



The flaky Cd film on Cu plate substrate: An active and efficient electrode for electrochemical reduction of CO₂ to formate



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ABSTRACT

Efficient electrochemical reduction of CO₂ to formate was studied on a Cu/Cd composite electrode in 0.5 M KHCO₃ aqueous solution, which was prepared by vacuum evaporation coating Cd film on the Cu plate substrate. The results showed that a novel flaky Cd film was deposited on the Cu plate substrate successfully. The performance of formate production on the Cu/Cd composite electrode was related to the electrolysis potential and the thickness of Cd film. The electrocatalytic activity of Cu/Cd composite electrode toward CO₂ reduction was enhanced in comparison with pure Cu plate and Graphite-Paper/Cd (G-P/Cd) electrodes. The maximum Faradaic efficiency of 76.2% for formate production has been obtained with high stability and current densities of 10.6 mA cm⁻² at -1.8 V (vs. Ag/AgCl) on the composite electrode with depositing a ~300 nm thick Cd film on the Cu substrate.

1. Introduction

In recent years, the electrochemical reduction of CO₂ for producing value-added chemicals in aqueous solutions has attracted much attention because it is energy-efficient compared with other methods [1–6]. Among many products from CO₂ reduction, formate is one of the relatively high economic value products [7]. It is well known that formate is a basic organic chemical raw materials, which was widely used in pesticides, leather, dyes, pharmaceutical and rubber industries [8]. It can also be directly as fuel for the fuel cells to generate electricity [9–11]. Thus, it is very attractive to convert CO₂ into value-added formate by electrochemical reduction.

So far, many kinds of catalysts have been used in the electrochemical reduction of CO₂, such as pure metals, metallic oxide, metal-organic compounds and alloys [12–17]. As a conventional electrode, metal and its alloy electrodes have been widely investigated due to its excellent performance on CO₂ reduction. For example, previous work has shown that on the Cd, Pb, Sn, Hg and In electrodes, CO₂ can be reduced to formate with high efficiency in aqueous solutions [18–22]. On the Zn, Ag and Au electrode, the main product of CO₂ reduction was CO [23–27]. Comparatively, Cu is a special electrode for CO₂ reduction because the product is widely distributed, including both hydrocarbons and formate, CO, methanol and ethanol [28–32]. Therefore, among the various metallic electrodes, Cu-based composite materials are the most

widely studied electrodes [33–35].

Although the Cu electrode exhibited excellent electrocatalytic activity of CO₂ reduction, poor stability was always observed during the process of electrolysis. It was usually deactivated at 20–30 min after the beginning of the electrolysis [36]. Moreover, the Faradaic efficiency of formate production is not high enough. For example, Qiao et al. prepared a fibrous copper electrode and achieved the highest Faradaic efficiency of 43% for producing formate [37]. Sen et al. explored the performance of CO₂ reduction on a porous Cu foams electrode and achieved Faradaic efficiency of 37% for producing formate [28]. In order to improve the performance of CO₂ reduction on Cu electrode, we consider depositing another metal which is efficiently for formate production on the Cu substrate electrode to prepare a Cu-based composite electrode. It has been known that the Cd has a high H₂ evolution potential and easy to produce formate efficiently in the process of CO₂ reduction [25]. In addition, the Cd electrode is well conductive and cost effective. Thus, Cd was selected as a nano-coating deposited on the Cu plate electrode to form a composite electrode, which can provide excellent electrocatalytic performance for CO₂ reduction to formate.

Furthermore, the performance of CO₂ reduction has a strong dependence on the preparation method of the composite electrode. Tang et al. has reported the differences in selectivity toward CO₂ reduction on Cu electrodes with three different morphologies, which were prepared by the electropolish, sputter coat, and nanoparticle coat methods,

