Electrocatalytic CO_2 reduction by cobalt octabutoxyphthalocyanine coated on graphite electrode

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Abstract

Electrocatalytic CO_2 reduction was studied by using a modified graphite electrode coated with cobalt octabutoxyphthalocyanine ($CoPc(BuO)_8$) and dipped in an aqueous electrolyte. The $CoPc(BuO)_8$ worked as a catalyst to produce CO with higher activity and selectivity than the non-substituted CoPc. Under typical conditions at pH 4.4, the most active and selective CO_2 reduction was achieved at -1.30 V with turnover number of the catalyst $\sim 1.1 \times 10^6$ h^{-1} and the selectivity of the produced $CO/H_2 \sim 4.2$. The high activity was ascribed to the electron-donating BuO substituents of the complex, which would facilitate the coordination of CO_2 as well as the electron transfer from the complex to the coordinated CO_2 molecule. The use of a poly(4-vinylpyridine) membrane to disperse the complex decreased the activity. The mechanism was investigated by the use of in situ potential-step chronoamperospectroscopy (PSCAS) in a homogeneous $CoPc(BuO)_8$/pyridine solution. In the absence of CO_2, distinct two-steps visible spectral changes were observed following the first and second reductions of the complex. However, under CO_2 atmosphere, only the one-electron reduced species was present under steady state. It was proposed that the third reduction of a CO_2-coordinated $CoPc(BuO)_8$ should take place for CO production.

Keywords: Electrocatalytic CO_2 reduction; Cobalt octabutoxyphthalocyanine; Potential-step chronoamperospectroscopy (PSCAS); Catalytic mechanism

1. Introduction

For constructing an artificial photosynthetic system, CO_2 reduction is an important reaction.

This CO_2 reduction should be carried out in a water phase since oxidation site (water oxidation) is in water. However, in an aqueous phase, proton reduction usually proceeds much more favorably than CO_2 reduction. CO_2 reduction has been studied extensively with various systems [1], but it has been difficult to achieve active and selective electrocatalytic CO_2 reduction in an aqueous phase by simple electrode systems [2]. In order to achieve selective CO_2

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reduction in water, metal complexes are one of the most promising candidates as the catalyst. We have studied electrochemical CO_2 reduction catalysts such as [Re(bpy)(CO)$_3$Br] (bpy; 2,2'-bipyridine) [3], [Co(terpy)$_2$]$^{2+}$ (terpy; 2,2':6',2"-terpyridine) [4] and cobalt phthalocyanine (CoPc) [5,6] by the use of electrode modification. CoPc has been reported to catalyze electrochemical CO_2 reduction in water [5–12]. We have found that CoPc incorporated into a poly(4-vinylpyridine) membrane coated on a graphite electrode achieves active and selective CO_2 reduction in water [5,6]. It is interesting and important as well to investigate the derivatives of CoPc for electrocatalytic CO_2 reduction to develop catalysts and to get insight into the mechanistic feature of the catalysis. Since the electron-donating groups at the Pc ring are expected to enhance CO_2 coordination and reduction, cobalt octabutoxyphthalocyanine (CoPc(BuO)$_8$) was studied. The mechanism of CO_2 reduction catalyzed by CoPc and its derivatives has not been established yet. To study the mechanism, CO_2 reduction in a homogeneous CoPc(BuO)$_8$/pyridine solution was also investigated by in situ potential-step chronoamperospectroscopy (PSCAS). In the present paper, catalytic activity of CoPc(BuO)$_8$ as well as its catalysis mechanism will be reported.

2. Experimental

2.1. Materials and preparation of a modified electrode coated with CoPc(BuO)$_8$

CoPc(BuO)$_8$ was synthesized in accordance with a previous report [13]. CoPc was purchased from Kanto Chemical. Preparation of modified electrode was carried out by casting a 4 μl DMF solution of 5 μM CoPc(BuO)$_8$ onto a basal-plane pyrolytic graphite (BPG) electrode (effective area: 0.17 cm^2) followed by solvent evaporation under air.

