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Identification of Single-Atom Ni Site Active toward Electrochemical CO₂ Conversion to CO

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single-atom Ni catalyst has been proposed as promising from experiments, but an idealized Ni–N₄ site shows an unfavorable energetics from theory, leading to many debates on the chemical nature responsible for high activity. To resolve this conundrum, here we investigated CO₂ electrolysis of Ni sites with well-defined coordination, tetraphenylporphyrin (N₄–TPP) and 21-oxatetraphenylporphyrin (N₃O–TPP). Advanced spectroscopic and computational studies revealed that the broken ligand-field symmetry is the key for active CO₂ electrolysis, which subordinates an increase in the Ni redox potential yielding Ni^I. Along with their importance in



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activity, ligand-field symmetry and strength are directly related to the stability of the Ni center. This suggests the next quest for an activity–stability map in the domain of ligand-field strength, toward a rational ligand-field engineering of single-atom Ni catalysts for efficient CO_2 electrolysis.

■ INTRODUCTION

Electrochemical carbon dioxide reduction reaction (CO_2RR) is a promising strategy for both balancing the global carbon cycle and production of fine chemicals.^{1,2} Among the various CO_2RR products, carbon monoxide is one of the simplest and most economically valuable substances by itself and serves as a feedstock for bulk chemical manufacturing.^{3,4} To achieve selective CO_2 -to-CO conversion, noble metals such as gold^{5–8} and silver^{9–13} have been widely investigated as irreplaceable electrocatalysts due to their apposite binding affinities with the CO_2RR intermediate (*COOH) and the product (*CO) in the scaling relationship.^{4,14,15} Nevertheless, noble metal catalysts have limitations such as high cost, vulnerability to impurities, and inadequate long-term durability.^{7,9,16} Hence, the development of new types of CO_2RR catalysts is in great demand.

As an outlier that breaks the conventional properties of metallic materials, single-atom metal catalysts, in which atomically dispersed metal ions are ligated to nonmetallic functional groups (e.g., Me–N–C catalysts, Me = Ni, Fe, Co, Zn, Mn, etc.), have recently attracted considerable attention for the selective CO production from CO_2RR .^{17–31} In particular, single-atom Ni catalysts have exhibited promising CO_2 -to-CO conversion activities, outperforming other Me–N–C catalysts and even comparable with noble metal catalysts.^{19–31} For example, the Ni–N–C catalyst synthesized by a topochemical transformation recorded near-unity CO selectivity of 99% at -0.81 V_{RHE} (reversible hydrogen

electrode).²⁷ In a gas diffusion electrode system, a similar Ni–N–C catalyst achieved a high CO partial current density of >200 mA cm⁻² as well as a stable CO Faradaic efficiency (FE) of ca. 85%, verifying its immense potential for future industrial applications.²¹

Notwithstanding the high efficiency of Ni–N–C catalysts, the molecular details of the catalytically active Ni moiety are still puzzling. Density functional theory (DFT) calculations, as a reliable supplement to experiments, have revealed a relatively weak binding affinity of *COOH to the porphyrin-like Ni–N₄ site, predicting a substantially large overpotential (>1.5 V).^{17,21,27} Considering the principles of organometallics, the poor ability of Ni^{II} (i.e., d⁸ species) to form an axial bond is predictable, as it strongly prefers the D_{4h} square-planar geometry.³² Accordingly, different local structures around the Ni center with broken D_{4h} symmetry—for instance, unsaturated or heteroatom-coordinated Ni–N sites (i.e., Ni–N_yX_{4-y}, X = vacancy or heteroatom besides N such as S and C)—have been suggested as possible catalytic sites preferable for CO production from CO₂RR.^{22–24,33} Another issue of interest is the oxidation state of Ni. Recently, Yang et al. reported the

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formation of an uncommon oxidation state of Ni^I on an N(/S)-doped graphene matrix, which was ascribed to the superior CO_2RR activity with 97% FE.³¹

For the rational design of Ni-N-C catalysts, we herein investigate the CO₂RR electrochemistry of Ni-porphyrin model compounds using advanced in operando spectroscopies and DFT calculations, with posing a fundamental questionwhich symmetry of the ligand field and which oxidation state are responsible for CO₂RR at the Ni center. The pyrolysis step at >800 °C required for the usual synthesis of Ni-N-C catalysts produces chemically inequivalent Ni species (e.g., metallic Ni, oxide, and various Ni $-N_yX_{4-y}$ sites),^{21,22} which renders the identification of the active Ni site highly vague. Therefore, we have employed molecular catalysts based on Nicomplexed porphyrins, tetraphenylporphyrin (N₄-TPP) and 21-oxatetraphenylporphyrin (N₃O-TPP). Their immobilization on a carbon substrate provided a heterogeneous catalytic platform with well-defined and equivalent organometallic active species, enabling us to unravel the structure-activity (and structure-stability) relationship in single-atom Ni electrocatalysis in CO₂RR.

