Electrocatalytic reduction of carbon dioxide by cobalt-phthalocyanine-incorporated polypyrrole

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Abstract
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Keywords
Electrocatalytic, reduction, carbon, dioxide, cobalt, phthalocyanine, incorporated, polypyrrole

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Electrochemical Reduction of Carbon Dioxide by Cobalt-Pthalocyanine-Incorporated Polyppyrole

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In the quest for catalysts for the electrocatalytic reduction of CO2, a cobalt phthalocyanine/polyppyrole (CoPc/PPy) composite electrode has been developed. The electrode is prepared by drop casting CoPc onto the PPy film from the CoPc/tetrahydrofuran solution (1 mg/mL). The onset potential for CO2 reduction occurred at potentials 160 mV more positive than observed with a simple PPy electrode. Furthermore, in the potentiostatic electrolysis, the catalytic current for CO2 reduction at CoPc/PPy was very stable, with a higher current density and current efficiency when compared to the PPy electrode.

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The advent of global warming, associated with increasing atmospheric carbon dioxide (CO2) concentrations, has stimulated research into the utilization of CO2. The transformation of CO2 to carbon monoxide or alcohols is a promising long-term objective. For the past decade, methods of reducing CO2 to CO, formaldehyde, methanol, methane, or oxalate, using electrochemical methods which consume less energy than traditional chemical reduction processes and can proceed at a moderate temperature and atmospheric pressure, have been developed.1-5

The direct electrochemical reduction of CO2 on various metal electrodes requires large overpotentials (more negative than −2 V vs saturated calomel electrode).6-10 It is therefore important to search for active electrocatalysts which can mediate the electrochemical reduction of CO2 at lower potentials. Numerous transition-metal (mainly Co and Ni) complexes, such as macrocyclic cobalt or nickel, cobalt phthalocyanine (CoPc), or porphyrin, have been reported to have such catalytic effects.11-13 The use of these catalysts, however, has generally been limited by their degradation during electrolysis. It is thus necessary to investigate the electrochemical reduction of CO2 at a modified electrode, on which the complex is more stable. Both Lieber and Lewis14 and Meshitsuka et al.15 reported the electroreduction of CO2 at a CoPc-modified graphite electrode in citrate buffer and obtained CO as the main product. The electrochemical reduction of CO2 at cobalt-octabutoxyphthalocyanine-coated graphite electrodes was investigated by Abe et al.16 The reduction of CO2 at a cobalt(II) tetrphenyldiporphyrin-pyridine-modified glassy carbon (GC) electrode showed a high catalytic activity for CO2 reduction to CO.17

In recent years, the combination of polymer and metal complex catalysts has provided an alternative route to the electrochemical reduction of CO2. The reduction of CO2 at Prussian blue/polymer/metal complex-based electrodes in the aqueous solution18-21 was investigated. CO2 was reduced at −0.8 V (vs Ag/AgCl) and the reaction products were formic acid, lactic acid, acetic acid, methanol, and ethanol. The electrocatalytic conversion of CO2 on polyppyrole (PPy)- or polyaniline-modified electrodes under high pressure in methanol resulted in the formation of CH3COOH as the main product.22-24

In this article, we present the study of electrocatalytic CO2 reduction at the CoPc/PPy-modified GC electrode in the 0.1 M LiClO4/ACN–H2O solution. The CoPc/PPy composite electrode was then investigated via a potentiostatic method and showed the enhanced electrocatalytic activity and stability for CO2 reduction.

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trocatalytic CO₂ reduction was observed in the CO₂-saturated non-
aqueous ACN solution, and the presence of H₂O is necessary and critical for the 
indirect reduction of CO₂. We assume that the reduction adsorption 
may be the adsorption of the substrate molecules via hydrogen 
bonding, so the transfer of a H_ads atom to the CO₂ molecule would 
be much easier and faster.

The inset of Fig. 1 shows the cyclic voltammograms obtained 
using the PPy-modified electrode in the nonaqueous 0.1 M 
LiClO₄/ACN electrolyte saturated with either N₂ or CO₂. No elec-
trocatalytic CO₂ reduction was observed in the CO₂-saturated electrolyte (vs Ag/AgCl). The inset shows CVs of the CoPc/PPy electrode in 0.1 M LiClO₄/ACN–H₂O under N₂ and CO₂, v = 50 mV/s.

