

Highly Tunable Syngas Product Ratios Enabled by Novel Nanoscale Hybrid Electrolytes Designed for Combined CO₂ Capture and Electrochemical Conversion

Tony G. Feric, Sara T. Hamilton, Byung Hee Ko, Gahyun Annie Lee, Sumit Verma, Feng Jiao, and Ah-Hyung Alissa Park*

Coupling renewable energy with the electrochemical conversion of CO₂ to chemicals and fuels has been proposed as a strategy to achieve a new circular carbon economy and help mitigate the effects of anthropogenic CO₂ emissions. Liquid-like Nanoparticle Organic Hybrid Materials (NOHMs) are composed of polymers tethered to nanoparticles and are previously explored as CO₂ capture materials and electrolyte additives. In this study, two types of aqueous NOHM-based electrolytes are prepared to explore the effect of CO₂ binding energy (i.e., chemisorption versus physisorption) on CO₂ electroreduction over a silver nanoparticle catalyst for syngas production. Poly(ethylenimine) (PEI) and Jeffamine M2070 (HPE) are ionically tethered to SiO₂ nanoparticles to form the amine-containing NOHM-I-PEI and ether-containing NOHM-I-HPE, respectively. At less negative cathode potentials, PEI and NOHM-I-PEI-based electrolytes produce CO at higher rates than 0.1 molal. KHCO₃ due to favorable catalyst-electrolyte interactions. Whereas at more negative potentials, H₂ production is favored because of the carbamate electrochemical inactivity. Conversely, HPE and NOHM-I-HPE-based electrolytes display poor CO₂ reduction performance at less negative potentials. At more negative potentials, their performance approached that of 0.1 molal. KHCO₃, highlighting how the polymer functional groups of NOHMs can be strategically selected to produce value-added products from CO₂ with highly tunable compositions.

the design and development of technologies that can directly convert and store excess renewable energy on the large scale could help mitigate the effects of climate change.^[3–6] For example, the renewables-powered electrochemical conversion of CO₂ to chemicals and fuels is an attractive means of avoiding and/or reducing CO₂ emissions, while creating a new circular carbon economy. When considering liquid solvent systems designed only for CO₂ capture, the solvent regeneration step is energy intensive, especially for aqueous systems where the heat capacity of water is very large (4.18 kJ kg^{−1} K^{−1}).^[7] Thus, it is proposed to drive the capture of CO₂ with subsequent electrochemical conversion, which is known to be a promising route to upgrade CO₂ to a variety of C₁ and C₂ compounds. The renewables-powered electrochemical CO₂ conversion would be a transformative pathway for closing the carbon cycle.

The electrochemical production of syngas, or a mixture of H₂ and CO, has been proposed for several applications which require specific H₂ to CO ratios. Examples include methanol synthesis

(H₂/CO ratio of 2), dimethyl ether formation (H₂/CO ratio of 1), syngas fermentation (H₂/CO ratio ranging from 1 to 3.33), and Fischer-Tropsch reactions (H₂/CO ratio of 2).^[8–11] The direct electrochemical production of some compounds is not currently possible with high selectivity and reactivity, thus

1. Introduction

Though renewable energy technologies have advanced rapidly over the last couple of decades, integration with the grid is currently challenged by intermittency and storage issues.^[1–3] Thus,


T. G. Feric, G. A. Lee, A.-H. A. Park
Department of Chemical Engineering
Columbia University
New York, NY 10027, USA
E-mail: ap2622@columbia.edu

T. G. Feric, S. T. Hamilton, G. A. Lee, A.-H. A. Park
Lenfest Center for Sustainable Energy
Columbia University
New York, NY 10027, USA

S. T. Hamilton, A.-H. A. Park
Department of Earth and Environmental Engineering
Columbia University
New York, NY 10027, USA

B. H. Ko, F. Jiao
Department of Chemical Engineering
University of Delaware
Newark, DE 19716, USA

S. Verma
Shell International Exploration and Production Inc.
Houston, TX 77082, USA

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/adfm.202210017>.

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the formation of syngas could be a useful first step to avoid costly downstream separations.^[8–11] Evidently, the optimal ratios of H₂/CO are quite different depending on the application of the syngas so the development of electrochemical systems that could produce a wide range of syngas compositions would be especially useful. An alternative approach would be to develop a system where a CO-producing unit exists separately from a H₂-producing electrolyzer so that they can be independently optimized. Several advances have been made in terms of catalyst^[5,12–14] and reactor^[5,14–16] design for the electrochemical conversion of CO₂, though aqueous CO₂ electroreduction is also limited due to the low solubility of CO₂ in the electrolyte phase.^[5,17,18] Thus, the development of innovative electrolytes with improved CO₂ solubilities has been proposed to improve the performance of the CO₂ electroreduction reaction (CO₂RR) and other electrochemical reactions relevant to energy storage applications, such as flow batteries.^[17–24]

The effects of incorporating ionic liquids,^[19,20,25,26] small ligands,^[27] surfactants,^[28,29] deep eutectic solvents,^[30–33] and/or amines^[28,33–36] to electrolytes for the CO₂RR have recently been studied. In addition to improving the CO₂ solubility of the electrolytes, in some cases, these additives behaved as co-catalysts for the CO₂RR as a reduction in overpotential, tuned product selectivity, and/or improved reaction rates were observed. Ionic liquids are promising candidates because they have been widely shown to significantly enhance the performance of the CO₂RR.^[37–41] Furthermore, a careful analysis of experimental and computational data has revealed that the ionic liquid plays a crucial role in stabilizing CO₂RR intermediates at the catalyst surface.^[19,20,40,42–44] As a result, electrolytes with an optimal CO₂ binding energy that can enhance the performance of the CO₂RR are highly sought after because an integration of CO₂ capture with the CO₂RR can remove the need for the energy-intensive CO₂ capture solvent regeneration.^[24,35]

Nanoparticle Organic Hybrid Materials (NOHMs) consist of an organic polymer tethered to an inorganic nanoparticle core via either covalent or ionic bond.^[45–48] Owing to their favorable properties, including negligible vapor pressure,^[46] oxidative-thermal stability,^[46,49–51] chemical tunability,^[52,53] and high conductivity,^[54,55] NOHMs have been extensively studied for CO₂ capture^[45,49,50,52,55–61] and several electrochemical applications.^[53,62–66] Because of the myriad of possible nanoparticle and polymer combinations, NOHMs are a highly versatile class of materials that can be designed for targeted applications. For electrochemical energy storage applications in particular, developing an understanding of the structural and transport properties of innovative electrolyte materials is essential to improving the overall system performance.^[67–72]

Though NOHMs possess several great properties for CO₂ capture, their application in the neat state is typically limited by a reduced polymer mobility and an order of magnitude larger viscosity when compared to untethered polymers.^[46,73–75] By mixing NOHMs with a secondary fluid, such as water, it was found that the viscosity dropped significantly.^[46] Thus, we have recently investigated the effect of the secondary fluid properties,^[74] ionic stimulus,^[71,75] NOHMs concentration,^[71] and bond type^[48] on the resulting transport behaviors and structure of the polymer canopy in NOHMs. The results of these studies have shown that the polymer canopy in NOHMs composed

with an ionic bond, in particular, are highly responsive to the chemical environment (i.e., solvent quality, ionic stimulus, and/or NOHMs concentration)^[71,74,75] making NOHMs promising candidates to study as electrolyte additives for a variety of energy storage processes. Because of their ability to increase the concentration of CO₂ in aqueous electrolytes, NOHMs have been proposed for combined CO₂ capture and conversion applications,^[62,76] though their exact role in the CO₂ conversion process has not been reported on. For this first in-depth study of NOHM-mediated CO₂ capture and conversion, a silver nanoparticle catalyst was selected because of its well-known ability to produce CO and H₂ at different ratios, depending on the applied potential.

In this study, we prepared two different types of NOHMs to explore the effect of polymer functional groups in the NOHMs canopy on the resulting CO₂ capture and conversion behaviors over a silver nanoparticle catalyst. We synthesized the amine-containing NOHM-I-PEI and the ether containing NOHM-I-HPE by ionically tethering branched poly(ethylenimine) (PEI) and Jeffamine M2070 (HPE), respectively, to ≈ 10 nm SiO₂ particles. The structures of the resulting materials are shown in **Figure 1a,b**, respectively. Additionally, we measured the CO₂ capture capacities of various polymer and NOHM-based fluids/electrolytes across a range of CO₂ partial pressures ($P_{\text{CO}_2} = 0.04$ –1 atm). Finally, we tested the CO₂RR performance of the CO₂-saturated untethered polymer and NOHM-based electrolytes on a silver nanoparticle catalyst at potentials ranging from -0.6 to -1.2 V versus RHE, and compared their performance to that of CO₂-saturated 0.1 molal. KHCO₃. The results from this study elucidate that NOHMs can be used as materials enabling combined CO₂ capture and conversion, and provide a unique reaction environment for the electrochemical reduction of CO₂.

2. Results and Discussion

2.1. CO₂ Capture Behaviors of PEI and NOHM-I-PEI Solutions as a Function of CO₂ Partial Pressure

Compared to non-aqueous solvents, water is significantly cheaper and safer, and thus, is more widely used in electrochemical applications.^[17] Unfortunately, its CO₂ solubility is limited to ≈ 34 mm, or 0.034 mmol CO₂ g⁻¹.^[5,17,18] As a result, when developing novel electrolytes for the integrated capture and conversion of CO₂, it will be necessary to determine the electrolyte CO₂ concentration at a wide range of CO₂ capture conditions and address any potential challenges associated with limited CO₂ solubility. In this study, we investigated the CO₂ capture kinetics and capacities of 8 wt.% PEI and 10 wt.% NOHM-I-PEI aqueous solutions at CO₂ partial pressures ranging from 0.04 to 1 atm. The total amount of CO₂ captured was expected to increase with the polymer/NOHMs concentration due to the increased amount of CO₂ binding functional groups in the solution. However, in our recently published studies, we found that the viscosity of untethered polymers around 2000 MW and the corresponding NOHMs began to increase rapidly above a concentration of 10 wt.%.^[74,75] Thus, here we employed a concentration of 10 wt.% NOHM-I-PEI to maximize the CO₂ loading

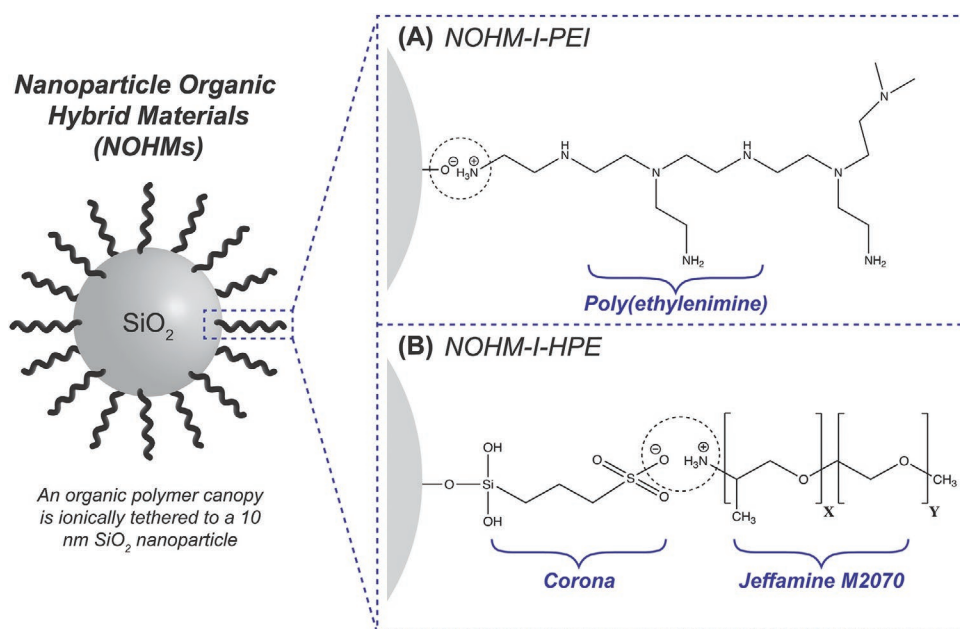
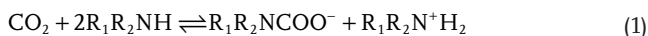


