



Electrocatalytic Reduction of CO₂ by Copper (II) Cyclam Derivatives

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ABSTRACT

This study investigates Cu(II) complexes of cyclam, propylene cross-bridged cyclam (PCB-cyclam), and propylene cross-bridged cyclam diacetate (PCB-TE2A) as homogeneous electrocatalysts for CO₂ reduction in comparison with Ni(II)-cyclam. It is found that Cu(II)-cyclam can catalyze CO₂ reduction at the potential close to its thermodynamic value (0.75 V vs. Ag/AgCl) in tris-HCl buffer (pH 8.45) on a glassy carbon electrode. Cu(II)-cyclam, however, suffers from severe demetalation due to the insufficient stability of Cu(I)-cyclam. Cu(II)-PCB-cyclam and Cu(II)-PCB-TE2A are revealed to exhibit much less demetalation behavior, but poor CO₂ reduction activities as well. The inferior electrocatalytic ability of Cu(II)-PCB-cyclam is ascribed to its redox potential that is too high for CO₂ reduction, and that of Cu(II)-PCB-TE2A to the steric hindrance preventing facile contact with CO₂ molecules. This study suggests that in addition to the redox potential and chemical stability, the stereochemical aspect has to be considered in designing efficient electrocatalysts for CO₂ reduction.

Keywords : Electrocatalyst, Carbon dioxide reduction, Cyclam, Copper, Cyclic voltammetry

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1. Introduction

The electrochemical reduction of CO₂ is a promising technology that could potentially provide carbon-neutral fuels with relatively high coulombic efficiency.¹⁻³⁾ The CO₂ reduction using homogeneous electrocatalysts has been extensively studied due to its intrinsic advantage of the relative low overpotential compared to the direct CO₂ reduction on metal electrodes [1-3]. Among the homogeneous electrocatalysts, Ni(II)-cyclam (cyclam: 1,4,8,11-tetraazacyclotetradecane) and its derivatives have been known

to exhibit remarkable efficiency and selectivity in converting CO₂ to CO [4-9]. It has been revealed that Ni(I)-cyclam, generated by one-electron-reduction of Ni(II)-cyclam, is the active catalytic species and the cyclam ligand stabilizes the Ni(I) state [5,7,10]. Ni(II)-cyclam, however, still exhibits rather high overpotential (ca. -0.6 V), leading to the low energy efficiency for CO₂ conversion. In addition, Ni(II)-cyclam necessitates a mercury electrode to avoid hydrogen evolution and shows much less electrocatalytic activities on other environmentally-benign electrodes [5-7].

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In contrast to the extensive works on Ni(II)-cyclam, the studies on the cyclam complexes of other transition metals (e.g., Co, Cu) are scarce [11-15]. It has been known that Cu(I)-cyclam is unstable so that Cu(I) ion is liberated from the complex upon a cathodic polarization, which is a serious drawback as an electrocatalyst [12,13]. This demetalation issue, however, has not been fully addressed yet. It was reported that the both the smaller and larger macrocyclic complexes than 14-membered cyclam leads to stabilization of Cu(I) state, and thus suppressed demetalation behavior [12,13]. It was also claimed that the N-alkylation of cyclam stabilizes the Cu(I)- and Ni(I)-cyclams both by increasing the cavity size and by decreasing the ligand field strength imparted by the nitrogen donor atom [15], which leads to a positive shift in the M(II)/M(I) potential [14,15]. In the prior works, however, the catalytic activities of the Cu(II)-complexes for CO₂ reduction were not reported.

In this study, Cu(II) complexes of cyclam, propylene cross-bridged cyclam (PCB-cyclam), and propylene cross-bridged cyclam diacetate (PCB-TE2A) (Fig. 1) were prepared, and investigated as homogeneous electrocatalysts for CO₂ reduction. With an aim to address the demetalation issue of Cu(II)-cyclam, N-alkylation with a cross-bridging propylene group in Cu(II)-PCB-cyclam was adopted with the following two rationales: (1) altering the macrocycle

size to stabilize the central Cu ion, (2) blocking one of the two open sites of Cu(II)-cyclam. In Cu(II)-PCB-TE2A, N-diacetate groups are supposed to add further steric and electronic effects on Cu(II)-PCB-cyclam. The redox properties and demetalation behaviors of the Cu(II)-complexes were examined using cyclic voltammetry in aqueous solution on glassy carbon electrode in comparison with Ni(II)-cyclam.