RESULTS AND DISCUSSION

Synthesis of the Ni-Porphyrin Compounds. The mesosubstituted porphyrins, i.e., N_4 -TPP and N_3O -TPP, were synthesized by modified Lindsey's methods (Figure 1a and



Figure 1. Synthesis and physical characterizations of the prepared porphyrins. (a) Synthetic scheme for Ni–N₄–TPP and Ni(–Cl)–N₃O–TPP by modified Lindsey's methods. (b) 3D molecular structure of Ni(–Cl)–N₃O–TPP determined by SC-XRD. (c) Ni K-edge XANES spectra of Ni–N₄–TPP, Ni(–Cl)–N₃O–TPP, and Ni foil.

Supporting Information Note 1), where 2,5-bis-(phenylhydroxymethyl)furan was used as a precursor for the preparation of N₃O-TPP (Figure S1).³⁴ After metalation,^{34,35} Ni-N₄-TPP and Ni(-Cl)-N₃O-TPP were recrystallized and used for subsequent analyses. Successful synthesis of the complexes was confirmed by matrix-assisted laser desorption ionization time-of-flight mass (MALDI-ToF MS), liquid chromatography (LC), ultraviolet-visible (UV-vis) absorption, and ¹H-/¹³C-nuclear magnetic resonance (NMR) spectra (Figures S2-S14). The oxidation state of the central Ni species was Ni^{II} for both Ni-porphyrin compounds, as revealed by the peaks at ca. 856.0 eV in X-ray photoelectron spectroscopy (XPS)-Ni_{2p} (Figure S15) and also by the Ni Kedge position of 8345 eV in the X-ray absorption near edge structure (XANES) spectra (Figure 1c and Figure S16).

The structure of $Ni(-Cl)-N_3O-TPP$ was further elucidated by single-crystal X-ray diffraction (SC-XRD; Figure 1b, Supporting Information Note 2, and Tables S1-S3). The result shows a five-coordinate Ni complex with a vertical distance of 0.303 Å between the Ni atom and O(1)N(2)-N(3)N(4) plane and the axial chloride ion at a distance of 2.279 Å apart. The η^1 -furan ligand is coordinated to the Ni atom with $\theta = 18.2^{\circ}$ (θ is the angle between the furan plane and Ni-O bond). This structural distortion, broken D_{4h} symmetry, is further verified by the silent $1s \rightarrow 4p_z$ transition at ca. 8339 eV in the XANES spectrum of Ni(-Cl)-N₃O-TPP (Figure 1c), a fingerprint of square-planar $Me-N_4$ moieties which can be clearly seen in that of Ni-N₄-TPP.³⁶ On the other hand, a pre-edge peak is observed at ca. 8335 eV for Ni(-Cl)-N₃O-TPP due to the increased dipole-allowed 1s \rightarrow 4p transition, which is evidence of the distorted D_{4h} symmetry inducing hybridization of the 3d and 4p orbitals. Thus, $\mathrm{Ni}^{\mathrm{II}}$ complexes with a four-coordinate dianionic ligand $(square-planar Ni-N_4-TPP)^{38}$ and a monoanionic ligand with an axial chloride ion (distorted Ni(-Cl)-N₃O-TPP)³⁴ were identified.

In Situ Characterizations of Porphyrin Compounds. Electrocatalysis of CO2RR on Ni-N4-TPP and Ni(-Cl)-N₃O-TPP was investigated in a 0.5 M KHCO₃ electrolyte using a rotating disk electrode (RDE). Electrodes were prepared by mixing the porphyrins with carbon black to provide sufficient electrical conductivity. Linear sweep voltammetry (LSV) measurements at a scan rate of 50 mV s⁻¹ reveal similar polarizations of Ni-N₄-TPP in Ar- and CO_2 -saturated electrolytes (Figure 2a; pH = ca. 8.9 and 7.2, respectively). On the other hand, $Ni(-Cl)-N_3O-TPP$ shows a substantial increase in the reductive current density in the CO_2 -saturated electrolyte, which is two times higher at -0.8V_{RHE} than that in the Ar-saturated electrolyte. The reductive currents are attributed to electrocatalysis on the Ni-porphyrin compounds, as confirmed by the much lower electrocatalytic activity on glassy carbon and carbon black without the model Ni-porphyrin compounds (Figure S17). Hence, the difference in the polarization curves, clearly observed on the Ni(-Cl)-N₃O-TPP electrode but not on the Ni-N₄-TPP electrode, implies better electrocatalytic CO₂RR activity of Ni(-Cl)- N_3O -TPP than that of Ni- N_4 -TPP.

To confirm the above hypothesis, electrocatalytic CO₂-to-CO conversion and competitive H₂ evolution, i.e., the two main reactions on the single-atom Ni catalysts under similar $CO_2 RR$ conditions,^{19–31} were monitored online by differential electrochemical mass spectroscopy (DEMS) coupled to a scanning flow cell (SFC) system (Figure S18). Under potentiodynamic polarizations at a scan rate of 5 mV s⁻¹, the CO_2 level (m/z = 44) in the electrolyte is stable in the highpotential region but starts to decrease at a potential below ca. -0.8 and -0.6 V_{RHE} for Ni-N₄-TPP and Ni(-Cl)-N₃O-TPP, respectively (Figure 2b and c). Simultaneously, the CO signal (m/z = 28) is newly evolved and intensified as the overpotential increases. These changes are hardly detectable in the Ar-saturated electrolyte, in which the gaseous product is only H_2 (Figure S19). Identical onset potentials for CO_2 consumption and CO evolution indicate that CO is produced