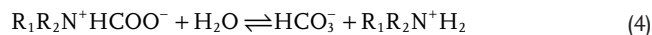
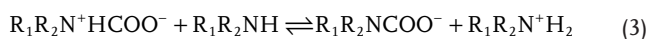
Figure 1. Schematic of a) NOHM-I-PEI and b) NOHM-I-HPE. The X and Y in the Jeffamine M270 (HPE) canopy represent the number of poly(propyleneoxide) groups (10) and poly(ethyleneoxide) groups (31).

in the electrolyte while minimizing mass transfer limitations. Since the NOHM-I-PEI is composed of roughly 20 wt.% SiO₂, an 8 wt.% solution of PEI would contain the same amount of polymer in solution as 10 wt.% NOHM-I-PEI, and was used as a comparison for all CO₂ capture and CO₂ reduction experiments in this study. Moreover, the concentrations of CO₂ were selected to represent industrial exhaust gases from gas turbines (4% CO₂), coal-fired power plants (10–15% CO₂), and cement manufacturing (14–33% CO₂).^[77,78] Concentrations of 65% CO₂ and 100% CO₂ were selected to further understand the CO₂ capture performance across a broad concentration range.

The CO₂ capture of aqueous amine-containing solutions has been well-studied throughout the literature.^[79–83] For every mole of amine, primary (R₁NH₂) and secondary amines (R₁R₂NH) are known to capture 0.5 moles of CO₂. The overall reaction can be represented by



though there has been some debate about the exact reaction mechanism. The two main mechanistic pathways which have been presented in the literature are the two-step zwitterion mechanism^[79–82] and the single-step termolecular mechanism.^[83] According to the zwitterion mechanism, the reaction of CO₂ with a primary or secondary amine results in the formation of a zwitterion (Equation 2) which is then deprotonated by another amine (Equation 3) or reacts with a water molecule to form bicarbonate (Equation 4).^[79–82] The zwitterion mechanism can be represented by the following

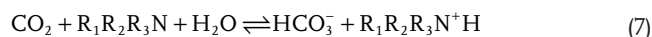


Conversely, Da Silva and Svendsen claimed that the zwitterion is not stable enough to be reliably detected and the reaction takes place in a single step whereby the CO₂ reacts with the base and the proton transfer occurs at the same time.^[83] More recent reports on mechanistic pathways of CO₂ capture by primary and/or secondary amines provide evidence for the zwitterion mechanism, as reaction intermediates have been clearly identified with spectroscopic tools.^[79–82]

Because they lack protons, the zwitterion formed upon reaction of tertiary amines (R₁R₂R₃N) with CO₂ can only be protonated by water molecules to form bicarbonate. Thus, the mechanism by which tertiary amines react with CO₂ is generally known to occur by the following reaction steps



The overall reaction mechanism can be represented by



whereby the theoretical uptake of 1 mole CO₂ per mole of amine can be achieved. It should be noted that because the formation of the charged carbamate species during the reaction of CO₂ with amines in solution leads to significantly improved conductivities,^[28,84] CO₂-loaded amine suspensions have recently been explored for CO₂ conversion applications.^[28,33–36,85]

The kinetic CO₂ uptake of 8 wt.% PEI and 10 wt.% NOHM-I-PEI solutions is presented in Figure 2a,b, respectively. As expected, the CO₂ capture rate and capacity increased with the CO₂ partial pressure. Additionally, polymer tethering in

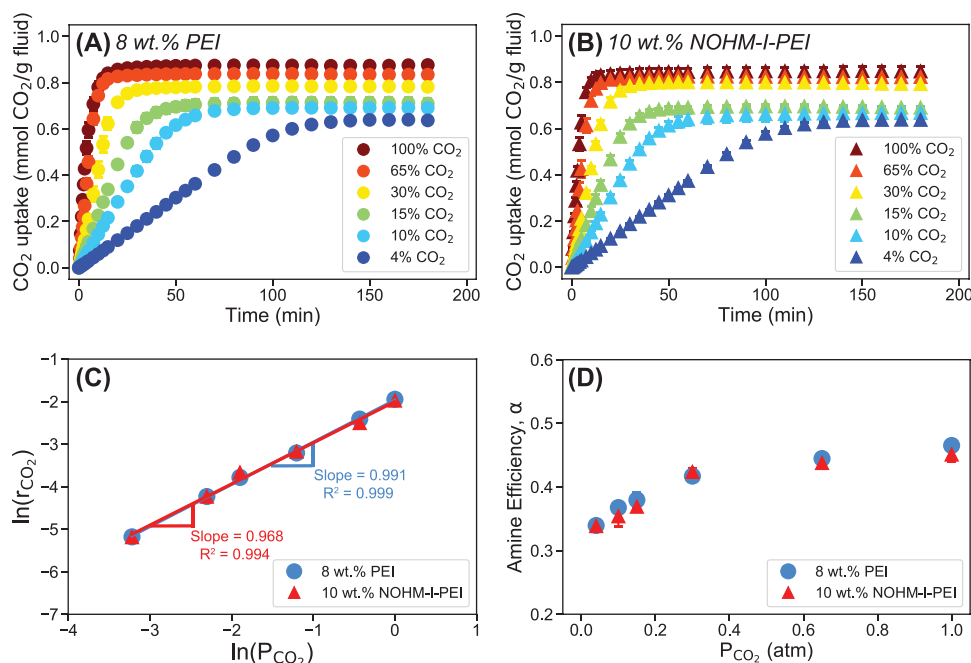


Figure 2. Kinetic CO₂ uptake of a) 8 wt.% PEI and b) 10 wt.% NOHM-I-PEI solutions measured at $P_{\text{CO}_2} = 0.04\text{--}1$ atm. c) Determination of the order of the reaction for CO₂ capture in 8 wt.% PEI and 10 wt.% NOHM-I-PEI. d) Amine efficiency plotted as a function of the CO₂ partial pressure for 8 wt.% PEI and 10 wt.% NOHM-I-PEI solutions.

NOHM-I-PEI does not appear to have a significant impact on the total CO₂ capture capacity suggesting that most of the amine groups in NOHMs are available to capture CO₂. Our prior studies have shown that NOHMs composed of an ionic bond display enhanced oxidative-thermal stability compared to the untethered polymer,^[45,46,49,51] thus highlighting that NOHMs can serve as robust materials for applications involving harsh reaction conditions.

The order of the reaction with respect to CO₂ was determined by the slope of the logarithm of the initial rate of CO₂ capture against the logarithm of the CO₂ partial pressure (see Figure 2c). It is apparent that the PEI and NOHM-I-PEI curves are overlapping which suggests that polymer tethering also does not pose constraints on the rate of CO₂ capture in NOHM-I-PEI. Additionally, the order of the reaction with respect to CO₂ was observed to be 1 in the case of 8 wt.% PEI and 10 wt.% NOHM-I-PEI, as has been reported for other amine-containing solutions.^[79] This signifies that the relationship between the CO₂ capture rate and the CO₂ partial pressure is linear, which could be an important design parameter when developing integrated CO₂ capture and conversion processes.

To understand how effectively the amine groups in the PEI are capturing CO₂ in the aqueous solutions of PEI and NOHM-I-PEI, the dimensionless amine efficiency was employed. The amine efficiency, α , describes the ratio of moles of CO₂ captured to the moles of amines in the solution and can be calculated by

$$\alpha = \frac{\text{mol CO}_2 \text{ captured}}{\text{mol N in solution}} \quad (8)$$

Knowing the CO₂ capture capacity and the number of amines (≈ 47 moles of amine per mole of PEI), the amine effi-

ciency was calculated and plotted as a function of the CO₂ partial pressure in Figure 2d for 8 wt.% PEI and 10 wt.% NOHM-I-PEI. As has been reported for similar aqueous suspensions of amines, the amine efficiency increased with CO₂ partial pressure and approached a value of ≈ 0.5 at $P_{\text{CO}_2} = 1$ atm, the theoretical maximum for primary and secondary amines in an aqueous solution.

2.2. Determining the Optimal KHCO₃ Concentration for CO₂RR in the Presence of Polymer and NOHM Additives

While PEI and NOHM-I-PEI solutions are ionically conductive, they are not as conductive as the conventional electrolytes. Thus, supporting electrolyte (i.e., 0.1 molal KHCO₃) was added to further improve the ionic conductivity of aqueous NOHM-based solutions and enhance their functionality for electrochemical applications. We studied the effect of KHCO₃ concentration on the CO₂ capture capacity and initial CO₂ capture rate of the aqueous suspensions of PEI and NOHM-I-PEI, at a partial pressure of $P_{\text{CO}_2} = 0.15$ atm, which is representative of CO₂ concentrations in flue gases.^[77,78] Figure 3a,b depict the kinetic CO₂ uptake data for 8 wt.% PEI and 10 wt.% NOHM-I-PEI, respectively, as the salt concentration was increased from 0.0 molal to 1.0 molal KHCO₃. An initial inspection of the data revealed that the initial rate of CO₂ capture did not change as the salt concentration increased, though the CO₂ capture capacity (per g of fluid) steadily decreased with salt addition. By plotting the initial rate of CO₂ capture and the amine efficiency (α) as a function of the salt concentration in Figure 3c,d, respectively, these trends can be more directly observed. The fact that the initial rate of CO₂ capture remained unaffected by