2. Experimental

2.1 Chemicals

1,4,8,11-tetraazacyclotetradecane (cyclam), Ni(ClO₄)₂, Cu(ClO₄)₂ were purchased from Aldrich. Ni(II)-cyclam was synthesized as perchlorate according to literature method [16]. To a solution of cyclam (0.075 mmol) in EtOH (10 mL), Ni(ClO₄)₂·6H₂O (1.87 mmol dissolved in EtOH (10 mL)), was added dropwise. The golden yellow precipitate was found to form immediately after the addition of nickel salt. The solution was then allowed to stir at room temperature for 16 h to ensure complete complexation [C-18, MeOH: 10% ammonium acetate (1:1)]. The solution was then evaporated to dryness under reduced pressure which was followed by recrystallization (acetone/Et₂O) to afford pure Ni(II)-cyclam complex (yield 49%). Cu(II)-cyclam was synthesized based on the similar method to Ni(II)-cyclam. PCB-cyclam and PCB-TE2A were synthesized according to the literature procedure [17].

Ni(II)-cyclam: ESIMS m/z calcd for C₁₀H₂₄N₄Ni [M+ClO₄]⁺ 357.084; found 357.102.

Cu(II)-cyclam: HRMS (FAB) m/z calcd for C₁₀H₂₄N₄Cu [M+ClO₄]⁺ 362.0782; found 362.0782.

Cu(II)-PCB-cyclam: HRMS (FAB) m/z calcd for C₁₃H₂₈CuN₄ [M+ClO₄]⁺ 402.1095; found: 402.1095.

Cu(II)-PCB-TE2A: HRMS (FAB) m/z calcd for C₁₇H₃₀N₄O₄Cu [M+Na]⁺ 440.1461; found: 440.1464.

2.2 Electrochemical measurements

A standard three-electrode configuration was employed for the cyclic voltammetry (CV) measurements. A glassy carbon (area = 0.07 cm²) was used as the working electrode. Prior to testing, the glassy carbon electrode was polished with 0.3 μm alumina. Ag/AgCl (Sat. KCl) and Pt wire were used for the reference and the counter electrodes, respectively. Electrochemical experiments were carried out with a VSP

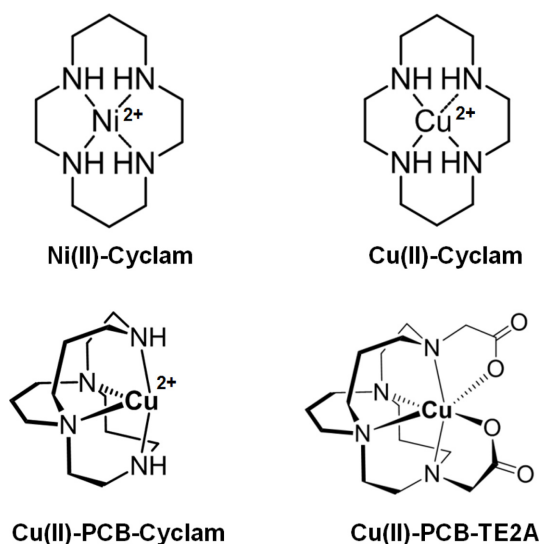


Fig. 1. Chemical structures of Ni(II)-cyclam, Cu(II)-cyclam, Cu(II)-PCB-cyclam, and Cu(II)-PCB-TE2A.

potentiostat (Biologic). All the CV measurements were performed at room temperature at a scan rate of 100 mVs^{-1} , otherwise mentioned. The electrolyte was 1 mM of Ni- or Cu-complexes in 50 mM tri-HCl buffer solution (pH 8.25). The electrolyte was purged with N_2 or CO_2 gas for 15 min before the CV measurement, and the gas stream was kept blown over the electrolyte during the measurement.