2.2. Electrochemical measurements

A single compartment electrochemical cell was equipped with a modified BPG working, a spiral platinum wire counter and a silver–silver chloride(Ag/AgCl) reference electrode. Electrochemical study was carried out by the use of a potentiostat (Hokuto Denko, HA-301) with a function generator (Hokuto Denko, HB-104), a coulomb meter (Hokuto Denko, HF-201) and a X-Y recorder (Shimadzu, XY-50). The measurement of cyclic voltammogram (CV) and potentiostatic electrolyses were run in an aqueous buffer solution in the range of pH 4.4 to 9.3. Gaseous products were analyzed by a gas chromatograph (Shimadzu, GC-4C) with a molecular sieve 5A column and helium carrier gas. Analysis of liquid products was carried out by a high performance liquid chromatograph (Hitachi, D-6000) with an anion exchange column (Showa Denko, Shodex KC-811).

2.3. Measurement for in situ potential-step chronoamperospectroscopy (PSCAS)

An in situ PSCAS measurement was carried out by a photodiode array spectrophotometer (Otsuka Electronics, IMUC-7000) in combination with the voltammetric apparatus. A thin layer electrochemical cell was equipped with a platinum mesh working, a spiral platinum wire counter and a silver (Ag/Ag$^+$) reference electrode. The potential of this Ag/Ag$^+$ reference electrode was -0.30 V versus Ag/AgCl in the pyridine solution. The measurement was run in a 5.0 × 10^{-4} M CoPc(BuO)$_8$/pyridine solution containing 0.5 M tetrabuthylammonium perchlorate (TBAP) as a supporting electrolyte.

3. Results and discussion

The redox behavior of CoPc(BuO)$_8$ is essentially similar to the other CoPc derivatives [5,6,14–16]. Fig. 1 shows a typical cyclic

voltammogram (CV) of the $CoPc(BuO)_8$ coated on a BPG electrode. The reversible wave of the first redox reaction $(Co^{II/I})$ was observed at $E = -0.58$ V (E is the midpoint potential between the anodic and cathodic peaks). However, the second redox reaction (the Pc ring) peak was not observed because of the high catalytic cathode current by proton reduction. The redox peak is relatively shifted to more negative potentials than that of the non-substituted CoPc [5]. This can be ascribed to the electron-donating property of the BuO groups.

By scanning to more negative potential region, the CV was also measured both under argon (A) and under CO_2 (B) as shown in Fig. 2. The cathodic currents are remarkably different for each voltammogram. Under CO_2 (B), the cathodic current started to increase at a slightly more positive potential than that under argon (A), and a specific shoulder peak, which has never been observed for $CoPc(BuO)_8$ alone, was observed around -1.30 V. In our previous report on the CoPc dispersed into poly(4-vinyl-pyridine) (CoPc/PVP), a similar shoulder peak

Fig. 2. Cyclic voltammograms at modified BPG electrode coated with $CoPc(BuO)_8$ under argon (A) and CO_2 (B) at pH 4.4. The coated amount of $CoPc(BuO)_8$ is 1.2×10^{-10} mol cm^{-2}. Scan rate, 200 mV s^{-1}.

was observed [6]. This shoulder peak can be ascribed to the catalytic reduction of a CO_2-coordinated species.