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Figure 2. Electrochemical and in situ spectroscopy studies. (a) Polarization curves of Ni–N₄–TPP and Ni(–Cl)–N₃O–TPP measured at a scan rate of 50 mV s⁻¹ in Ar-/CO₂-saturated 0.5 M KHCO₃ electrolytes. (b, c) Online SFC-DEMS results of Ni–N₄–TPP (b) and Ni(–Cl)–N₃O–TPP (c). The CO₂ (m/z = 44), CO (m/z = 28), and H₂ (m/z = 2) signals were collected during two cycles of CV from 0 to –0.9 V_{RHE} in a CO₂-saturated 0.5 M KHCO₃ electrolyte. The potential profile during the DEMS measurements is indicated by a dotted line. (d) CV results of Ni–N₄–TPP and Ni(–Cl)–N₃O–TPP measured at a scan rate of 50 mV s⁻¹ in a potential range from –0.5 to 0.4 V_{RHE} in a CO₂-saturated electrolyte. Redox couple A is indicated by an arrow. (e) In situ XANES spectra of Ni–N₄–TPP and Ni(–Cl)–N₃O–TPP measured at the OCP and –0.65 V_{RHE} are also shown (dotted line). (f) Linear combination fitting of the Ni K-edge XANES spectrum of Ni(–Cl)–N₃O–TPP collected at –0.65 V_{RHE}.

by the electrochemical reduction of CO_2 dissolved in the electrolyte. Along with the higher onset potential, more substantial ionic current changes in CO_2 consumption and CO evolution are recorded for Ni(-Cl) $-N_3O-TPP$ than for Ni-N₄-TPP. Therefore, these results reveal a better CO_2 -to-CO conversion on Ni(-Cl) $-N_3O-TPP$ than on Ni-N₄-TPP.

To clarify the origin of the diametrically opposite CO₂-to-CO conversion activities between the Ni-porphyrins, variations in the Ni oxidation state, which has been debated as a key parameter determining CO₂RR performance,^{21-23,30,31} were investigated under the polarization conditions. Cyclic voltammetry (CV) measurement for the Ni-N₄-TPP shows a double-layer capacitive characteristic without noticeable redox signals of the central Ni ion in the CO2-saturated electrolyte (Figure 2d), indicating stabilization of the initial oxidation state of Ni^{II} in a potential range from 0.4 to -0.5 V_{RHE} (even to -0.8 V_{RHE} , Figure S20). In the CV result of $Ni(-Cl)-N_3O-TPP$, however, a clear redox couple is observed at ca. $-0.22 V_{RHE}$ (peak A), a much lower value of the open circuit potential (OCP) of ca. 0.98 V_{RHE} at which the initial oxidation state of Ni^{II} is thermodynamically stable. Because $Ni(-Cl)-N_3O-TPP$ is adsorbed on the electrode, i.e., a surface-confined redox reaction, the peak current is linearly proportional to the scan rate (Figure S21).^{39,40} Considering the amount of Ni(-Cl)-N₃O-TPP on the electrode and the charge passed during the reaction, the number of electrons in redox couple A can be estimated to be ca. 1.9. Similar results are obtained in the Ar-saturated electrolyte (Figure S22), but the redox potential (E^0) of $Ni(-Cl)-N_3O-TPP$ is positively shifted by ca. 110 mV on the RHE scale. However, on the standard hydrogen electrode (SHE) scale without pH compensation, the redox couple A is located at an identical E^0 of -0.62 V_{SHE} in both Ar- and CO₂saturated electrolytes (Figure S23). Therefore, the voltammogram results indicate that the redox reaction A accompanies two-electron transfer without proton transfer.

The variation of the oxidation state of the Ni^{II} center was further studied by in situ XANES analysis. The XANES spectra were recorded in a CO₂-saturated electrolyte at the OCP and $-0.65 V_{RHE}$ (Figure 2e and Figure S24); the latter potential is lower than the redox potential of $Ni(-Cl)-N_3O-TPP$ (i.e., -0.22 V_{RHE}), and CO_2RR is maximized at this potential (discussed later). For Ni-N₄-TPP, the XANES spectrum measured at -0.65 V_{RHE} is almost identical to that measured at the OCP. However, the Ni K-edge position of Ni(-Cl)-N₃O-TPP decreases by 2 eV once the electrode is polarized at -0.65 V_{RHE}. The absorption edge position at 8.343 eV corresponds to the average Ni oxidation state of ca. +1.6 (Figure S16), indicating a part of Ni^{II} reduced to Ni⁰ and/or Ni^I. Therefore, it can be presumed that the electronic state of the Ni site may play a decisive role in the electrochemical CO₂to-CO conversion, and either metallic or monovalent Ni sites are likely to be responsible for efficient CO evolution rather than Ni^{II} moieties.