3. Results and discussion

Before investigating the electrocatalytic activity of Cu(II)-cyclam derivatives, the redox reactions of Ni(II)-cyclam, the most representative electrocatalyst for CO_2 reduction, was examined for comparison. The cyclic voltammograms (CVs) of Ni(II)-cyclam in tri-HCl buffer solution (pH 8.25) are presented in Fig. 2. In a N_2 -saturated condition, an irreversible reduction wave of Ni(II)/Ni(I) couple appears at -1.22 V , which matches with prior studies reporting irreversible behaviors of Ni(II)/Ni(I) redox couple on a glassy carbon electrode in tri-HCl buffer and KCl solution [7,8]. Some other studies, however, reported quasi-reversible behaviors for the Ni(II)/Ni(I) couple [5,6]. It seems that the reversibility of Ni(II)/Ni(I)-cyclam is affected by the experimental conditions (e.g., supporting electrolyte, pH, working electrode materials), which deserves further study. In a CO_2 -saturated solution, a large reduction current corresponding to electrocatalytic CO_2 reduction is

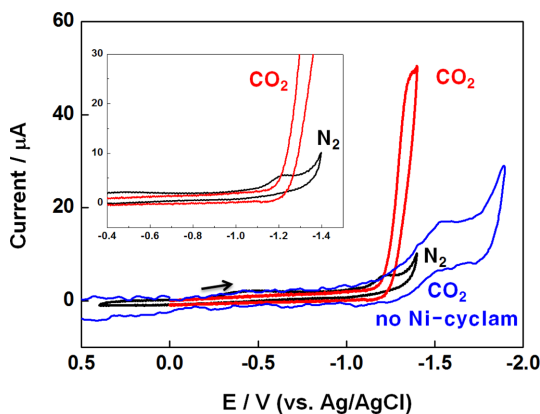


Fig. 2. Cyclic voltammograms of 1 mM Ni(II)-cyclam in 50 mM tri-HCl buffer (pH 8.25) purged with N_2 or CO_2 . The cyclic voltammogram without Ni(II)-cyclam in buffer solution with CO_2 is shown for comparison. Glassy carbon working electrode, $50 \text{ mV}\cdot\text{s}^{-1}$ scan rate. Inset in Fig. 2: an enlarged view over negative potential limit.

observed. The onset potential of the CO_2 reduction is determined to be -1.18 V , which is consistent with prior studies [5-8].

The CVs of Cu(II)-cyclam in tris-HCl buffer with and without CO_2 are shown in Fig. 3. The reduction of Cu(II)-cyclam takes place through two steps. A Cu(II)/Cu(I) peak appears at -0.85 V (peak A), a Cu(I)/Cu(0) peak at -1.05 V (peak B) [12], and the solvent decomposition current follows at below -1.2 V . In a CO_2 -saturated solution, the reduction currents are notably increased and the peak potentials are shifted to positive direction (i.e., -0.81 V (peak A') and -0.97 V (peak B')). The onset potential of CO_2 reduction by Cu(II)-cyclam is determined about -0.7 V , which is much less negative than that by Ni(II)-cyclam (-1.18 V). The theoretical potential for the CO_2/CO conversion is known to be -0.78 V vs. Ag/AgCl in pH 8 tris-HCl buffer solution saturated with 1 atm CO_2 [8]. Despite the slightly different experimental conditions, it can be stated that the electrocatalytic CO_2 reduction by