Figs. 3–5 show the results of the potentiostatic electrolyses at modified electrode coated with $CoPc(BuO)_8$ (A) at pHs 4.4, 6.8 and 9.3, respectively. The data are compared with the non-substituted CoPc system (B) under the same conditions. The coated amount of the complex is $\sim 1.2 \times 10^{-10}$ mol/cm^2. In the present systems, only CO and H_2 were confirmed as the reductive products. Any other liquid products were not detected in the aqueous phase. In the electrolysis data at various pH conditions, the characteristic features are that (i) much larger amount of CO production was confirmed in the $CoPc(BuO)_8$ system than in the CoPc system, and (ii) more active CO_2 reduction by $CoPc(BuO)_8$ was achieved at more positive potentials than by CoPc, especially under acidic conditions. Much higher activity of $CoPc(BuO)_8$ can also be shown by the turnovernumber (TN) of the catalyst species. For instance, at -1.30 V in a pH 4.4 electrolyte solution, the TN values
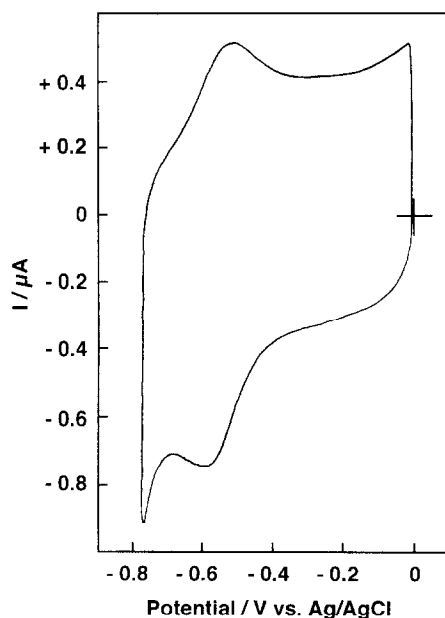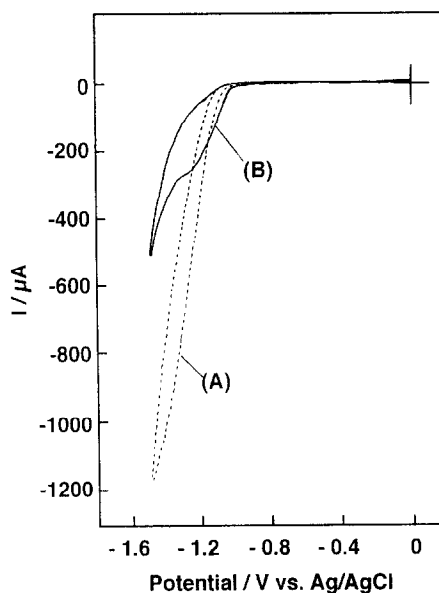

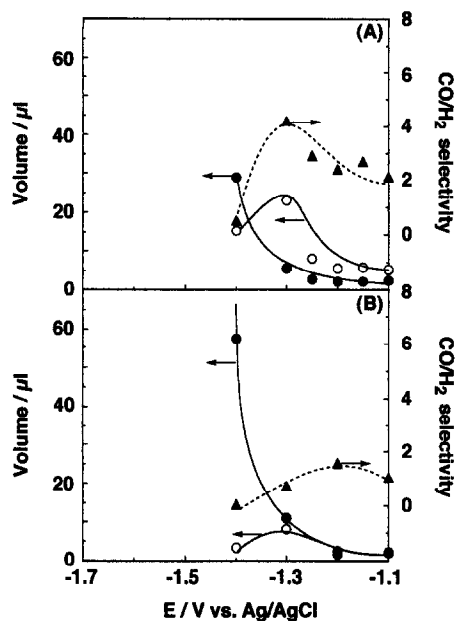Fig. 1. Cyclic voltammogram at BPG electrode (effective area: 0.17 cm^2) coated with $CoPc(BuO)_8$ (1.2×10^{-10} mol cm^{-2}) at pH 4.4. Scan rate, 200 mV s^{-1}.

Fig. 3. Results of potentiostatic electrolyses at modified BPG electrode coated with CoPc(BuO)$_8$ (A) and CoPc (B) at pH 4.4 and relationship of the produced CO/H$_2$ selectivity with respect to the applied potentials. The coated amount of catalyst is 1.2× 10^{-10} mol cm^{-2} in each system. Potentiostatic electrolysis was run for 1 h. Product: CO (○), H$_2$ (●).
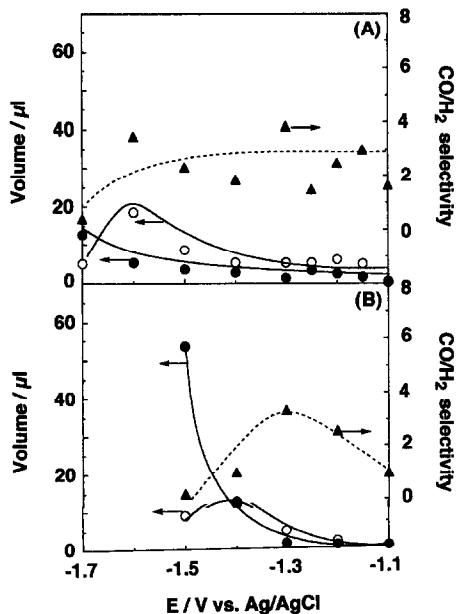