However, the XANES spectrum of Ni(-Cl) $-N_3O-TPP$ at $-0.65 V_{RHE}$ shows a poor fitting value (*R*-factor = 0.075) in linear combination with the spectra of Ni⁰ (Ni foil) and Ni^{II} (Ni(-Cl) $-N_3O-TPP$ at the OCP) components (Figure 2f). The downshift of the edge in the region is assigned to Ni^{1.6+} (negative residual at edge) but the overestimation of the Ni^{II} contribution (positive residual at the white line). The failure of the fitting thus points out that the redox couple A of Ni(-Cl) $-N_3O-TPP$ at $-0.22 V_{RHE}$ is not fully attributed to the electron transfer process between Ni^{II} and Ni⁰. Accordingly, one-electron reduction of Ni^{III} to monovalent Ni^I could be reasonably considered, which accompanies another one-electron reduction of the N₃O-TPP ligand because the redox couple A follows the two-electron process

as verified by CV (Figure 2d). It is worth noting that the stabilization of monovalent Ni^I as well as Ni^{II} has been successfully achieved using monoheteroatom porphyrin ligands similar to N₃O–TPP,^{34,41,42} while this character is rarely found in typical N₄-porphyrins due to the formation of porphyrin π -anion radicals.⁴³

Electronic State of Active Ni Species in Operando and CO₂RR Chemistry. Using DFT (Supporting Information Note 4), which was confirmed to predict reliable E^0 for various Me-N₄-TPP systems (Me = Fe, Co, Ni, Cu, and Zn) (Table S6), the E^0 of Ni-porphyrin compounds was theoretically investigated. DFT predicts the one-electron reduction potential of Ni-N₄-TPP as -1.04 V_{SHE} and the additional electron to be added to the π^* -orbital of N₄-TPP (Figure S25), which are in agreement with the previous experimental^{44,45} and theoretical studies.⁴⁶ Thus, DFT results support that the Ni^{II} center of Ni-N₄-TPP is redox-innocent in the potential range for CO₂RR.

The two-electron redox of $Ni(-Cl)-N_3O-TPP$ is considered to occur via the following reaction.

$$Ni(-Cl) - N_{3}O - TPP + 2e^{-}$$

$$\approx Ni - N_{3}O - TPP^{-} + Cl^{-}(aq)$$
(1)

DFT predicts the E^0 of eq 1 as $-0.54 V_{SHE}$. This corresponds to our experimental observation of the redox couple A located near $-0.62 V_{SHE}$. During two-electron reduction, DFT further reveals that one electron reduces the Ni^{II} center to Ni^I as supported by the spin density plot of the Ni $-N_3O-TPP^{10}$ species (Figure S26a) and the +0.98 Mulliken spin population at the Ni center. The other electron is found to occupy the π^* orbital of N₃O-TPP with marginally changing the Mulliken spin population at the Ni center from +1 but significantly increasing the spin density in the porphyrin π -system (Figure S26b). For a detailed understanding about the electronic structural changes during the reduction of Ni^{II} $-N_4-TPP$ and Ni^{II} $(-Cl)-N_3O-TPP$, readers are referred to the Supporting Information Note 5 (and Figures S25–S30).

Consequently, Ni^{II} of Ni-N₄-TPP and Ni^I of Ni-N₃O-TPP^{|-} are the actual chemical species responsible for the CO₂RR. Thus, the CO₂RR chemistry at these two different Ni centers is of interest. In order to decouple the effect of change in oxidation state and ligand field, a hypothetical system of $Ni-N_3O-TPP^{+}$, which can be formed by removing the axial chloride from Ni(-Cl)-N₃O-TPP without redox, is additionally examined using DFT. Unlike Ni(-Cl)-N₃O-TPP, the lack of fifth coordination of Ni-N₃O-TPP^{]+} stabilizes the low-spin Ni^{II} state (S = 0) with virtually no out-of-plane distortion (Figure S31). Thus, the metal oxidation state and coordination geometry of both Ni-N₃O-TPP^{]+} and Ni-N₄-TPP are nearly the same, but the D_{4h} ligand field is broken only for $Ni-N_3O-TPP^{\uparrow+}$ due to the substitution of one N with O. In Figure 3, the CO_2RR free energies are shown for Ni–N₄– TPP (Ni^{II} with D_{4h} ligand field) and Ni-N₃O-TPP^{]-} (Ni^I with broken D_{4h} ligand field) when a potential of $-0.6 V_{RHE}$ is applied. At the *COOH step, which shows the most unfavorable energetics, Ni^{II} of Ni-N₄-TPP exhibits the low stabilization ability of *COOH, predicting a large overpotential. On the contrary, the active species of Ni(-Cl)-N₃O-TPP in operando, Ni^I of Ni-N₃O-TPP¹⁻, can substantially stabilize *COOH, yielding a much reduced overpotential. Interestingly, the hypothetical active site of Ni^{II} of Ni-N₃O-TPP^{]+} shows comparable CO₂RR energetics



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Figure 3. Suggested CO₂RR mechanism. (a) Catalytic cycles of Ni– N₄–TPP (left) and Ni(–Cl)–N₃O–TPP (right) and (b) corresponding DFT-calculated free energy profiles when a potential of –0.6 V_{RHE} is applied. CO₂ adsorption to the Ni site is an uphill process at a long distance (Figure S32), and thus the CO₂-adsorbed species is considered to be a transient configuration (denoted using parentheses).

to Ni¹ of Ni–N₃O–TPP^{1–} (Figure S33). For an active CO₂RR, it is thus concluded that breaking the symmetry of the in-plane ligand field is pivotal. Additional CV experiments and DFT calculations further supported the in situ generation of the Ni active center with a weakened D_{4h} ligand field during CO₂RR of another high-performing single-atom Ni catalyst of Ni-complexed phthalocyanine (NiPc; Supporting Information Note 6). Thus, our conclusion is not a specific nature of Ni(-Cl)–N₃O–TPP but is general for single-atom Ni catalysts for CO₂RR.