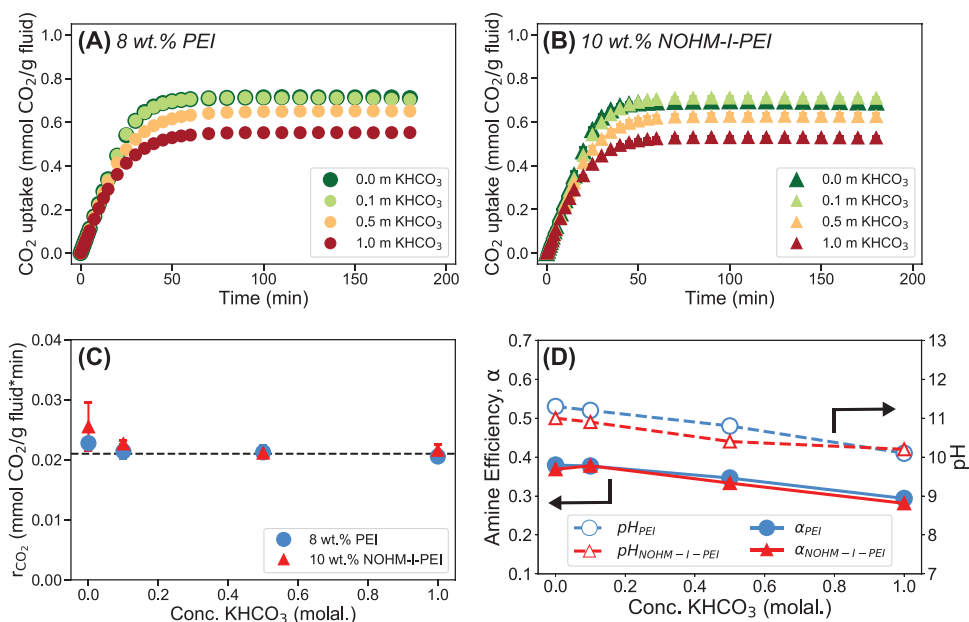
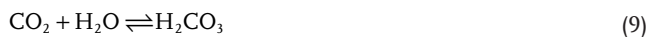


Figure 3. Effect of KHCO_3 concentration on the CO_2 capture behaviors of a) 8 wt.% PEI and b) 10 wt.% NOHM-I-PEI, at $P_{\text{CO}_2} = 0.15$ atm. c) Initial CO_2 uptake rate and d) amine efficiency and pH plotted as a function of the KHCO_3 concentration for 8 wt.% PEI and 10 wt.% NOHM-I-PEI solutions.

the salt concentration is an excellent finding which suggests that the salt ions (i.e., K^+ , HCO_3^- and/or CO_3^{2-}) do not impede the ability of the amine functional groups of the PEI polymer to capture CO_2 .

Moreover, the reduced CO_2 capture capacity of the electrolytes as the salt is added can be explained by a combination of solution pH and CO_2 equilibrium effects. Since CO_2 is a weakly acidic gas, a higher pH value (i.e., more basic solution) will ensure a higher driving energy for CO_2 capture.^[85] Figure 3d also displays the measured pH values of 8 wt.% PEI and 10 wt.% NOHM-I-PEI electrolytes as a function of KHCO_3 concentration, and as salt was added, the pH steadily declined. Additionally, the HCO_3^- anion is known to partition between the CO_3^{2-} and CO_2 species in aqueous solutions as shown in the following equilibrium reactions



Thus, the addition of a significant amount of KHCO_3 in the solutions could introduce more CO_3^{2-} and HCO_3^- species initially, which would then limit additional CO_2 loading in the amine solutions.

Because there was almost no difference between the total CO_2 capture capacity when there was no salt and 0.1 molal. KHCO_3 loaded into the electrolytes, this salt concentration was selected for CO_2 RR experiments over the silver nanoparticle catalyst. Similar concentrations of KHCO_3 have been reported for use in the CO_2 RR throughout the literature because of the ability of the bicarbonate ion to serve as an excellent

buffer^[17,86,87] and increase local concentrations of CO_2 near the electrochemical interface.^[88] In a similar fashion, we also confirmed that the addition of 0.1 molal. KHCO_3 did not reduce the CO_2 capture capacity ($P_{\text{CO}_2} = 1$ atm) of the 8 wt.% HPE and 10 wt.% NOHM-I-HPE solutions (see Figure S1, Supporting Information).

2.3. Impact of Polymer Functional Groups on CO_2 Capture Capacity and Electrolyte pH and Conductivity

The goal of this study was to employ NOHMs of variable CO_2 binding energy (i.e., chemisorption versus physisorption) to understand the resulting effect on the CO_2 RR. Thus, we synthesized NOHMs composed of polymers with ether groups (i.e., NOHM-I-HPE) and amine groups (i.e., NOHM-I-PEI) ionically tethered to SiO_2 nanoparticles. It is widely known that aqueous amine solutions capture CO_2 via chemisorption and ether groups interact with CO_2 via physisorption. Figure 4 presents the CO_2 capture capacity of the 8 wt.% PEI, 10 wt.% NOHM-I-PEI, 8 wt.% HPE, 10 wt.% NOHM-I-HPE and an aqueous solution of 0.1 molal. KHCO_3 , at $P_{\text{CO}_2} = 1.0$ atm. It is clear that the addition of any of the polymers or NOHMs studied led to an increase in the CO_2 capture capacity. Additionally, it was found that the amine containing polymers/NOHMs had about an order of magnitude higher CO_2 capture capacity than their ether containing counterparts.

As mentioned previously, the concentrations of polymers and NOHMs tested were strategically selected to normalize for the mass of inert SiO_2 present in the NOHMs samples. Thus, it was expected for the CO_2 capture capacity to be very similar between the corresponding untethered polymer and NOHM-based solutions. However, the 8 wt.% HPE displayed a CO_2 capture capacity which was notably higher than that of the 10 wt.%

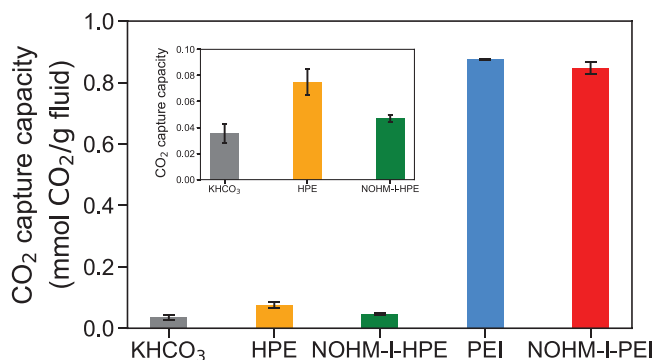


Figure 4. CO₂ capture capacity represented for 0.1 molal. KHCO₃, 8 wt.% HPE, 10 wt.% NOHM-I-HPE, 8 wt.% PEI and 10 wt.% NOHM-I-PEI at 25 °C and $P_{\text{CO}_2} = 1$ atm. Polymer and NOHM-based fluids were not doped with any salt.

NOHM-I-HPE. This can be explained by the presence of free -NH_2 groups in the untethered Jeffamine M2070 polymer (see Figure 1b for the structure of HPE), which would be expected to capture some CO₂ via chemisorption. More specifically, in the HPE chain, there is ≈ 1 primary amine group per polymer chain, which has ≈ 41 repeat units. In NOHM-I-HPE, the amine terminus is used as the site of ionic tethering to the SiO₂ nanoparticle, and thus would not be expected to participate in CO₂ capture in the same manner as a primary amine. Similarly, NOHM-I-PEI was observed to have a slightly lower CO₂ capture

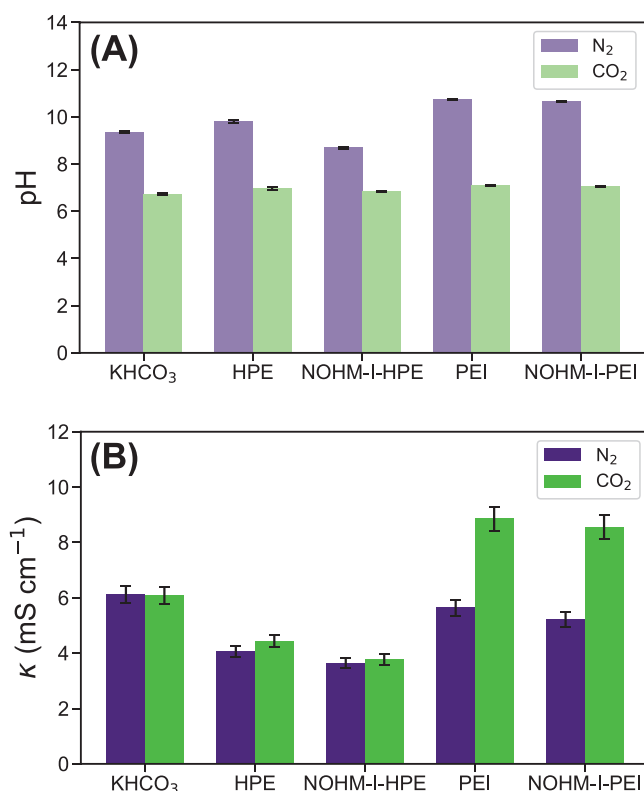


Figure 5. Measured a) pH and b) ionic conductivity of 0.1 molal. KHCO₃, 8 wt.% HPE, 10 wt.% NOHM-I-HPE, 8 wt.% PEI and 10 wt.% NOHM-I-PEI after being purged with N₂ or CO₂ for 30 min. All polymer and NOHMs samples were doped with 0.1 molal. KHCO₃.

capacity than the corresponding PEI solution, though the difference was much less significant due to the larger number of amine groups present in the polymer backbone.

The electrolyte pH^[89–91] and conductivity^[32,87] have also been shown to influence product selectivity and formation rates in electrochemical CO₂ reduction. Thus, we measured the pH and conductivity of 0.1 molal. KHCO₃ and the 4 polymer/NOHMs solutions mentioned above doped with 0.1 molal. KHCO₃, after being purged with N₂ and CO₂ for 30 min. The results are displayed in Figure 5. When purged with N₂, the pH of all of the solutions were variable and ranged from 8.7 to 10.8, due to the different functional groups present. Conversely, upon CO₂ capture, the solutions all displayed a pH very close to 7. As the pH of the electrolyte has been shown to affect the CO₂RR performance,^[89–91] it is important that the bulk pH is well controlled and accounted for in CO₂RR experiments. Since this was the case, no further pH control technique was applied to the CO₂-purged electrolytes employed in this study.

The conductivity of the 0.1 molal. KHCO₃ (6.12 ± 0.31 mS cm⁻¹), 8 wt.% PEI (5.64 ± 0.28 mS cm⁻¹), and 10 wt.% NOHM-I-PEI (5.22 ± 0.26 mS cm⁻¹) electrolytes purged with N₂ were quite similar. PEI is reportedly known to possess a conductive nature due to the large number of amine groups, some of which can become protonated when dissolved in water.^[53] Thus, it was not expected to see a significant drop in the conductivity of the PEI and NOHM-I-PEI-based electrolytes compared to the 0.1 molal. KHCO₃. Contrarily, the conductivity of the 8 wt.% HPE (4.05 ± 0.20 mS cm⁻¹) and 10 wt.% NOHM-I-HPE (3.63 ± 0.18 mS cm⁻¹) electrolytes were notably lower than that of the 0.1 molal. KHCO₃, suggesting that the ether groups along the HPE backbone do not contribute to solution conductivity and the addition of bulky polymer components reduced the overall mobility of ions in solution. Upon CO₂ exposure for 30 min, the conductivity of 0.1 molal. KHCO₃ (6.08 ± 0.30 mS cm⁻¹), 8 wt.% HPE (4.43 ± 0.22 mS cm⁻¹), and 10 wt.% NOHM-I-HPE (3.77 ± 0.19 mS cm⁻¹) remained relatively unchanged. As mentioned previously, the reaction of CO₂ with amines in aqueous suspensions leads to the formation of charged carbamate species^[28] (see Equation 1), and thus, the conductivity of 8 wt.% PEI (8.85 ± 0.44 mS cm⁻¹) and 10 wt.% NOHM-I-PEI (8.56 ± 0.43 mS cm⁻¹) increased by a factor of ≈ 1.5 . It should be noted that the conductivity of the NOHMs were slightly lower than that of the corresponding untethered polymer.