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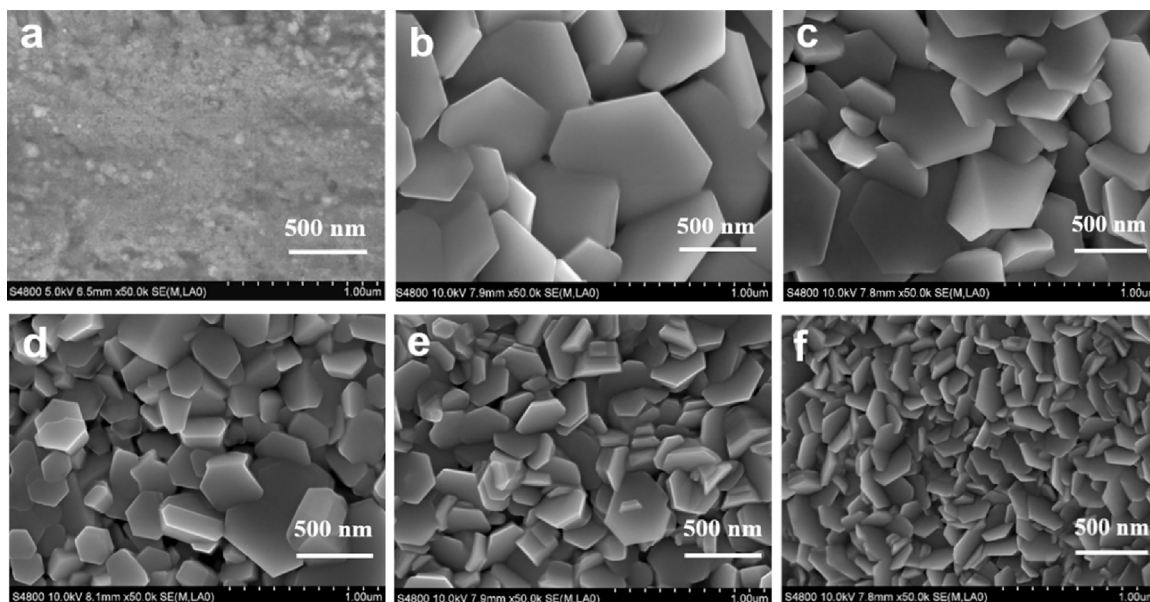


Fig. 1. SEM images of the pure Cu plate electrode for (a) and Cu/Cd composite electrodes obtained by vacuum evaporation coating different thickness of Cd films on Cu plate substrates for (b) 100 nm. (c) 200 nm. (d) 300 nm. (e) 400 nm. (f) 500 nm.

respectively. They found that the last two methods tended to generate hydrocarbons compared with the electropolish [38]. Especially, the Faradaic efficiency of formate production the Cu-based composite electrodes prepared by electrodeposition and electroplating methods is not efficient enough. For example, Hori et al. in-situ electrodeposited Cd on Cu electrodes and found that a small amount of Cd heavily promoted the reduction of CO₂ to CO, but the Faradaic efficiency for producing formate had no obvious change compared with the Cu electrode [39]. Watanabe et al. prepared Cu-Cd alloy by electroplating from conventional plating baths and obtained the highest Faradaic efficiency only of 43% [25].

In this work, a novel flaky Cd film was deposited on the Cu plate substrate through the vacuum evaporation deposition method. This method allows a large-scale preparation of homogeneous composite electrode in industry. In order to achieve the optimal experimental conditions, the effect of thickness of Cd film and applied potential on the electrocatalytic activity toward CO₂ reduction have been investigated.

2. Experimental

2.1. Preparation of composite electrodes

A substrate electrode was fabricated out of a Cu plate (1 × 1 cm, 0.1 cm), which was polished by 400 grade sandpaper firstly and then was ultrasonic cleaned by acetone, 0.5 M hydrochloric acid, deionized water, respectively. The Cd metal particles as a Cd source for vacuum evaporation coating Cd films were purchased (≥99.99%) from Shanghai Macklin Biochemical Co., Ltd, and without any further pre-treatment before used. The Cu/Cd composite electrode was prepared by vacuum evaporation coating Cd film on the Cu plate substrate by the ZHD300 high vacuum resistance evaporative coating machine (Beijing Ticonuo Technology Co., Ltd, China) in this experiment. The rate for depositing Cd film was 10 Å s⁻¹ and the thicknesses of Cd film deposited on Cu plate substrate were controlled to 100, 200, 300, 400 and 500 nm, respectively. In addition, the Graphite-Paper/Cd (G-P/Cd) composite electrode was obtained by vacuum evaporation coating a 300 nm thick Cd film on the inert graphite paper electrode, which was used in the comparative experiment.