Fig. 5. Results of potentiostatic electrolyses at modified BPG electrode coated with CoPc(BuO)$_8$ (A) and CoPc (B) at pH 9.3 and relationship of the produced CO/H$_2$ selectivity with respect to the applied potentials. The coated amount of catalyst is 1.2× 10^{-10} mol cm^{-2} in each system. Potentiostatic electrolysis was run for 1 h. Product: CO (○), H$_2$ (●).
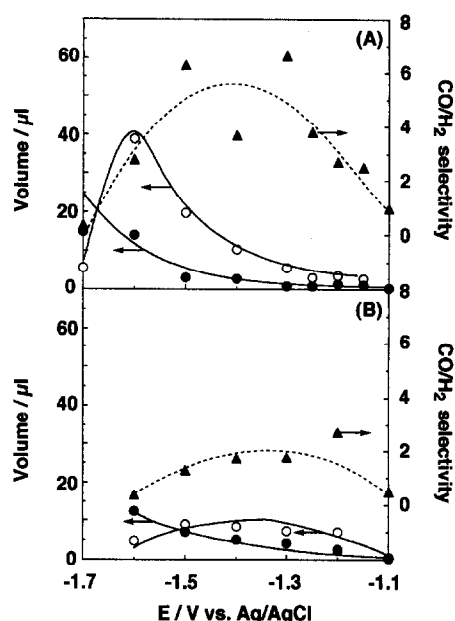

Fig. 4. Results of potentiostatic electrolyses at modified BPG electrode coated with CoPc(BuO)$_8$ (A) and CoPc (B) at pH 6.8 and relationship of the produced CO/H$_2$ selectivity with respect to the applied potentials. The coated amount of catalyst is 1.2× 10^{-10} mol cm^{-2} in each system. Potentiostatic electrolysis was run for 1 h. Product: CO (○), H$_2$ (●).

of CoPc(BuO)$_8$ and CoPc were obtained as 1.1 × 10^6 and 5.5 × 10^4 h^{-1}, respectively, showing that the TN of the CoPc(BuO)$_8$ is 20 times as high as that of CoPc.

It should be noted that in both CoPc(BuO)$_8$ and CoPc systems H$_2$ production is favored and CO production is suppressed at negative potentials. In the modified BPG electrode coated with CoPc, it was found that the rate of the electrocatalytic proton reduction via the complex was lower than that of the direct reduction on the electrode surface [6]. The efficient H$_2$ production at negative potentials can be ascribed to the direct proton reduction on the BPG electrode surface, and it seems that this results in the suppression of CO production. At negative potentials the electrons would not be transported efficiently because of the high rate proton reduction. CoPc(BuO)$_8$ keeps high catalytic activity at more negative potentials than CoPc. CoPc(BuO)$_8$ would have a high ability of electron transport to CO$_2$ molecule due to the higher

electron-donating property than CoPc (see also the discussion about CV). The produced CO/H_2 selectivity is also shown in Figs. 3–5. Much higher CO/H_2 selectivity was obtained by the $CoPc(BuO)_8$ system than by the CoPc. The selectivity is associated with the relative rate ratio of catalytic CO_2 reduction on the complex and proton reduction on the electrode.

We have studied catalyst membranes composed of a complex and functional polymer such as Nafion® and poly(4-vinlpyridine) for electrocatalytic CO_2 reduction [3–6]. These results showed higher catalytic activity of the complex incorporated in a membrane than the neat complex. Poly(4-vinylpyridine) (PVP) membrane containing $CoPc(BuO)_8$ ($CoPc(BuO)_8$/PVP) was prepared by the method reported by the present authors [6]. In the CoPc/PVP system [6], the properties of PVP such as weakly basic and coordinative characteristics brought about the increase of the catalytic activity of CoPc. For the $CoPc(BuO)_8$/PVP, typical electrolysis data are shown in Table 1. It was found that CO_2 reduction is never achieved efficiently by $CoPc(BuO)_8$/PVP. The low catalytic activity of $CoPc(BuO)_8$/PVP system would come from its electrochemical inertness due to some specific interaction between the hydrophobic substituents and PVP.