Overall, the change in functional groups in the polymer canopy of NOHMs will ultimately affect the electrolyte CO₂ capture capacity, pH, and conductivity. Ideally, electrolytes with high CO₂ capture capacity and conductivity are desired for CO₂RR applications. However, it was important to understand whether the captured CO₂ in NOHM-based electrolytes was electrochemically active.

2.4. Effect of Varying CO₂ Binding Energy of NOHMs on CO₂ Electrochemical Conversion Over a Silver Nanoparticle Catalyst

After demonstrating the improved CO₂ capture capacity of the NOHM-I-PEI and NOHM-I-HPE electrolytes compared to one of the conventional CO₂RR electrolytes (i.e., 0.1 molal. KHCO₃), we explored the effect of the NOHMs on the CO₂RR

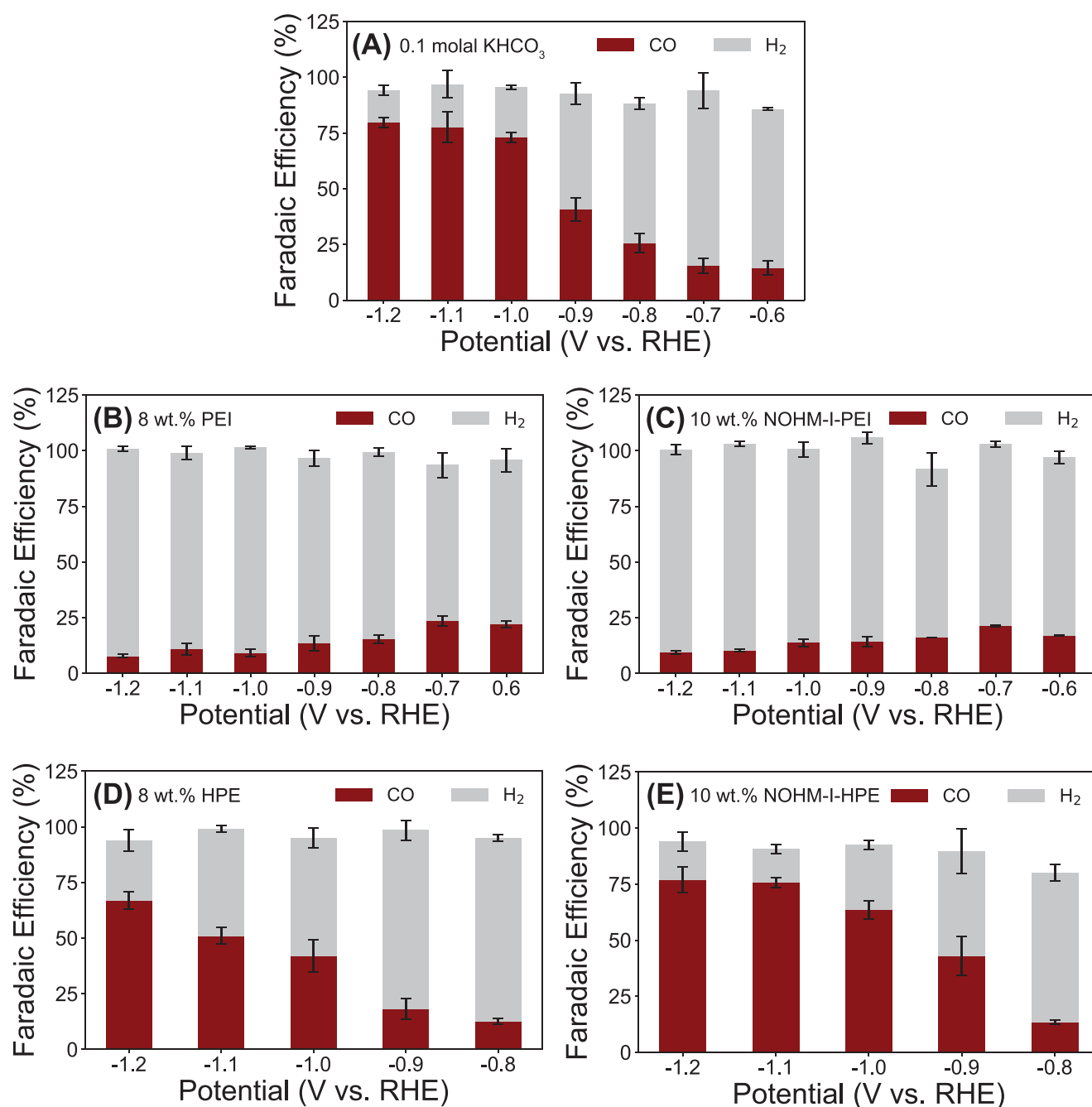


Figure 6. Faradaic efficiency distribution of the 1-hr chronoamperometry of CO_2 -purged a) 0.1 molal. KHCO_3 , b) 8 wt.% PEI, c) 10 wt.% NOHM-I-PEI, d) 8 wt.% HPE, and e) 10 wt.% NOHM-I-HPE over a silver nanoparticle catalyst. All polymer and NOHMs samples were doped with 0.1 molal. KHCO_3 and three experimental trials were conducted at each iR-corrected potential.

by performing 1-hr chronoamperometry experiments over a silver nanoparticle catalyst, in an H-cell. The gas-phase products of the aqueous CO_2 RR, namely H_2 and CO, were measured throughout the course of the reaction and the Faradaic efficiency (FE) of the reactions is depicted in Figure 6 for the 5 electrolytes employed in this study. Additionally, the measured current density responses are reported in Figure S2 (Supporting Information) as a function of time. Figure 6a shows the gas-phase product distribution for the electrolysis of a CO_2 -

purged 0.1 molal. KHCO_3 solution. As is typically observed for silver catalysts, the CO selectivity increased significantly as the applied cathode potential became more negative.^[28,29,92,93] It should be noted that the H_2 and CO faradaic efficiencies and current densities observed in this study for 0.1 molal KHCO_3 at -1.0 V versus RHE were in good agreement with the literature for silver catalysts employed for the CO_2 RR, thus ensuring our confidence in the results (see Table S1, Supporting Information).

Upon inspection of the data presented in Figure 6b,c, the selectivity of the CO₂RR was clearly distinct when the electrolyte was changed to 8 wt.% PEI or 10 wt.% NOHM-I-PEI. For example, at less negative potentials (i.e., −0.6 and −0.7 V versus RHE) the FE_{CO} was ≈ 5% higher when compared to the FE_{CO} of CO₂RR in 0.1 molal. KHCO₃. This observation suggests that the conversion of “free” CO₂ at low applied potentials was facilitated in the presence of the absorbed PEI or NOHM-I-PEI layer on the surface of the electrode. CO₂ confined in that electrolyte layer seemed to have different electrochemical reaction behaviors and our future studies will further probe this effect. On the other hand, as the potential became more negative, the FE_{CO} slightly decreased in 8 wt.% PEI or 10 wt.% NOHM-I-PEI-based electrolytes, suggesting that catalyst-electrolyte interactions and/or the strength of the carbamate bond limit the ability of captured CO₂ to be converted electrochemically. Thus, while a strong CO₂ binding energy (e.g., carbamate bonds) is favored in terms of achieving a high CO₂ loading in the electrolyte, it challenges the conversion of captured CO₂ unless energy is added to release CO₂ into an electrochemically active form (e.g., a thermal swing similar to the solvent regeneration step used for CO₂ capture technologies).

Conversely, the electrolytes containing HPE and NOHM-I-HPE displayed a much more similar FE distribution of the H₂ and CO to the 0.1 molal. KHCO₃ case (see Figure 6d,e), especially at more negative applied potentials (i.e., −1.0, −1.1, and −1.2 V versus RHE). At less negative potentials, such as −0.8 and −0.9 V versus RHE, the H₂ evolution reaction (HER) was observed to dominate in HPE and NOHM-I-HPE containing electrolytes. These results demonstrate that the chemistry of the polymer canopy and the resulting binding energy for CO₂ can be used to tune the selectivity of the NOHM-mediated CO₂RR.

Furthermore, in the case of PEI and NOHM-I-PEI-based electrolytes, polymer tethering did not appear to significantly change the distribution of the product formation as the FE for H₂ and CO remained more or less equivalent across the potential range. However, the FE_{CO} was 10–15% higher for NOHM-I-HPE-based electrolytes when compared to the untethered HPE-based electrolytes. In our recent mechanistic study of NOHM-mediated Zn electrodeposition, we showed that the polymer tethering in NOHM-I-HPE led to noticeable differences in the electrochemical deposition of Zn over a glassy carbon electrode, when compared to the untethered HPE. Briefly, the HPE canopy organization around the bulky SiO₂ nanoparticle was demonstrated to affect the delivery of Zn²⁺ ions to the electrode surface, as evidenced by enhancements in the overall current density of the deposition reaction and the exchange current density after Zn deposition.^[66] The adsorbed layer of NOHMs on the electrode surface led to multiple transport pathways. Based on the improvement of FE_{CO} in the NOHM-I-HPE compared to the untethered HPE in this study, a slight benefit of the polymer structure in the NOHM-I-HPE was also observed. Taken together, the findings presented in this study, therefore, suggest that the polymer functional groups and their structure/conformation may also play a significant role at the electrochemical interface, in particular for heterogeneous reactions such as the CO₂RR.

The results presented in Figure 6 illustrate that the NOHMs play a role in tuning the products of CO₂RR, however, they do

not give any indication of the effect of NOHMs on the rate of CO₂ conversion. Thus, the partial current density of H₂ (j_{H_2}) and CO (j_{CO}) formation at a given potential were determined by multiplying the calculated FE (see Figure 6) by the respective total steady state current density (j_{tot}) of the CO₂RR (see Figure S2, Supporting Information). For example, the following can be used to determine j_{H_2} and j_{CO} , respectively

$$j_{H_2} = j_{tot} \times FE_{H_2} \quad (12)$$

$$j_{CO} = j_{tot} \times FE_{CO} \quad (13)$$

Using Equations 12 and 13, the partial current densities of H₂ and CO were calculated and plotted in Figure 7 as a function of the applied potential for the 5 electrolytes explored in this study. It should be noted that the total current density of CO₂RR produced by electrolytes containing HPE and NOHM-I-HPE was notably lower than the other electrolytes studied (see Figure S2, Supporting Information). It is suggested that strong catalyst-electrolyte interactions between the HPE canopy and the electrode limited the overall current density, since the applied potentials for all bulk electrolysis experiments were iR-corrected. Thus, using the same experimental conditions (i.e., electrode area and CO₂ sweep gas flowrate), accurate product detection was not possible at −0.6 and −0.7 V versus RHE for these HPE and NOHM-I-HPE-based electrolytes.

In Figure 7a, it is evident that the HPE-based electrolyte displayed a similar amount of H₂ production compared to 0.1 molal. KHCO₃ in the entire potential range tested, while the 10 wt.% NOHM-I-HPE-based electrolyte displayed a slight suppression in the rate of H₂ formation, which is highly desired for CO₂RR applications. However, the rate of CO production in the HPE and NOHM-I-HPE electrolytes was slightly reduced compared to that of the 0.1 molal. KHCO₃, likely due to strong interactions between the HPE and the electrode surface blocking some of the catalytic active sites. The overall potential-dependent CO₂RR performance of electrolytes containing HPE and NOHM-I-HPE matched the trends observed in the 0.1 molal. KHCO₃. For example, the rate of H₂ formation remained relatively constant at potentials more negative than −0.8 V versus RHE while the rates of CO production continually increased as more negative potentials were applied.