Electrocatalytic CO₂ reduction at CoPc/PPy electrode.— To im-
prove the catalytic performance of PPy, the CoPc-modified PPy film was prepared by coating with the CoPc/THF material. The scanning electron microscopy (SEM) images of the PPy film with/without CoPc are shown in Fig. 2. The pure PPy displays a very smooth 
surface morphology (Fig. 2a), while the CoPc-modified PPy film 
(Fig. 2b) has a crystalline porous structure due to the CoPc coating.

After the preparation of the CoPc/PPy electrode, it was investi-
gated for electrocatalytic CO₂ reduction under identical conditions 
used for the pure PPy electrode. The CVs using either PPy or CoPc/ 
PPy as working electrodes were obtained in a CO₂-saturated 0.1 M 
electrolyte (Fig. 3). The electrocatalytic reduction of CO₂ took place 
at −0.18 V using the CoPc/PPy electrode, which showed a positive 
160 mV shift in the onset of the reduction potential compared to that 
of pure PPy electrode (−0.34 V). This illustrates that the CoPc/PPy 
has a much better catalytic influence on CO₂ reduction than pure 
PPy. Furthermore, a higher catalytic peak current of CO₂ reduction 
is observed at −0.45 V using the CoPc/PPy electrode, which is 
probably caused by the increase in the number of active centers 
where the reduction of CO₂ takes place.20

Compared to the CV of the CoPc/PPy electrode in the 
N₂-saturated 0.1 M LiClO₄/ACN–H₂O solution, the inset of Fig. 3 
shows that the oxidation peak of Co(I)Pc to Co(II)Pc disappeared in the 
presence of CO₂. The corresponding reduction peak of Co(II)Pc to 
Co(I)Pc under N₂ coincides less with that under CO₂ so that it is 
unclear whether the corresponding reduction peak is present in the 
CV under the CO₂ peak or not at all. The possible mechanism for 
this is that when H⁺ is reduced to H_ads and H_ads is continuously 
consumed to reduce CO₂, it causes the oxidation of Co(I)Pc to 
Co(II)Pc.20 It also suggests that a much stronger generation of H_ads 
occurred at the PPy and CoPc interfaces; therefore the CoPc/PPy 
composite electrode promoted the electrocatalytic reduction of CO₂ 
with enhanced catalytic activity compared to PPy alone.

Potentiostatic CO₂ reduction at PPy and CoPc/PPy elec-
trodes.— CO₂ reduction was performed at a constant potential −0.8 
V (vs Ag/AgCl) at both PPy and CoPc/PPy electrodes in the 
CO₂-saturated 0.1 M LiClO₄/ACN–H₂O (v:v = 1:1) solution. Fig-
ure 4 shows the I-t curve for catalytic CO₂ reduction at the CoPc/ 
PPy electrode normalized from the pure PPy electrode with a stable 
current density of 20 mA/g. The higher catalytic current observed at 
the CoPc/PPy electrode again confirms that the PPy incorporated 
with CoPc has a better catalytic performance for CO₂ reduction than 
the PPy electrode itself (see inset of Fig. 4).

The product detected by HPLC was formic acid. No evolution of 
gaseous products was observed during the controlled potential elec-
trolysis. This is consistent with the mechanism described in the first 
subsection for electrocatalyzed CO₂ reduction. This is possibly due
Figure 4. (Color online) (a) I-t curve for CO\textsubscript{2} reduction at the CoPc/PPy electrode normalized from the PPy electrode in 0.1 M LiClO\textsubscript{4}/ACN–H\textsubscript{2}O (vs Ag/AgCl). The inset is the I-t curve of the PPy- and CoPc/PPy-modified electrodes under CO\textsubscript{2}, \(E = -1.0\) V (vs Ag/AgCl). (b) Current efficiency–time diagrams of CO\textsubscript{2} reduction at PPy and CoPc/PPy electrodes.

The inset is the I-t curve for CO\textsubscript{2} reduction at the CoPc/PPy composite electrode from \(-0.34\) (PPy) to \(-0.18\) V. Furthermore, during potentiostatic electrolysis, the catalytic current for CO\textsubscript{2} reduction at CoPc/PPy was very stable with a higher current efficiency when compared to a single PPy electrode.

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