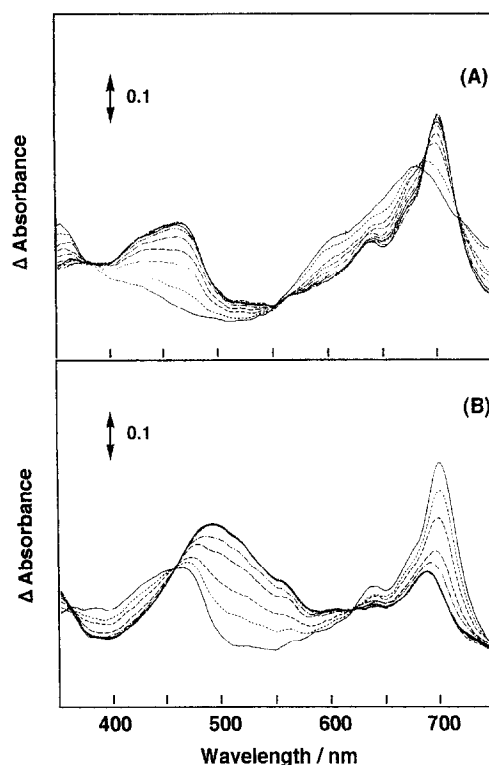In situ potential-step chronoamperospectroscopy (PSCAS) was carried out to elucidate

Fig. 6. Development of electronic absorption spectra with time during the reduction of [$Co^{II}Pc(BuO)_8$] at -0.85 V versus Ag/Ag^+ (A) and [$Co^IPc(BuO)_8$] at -1.65 V versus Ag/Ag^+ (B) in 0.5 M TBAP/pyridine solution under argon. [$CoPc(BuO)_8$] $= 0.5$ mM.

Table 1
Results of typical potentiostatic electrolyses (1 h) by using modified electrode coated with $CoPc(BuO)_8$ or $CoPc(BuO)_8$ /PVP at pH 4.4

Catalyst [a]	E / V (versus Ag/ AgCl)	CO (μl)	H_2 (μl)	Selectivity of CO/H_2
$CoPc(BuO)_8$	-1.30	23.1	5.5	4.2
$CoPc(BuO)_8$ /PVP [b]	-1.30	2.1	4.3	0.49

[a] Total amount of catalyst coated on the electrode surface: 1.2×10^{-10} mol cm^{-2}.
[b] The modified electrode was prepared with casting a 0.5 wt% poly(4-vinylpyridine)/DMF solution containing 5 μM $CoPc(BuO)_8$.

the catalytic mechanism. Unfortunately, for the $CoPc(BuO)_8$ coating system, the PSCAS measurement can not be carried out due to a low absorbance change of the complex during electrolysis and also due to the intransparency of the BPG base electrode. In a homogeneous solution system, the PSCAS study can not also be carried out on $CoPc(BuO)_8$/DMF system due to the low solubility of the complex.

The PSCAS results in a potential-step from 0 to -0.85 V (versus Ag/Ag^+) in a homogeneous 0.5 mM $CoPc(BuO)_8$/pyridine solution containing TBAP as a supporting electrolyte under argon are shown in Fig. 6(A), and the results in a potential-step from -0.85 to -1.65 V are shown in Fig. 6(B). The spectral changes in the first (A) and second (B) steps under argon are ascribed to the reduction of the central Co^{II}

ion and the ligand (Pc ring), respectively. The spectral features of each reduction species are similar to those of CoTNPc (TN; 2,9,16,23-tetraneopentoxy) [17]. The first order rate constants for both the first and the second reductions under argon were obtained as $k_1 = 6.3 \times 10^{-3}$ s^{-1} and $k_2 = 3.3 \times 10^{-2}$ s^{-1} (from Fig. 6(A) and (B)), respectively.