Moreover, the PEI and NOHM-I-PEI-based electrolytes displayed opposing H₂ and CO production trends compared to those described for 0.1 molal. KHCO₃. In particular, the rates of H₂ production continually increased as more negative potentials were applied, whereas the CO production appeared to plateau as the potential reached −1.2 V versus RHE. These findings revealed that at less negative applied potentials, favorable interactions between the amine functional groups of the PEI and NOHM-I-PEI-based electrolytes could promote the electrochemical conversion of “free” CO₂. Conversely, at more negative potentials, the room temperature electrochemical stability of the carbamate bond^[35,36,94] and/or unique catalyst-electrolyte interactions led to a favoring of the HER, over a silver nanoparticle catalyst. These observations are in good agreement with recent literature reports documenting the CO₂ reduction behaviors of aqueous amine-electrolytes under similar reaction conditions (see Table S2, Supporting Information).

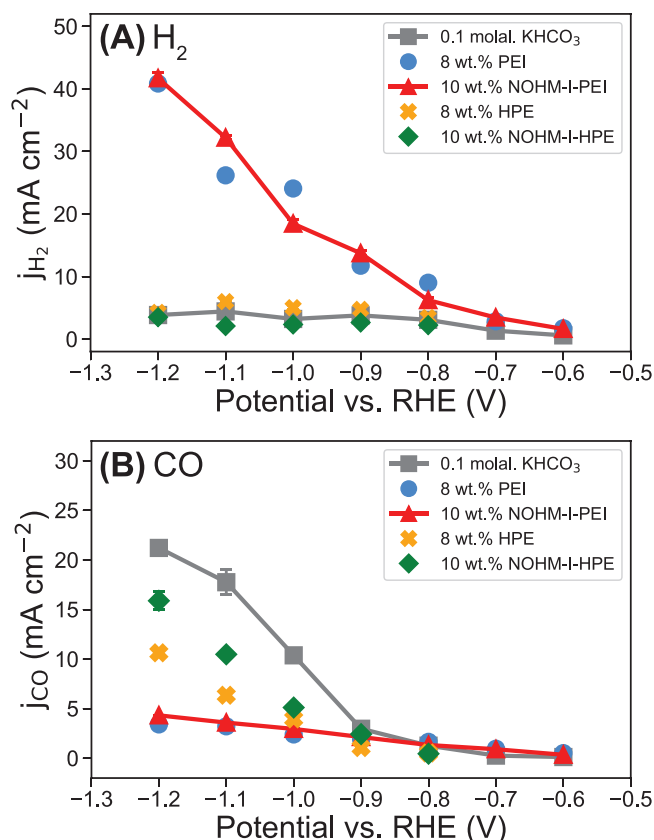


Figure 7. Partial current density of a) H_2 and b) CO formation represented as a function of the iR-corrected potential for CO_2 -purged 0.1 molal. KHCO_3 , 8 wt.% PEI, 10 wt.% NOHM-I-PEI, 8 wt.% HPE and 10 wt.% NOHM-I-HPE, during 1-hr chronoamperometry over a silver nanoparticle catalyst. All polymer and NOHMs samples were doped with 0.1 molal. KHCO_3 and three experimental trials were conducted at each applied potential.

Because the formation of some compounds via CO_2RR is currently limited by low selectivity and reaction rate (i.e., methanol synthesis), the production of tunable syngas ratios via electrochemical pathways can be an invaluable tool for the development of chemical precursors for a variety of processes.^[8,9] The syngas ratios (H_2/CO) for the aqueous CO_2RR of a silver nanoparticle catalyst in the 5 electrolytes explored in this study are reported in Figure 8 as a function of the applied potential and Figure 9 illustrates the effect of the polymer canopy's CO_2 binding energy on the observed CO_2RR behaviors in NOHM-based electrolytes. Overall, the polymer and NOHM-based electrolytes were able to form syngas at H_2/CO ratios ranging from 0.22 ± 0.08 (NOHM-I-HPE at -1.2 V versus RHE) to 11.85 ± 1.24 (NOHM-I-PEI at -1.2 V versus RHE), highlighting their ability to be used in applications with varying H_2 and CO concentration requirements, such as, methanol synthesis (H_2/CO ratio of 2), dimethyl ether formation (H_2/CO ratio of 1), syngas fermentation (H_2/CO ratio ranging from 1 to 3.33) and Fischer-Tropsch reactions (H_2/CO ratio of 2).^[8–11] It is important to note that the addition of NOHMs to the electrolyte was observed to reduce the current density of desired CO_2RR products at most applied potentials, when compared to the 0.1 molal. KHCO_3 . However, the results of this study have informed the design

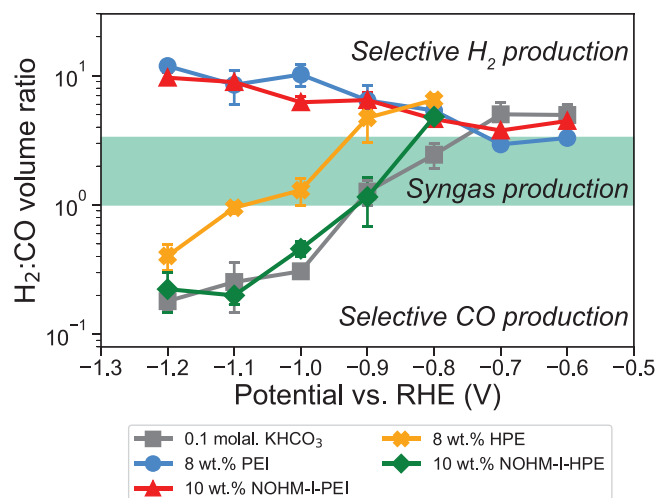


Figure 8. Effect of iR-corrected potential on the $\text{H}_2:\text{CO}$ product ratio for CO_2 -purged 0.1 molal. KHCO_3 , 8 wt.% PEI, 10 wt.% NOHM-I-PEI, 8 wt.% HPE and 10 wt.% NOHM-I-HPE, during 1-hr chronoamperometry over a silver nanoparticle catalyst. All polymer and NOHMs samples were doped with 0.1 molal. KHCO_3 and three experimental trials were conducted at each applied potential.

of NOHMs which can facilitate the efficient delivery of CO_2 to the electrode surface for conversion to upgraded chemicals and fuels. For example, conductive polymers with an intermediate CO_2 binding energy and a stimuli responsive (e.g., magnetic field, light etc.) nanoparticle are desired to enable the facile reaction of CO_2 at the electrode interface and tune the composition of the electrolyte double layer, respectively. Furthermore, CO_2 bound strongly to NOHMs containing amine moieties could be promoted for electrochemical reduction through a moderate thermal swing process (e.g., temperature of $60\text{--}75^\circ\text{C}$), as has recently been demonstrated.^[35,36] This energy transfer could be efficiently applied through careful selection of the nanoparticle core. Both electrolyte and reactor/process design will be critical to effectively combine CO_2 capture with conversion at industrially relevant rates.

2.5. Exploring Catalyst-NOHMs Interactions via SEM-EDS Imaging

It was hypothesized that strong catalyst-polymer interactions led to the observed differences in the product distributions and current densities associated with the iR-corrected CO_2 electrolysis when PEI, NOHM-I-PEI, HPE or NOHM-I-HPE were introduced to the electrolyte, compared to the 0.1 molal. KHCO_3 . Throughout the literature, probing the catalyst-electrolyte interactions has been demonstrated to be insightful in further understanding the effect of novel electrolytes in CO_2 conversion.^[19,20,30,40,42–44] As a result, we employed a scanning electron microscope (SEM) coupled with energy dispersive X-ray spectroscopy (EDS) analysis to detect the presence of polymers and NOHMs on the silver nanoparticle electrode surface after CO_2 conversion.

The SEM images of the neat electrode and after 1-hr electrolysis in the 5 electrolytes tested in this work are shown

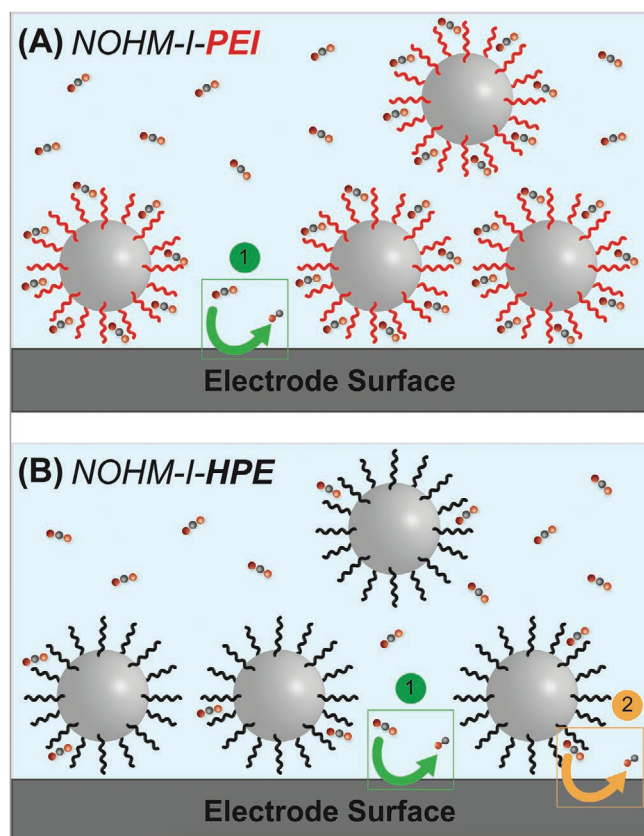


Figure 9. Schematic representing the different proposed CO_2 reduction pathways in NOHM-based electrolytes. a) When the binding energy between the functional groups in the polymer canopy of NOHMs is too strong and results in carbamate formation, only “free” CO_2 can be converted under ambient temperature, as depicted by Pathway 1. b) When the CO_2 is captured by NOHMs via physisorption, the weakly bound CO_2 can be converted (e.g., Pathway 2) in addition to the “free” CO_2 .

in Figures S3–S5 (Supporting Information), at three different magnification levels. After CO_2RR was completed, the electrodes were rinsed and then dried overnight with a vacuum oven. Then, an EDS technique was applied to map the elemental composition of the electrode surface with the aim of detecting species unique to the polymer and NOHM-based electrolytes (i.e., N and/or Si). The elemental mapping obtained from the EDS analysis is shown in **Figure 10** and the results clearly depict the detection of N on the electrodes which had CO_2RR performed in 8 wt.% PEI and 10 wt.% NOHM-I-PEI, as expected. Additionally, the electrodes which were employed for CO_2 reduction in 10 wt.% NOHM-I-PEI and 10 wt.% NOHM-I-HPE displayed the presence of Si peaks, demonstrating the surface adsorption of NOHMs. It should be noted that the N and Si peaks detected are quite small, but the electrodes were analyzed after applying a rinsing procedure, which suggests that the polymer and/or NOHMs detected on the surface of the electrode are quite strongly adsorbed during the CO_2RR . Overall, these findings revealed that the polymers and NOHMs employed in this study have unique interactions with the Ag nanoparticle catalyst, though more in-depth electrode surface characterization tools are required to probe the exact nature

of the catalyst-electrolyte interactions. The results of this study illustrate that not only is it important to improve the solubility of CO_2 in the electrolyte, but the catalyst-electrolyte interactions need to promote the subsequent conversion of the captured CO_2 . By probing the nature of the electrochemical interface during the CO_2RR , polymer canopies with optimized functional groups (i.e., CO_2 binding energy, conductivity, pH, viscosity) can be identified for enhanced CO_2 conversion performance.