As shown in Figure 4a and b, $Ni^{I}-N_{3}O-TPP^{-}$ can form a stronger Ni-C bond than $Ni^{II}-N_{4}-TPP$, which is the origin



Figure 4. Origin of different activities. DFT-optimized structures of COOH-bound (a) Ni–N₄–TPP and (b) Ni–N₃O–TPP^{1–}. Binding energy of ·COOH to the Ni center is also displayed, where the more negative value means the stronger binding. (c) A schematic MO diagram is shown. To form a strong Ni–COOH bond, the electronrich Ni center needs to redistribute its electron density to the N₃X ligand (orange arrow); the energy cost for such an electron redistribution becomes large when the ligand-field splitting, Δ , increases.

of the larger electrochemical reactivity of Ni^I-N₃O-TPP^{]-}. To explain this, a schematic molecular orbital (MO) diagram is shown in Figure 4c. As most of the d orbitals of the low-valent Ni species, such as Ni^{II} and Ni^I, are filled, the Ni center has a low Lewis acidity, prohibiting the formation of a strong Ni-C bond with COOH. To form a strong Ni-C bond with COOH, therefore, the Ni center needs to redistribute its electron density to the ligand. When the strong ligand field produces a large splitting of Δ , as in the case of the N₄-TPP ligand, the energy cost required for the charge redistribution becomes significant (see Figure 4c), which substantially weakens the Ni-C bond strength. Therefore, when the symmetry of the inplane ligand field is broken and/or weakened, which is what happened to the N₃O-TPP ligand, the Ni center can form a stronger Ni-C bond to stabilize the *COOH, which is the key to achieving a favorable energetics for CO₂RR at the Ni center. But, it also accompanies a substantial positive shift of the Ni reduction potential as the empty d orbital of the Ni center is being lowered, facilitating the generation of a +1 oxidation state under polarization.

Electrochemical CO₂-to-CO Conversion. Along with the fundamental understandings based on the operando spectroscopic and computational studies, the gaseous products were analyzed by online gas chromatography (GC) in a two-compartment H-cell to determine the FE and partial current density for CO₂RR. Figure 5a shows the FEs of formation of CO and H₂ measured under potentiostatic polarization conditions for 1 h CO₂RR operation. In both Ni-porphyrin electrodes, the sum of FE_{CO} and FE_{H2} reached almost 100%, indicating that the formation of other products was almost negligible. The ¹H NMR spectrum also confirmed the absence



Figure 5. CO₂-to-CO conversion in an H-type electrochemical cell. (a) FE_{Total} and FE_{CO} and (b) j_{Total} and $j_{CO'}$ acquired for 1 h CO₂RR operation at various potentials in a two-compartment H-cell. FE_{Total} was estimated by the sum of FE_{CO} and FE_{H2} (not shown). (c) Baseline-subtracted oxidation peaks for Ni(-Cl)-N₃O-TPP measured by CV with different LPLs. The voltammograms were recorded by changing the LPL sequentially from -0.5 to -0.8 V_{RHE} at a scan rate of 50 mV s⁻¹ in the CO₂-saturated 0.5 M KHCO₃ electrolyte. The peaks (A and B) are indicated by arrows. (d) Raman spectra of Ni(-Cl)-N₃O-TPP before and after sequential CV measurements from 0.4 to -0.8 V_{RHE}. NiO signals in the Raman spectrum are indicated by dotted lines.

(or imperceptible amount) of liquid products (e.g., formate or methanol) in the electrolyte after the reaction (Figure S34). During electrolysis, Ni–N₄–TPP exhibits predominant H₂ formation over the whole potential range (Figure S35), but minor CO formation is detected at a high overpotential region below $-0.75 V_{RHE}$ with a maximum FE_{CO} of only ca. 2% (Figure 5a and b). On the other hand, Ni(–Cl)–N₃O–TPP shows an onset potential of CO formation at approximately $-0.55 V_{RHE}$, and its maximum FE_{CO} reaches ca. 80% at $-0.65 V_{RHE}$. The FE_{CO} of Ni(–Cl)–N₃O–TPP and the partial current density of CO formation, however, are deteriorated in the high-overpotential region, while H₂ production is significantly enhanced (Figure 5a). This is in contrary to the result measured by online SFC-DEMS, which shows enhanced CO evolution as the overpotential increases.