The PSCAS measurement was carried out also under CO_2, and the results are shown in Fig. 7. The spectral changes in Fig. 7(A) were very similar to Fig. 6(A) in a potential-step from 0 to -0.85 V (versus Ag/Ag$^+$). However, spectral changes as seen in Fig. 6(B) were not observed at all in Fig. 7(B) although the applied potential was negative enough to form ligand reduced species, and only the central metal-reduced species (one-electron reduced
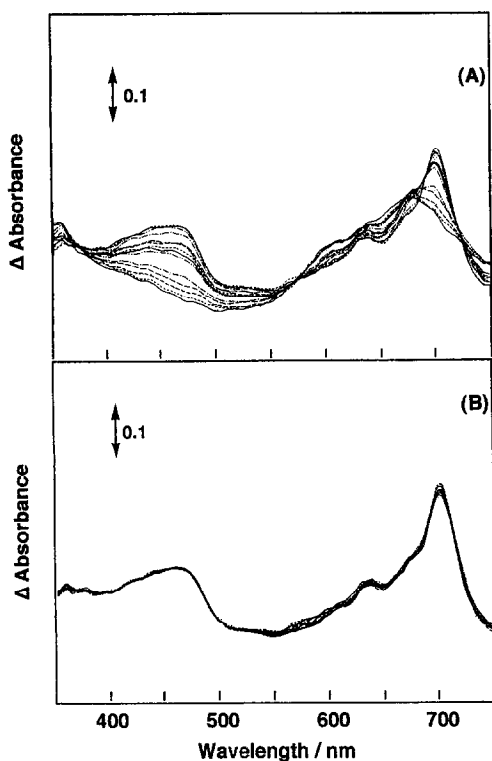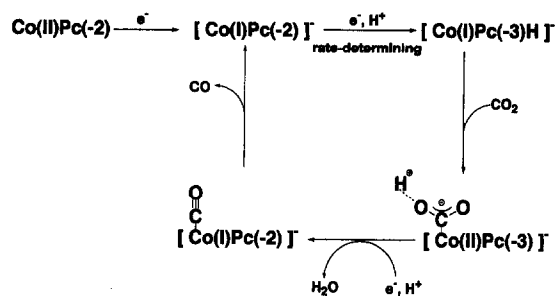

Fig. 8. A proposed mechanism for electrochemical CO_2 reduction catalyzed by CoPc(BuO)$_8$.

species) was present under steady state. In fact, at this potential (-1.65 V versus Ag/Ag$^+$) CO production was also confirmed during potentionstatic electrolysis in this solution system. From these PSCAS measurements, it is proposed that the third reduction of the catalyst takes place to result in a steady-state one-reduction CoPc(BuO)$_8$ species.

The mechanism can be represented by Fig. 8. Probably, the basicity of one-electron reduced species would be too weak to form an intermediate with CO_2 molecule. Therefore, as seen in other macrocyclic cobalt complex system, the two-electron reduced species, which is highly nucleophilic, would coordinate to CO_2 molecule (η^1-CO_2-coordinated species) [18–21]. The electron density of CoPc(BuO)$_8$ is higher than that of CoPc, so that the CoPc(BuO)$_8$ could not only result in higher intermediate concentration but also donate an electron more efficiently from the catalyst to coordinated CO_2 molecule than the non-substituted CoPc. The results of the in situ PSCAS as well as the electrolysis support a few previous reports which indirectly suggested the presence of the third reduction of CoPc and its derivatives [22–24]. It should be noted that the efficient proton consumption for H_2 production at negative potentials suppresses the dehydration process in CO production and also the electron transport from the electrode surface to the catalyst.

Fig. 7. Development of electronic absorption spectra with time during the reduction of [Co^{II}Pc(BuO)$_8$] at -0.85 V versus Ag/Ag$^+$ (A) and [Co^{I}Pc(BuO)$_8$] at -1.65 V versus Ag/Ag$^+$ (B) in 0.5 M TBAP/pyridine solution under CO_2. [CoPc(BuO)$_8$] = 0.5 mM.

4. Conclusion

The cobalt octabutoxyphthalocyanine $(CoPc(BuO)_8)$ containing the electron-donating BuO groups worked as an active and selective catalyst for the electrocatalytic CO_2 reduction to give CO. The increase of its catalytic activity compared to the non-substituted CoPc was ascribed to the electronic property of the complex. Entirely different from the CoPc system, the activity of $CoPc(BuO)_8$ was remarkably low when it was used by incorporating into a poly(4-vinylpyridine) membrane.

From the PSCAS measurement, it was found that the one-electron reduced species of $CoPc(BuO)_8$ is present under the steady state during the electrocatalytic CO_2 reduction, showing that the third reduction of a CO_2-coordinated $CoPc(BuO)_8$ takes place for CO production. In the present work, it was shown that the combination of the electrolysis experiment with an in situ PSCAS study is useful for understanding electrocatalytic reaction processes.

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