3. Conclusions

In this study, we observed that the NOHM-mediated electrochemical conversion of CO_2 on a silver nanoparticle catalyst led to a change in the selectivity and reaction rate of the product formation when compared to the conventional aqueous electrolyte (i.e., 0.1 molal. KHCO_3). In particular, we explored the effect of the polymer functional groups of NOHMs on the electrochemical conversion of CO_2 . For example, the CO_2 -loaded PEI and NOHM-I-PEI containing electrolytes displayed increased total reaction rates at all applied potentials. At -0.8 V versus RHE, the PEI and NOHM-I-PEI containing electrolytes were found to produce CO at a slightly higher rate (1.65 ± 0.03 and 1.33 ± 0.01 mA cm^{-2}) than the 0.1 molal. KHCO_3 (1.26 ± 0.05 mA cm^{-2}). Alternatively, at -1.2 V versus RHE, the CO formation reached a plateau for PEI and NOHM-I-PEI containing electrolytes (3.41 ± 0.03 and 4.32 ± 0.03 mA cm^{-2}) while the CO formation significantly increased as the applied potential became more negative for 0.1 molal. KHCO_3 (21.21 ± 0.47 mA cm^{-2}). This was explained to be a result of the inability of the carbamate bond to be broken electrochemically at 25°C ^[35,36,94] and/or unique interactions between the functional groups of the PEI polymer and the surface of the electrode promoting the HER. Furthermore, at all applied potentials the total current density was slightly lower for HPE and NOHM-I-HPE electrolytes compared to the 0.1 molal. KHCO_3 . At -0.8 V versus RHE, CO formation rates in the HPE and NOHM-I-HPE electrolytes were noticeably lower (0.53 ± 0.01 and 0.45 ± 0.01 mA cm^{-2}), while at -1.2 V versus RHE their performance approached that of the 0.1 molal. KHCO_3 (10.63 ± 0.41 and 15.89 ± 0.93 mA cm^{-2}). Under most of the conditions explored, the NOHM-based electrolytes performed as well as or better than the corresponding untethered polymer-based electrolytes. Additionally, liquid-like NOHMs composed of an ionic bond have been shown to display a higher oxidative-thermal stability than the corresponding untethered polymers,^[45,49,51,74] thus illustrating their robustness as functional materials under harsh oxidizing conditions. Moreover, the multitude of polymer, linker, and nanoparticle combinations will allow for the design of materials that are responsive to a change in the environment (i.e., temperature, pH, ionic stimulus, and/or magnetic field) that can be used in a variety of integrated CO_2 capture and conversion applications. Overall, the results of this work demonstrated that NOHMs appear to be promising electrolyte additives for combined CO_2 capture and conversion applications, and the further design of NOHM-based electrolytes should focus on more conductive polymer canopies with intermediate CO_2 binding energy and NOHMs with functionalized cores.

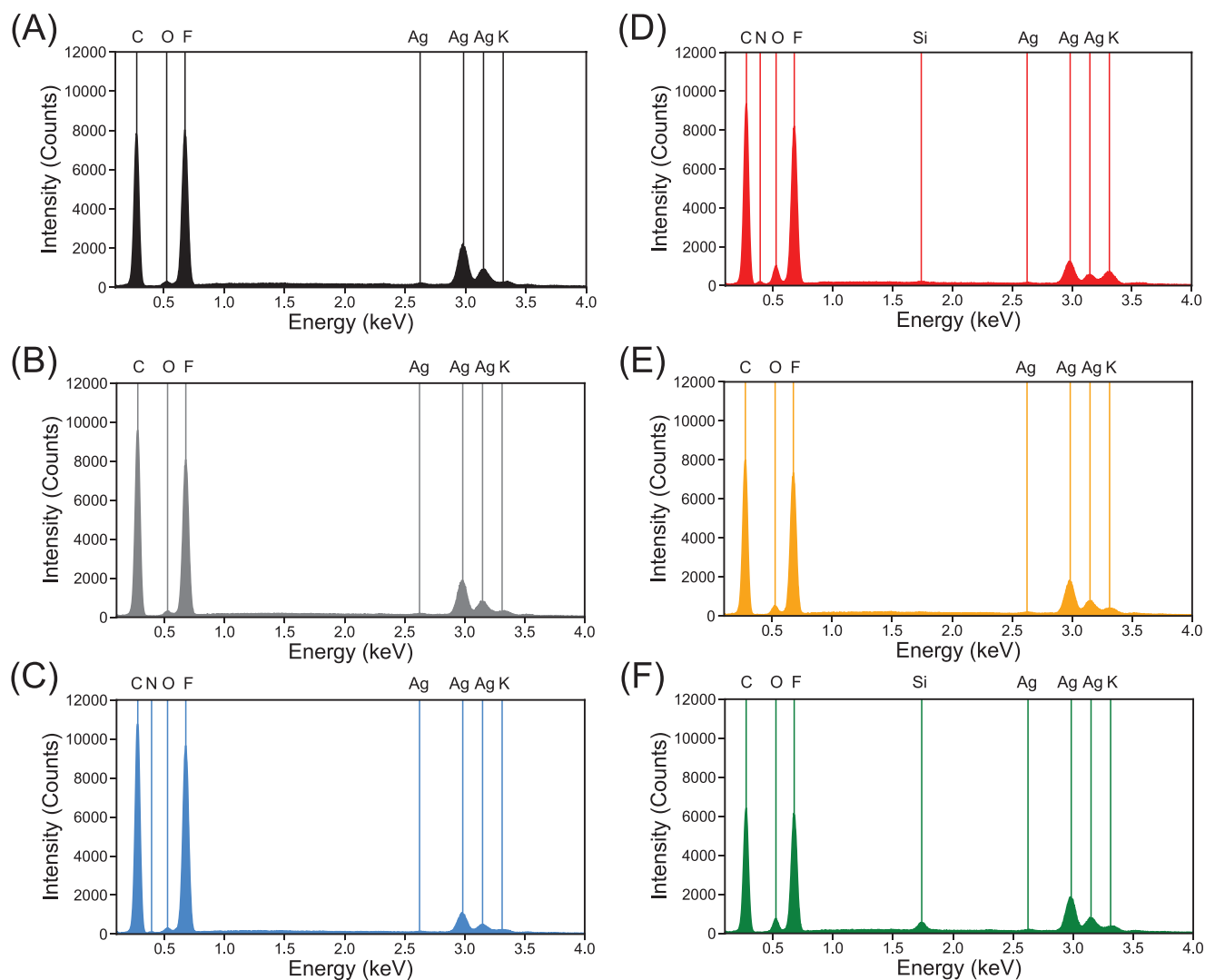


Figure 10. EDS identification of the elements present on the a) neat Ag nanoparticle surface and after 1 hr of CO₂ electrolysis at −1.2 V vs. RHE in b) 0.1 molal. KHCO₃, c) 8 wt.% PEI, d) 10 wt.% NOHM-I-PEI, e) 8 wt.% HPE and f) 10 wt.% NOHM-I-HPE. The electrolytes containing polymer or NOHMs were doped with 0.1 molal. KHCO₃. Elements present on each electrode are identified.

4. Experimental Section

Synthesis of NOHM-I-PEI: Liquid-like NOHM-I-PEI was synthesized as previously reported and a representative structure is shown in Figure 1a.^[45,52,53] Briefly, a 3 wt.% mixture of 10 nm diameter SiO₂ nanoparticles (Ludox SM-30, obtained from Sigma Aldrich) in deionized water was prepared and then stirred for at least 30 min. To replace any positively charged cations with protons, the diluted silica suspension was then run through a cation exchange column filled with 50 g of Dowex Marathon C hydrogen form (Sigma-Aldrich). Next, the silica nanoparticles were functionalized by the dropwise addition of a 20 wt.% solution of branched poly(ethylenimine) (MW = 2000 g mol^{−1}, Polysciences Inc.) in deionized water, while stirring. According to the manufacturer, the poly(ethylenimine) (referred to as PEI) contains primary, secondary, and tertiary amines at an approximate ratio of 40/36/24. Once all of the PEI had been added to the nanoparticles, the solution was then left to stir for several hours. Then, this solution was placed in a vacuum oven set to 60 °C overnight to evaporate the excess water. In this study, the mass ratio of PEI to SiO₂ is roughly 80:20 in the resulting NOHM-I-PEI. Before preparing any samples, neat PEI and

NOHM-I-PEI were placed in the vacuum oven at 75 °C for 2 hr to ensure the removal of any absorbed moisture and/or CO₂.

Synthesis of NOHM-I-HPE: Liquid-like NOHM-I-HPE was synthesized using previously described methods and a representative structure is shown in Figure 1b.^[46,51,57–59,74,95–97] 18.3 g of a 30 wt.% colloidal suspension of 10 nm diameter SiO₂ nanoparticles (Ludox SM-30 obtained from Sigma-Aldrich) was diluted to a concentration of 4 wt.% in deionized water. 30 g of a 35 wt.% 3-(trihydroxysilyl)-1-propane-sulfonic acid solution (Gelest Inc.) was further diluted to a final concentration of 7 wt.%. The silica suspension was then added to the silane solution in a dropwise manner. Then, 1 M NaOH was added dropwise to this solution to a pH 5 and the final solution was stirred at 70 °C for 24 h. Excess silane linker molecules were removed by dialyzing the solution against deionized water for a total of 48 h (SnakeSkin Dialysis Tubing 3500 MW cutoff, Thermo Scientific) with frequent water changing. To protonate the sulfonate groups on the linker molecules and remove any other cations, the surface functionalized silica nanoparticles were then passed through a cation-exchange resin (Dowex Marathon C hydrogen form, Sigma-Aldrich).

Next, an amine-terminated polyether, Jeffamine M2070 (MW = 2000 g mol^{−1}, acquired from Huntsman Co.), was ionically

tethered to the functionalized nanoparticles. A 20 wt.% solution of Jeffamine M2070 (referred to as HPE) in deionized water was titrated into the functionalized silica nanoparticles solution until the equivalence point was reached (pH 6.5), where all the linker groups were neutralized. The resulting solution containing the ionically tethered polymers was placed in a vacuum oven at 60 °C for 24 h to remove the water used in the previous steps. Prior to performing any experiments, neat HPE and NOHM-I-HPE were placed in a vacuum oven at 75 °C for at least 2 hr, in order to remove any absorbed moisture.