Additional CV analysis for Ni(-Cl)-N₃O-TPP with a different lower potential limit (LPL) provides a clue to the understanding of the discrepancy in CO selectivity (Figure 5c and Figure S36). When the LPL decreases below $-0.7 V_{RHE}$, the redox couple A of Ni(-Cl)-N₃O-TPP at ca. -0.22 V_{RHE} in the CO₂-saturated electrolyte disappears. Meanwhile, a broad redox couple newly grows up at ca. 0.07 V_{RHE} (Figure 5c; peak B), which can be more clearly differentiated in the Arsaturated electrolyte into two different redox couples at ca. 0.13 and 0.07 V_{RHE} (peaks B1 and B2, respectively; Figure S36 and Supporting Information Note 3). The peak B at ca. 0.07 V_{RHE} in the CO₂-saturated electrolyte (or peak B1 at ca. 0.13 V_{RHE} in the Ar-saturated electrolyte) is responsible for the redox couple of Ni-free N₃O-TPP (Figure S37), indicating the instability (i.e., demetalation) of the Ni-coordination structure at a potential of <-0.6 V_{RHE}. Considering the Pourbaix diagram,47 the precipitation of dissolved Ni ions to metallic Ni or oxidized NiO and Ni(OH)₂ is an exergonic process in our pH conditions (i.e., pH = 7.2-8.9), and their standard E^0 are ca. 0.13 ($E^0_{Ni/NiO}$) and 0.11 ($E^0_{Ni/NiOH2}$) V_{RHE} , respectively. More evidently, the formation of bulk NiO phase was clearly confirmed by the Raman spectrum of the Ni(-Cl)-N₃O-TPP electrode after CVs from -0.8 to 0.4 V_{RHE} (Figure 5d).⁴⁸ It is of note that these bulk Ni phases are highly active toward H₂ evolution reaction.^{49,50} Although the working electrode was replaced with a new one at each potential in the H-cell measurements, the 1 h operating time is much longer than a few minutes (only 80 s in potential below -0.7 V_{RHE}) of the CV protocol in SFC-DEMS analysis, consequently resulting in a much more severe degradation of $Ni(-Cl)-N_3O-TPP$ in the H-cell study. Despite the quick measurements in the SFC-DEMS, the instability of Ni(-Cl)-N₃O-TPP can also be seen by the considerably decreased ionic current from CO₂ consumption and CO evolution at the second CV polarization (Figure 2c).

OUTLOOK AND CONCLUSIONS

Our experimental and theoretical findings on the electrochemistry of the two Ni-porphyrins offer important insights into the rational design strategy of highly efficient Ni catalysts for CO_2RR . Given the similar case of single-atom Fe catalysts for O_2 reduction in fuel cells, it has been reported that, despite the high instability of Fe-porphyrins, incorporation of their active Fe moieties into a carbon lattice (i.e., Fe–N–C) can effectively minimize the undesirable Fe demetalation even under highly corrosive acidic conditions.⁵¹ In that sense, anchoring the active Ni moieties on the carbon lattice (i.e., Ni–N–C) can thus be one promising approach to stabilization of the Ni sites without their dissolution. In many recent works, indeed, this synthetic strategy has been successfully implemented by pyrolyzing a mixture of Ni, N, and C precursors, demonstrating their durable CO₂-to-CO conversions over tens of hours of operation.^{21,25,31}

The next challenge will thus become how one can suppress the in-plane ligand field and at the same time prevent the Ni leaching under the reaction conditions. To provide further synthetic guidelines, additional DFT calculations were performed to investigate the $Ni-N_3X$ sites, where X = N, O, C, S, and vacancy (V) using various active site models embedded in the carbon lattice (Figure \$38). The Ni binding energies to N₃X sites and *COOH binding energies to the Ni center demonstrate an inverse proportionality (Figure S39), implying a trade-off relation between the stability of the metal site and CO₂RR activity. Accordingly, it is important to engineer the ligand-field strength to be optimal for both metalsite stability and *COOH binding strength. Therefore, the present understandings suggest that the next challenge is the development of new synthetic routes to control the ligand-field strength of the pyrolyzed Ni-N-C catalysts. With varying heteroatom species and contents during pyrolysis, for example, the ligand-field strength can be gradually tuned. We then expect to map out the activity and stability in the domain of ligand-field strength, which will enable a rational design of Ni-N-C catalysts with achieving high CO₂RR performance.

EXPERIMENTAL SECTION

Experimental details for the synthesis of Ni-porphyrins and computational predictions are given in Supporting Information Notes 1 and 4, respectively.