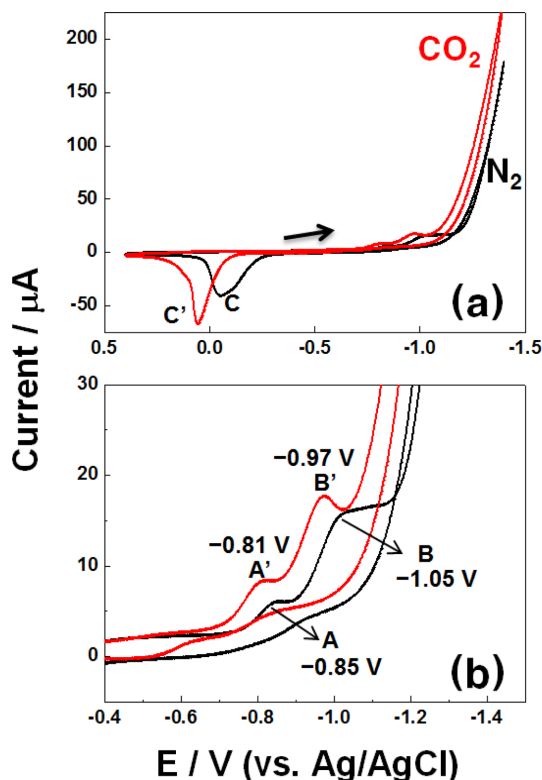


Fig. 3. (a) Cyclic voltammograms of 1 mM Cu(II)-cyclam in 50 mM tri-HCl buffer (pH 8.25) purged with N_2 or CO_2 . Glassy carbon working electrode, $100 \text{ mV}\cdot\text{s}^{-1}$ scan rate. (b) an enlarged view of (a).

Cu(II)-cyclam takes place near the thermodynamic potential. During the anodic scan, however, a large oxidation peak (peak C or peak C') appears at around 0.0 V, which is attributed to the oxidation of Cu(I) ion/Cu atom released from Cu(I)-cyclam [12]. This manifests a severe demetalation behavior of Cu(II)-cyclam, which is a critical drawback as an electrocatalyst for CO₂ reduction.

The CVs of Cu(II)-PCB-cyclam and Cu(II)-PCB-TE2A, which were rationally designed to mitigate the demetalation behavior of Cu(II)-cyclam are shown in Fig. 4. It is noted that N-alkylation affects the redox properties of Cu(II)-cyclam in the following three aspects: (1) Cu(II)-PCB-cyclam exhibits only a quasi-reversible redox peak of Cu(II)/Cu(I) couple without showing Cu(I)/Cu redox reaction (Fig. 4a). (2) the redox potential of Cu(II)/Cu(I) couple is much more positive (-0.50 V) than that of un-substituted Cu(II)-cyclam (-0.85 V). (3) Cu(II)-PCB-cyclam

shows much smaller (< 50%) Cu oxidation current, indicating mitigated demetalation compared to Cu(II)-cyclam.

These results are consistent with the previous claims that the N-alkylation of cyclam stabilizes the Cu(I)- and Ni(I)-cyclams, leading to a positive shift in the M(II)/M(I) potential [14,15]. It can be viewed that the stabilized Cu(I)-PCB-cyclam also resulted in the absence of M(I)/M redox reaction and in the diminished demetalation. However, the cathodic behavior of Cu(II)-PCB-cyclam is hardly increased under CO₂, implying that the presence of a cross-bridging propylene group seriously deactivates the electrocatalytic ability of Cu(II)-cyclam. The negligible electrocatalytic activity of Cu(II)-PCB-cyclam seems to be due to the too positive reduction potential (-0.50 V) for the theoretical CO₂ reduction potential (-0.78 V). It is supposed that the optimum reduction potential of an electrocatalyst would be only slightly more negative than the CO₂ reduction potential.

Cu(II)-PCB-TE2A also exhibits a quasi-reversible Cu(II)/Cu(I) redox reaction centered at -0.82 V. The reduction potential of Cu(II)/Cu(I) couple is -0.88 V, which is similar to that of un-substituted Cu(II)-cyclam (-0.85 V) but much more negative than Cu(II)-PCB-cyclam (-0.50 V). It seems that diacetic groups in a PCB-cyclam backbone increase the electron density around a Cu(II) ion, and thus make the Cu(II)/Cu(I) reduction of Cu(II)-PCB-TE2A unfavored compared to more Cu(II)-PCB-cyclam. It seems also possible that the presence of diacetic groups returns the cavity size of Cu(II)-PCB-cyclam to that of Cu(II)-cyclam, probably by generating a counter-strain at the other side of cyclam plane of a cross-bridged propylene group.