Gravimetric Measurement of CO₂ Capture Capacity: The CO₂ capture capacity of various polymer and NOHM-based fluids/electrolytes were measured gravimetrically. Gas tanks containing different mixtures of CO₂ and N₂ were used to simulate flue gases with different partial pressures of CO₂ ranging from 0.04 to 1 atm. About 20 g of the polymer or NOHM-based fluid/electrolyte was loaded into a 3-neck valve fitted with a 2 μm gas sparger (Fisher) on one of the ports. The two remaining ports were fitted with small outlet vents to prevent pressure buildup within the cell. The CO₂ containing gas stream was continuously fed at 100 mL min⁻¹ to the port fitted with the gas sparger after first passing through a bubbler to minimize solvent evaporation. During the course of the reaction, the 3-neck cell was weighed at several time points using an analytical balance (AB104-S/FACT, Mettler Toledo, precision of 10⁻⁴ g), and the increase in mass was converted to absorbed moles of CO₂ (MW = 44.01 g mol⁻¹). The reaction was performed at room temperature, ≈ 25 °C.

pH and Ionic Conductivity Measurement: The pH and ionic conductivities of the 0.1 molal. KHCO₃, 8 wt.% PEI, 10 wt.% NOHM-I-PEI, 8 wt.% HPE and 10 wt.% NOHM-I-HPE were measured after being purged with N₂ or CO₂ for 30 min. It should be noted that all polymer and NOHM-based electrolytes were doped with 0.1 molal. KHCO₃. The pH of these electrolytes was measured at room temperature using a previously calibrated benchtop pH meter (Fisher Scientific). The ionic conductivities of these electrolytes were measured at 25 ± 1 °C using an S230 SevenCompact benchtop conductivity meter (Mettler Toledo) equipped with a micro 2 platinum poles conductivity probe (Cond probe InLab 752—6 mm, Mettler Toledo), which can measure conductivities in the range of 0.01–112 mS cm⁻¹. The uncertainty in conductivity was determined to be within ± 5% for all samples.

Ag Nanoparticle Electrode Preparation: The electrodes employed in this study were prepared using a previously reported method.^[98] Briefly, the catalyst ink was prepared by mixing 100 mg Ag nanoparticles (<100 nm, 99.5%, Sigma-Aldrich) and 10 wt.% (metal basis) Nafion ionomer (5 wt.% in 50/50 water and isopropanol, Fuel Cell Store) in 10 mL deionized water and 10 mL isopropanol. After sonicating for 1 hr, the catalyst ink was air-sprayed onto Sigracet 39 BB gas diffusion layer (Ion Power) at 100 °C until ≈ 0.25 mg cm⁻² was loaded.

Bulk CO₂ Electrolysis and Product Analysis: 1-hr bulk CO₂ electrolysis experiments were performed using a custom-built H-cell (Pine Research) coupled with an online microGC for gaseous product detection. Using a PMC-500/LO Potentiostat (Princeton Applied Research), the chronoamperometry experiments were performed by holding the potential at values between -0.6 and -1.2 V versus RHE. For all experiments, the working, reference and counter electrodes were a fresh sheet of the silver nanoparticle catalyst (≈ 1 cm²), Ag|AgCl (Pine Research) and a 3 mm diameter graphite rod (Sigma Aldrich), respectively. The two halves of the H-cell were separated by a Nafion 115 membrane (Fuel Cell Store). The working half-cell was sealed so that it was gas tight and contained 30 mL of the CO₂-purged electrolyte, the working electrode, and the reference electrode. Bulk CO₂ electrolysis was carried out in 5 different electrolytes: 0.1 molal. KHCO₃, 8 wt.% PEI, 10 wt.% NOHM-I-PEI, 8 wt.% HPE and 10 wt.% NOHM-I-HPE, where all polymer and NOHM-based electrolytes were doped with 0.1 molal. KHCO₃. In every experiment, the counter half-cell contained 30 mL of CO₂-purged 0.1 molal KHCO₃ and the counter electrode. The counter half-cell was left open to the atmosphere to prevent any pressure buildup within the H-cell. Prior to starting the 1-hr chronoamperometry experiments, the silver nanoparticle catalysts were cleaned using a cyclic voltammetry sweep program and the resistance of the solution was compensated for using an iR detection function on the potentiostat.

The gas-phase products (i.e., H₂ and CO) were analyzed using a previously calibrated microGC Fusion Analyzer (Inficon) during the course of the reaction. A constant stream of CO₂ (45–50 mL min⁻¹) flowed through the working half-cell and passed through a gas dryer before arriving at the microGC, where a custom program was developed for the online gas collection, with sampling occurring every ≈ 5 min. A schematic of our setup for the online CO₂RR product measurement is displayed in Figure S6 (Supporting Information). The main species detected were H₂, CO, and CO₂, with trace amounts of N₂ and O₂ observed as well. Using the properties of the gases and the measured flowrate, the detected volume concentrations of H₂ and CO were converted to mole concentrations and then integrated with respect to time to determine the total number of moles of each product collected over the course of each 1-hr electrolysis experiment. The Faradaic efficiency (FE) was calculated using the following equation

$$FE (\%) = \frac{nFmol_i}{C} \times 100\% \quad (14)$$

where n is the number of electrons transferred per mole of product ($n = 2$ for both H₂ and CO formation), F is Faraday's constant (96485 C mol⁻¹ electron), mol_i refers to the total moles of compound i formed at time, t , and C is the total charge transferred at time, t .

Imaging and Elemental Mapping of the Ag Nanoparticle Electrodes: To visualize the effect of PEI, NOHM-I-PEI, HPE, and NOHM-I-HPE addition on the CO₂RR and to confirm the presence of polymers/NOHMs on the electrode surface, SEM imaging and elemental mapping were performed. The electrode was analyzed using a scanning electron microscope with 5 and 10 kV (Zeiss Sigma VP SEM) equipped with energy-dispersive spectroscopy (EDS), 10 kV, (Bruker XFlash 6j 30 EDS). The electrodes were characterized after being held at -1.2 V versus RHE for 1 hr in each of the 5 CO₂-purged electrolytes studied: 0.1 molal. KHCO₃, 8 wt.% PEI, 10 wt.% NOHM-I-PEI, 8 wt.% HPE and 10 wt.% NOHM-I-HPE. All polymer and NOHM-based electrolytes were doped with 0.1 molal. KHCO₃. Before imaging the electrodes, they were rinsed with DI water immediately after the reaction was completed and then dried overnight under vacuum at 25 °C to remove any residual moisture.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

CO₂ capture and conversion, CO₂ reduction, CO₂RR, electrochemistry, electrolyte, nanoparticle organic hybrid materials (NOHMs), nanoparticles, polymers