2.2. Electrochemical experiments

A three electrode test was carried out in a sealed H-cell which was separated by Nafion N117 membrane. A Cu/Cd composite electrode was used as the working electrode. The counter and reference electrodes are Ag/AgCl and Pt plate (1 × 1 cm), respectively. A CHI630C electrochemical analyzer (Shanghai chenhua instrument co. LTD, China) was used in all the electrochemical experiments. Cyclic voltammetry (CV) and Constant potential electrolysis (i-t) experiments were studied in 0.5 mol L⁻¹ KHCO₃. Before the start of experiments, constant bubbling N₂ (99.99%) and CO₂ (99.99%) for 30 min to remove O₂ from the H-cell and electrolyte. The flow rate of CO₂ was 40 mL min⁻¹ in the process of CO₂ reduction. Current density (*j_a*) was determined on the geometrical area of the working electrode (1 cm²). All the experiments were studied at atmospheric pressure and room temperature (25 ± 3 °C).

2.3. Characterization and analysis

The scanning electron microscope (SEM) pictures were obtained through the Hitachi S-4800 high-resolution electron microscope without any conductive coating.

The atomic force microscope (AFM) images were provided by the Agilent Technologies 5500 scanning probe microscope in the tapping mode. The images with an area of 2.5 μm × 2.5 μm were investigated.

X-ray diffraction (XRD) patterns were obtained on the D8 advance X-ray Diffractometer from Bruker with Cu Kα radiation (λ = 1.541 Å). The XRD were recorded in the range of 10 to 80°, with degree steps of 0.02 and acquisition times of 0.1 s step⁻¹.

Liquid phase products were quantified by a high performance liquid chromatography (HPLC, Agilent 1200) with the Aminex HPX-87H Ion Exclusion columns. The mobile phase was 5 mM H₂SO₄, and injection rate was 0.5 mL min⁻¹. The amount of measurement was 10 μL every time.

Faradaic efficiency (*η*) of formate production was achieved by the formula:

$$\eta = 2nF/Q$$

where *η* is Faradaic efficiency of formate; 2 represents the number of electrons required to form formate from CO₂; *n* represents the total number of moles of formate production, which was measured by HPLC;

F represents Faraday constant (96485); and the Q corresponds to the amount of cumulative charge in the process of CO₂ reduction, which was provided by the electrochemical workstation.

3. Results and discussion

Shown in Fig. 1 are surface images of the pure Cu plate and Cu/Cd electrodes obtained by vacuum evaporation depositing different thickness of Cd films on Cu plate substrates. The image (a) shows that the surface morphology of the pure Cu electrode is still a bit rough after being polished by 400 grade sandpaper. The images (b), (c), (d), (e) and (f) correspond to 100 nm, 200 nm, 300 nm, 400 nm and 500 nm thickness of Cd film, respectively. It can be seen that the morphology of Cd particles were vacuum evaporation deposited on the Cu plate substrate are mostly irregular flakes and have been coated on the Cu plate substrate successfully. From Fig. 1(b)–(f), as the controlled thickness of coating film increases further, the Cd flakes deposited on Cu plate substrate become smaller, resulting in denser accumulation of Cd flakes. This could be caused by the reason that the internal stress of the film increases when the thickness of film increases further.

AFM images of Cu/Cd composite electrode with 300 nm thick Cd film is shown in Fig. 2 to explore the surface roughness of the electrode. The images reveal that the

Cd flakes are with multiple shapes and piled up randomly. The deposited Cd film has highly rough and porous surface morphology. The analysis of the AFM images shows that the average surface roughness of the film is 58.7 nm. The porous structure and rough surface of the Cd film are useful to increase electrocatalytic activity sites of CO₂ reduction and the electrocatalytic performance of composite electrode on CO₂ reduction could be enhanced in this way.