Notably, the Cu oxidation current is greatly suppressed in Cu(II)-PCB-TE2A. The excellent resistance of Cu(II)-PCB-TE2A to reduction-induced demetalation is ascribed to thorough protection of Cu(II)-cyclam backbone by the two Cu-coordinating acetate groups as well as by a cross-bridging propylene moiety [17]. Cu(II)-PCB-TE2A, however, shows only marginal electrocatalytic activity for CO₂ reduction. This poor electrocatalytic activity of Cu(II)-PCB-TE2A is rather unexpected when considering the redox potential (-0.82 V) suitable for the CO₂ reduction (-0.78 V) and the enhanced stability of Cu(I) state of the complex. Although further investigation is needed, it is supposed that the steric hin-

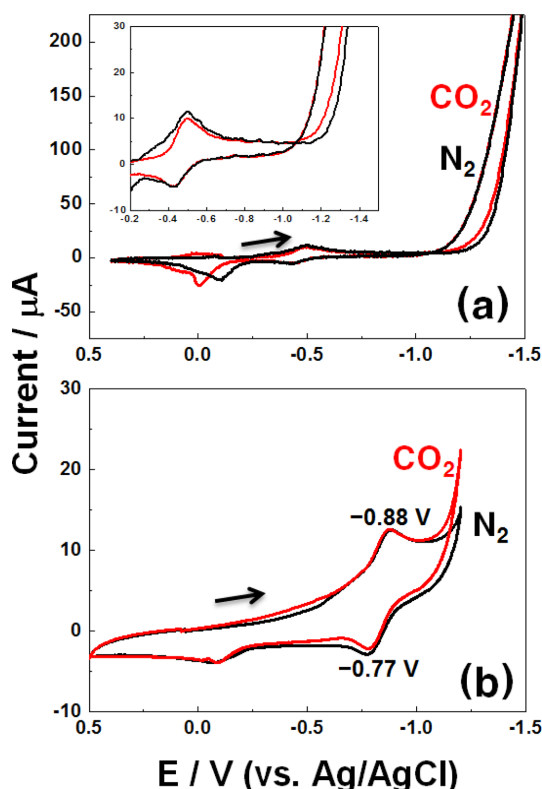


Fig. 4. Cyclic voltammograms of (a) 1 mM Cu(II)-PCB-cyclam and (b) 1 mM Cu(II)-PCB-TE2A in 50 mM tri-HCl buffer (pH 8.25) with and without CO₂. Glassy carbon working electrode, 100 mV·s⁻¹ scan rate. Inset in Fig. 4a: an enlarged view over negative potential limit.

drance around the central Cu ion in Cu(II)-PCB-TE2A is too large to allow the intimate interaction with CO₂ molecules.

Based on the results obtained so far, it can be inferred that, to design efficient electrocatalysts for CO₂ reduction, one should consider the stereochemical factor to allow facile interaction with CO₂ molecules in addition to the proper redox potential and chemical stability of the catalysts. The lessons learned from this study would be helpful to understand the detailed CO₂ reduction mechanism of homogeneous electrocatalyst and to develop novel catalysts surpassing Ni(II)-cyclam, the current most efficient electrocatalyst for CO₂ reduction.

4. Conclusions

Cu(II)-cyclam, Cu(II)-PCB-cyclam, and Cu(II)-PCB-TE2A were compared as homogeneous electrocatalysts for CO₂ reduction in tris-HCl buffer (pH 8.45) on a glassy carbon electrode. It was revealed that Cu(II)-cyclam catalyzes CO₂ reduction at much lower overpotential than Ni(II)-cyclam, the current most representative electrocatalyst. However, Cu(II)-cyclam showed severe demetalation behavior owing to the insufficient stability of Cu(I) state. The demetalation issue was greatly mitigated in Cu(II)-PCB-cyclam, in which a cross-bridging propylene is supposed to stabilize Cu(I)-PCB-cyclam. Cu(II)-PCB-cyclam, however, exhibited poor electrocatalytic activity, which is possible ascribed to its redox potential too high for CO₂ reduction. Cu(II)-PCB-TE2A exhibited further suppressed demetalation and appropriate redox potential for CO₂ reduction, but was turned out to show only marginal electrocatalytic activity, which is attributed to large steric hindrance preventing facile contact with CO₂ molecules. This study also suggests that stereochemical factor is as crucial as the redox potential and chemical stability of the electrocatalysts for CO₂ reduction.

Acknowledgements

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