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- [1] S. R. Sinsel, R. L. Riemke, V. H. Hoffmann, *Renew. Energy* **2020**, *145*, 2271.
- [2] G. Glenk, S. Reichelstein, *Nat. Energy* **2019**, *4*, 216.
- [3] W. Ren, C. Zhao, *Natl. Sci.* **2020**, *7*, 7.
- [4] Y. Y. Birdja, E. Pérez-gallent, M. C. Figueiredo, A. J. Göttle, F. Callevallejo, M. T. M. Koper, *Nat. Energy* **2019**, *4*, 732.
- [5] M. B. Ross, P. De Luna, Y. Li, C. Dinh, D. Kim, P. Yang, E. H. Sargent, *Nat. Catal.* **2019**, *2*, 648.
- [6] D. T. Whipple, P. J. A. Kenis, *J. Phys. Chem. Lett.* **2010**, *1*, 3451.
- [7] T. Ping, Y. Dong, S. Shen, *ACS Sustainable Chem. Eng.* **2020**, *8*, 18071.
- [8] B. Qin, Y. Li, H. Fu, H. Wang, S. Chen, Z. Liu, F. Peng, *ACS Appl. Mater. Interfaces* **2018**, *10*, 20530.
- [9] Z. Liang, L. Song, M. Sun, B. Huang, Y. Du, *Sci. Adv.* **2021**, *7*, 1.
- [10] S. Cui, C. Yu, X. Tan, H. Huang, X. Yao, J. Qiu, *ACS Sustainable Chem. Eng.* **2020**, *8*, 3328.
- [11] S. A. Ghoneim, R. A. El-Salamony, S. A. El-Temtamy, *World J. Eng. Technol.* **2016**, *04*, 116.
- [12] Q. Lu, F. Jiao, *Nano Energy* **2016**, *29*, 439.
- [13] N. Han, P. Ding, L. He, Y. Li, Y. Li, *Adv. Energy Mater.* **2019**, *10*, 1902338.
- [14] L. Fan, C. Xia, F. Yang, J. Wang, H. Wang, Y. Lu, *Sci. Adv.* **2020**, *6*.
- [15] S. Malkhandi, B. S. Yeo, *Curr. Opin. Chem. Eng.* **2019**, *26*, 112.
- [16] S. Liang, N. Altaf, L. Huang, Y. Gao, Q. Wang, *J. CO₂ Util.* **2020**, *35*, 90.
- [17] M. König, J. Vaes, E. Klemm, D. Pant, *iScience* **2019**, *19*, 135.
- [18] S. Sharifi Golru, E. J. Biddinger, *Chem. Eng. J.* **2022**, *428*, 131303.
- [19] H.-K. Lim, Y. Kwon, H. S. Kim, J. Jeon, Y.-H. Kim, J.-A. Lim, B.-S. Kim, J. Choi, H. Kim, *ACS Catal.* **2018**, *8*, 2420.
- [20] B. A. Rosen, J. L. Haan, P. Mukherjee, B. Braunschweig, W. Zhu, A. Salehi-Khojin, D. D. Dlott, R. I. Masel, *J. Phys. Chem. C* **2012**, *116*, 15307.
- [21] B. A. Rosen, I. Hod, *Adv. Mater.* **2018**, *30*, 1706238.
- [22] C. V. Amanchukwu, *Joule* **2020**, *4*, 281.
- [23] M. M. de Salles Pupo, R. Kortlever, *ChemPhysChem* **2019**, *20*, 2926.
- [24] I. Sullivan, A. Goryachev, I. A. Digdaya, X. Li, H. A. Atwater, D. A. Vermaas, C. Xiang, *Nat. Catal.* **2021**, *4*, 952.
- [25] L. Sun, G. K. Ramesha, P. V. Kamat, J. F. Brennecke, *Langmuir* **2014**, *30*, 6302.
- [26] B. A. Rosen, A. Salehi-Khojin, M. R. Thorson, W. Zhu, D. T. Whipple, P. J. A. Kenis, R. I. Masel, *Science* **2011**, *334*, 643.
- [27] Z. P. Jovanov, J. F. De Araujo, S. Li, P. Strasser, *J. Phys. Chem. C* **2019**, *123*, 2165.
- [28] L. Chen, F. Li, Y. Zhang, C. L. Bentley, M. Horne, A. M. Bond, J. Zhang, *ChemSusChem* **2017**, *10*, 4109.
- [29] F. Quan, M. Xiong, F. Jia, L. Zhang, *Appl. Surf. Sci.* **2017**, *399*, 48.
- [30] S. Garg, M. Li, T. E. Rufford, L. Ge, V. Rudolph, R. Knibbe, M. Konarova, G. G. X. Wang, *ChemSusChem* **2019**, *13*, 304.
- [31] D. V. Vasilyev, A. V. Rudnev, P. Broekmann, P. J. Dyson, *ChemSusChem* **2019**, *12*, 1635.
- [32] S. Verma, X. Lu, S. Ma, R. I. Masel, P. J. A. Kenis, *Phys. Chem. Chem. Phys.* **2016**, *18*, 7075.
- [33] N. Ahmad, X. Wang, P. Sun, Y. Chen, F. Rehman, J. Xu, X. Xu, *Renew. Energy* **2021**, *177*, 23.
- [34] M. Abdinejad, Z. Mirza, X. Zhang, H.-B. Kraatz, *ACS Sustainable Chem. Eng.* **2020**, *8*, 1715.
- [35] E. Pérez-Gallent, C. Vankani, C. Sánchez-Martínez, A. Anastasopol, E. Goetheer, *Ind. Eng. Chem. Res.* **2021**, *60*, 4269.
- [36] G. Lee, Y. C. Li, J. Y. Kim, T. Peng, D. H. Nam, A. Sedighian Rasouli, F. Li, M. Luo, A. H. Ip, Y. C. Joo, E. H. Sargent, *Nat. Energy* **2021**, *6*, 46.
- [37] Y. Cui, B. He, X. Liu, J. Sun, *Ind. Eng. Chem. Res.* **2020**, *59*, 20235.
- [38] B. A. Rosen, A. Salehi-Khojin, M. R. Thorson, W. Zhu, D. T. Whipple, P. J. A. Kenis, R. I. Masel, *Science* **2011**, *334*, 643.
- [39] M. Asadi, K. Kim, C. Liu, A. V. Addepalli, P. Abbasi, P. Yasaei, P. Phillips, A. Behranginia, J. M. Cerrato, R. Haasch, P. Zapol, B. Kumar, R. F. Klie, J. Abiade, L. A. Curtiss, A. Salehi-Khojin, *Science* **2016**, *353*, 467.
- [40] A. Atifi, D. W. Boyce, J. L. DiMeglio, J. Rosenthal, *ACS Catal.* **2018**, *8*, 2857.
- [41] W. Ren, X. Tan, X. Chen, G. Zhang, K. Zhao, W. Yang, C. Jia, Y. Zhao, S. C. Smith, C. Zhao, *ACS Catal.* **2020**, *10*, 13171.
- [42] H. K. Lim, H. Kim, *Molecules* **2017**, *22*, 536.
- [43] B. Ratschmeier, B. Braunschweig, *J. Phys. Chem. C* **2021**, *125*, 16498.
- [44] L. Sun, G. K. Ramesha, P. V. Kamat, J. F. Brennecke, *Langmuir* **2014**, *30*, 6302.
- [45] K.-Y. A. Lin, A.-H. A. Park, *Environ. Sci. Technol.* **2011**, *45*, 6633.
- [46] C. Petit, S. Bhatnagar, A.-H. A. Park, *J. Colloid Interface Sci.* **2013**, *407*, 102.
- [47] K.-Y. A. Lin, C. Petit, A.-H. A. Park, *Energy Fuels* **2013**, *27*, 4167.
- [48] T. G. Feric, S. T. Hamilton, A. Haque, J. Jeddi, J. Sangoro, M. D. Dadmun, A.-H. A. Park, *Adv. Funct. Mater.* **2022**, *32*, 2203947.
- [49] K.-Y. A. Lin, Y. Park, C. Petit, A.-H. A. Park, *RSC Adv.* **2014**, *4*, 65195.
- [50] C. Petit, K.-Y. A. Lin, A.-H. A. Park, *Langmuir* **2013**, *29*, 12234.
- [51] T. G. Feric, S. T. Hamilton, A. H. A. Park, *Energy Fuels* **2021**, *35*, 19592.
- [52] G. Rim, T. G. Feric, T. Moore, A.-H. A. Park, *Adv. Funct. Mater.* **2021**, *31*, 2010047.
- [53] N. M. Cantillo, M. Bruce, S. T. Hamilton, T. G. Feric, A.-H. A. Park, T. Zawodzinski, *J. Electrochem. Soc.* **2020**, *167*, 116508.
- [54] J. L. Schaefer, S. S. Moganty, D. A. Yanga, L. A. Archer, *J. Mater. Chem.* **2011**, *21*, 10094.
- [55] S. Srivastava, S. Choudhury, A. Agrawal, L. A. Archer, *Curr. Opin. Chem. Eng.* **2017**, *16*, 92.
- [56] Y. Park, K.-Y. A. Lin, A.-H. A. Park, C. Petit, *Front. Energy Res.* **2015**, *3*, 1.
- [57] Y. Park, J. Decatur, K.-Y. A. Lin, A.-H. A. Park, *Phys. Chem. Chem. Phys.* **2011**, *13*, 18115.
- [58] S. Choi, S. Moon, Y. Park, *Langmuir* **2020**, *36*, 9626.
- [59] C. Petit, Y. Park, K.-Y. A. Lin, A.-H. A. Park, *J. Phys. Chem. C* **2012**, *116*, 516.
- [60] Y. Park, C. Petit, P. Han, A.-H. A. Park, *RSC Adv.* **2014**, *4*, 8723.
- [61] Y. Park, D. Shin, Y. N. Jang, A.-H. A. Park, *J. Chem. Eng. Data* **2012**, *57*, 40.
- [62] S. Overa, T. G. Feric, A.-H. A. Park, F. Jiao, *Joule* **2021**, *5*, 8.
- [63] A. Agrawal, S. Choudhury, L. A. Archer, *RSC Adv.* **2015**, *5*, 20800.
- [64] S. Choudhury, A. Agrawal, S. Wei, E. Jeng, L. A. Archer, *Chem. Mater.* **2016**, *28*, 2147.
- [65] M. D. Tikekar, L. A. Archer, D. L. Koch, *J. Electrochem. Soc.* **2014**, *161*, A847.
- [66] S. T. Hamilton, T. G. Feric, G. Andrzej, N. M. Cantillo, T. A. Zawodzinski, A. A. Park, *ACS Appl. Mater. Interfaces* **2022**, *14*, 22016.
- [67] Y. Zhang, D. Poe, L. Heroux, H. Squire, B. W. Doherty, Z. Long, M. Dadmun, B. Gurkan, M. E. Tuckerman, E. J. Maginn, *J. Phys. Chem. B* **2020**, *124*, 5251.

- [68] J. M. Klein, H. Squire, W. Dean, B. E. Gurkan, *J. Phys. Chem. B* **2020**, 124, 6348.
- [69] N. K. Jayakody, C. C. Fraenza, S. G. Greenbaum, D. Ashby, B. S. Dunn, *J. Phys. Chem. B* **2020**, 124, 6843.
- [70] S. Liu, M. Walton, N. V. Tarakina, P. Akcora, *J. Phys. Chem. B* **2020**, 124, 4843.
- [71] M. D. Dadmun, M. A. Haque, T. G. Feric, S. T. Hamilton, A.-H. A. Park, *J. Phys. Chem. C* **2021**, 125, 5327.
- [72] J. M. Klein, H. Squire, B. Gurkan, *J. Phys. Chem. C* **2020**, 124, 5613.
- [73] E. U. Mapesa, N. M. Cantillo, S. T. Hamilton, M. A. Harris, T. A. Zawodzinski, A. A. Park, J. Sangoro, *Macromolecules* **2021**, 54, 2296.
- [74] T. G. Feric, S. T. Hamilton, N. M. Cantillo, A. E. Imel, T. A. Zawodzinski, A.-H. A. Park, *J. Phys. Chem. B* **2021**, 125, 9223.
- [75] S. T. Hamilton, T. G. Feric, S. Bhattacharyya, N. M. Cantillo, S. G. Greenbaum, T. A. Zawodzinski, A.-H. A. Park, *JACS Au* **2022**, 2, 590.
- [76] W. Yu, T. Wang, A.-H. A. Park, M. Fang, *Nanoscale* **2019**, 11, 17137.
- [77] S. Liguori, J. Wilcox, in *Current Trends and Future Developments on (Bio-) Membranes: Carbon Dioxide Separation/Capture by Using Membranes* (Eds: A. Basile, E. P. Favvas), Elsevier **2018**, pp. 385–413.
- [78] X. Wang, C. Song, *Front. Energy Res.* **2020**, 8, 560849.
- [79] R. R. Bhosale, A. Kumar, F. Almomani, U. Ghosh, A. Alnouss, J. Scheffe, R. B. Gupta, *Ind. Eng. Chem. Res.* **2016**, 55, 5238.
- [80] H. M. Stowe, G. S. Hwang, *Ind. Eng. Chem. Res.* **2017**, 56, 6887.
- [81] B. Lv, B. Guo, Z. Zhou, G. Jing, *Environ. Sci. Technol.* **2015**, 49, 10728.
- [82] S. Zhang, Y. Shen, P. Shao, J. Chen, L. Wang, *Environ. Sci. Technol.* **2018**, 52, 3660.
- [83] E. F. Da Silva, H. F. Svendsen, *Ind. Eng. Chem. Res.* **2004**, 43, 3413.
- [84] H. Guo, C. Li, X. Shi, H. Li, S. Shen, *Appl. Energy* **2019**, 239, 725.
- [85] D. Filotás, T. Nagy, L. Nagy, P. Mizsey, G. Nagy, *Electroanalysis* **2018**, 30, 690.
- [86] C. Delacourt, P. L. Ridgway, J. B. Kerr, J. Newman, *J. Electrochem. Soc.* **2008**, 155, B42.
- [87] M. R. Singh, E. L. Clark, A. T. Bell, *Phys. Chem. Chem. Phys.* **2015**, 17, 18924.
- [88] M. Dunwell, Q. Lu, J. M. Heyes, J. Rosen, J. G. Chen, Y. Yan, F. Jiao, B. Xu, *J. Am. Chem. Soc.* **2017**, 139, 3774.
- [89] A. S. Varela, M. Kroschel, T. Reier, P. Strasser, *Catal. Today* **2016**, 260, 8.
- [90] P. Bumroongsakulsawat, G. H. Kelsall, *Electrochim. Acta* **2014**, 141, 216.
- [91] M. R. Singh, Y. Kwon, Y. Lum, J. W. Ager, A. T. Bell, *J. Am. Chem. Soc.* **2016**, 138, 13006.
- [92] L. Q. Zhou, C. Ling, M. Jones, H. Jia, *Chem. Commun.* **2015**, 51, 17704.
- [93] E. L. Clark, S. Ringe, M. Tang, A. Walton, C. Hahn, T. F. Jaramillo, K. Chan, A. T. Bell, *ACS Catal.* **2019**, 9, 4006.
- [94] M. Bhattacharya, S. Sebghati, Y. M. Vercella, C. T. Saouma, *J. Electrochem. Soc.* **2020**, 167, 086507.
- [95] K.-Y. A. Lin, C. Petit, A.-H. A. Park, *Energy Fuels* **2013**, 27, 4167.
- [96] Y. Park, D. Shin, Y. N. Jang, A.-H. A. H. A. Park, *J. Chem. Eng. Data* **2012**, 57, 40.
- [97] S. Moon, Y. Lee, S. Choi, S. Hong, S. Lee, A.-H. A. Park, Y. Park, *Org. Process Res. Dev.* **2018**, 22, 1723.
- [98] B. H. Ko, B. Hasa, H. Shin, E. Jeng, S. Overa, W. Chen, F. Jiao, *Nat. Commun.* **2020**, 11, 5856.