Shown in Fig. 3 is the X-ray diffractogram (XRD) of the pure Cu electrode, the Cu/Cd and G-P/Cd composite electrodes, which were deposited 300 nm thick Cd films on the Cu plate and graphite paper substrate, respectively. The result indicate that the Cu/Cd composite electrode exhibits high crystallinity and the peaks at 43.3°, 50.4° and 74.1° correspond to (111), (200) and (220) crystal facets of Cu plate (PDF# 04-0836), respectively. These at 31.8°, 34.7°, 38.4° and 66.6° are assigned to (002), (100), (101) and (004) crystal facets of the deposited Cd film (PDF# 05-0674), respectively. Obviously, the crystal structures of Cu and Cd were not destroyed and there was no alloying in the process of preparing composite electrode. Furthermore, the ratio of the diffraction intensity of (002) and (101) crystal facets is 10.2 for the Cu/Cd composite electrode. For comparison, this ratio is 7.7 for the G-P/Cd composite electrode. Although identical crystal facets are observed in both electrodes, the intensity of (002) facet on the Cu/Cd is ~33% higher than that on the G-P/Cd composite electrode. This difference suggests the preferential growth low index crystal face on Cu/

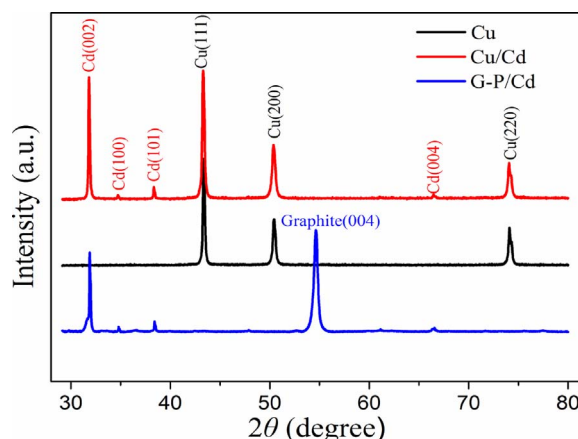


Fig. 3. XRD patterns of the pure Cu electrode, Cu/Cd and G-P/Cd composite electrodes.

Cd and may be beneficial to the efficiency of formate production in the electrochemical reduction of CO₂ [40,41].

Fig. 4a shows the cyclic voltammogram of Cu/Cd composite electrode which is deposited 300 nm thick Cd film on the Cu plate substrate in 0.5 M KHCO₃ electrolyte solution. As shown in the inset, the onset reduction potential under N₂ (−1.1 V) is more negative than that under CO₂ (−0.95 V). The result reveals that the Cu/Cd composite electrode exhibits excellent electrocatalytic activities toward electrochemical reduction of CO₂. It is also observed that the current density increases sharply in both N₂ and CO₂ at more negative potentials and the current density under N₂ is lower than that under CO₂. The Cu/Cd composite electrode exhibits excellent electrocatalytic activities toward CO₂ reduction. The sharp increase of the current density under N₂ should be attributed to the electrolysis of water (H₂ evolution reaction) and the current density under CO₂ is attributed to both the electrolysis of water and reduction of CO₂ [42]. Fig. 4b shows the cyclic voltammograms of Cu/Cd and G-P/Cd composite electrodes in 0.5 M KHCO₃ electrolyte solution purged with CO₂ and the sweep rate is 50 mV s^{−1}. Obviously, the Cu/Cd composite electrode possess higher activity than the G-P/Cd electrode, as manifest a higher current density of CO₂ reduction. The current density of the Cu/Cd composite electrode is almost twice that of the G-P/Cd electrode. Shown in Fig. 4c are the CVs of Cu/Cd composite electrode obtained at different sweep rates and the inset of Fig. 4c are the CVs of the Cu, G-P/Cd and Cu/Cd electrodes at 50 mV s^{−1}, respectively. It can be seen that, there are no redox reactions on the G-P/Cd electrode in the potential range of −0.3 V to 0.3 V. Therefore, the oxidation peaks of Cu/Cd electrode at ca. 0.05 V and 0.10 V should correspond the reaction process that Cu is oxidized to Cu¹⁺ and the reaction process that Cu¹⁺ continues to be oxidized to Cu²⁺,