Physical Characterizations. Liquid chromatography electrospray ionization mass spectrometry (LC-ESI-MS) was performed using an Agilent 1260 infinity liquid chromatography system with an Agilent 6120 single-quadrupole mass spectrometer. A binary mobile phase system (solvent A: H₂O + 0.1% trifluoroacetic acid (99.5%, Acors Organics); solvent B: CH₃CN) was used. The sample for LC-ESI-MS was prepared as 100 μ M solution in methanol (\geq 99.9%, Fisher Scientific). MALDI-ToF MS was carried out with a Bruker AutoflexTM speed MALDI-ToF spectrometer. The samples for MALDI-ToF MS were prepared by mixing the porphyrin samples with a CHCA matrix (saturated α -cyano-4-hydroxycinnamic acid (Sigma-Aldrich) in 30% CH₃CN (≥99.9%, Fisher Scientific) and 70% H₂O containing 0.1% trifluoroacetic acid (\geq 99.0%, Sigma-Aldrich)). The spectra were recorded in a reflector positive ion mode using a pulsed nitrogen laser as the ionization source. Data are reported as m/z for both ESI-MS and MALDI-ToF MS. The UV-vis absorption spectra were obtained on a GE Healthcare Ultrospec 2100 Pro in a quartz cell with a 1 mm path length. The measurements were performed in open air at room temperature. Each spectrum was expressed after proper baseline correction with dichloromethane (≥99.9%, Sigma-Aldrich). ¹H NMR and ¹³C NMR spectra were recorded with a JEOL ECS400 (400 MHz for ¹H and 100 MHz for ¹³C) spectrometer in CDCl₃ (D, 99.96%, Cambridge Isotope Laboratories). The spectra were referenced to residual CHCl₃ (7.26 ppm for ¹H, 77.23 ppm for ¹³C). Chemical shifts are reported in ppm, and signal multiplicities are indicated as s (singlet), d (doublet), and m (multiplet). Elemental analysis was performed using an Elementar vario MICRO cube. The chemical structure and atomic composition of Ni-N₄-TPP and Ni(-Cl)-N₃O-TPP were analyzed by XPS (PHI 5000 VersaProbe) with an Al K α monochromator X-ray source. The binding energies were calibrated against the C–C signal at 284.5 eV. The SC-XRD measurement was conducted on a Bruker APEX-II CCD-based diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.7107$ Å), and further details are given in Supporting Information Note 2. Ex situ X-ray absorption spectroscopy (XAS) was

performed using a synchrotron radiation light source at the Pohang Accelerator Laboratory (8C-Nano XAFS). The samples were loaded in a sample holder ($w \times l \times d = 3 \times 5 \times 1 \text{ mm}^3$) sealed by Kapton tape. Before the measurement, the energy was calibrated using a Ni foil standard. The XANES data were analyzed by Athena implemented in the Demeter program package (ver. 0.9.26).

Electrochemical Analysis. Electrochemical measurements were conducted with a RDE apparatus (RRDE-3A, ALS) and a potentiostat (VMP3, Bio-Logic Science Ins.) in a three-electrode system. A graphite rod and saturated Ag/AgCl reference electrode (RE-16, EC-Frontier) were used as the counter and reference electrodes, respectively. The electrochemical cell was made of Teflon, and the reference electrode was separated by a double junction configuration to avoid interference from glassware dissolution and halogen.⁵² A glassy carbon RDE (diameter = 3 mm) was used as a working electrode after mirror polishing with alumina slurry (1.0 and 0.05 μ m, R&B Inc.). For a sufficient electrical conductivity and homogeneous dispersion of Ni-porphyrins, the Ni-porphyrins and Ketjenblack EC-600JD were mixed together in dichloromethane (\geq 99.9%, Sigma-Aldrich) with a target Ni loading of 1 wt %. It is of note that the absence of the carbon black renders the electrochemical responses rather irreversible in our case as compared to that with the carbon black (data not shown). In the case of Ni-free porphyrins, an identical number of porphyrins were introduced into the solution. After evaporation of the solvent, catalyst inks were prepared by dispersing 5 mg of the Ni-porphyrin/carbon mixture and $23 \ \mu L$ of the Nafion ionomer (5 wt %) in 4.3 mL of deionized (DI) water (>18.2 M Ω , Arium mini, Sartorius). The thin film electrode was fabricated by pipetting the inks onto the glassy carbon electrode (0.071 $\mbox{cm}^2)$ with a targeted Ni loading of 1 μ g cm⁻². For comparison, a NiPc (Sigma-Aldrich) electrode was fabricated identically. The electrolyte was 0.5 M KHCO₃ solution, prepared using DI water and KHCO₃ (99.7%, Sigma-Aldrich). The reference electrode was calibrated in a H₂saturated 0.5 M KHCO₃ electrolyte. All potentials reported in this work are given with respect to the RHE scale. Prior to the electrochemical measurements, 30 cycles of CV were conducted in the potential range of 0.05–1.00 V_{RHE} at a scan rate of 200 mV s⁻¹ to stabilize the voltammetric response. The LSV measurements were conducted at a scan rate of 50 mV s⁻¹ at 1600 rpm rotation speed in an Ar- or CO_2 -saturated electrolyte (pH = ca. 8.9 and 7.2, respectively). The electrolyte pH was measured using an HM-30P pH meter (DKK-TOA). The redox characteristics were measured at a scan rate of 50 mV s⁻¹ by CV from 0.4 V_{RHE} to different LPLs, decreasing from -0.5 to -0.8 V_{RHE} (by 0.1 V). Before and after the CV treatment, the precipitation of dissolved Ni ions into bulk phases was investigated by Raman spectroscopy (micro-Raman spectroscopy system, Renishaw) using a 514.5 nm laser (50 mW). The correlation between the peak current of the redox couple and the scan rate was analyzed at different scan rates (10, 20, 50, 100, 150, and 200 mV s^{-1}).

