

“Deactivation of copper electrode” in electrochemical reduction of CO₂

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Abstract

Metallic Cu electrode can electrochemically reduce CO₂ to CH₄, C₂H₄ and alcohols with high yields as revealed by the present authors. Many workers reported that formation of CH₄ and C₂H₄ rapidly diminishes during electrolysis of CO₂ reduction. This paper shows that such deactivation of Cu electrode is reproduced with electrolyte solutions prepared from reagents used by these workers. Deactivated Cu electrodes recovered the electrocatalytic activity for CO₂ reduction by anodic polarization at –0.05 V versus *she* in agreement with the previous reports. Features of the deactivation depend greatly on the individual chemical reagents. Purification of the electrolyte solution by preelectrolysis with a Pt black electrode effectively prevents the deactivation of Cu electrode. Anode stripping voltammetry of Cu electrodes, which were deactivated during electrolysis of CO₂ reduction, showed anodic oxidation peaks at ca. –0.1 or –0.56 V versus *she*. The severer the deactivation of the Cu electrode was, the higher electric charge of the anodic peak was observed. It is presumed that some impurity heavy metal, originally contained in the electrolyte, is deposited on the Cu electrode during the CO₂ reduction, poisoning the electrocatalytic activity. On the basis of the potential of the anodic peaks, Fe²⁺ and Zn²⁺ are assumed to be the major contaminants, which cause the deactivation of the Cu electrode. Deliberate addition of Fe²⁺ or Zn²⁺ to the electrolyte solutions purified by preelectrolysis exactly reproduced the deactivation of a Cu electrode in CO₂ reduction. The amount of the deposited Fe or Zn on the electrode was below the monolayer coverage. Electrothermal atomic absorption spectrometry (*etaas*) showed that Fe originally contained in the electrolyte solution is effectively removed by the preelectrolysis of the solution. Mechanistic difference is discussed between Fe and Zn in the deterioration of the electrocatalytic property of Cu electrode in the CO₂ reduction. The concentration of the impurity substances originally contained in the chemical reagents as Fe or Zn is estimated to be far below the standard of the impurity levels guaranteed by the manufacturers. Presence of trimethylamine in the electrolyte solution also severely poisons a Cu electrode in the CO₂ reduction. It was concluded that the deactivation of Cu electrode in CO₂ reduction is not caused by adsorption of the products or the intermediates produced in CO₂ reduction.

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1. Introduction

1.1. “Deactivation” of copper electrode in electrochemical reduction of CO₂ reported in the previous works

CO₂ is electrochemically reduced to CH₄, C₂H₄ and alcohols in high yields at Cu electrode in aqueous electrolytes as

firstly revealed by the present authors [1–3]. With regard to this reaction, many workers reported “poisoning” or “deactivation” of the copper electrode. Most of them described that the formation of CH₄ and C₂H₄ at Cu electrode diminishes rapidly and the hydrogen evolution prevails in 10–30 min after the start of the CO₂ electrolysis.

DeWulf et al. [4] studied CO₂ reduction at high purity copper foil electrodes, employing 0.5 M KHCO₃ as the electrolyte solution prepared from an ACS reagent grade, MCB Manufacturing Chemists Inc. and Milli Q water without further purification. The current density in their study was 30–35 mA cm^{–2} at –2.00 V versus standard calomel elec-

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trode (*sce*). The total Faradaic efficiency of CH_4 and C_2H_4 reached 65% after 20 min of electrolysis, and gradually decayed to 0% after 120 min. Meanwhile the electrode surface was blackened, and they detected graphitic carbon on the electrode surface by X-ray photoelectron spectroscopy (*xps*) and Auger electron spectroscopy (*aes*) measurements. They presumed that some products or intermediates formed in the CO_2 reduction are adsorbed on the electrode surface, suppressing the reaction. They also pointed out a possibility that the poisoning or deactivation could be derived from deposition on the electrode surface of impurities originally contained in the electrolyte solution.

Wasmus et al. [5] reported CO_2 reduction studied with on line electrochemical mass spectrometry. The measurements were performed in 0.5 M KHCO_3 (Fluka p.a.) solution prepared from Millipore water without further purification. They showed that CH_4 and C_2H_4 formation at a bulk copper electrode decayed during successive cathodic scans to -2.0 V versus *sce* or less for 10 min with the electrode blackened meanwhile. The activity of the electrode was regenerated by anodic polarization at -0.15 V versus *sce*.

