of CoPc-P4VP and CoPc(py)-P2VP are due to a specific proton relay effect imbued by the pyridyl moieties and not a general behavior of polymers without proton relays. Note that similar proton inventory behavior is shown in the catalytic systems in this study of polymers without proton relays. Note that similar proton inventory behavior is shown in the catalytic systems in this study.

**Polymer loading dependence on KIE and Z.** Our KIE and proton inventory studies provide strong evidence that pyridyls within the polyvinylpyridine polymers act as proton relays to control proton delivery to the CoPc active sites, and the weak-inverse isotope effect from the pyridyl moieties moderates the KIE for CoPc-P4VP compared to CoPc(py). Based on these observations, we postulate that increasing the ratio of pyridyl to KIE for CoPc-P4VP compared to CoPc(py) based proton relays with weak inverse isotope effects in the polyvinylpyridine polymers. Note that the CO\(_2\)RR activity slightly increases with increasing P4VP loading. We postulate that this may be due to increased CO\(_2\) partitioning within largely-hydrophobic polymer layer which may lead to higher overall catalytic activity\(^{20,22}\).

**Discussion**

We believe the experimental techniques applied in and the mechanistic insights derived from this work can serve as a model for understanding the catalytic mechanisms of related heterogeneous electrocatalysts. For example, previous studies of CO\(_2\) reduction with CoPc adsorbed onto graphitic carbon show non-selective CO\(_2\) reduction to CO with \( k_{CO} \) ranging from ~40% to ~60% with appreciable competitive H\(_2\) evolution\(^{19,21,22,56,57}\), which is consistent with this study. However, recent reports show that CoPc adsorbed onto highly-oxygenated carbon nanotubes (CNTs) synthesized from high-temperature calcination of carbon-precursors in air selectively reduces CO\(_2\) with \( k_{CO} \approx 80\% \) at optimized potential, pH, and loading conditions\(^{40,56,57}\). It has been postulated that the \( \pi-\pi \) interactions between the CNTs and the macrocyclic CoPc complexes may explain the increased activity of CoPc and related systems when absorbed onto CNTs\(^{40,56,57}\). We propose that an additional reason for the increased activity of CoPc adsorbed onto CNTs may be axial-coordination of impurities in the CNTs structure, such as oxidized and hydroxyl-defect sites, with the adsorbed CoPc. These proposed axial interactions in the CoPc-CNT system are analogous to the axial-coordination of pyridine and P4VP to CoPc in our studies. Note that similar increases in activity for O\(_2\) reduction by macrocyclic Co and Fe complexes adsorbed onto defect-rich carbon supports has been previously observed\(^{38-42}\), and was largely attributed to axial-coordination of the metal complexes to organic functional groups on the carbon surfaces\(^{59-62}\). While directly probing the nature of the CoPc-CNTs interactions is beyond the scope of our current study, we suggest that similar electrochemical KIE measurements to those conducted here can be used as a tool to determine the nature of the rate-determining step of CO\(_2\) reduction by CoPc adsorbed onto CNTs and thereby determine the nature of the CoPc-CNTs interactions.

Perhaps one of the most-promising CO\(_2\)RR materials mechanically related to the CoPc and CoPc-P4VP systems is MNC materials—extended graphitic structures with discrete functional groups.

**Table 2 Results of Kinetic Isotope Effects and Proton Inventory Measurements for CoPc-P4VP with different P4VP loadings**

| P4VP (%) | py/CoPc | py\(^+\) · CoP | \( j_{H, D} \) (mA·cm\(^{-2}\)) | \( TOF_{CO} \) (s\(^{-1}\)) | KIE | Proton Inventory Parameters |
|---|---|---|---|---|---|---|
| 0.1 | 190 | 38 | (H) \(-2.09 \pm 0.06\) | 2.3 \pm 0.2 | \( \phi \) | 
| 0.5 | 950 | 190 | (H) \(-2.67 \pm 0.10\) | 2.2 \pm 0.1 | \( Z \) | 
| 1 | 1900 | 380 | (H) \(-2.90 \pm 0.02\) | 2.1 \pm 0.1 | \( \phi \) | 
| 2 | 3800 | 760 | (H) \(-1.37 \pm 0.01\) | 1.9 \pm 0.1 | \( Z \) | 
| 3 | 5700 | 1140 | (H) \(-3.03 \pm 0.09\) | 1.7 \pm 0.1 | \( \phi \) | 

All measurements conducted at \(-1.25\) V vs. SCE. All reported values are averages from three or more independent measurements, and all errors are given as standard deviations.

\( \phi = \frac{\text{Ratio of } \text{py} / \text{CoPc}}{0.20} \times \frac{\text{Hydroxyl-defect CoPc}}{\text{Pyridyl-CoPc}} \)

\( \text{Proton relays with weak inverse isotope effects in the polyvinylpyridine polymers. Note that the CO}_2\text{RR activity slightly increases with increasing P4VP loading. We postulate that this may be due to increased CO}_2\text{ partitioning within largely-hydrophobic polymer layer which may lead to higher overall catalytic activity}^{20,22}. \)

\( \text{Data not shown.} \)

\( \text{Data not measured.} \)
We have investigated the electrochemical CO₂-RR mechanism for CoPc encapsulated in a coordinating polymer using a combination of KIE measurements and proton inventory studies. Specifically, KIE studies suggest that axial-coordination of pyridyl/pyridine to CoPc to form a putative five-coordinate species changes the rate-determining step of the catalytic mechanism from a CO₂-binding step (step (i), Fig. 3a) in the case of CoPc to a subsequent protonation step (step (iii), Fig. 3a) in the case of the five-coordinate species. The axially-coordinated pyridine/pyridyl can be either a discrete ligand (CoPc(py), CoPc(py)P-2VP, CoPc(py)-PS) or be attached to an encapsulating polymer (CoPc-P4VP). Moreover, our proton inventory studies strongly suggest that proton delivery to the CoPc active sites in the polyvinylpyridine-encapsulated systems is controlled by a polymer-based proton relay mechanism involving the pyridyl moieties. Our work here provides a strategy to modulate the catalytic activity of this class of catalyst-polymer composite systems by (1) controlling the extent of axial-coordination to the catalyst center and (2) controlling the fractional protonation of the polymer to modulate the nature and extent of the proton relays in the encapsulating polymer. The mechanistic insights for the CoPc-P4VP and related systems introduced in this work reinforce the findings of previous studies of catalytic mechanism at M-N₄ active sites in heterogeneous MNC materials. The systems and experimental techniques developed in this work will serve as a useful model for further probing catalytic activity and mechanisms in future MNCs and polymer-encapsulated catalyst materials which will facilitate the development of new, more-active electrocatalytic systems for selective CO₂ reduction.

Methods

Electrolyte solution preparation and pH measurements. All pH measurements were conducted with a Fisher Scientific Accumet AB200 pH meter with an Accumet pH/ATC Epoxy Body Combination Electrode calibrated with a three-point calibration curve at pH = 4.01, 7.06, and 10.01. For estimating pH,

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Author contributions
C.C.L.M. conceived the project. C.C.L.M. and Y.L. designed the experiments. Y.L. performed the data analysis. C.C.L.M. and Y.L. interpreted the results and wrote the manuscript. All authors discussed the results and commented on the manuscript at all stages.

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