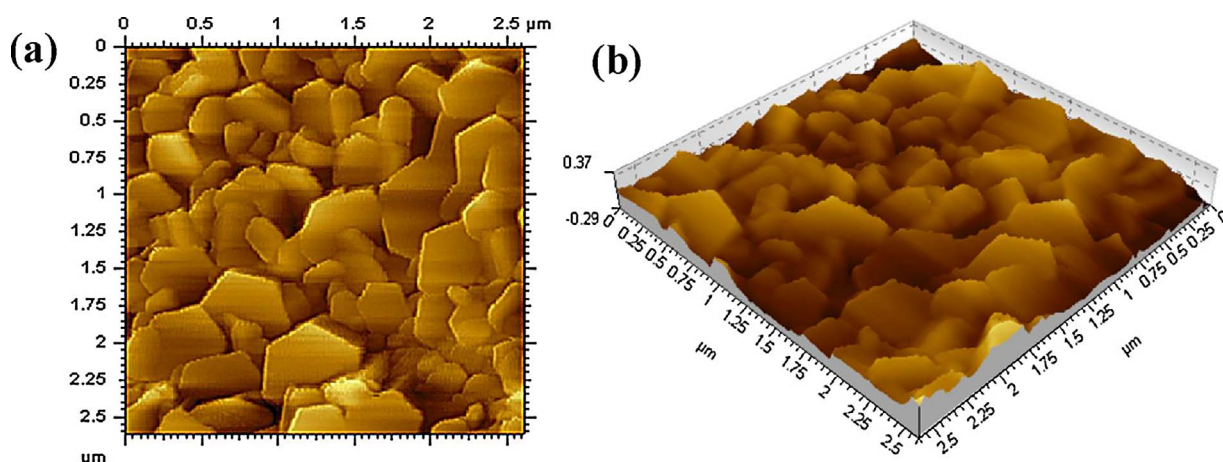


Fig. 2. AFM images of the Cu/Cd composite with 300 nm thick Cd film on the Cu plate substrate for (a) 2 D figure; (b) 3 D figure.