Kyriacou and Anagnostopoulos [6] reported deactivation in the CO_2 reduction using high purity copper foil electrodes in 0.5 M KHCO_3 (Aldrich, reagent grade) solution prepared from doubly distilled water. In their electrolysis measurements at -1.85 V versus *sce*, the current efficiencies of the products reached maxima (CH_4 31%, C_2H_4 10%, CO 3%), and diminished to less than 5% in 10 min. Shiratuchi et al. [7] reported poisoning of a Cu electrode in CO_2 reduction in 0.1 M KHCO_3 . They could suppress the poisoning of the electrode by applying anodic polarization pulses to the Cu electrode periodically during the cathodic reduction of CO_2 . Jermann and Augustynski [8] observed severe deactivation of a Cu electrode. They used 0.5 M NaHCO_3 and KHCO_3 (pro analysi, Merck) as the electrolyte solutions prepared from doubly distilled water. Friebe et al. [9], Lee and Tak [10], and Yano et al. [11] also reported the deactivation of Cu electrode in electrochemical reduction of CO_2 . Some authors investigated deactivation of Au or Ag metal electrode in CO_2 reduction. The behaviors of these metal electrodes are similar to those of Cu electrode.

Frese referred in his monograph [12] to the deactivation possibly derived from impurity metals deposited on the surface of the Cu electrode after electrolytic reduction of CO_2 in 0.5 M KHCO_3 . He suggested that main impurity substances are Fe and Zn.

Kyriacou and Anagnostopoulos [6], and Jermann and Augustynski [8] attempted to examine the reason of the deactivation. Both of them preelectrolyzed the electrolyte solution with platinum electrodes, and found little improvement in suppression of the deactivation. They analyzed the surface of the used electrode by energy dispersive spectroscopy (*eds*) [6] or *xps* [8], and did not detect impurity metallic traces on the electrode surface. Both of them concluded that deposition of metallic impurities of the solution is not the main cause of the electrode poisoning. They presumed that the “deactivation”

was derived from adsorption of organic intermediate formed in CO_2 reduction [6], or formation of a substance related with oxide or hydroxide formed on the copper electrode [8].

1.2. Possible causes of the “deactivation” of Cu electrode

The electrochemical reduction of CO_2 is an interfacial reaction, and must naturally be sensitive to the state of the electrode surface. Thus one could presume that the “deactivation” of Cu electrode may be derived from the following causes.

- (1) Heavy metal impurities contained in reagent chemicals at extremely low level are introduced to the electrolyte solution. Such heavy metal ions in the electrolyte solution will be cathodically reduced and deposited at the electrode during the CO_2 reduction. Metal electrodes other than Cu do not have electrocatalytic activity for hydrocarbon formation in CO_2 reduction. Thus, any deposited heavy metals except Cu will deteriorate the electrocatalytic activity of Cu electrode for CO_2 reduction.
- (2) Very small amount of organic substances are possibly contained in water, such as surface active reagents. They are sometimes hard to remove even by distillation [13]; these substances may be adsorbed on the electrode during the CO_2 reduction, subsequently deactivating the electrode.
- (3) In accordance with some previous workers mentioned above, some intermediate species or products formed during the CO_2 reduction, adsorbed on the electrode, might poison the subsequent reaction.

As described in the preceding section, the “deactivation” or “poisoning” has a common concept that the formation of CH_4 or C_2H_4 is depressed during the CO_2 reduction. However, it is noticeable that the time elapsed till appearance of the deactivation scatters widely, depending greatly on the research groups. The appearance of the surface after the electrolysis depends on the individual research groups. Some workers reported surface blackening and others not. These widely scattered facts strongly suggest that the “poisoning” or “deactivation” may be involved with experimental procedure of each research group, not from any intrinsic factors, such as adsorption of intermediate species or products formed during CO_2 reduction.

1.3. Purpose of this article

It is well-known that trace amount of impurities interferes with the surface process in electrochemical reactions on the electrodes. Many workers studied hydrogen evolution reaction (*her*) on various metal electrodes since Tafel's work. They attempted to obtain the correlation between the hydrogen overvoltage and the properties of the electrode material. During the course of these works, widely scattered voltage

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