In Situ XANES Measurements. In situ XANES analysis was performed with a synchrotron radiation light source at the Pohang Accelerator Laboratory (1D, XRS KIST-PAL). A flow-type in situ XAS cell, equipped with an electrolyte flow channel and a window for X-ray radiation, was employed. The window was made of a carboncoated Kapton film (200RS100, 0.05 mm, DuPont), and it was directly used as a working electrode after coating with the Niporphyrin/carbon mixture (Ni loading = 110 μ g cm⁻²). Due to the low Ni content in the porphyrin/carbon mixture used for the electrochemical measurements (ca. 1 wt % Ni), a mixture with a higher Ni-porphyrin content on the carbon (7.5 wt % Ni) was separately prepared for the in situ XANES measurements. Pt wire and Ag/AgCl electrodes were used as counter and reference electrodes, respectively, which made an electrochemical contact at the outlet of the electrolyte stream. The electrolyte flow rate was set to 1 mL $\min^{-1}.$ The in situ XANES spectra were collected in the fluorescence mode under the OCP and $-0.65~V_{\text{RHE}}$ in a CO2-saturated 0.5 M KHCO₂

SFC-DEMS Analysis. The SFC connected to a mass spectrometer (Max 300 LG, Extrel) was constructed for DEMS analysis. The SFC

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was equipped with a 10 mm opening at the bottom of the cell for electrical contact with the 3 mm diameter glassy carbon working electrode. During the reactions, volatile and gaseous products were

directly collected by a tip equipped with a porous Teflon membrane positioned ca. 100 μ m above the working electrode. The graphite tube (inner diameter = 3 mm) and reference electrode were electrically connected by the U-shaped electrolyte channel. The working electrode was fabricated in an identical manner to the setup for the electrochemical measurements (Ni loading of 1 μ g cm⁻²). The SFC-DEMS measurements were conducted using two consecutive slow CVs at a scan rate of 5 mV s⁻¹ in Ar- or $\widetilde{CO_2}$ -saturated electrolytes. The electrolyte flow rate was set to 0.07 mL min⁻¹. The mass signals of H₂ (m/z = 2), CO (m/z = 28), and CO₂ (m/z = 44) were collected simultaneously with the electrode polarizations. Due to the fragmentation of CO₂ to CO during its ionization, the contribution of CO₂ was subtracted (11%) from the ionic current collected at m/z =28.

Online GC Measurement. Electrochemical CO₂RR of the Niporphyrins was conducted with a potentiostat (Ivium Statpotentiostat, Ivium Tech) in a two-compartment customized electrochemical cell, where the cathode and anode regions were separated using an anion exchange membrane (Selemion AMV). The saturated calomel electrode (SCE) and Pt foil (0.05 mm, 99.99%, Alfa Aesar) were used as the reference and counter electrodes, respectively. The catalyst ink solution was prepared with 5 mg of the Niporphyrin/carbon mixture and 40 μ L of the Nafion solution (5 wt %) in 3.78 mL of DI water. To prevent catalyst detachment, a higher Nafion-to-catalyst ratio in the ink solution was employed for the CO2 electrolysis than that for the half-cell/SFC-DEMS studies. A working electrode was fabricated by spray coating of the catalyst ink solution on a glassy carbon substrate (active area = 0.28 cm^2 , Alfa Aesar). The Ni loading on the glassy carbon was targeted at 100 μ g cm⁻². The catalytic performance was examined through step-potential electrolysis with periodic quantification of the gaseous products by online GC (6500 GC, Young Lin Instrument Co. Ltd.). The products from CO₂ electrolysis were CO and H₂, and the net total FE was nearly 100%. The electrolyte was a CO₂-bubbled 0.5 M KHCO₃ aqueous solution. All potentials were compensated for the *iR* loss. The GC was equipped with a pulsed discharge ionization detector (PDD) and a capillary molecular sieve column (Restek, RT-Msieve 5A), using ultrahigh purity He (99.9999%) as the carrier gas. During the measurement, CO2 gas was continuously flowed through the electrochemical cell at a velocity of 20 mL min⁻¹. This helps to sustain the steady reaction condition with almost unchanged electrolyte pH during the electrolysis.53 After 1 h CO₂RR using Ni(-Cl)-N₃O-TPP at -0.65 V_{RHE}, 540 μ L of the catholyte was collected and mixed with 30 µL of standard solution-D2O solvent (99.9%, Cambridge Isotope Laboratories) containing 2 mM dimethyl sulfoxide (DMSO; ≥99.9%, Sigma-Aldrich) and 10 mM phenol (≥99.0%, Sigma-Aldrich)—to confirm the imperceptible formation of the liquid products using 700 MHz ¹D ¹H NMR spectroscopy (Bruker Avance).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c11008.

General methods; experimental procedure for the preparation of porphyrins; X-ray crystallographic data for $Ni(-Cl)-N_3O-TPP$; assignment of redox couples evolved after Ni dissolution from $Ni(-Cl)-N_3O-TPP$; computational details; detailed analyses of electronic structure changes; catalytic nature of Ni-complexed phthalocyanine (NiPc) in CO₂RR (PDF)

Crystallographic data in CIF format (CIF)

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Notes

The authors declare no competing financial interest.

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