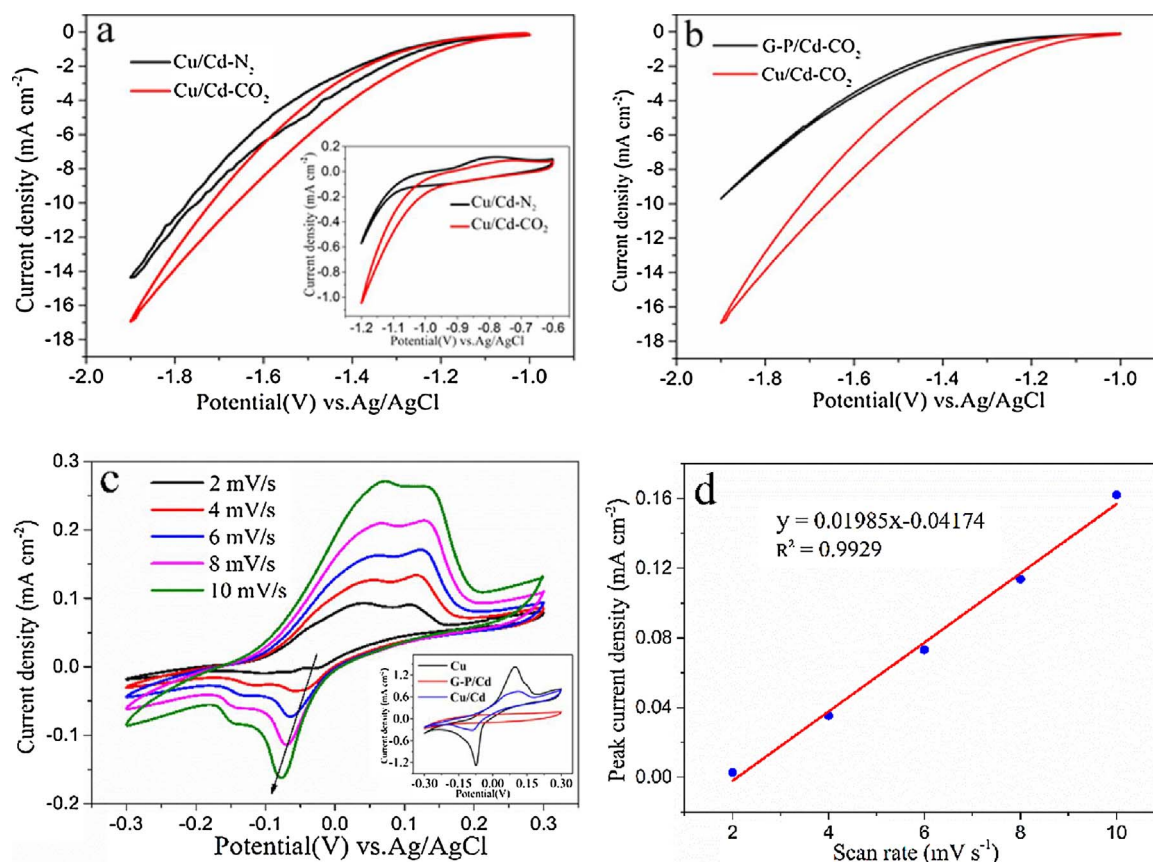


Fig. 4. The cyclic voltammogram scanning results (a) CV of Cu/Cd composite electrodes in 0.5 M KHCO₃ saturated with N₂ and CO₂, respectively. The inset of (a): CV at the potentials range from -0.6 to -1.2 V. (b) CV of Cu/Cd and G-P/Cd composite electrodes in CO₂ saturated 0.5 M KHCO₃. (c) CV of Cu/Cd composite electrode measured at different scan rate from 2 to 10 mV s⁻¹. The inset of (c): CV of Cu, G-P/Cd and Cu/Cd electrodes at 50 mV s⁻¹. (d) Variations of peak current densities with the sweep rates.

respectively; The reduction peaks at ca. -0.07 V and -0.15 V are assigned to the process that Cu²⁺ is reduced to Cu¹⁺ and the process that Cu¹⁺ continues to be reduced to Cu, respectively. Fig. 4d depicts the variations of peak current densities with the sweep rates corresponding to Fig. 4c. The sweep rates are linearly dependent with the current densities, confirming the electrochemical process is adsorption-limited [43].

Shown in Fig. 5 is the chronoamperogram of the Cu/Cd composite electrode in 0.5 M KHCO₃ electrolyte solution purged with CO₂ at different electrolysis potentials. The results indicate that the current densities increase gradually from 2.2 to 18.1 mA cm⁻² with the applied potentials increasing from -1.4 to -1.9 V. It also can be seen that the

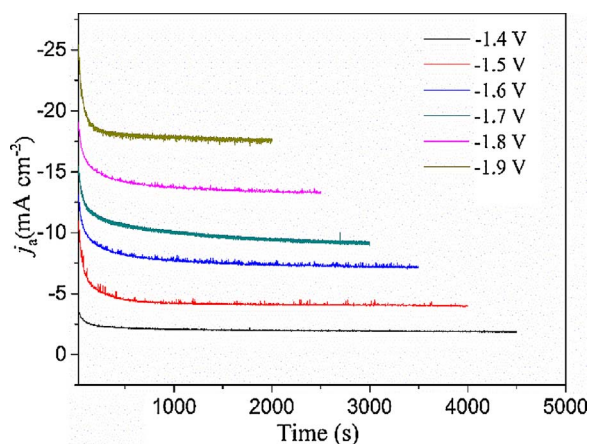


Fig. 5. Chronoamperogram of the Cu/Cd composite electrode in 0.5 M KHCO₃ electrolyte solution purged with CO₂.

current density fluctuates at more negative potentials, which is probably caused by the enhancement of H₂ evolution reaction at more negative potentials [9]. The violent H₂ evolution reaction resulted in a large amount of bubbles produced on the electrode surface during the electrochemical reduction of CO₂ at more negative potentials, which interfered with the equilibrium state of the electrode surface. This is consistent with the experimental phenomena that we observed during the electrolysis process.

Fig. 6 depicts the dependence of Faraday efficiency of formate production on the electrolysis potentials on the Cu/Cd composite electrode with 100 nm thick Cd film during the CO₂ reduction. The result shows that the Faradaic efficiency of formate production increases from -1.4 to -1.8 V and then decreases for -1.9 V. The

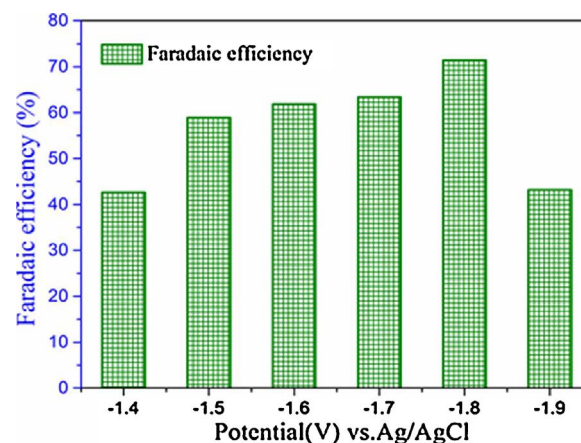


Fig. 6. The dependence of Faraday efficiency on the electrolysis potentials.

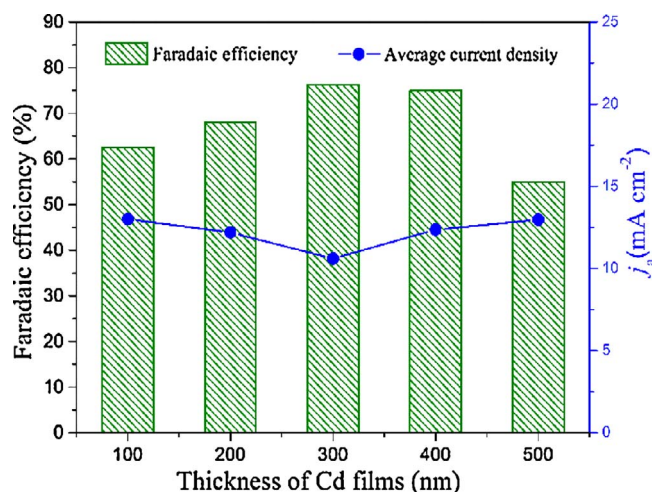


Fig. 7. Variations of the average current density and Faradaic efficiency of formate production with the thickness of Cd films deposited on Cu plate substrates.

maximum value (71.4%) is obtained at -1.8 V. The Faradaic efficiency decreases as the electrolysis potential increases further, which can be explained by electrolysis of water results in electric power consumption at more negative potentials. The above results indicate that the appropriate potential toward electrochemical reduction of CO₂ on Cu/Cd composite electrode could be -1.8 V versus the Ag/AgCl reference electrode.

The effects of the thickness of Cd film on the electrocatalytic activity of the Cu/Cd composite electrode were investigated. It has been known from Fig. 6 that the optimal applied potential is around 1.8 V. Thus, the experiment of Cd film thickness effect was carried out with potential of -1.8 V. As shown in Fig. 7, a slight change of current density was observed with the thickness of Cd film increasing from 100 to 500 nm. When the thickness of the Cd film was 300 nm, the maximum Faradaic efficiency (76.2%) for producing formate was achieved, which could be attribute to the appropriate size and accumulation of the Cd flakes at 300 nm. It has been known that the potential for H₂ evolution reaction on Cu is lower than that on Cd [25]. According to the SEM images, the size of the Cd flakes increase with the thickness of the films decrease, which resulting in the larger pore size between the Cd flakes. The surface of Cu plate substrate is more easily exposed to the electrolyte and start the H₂ evolution reaction, resulting in a lower Faradaic efficiency; In contrast, with the decrease in the size of Cd flakes, the films are denser. Thus, CO₂ is difficult to diffuse to the surface of Cu plate substrate, the electrocatalytic activity of Cu plate is weakened during the process of CO₂ reduction. Therefore, the optimal thickness of the Cd film deposited the Cu plate substrate is around 300 nm due to the proper surface roughness and accessibility of Cu substrate.

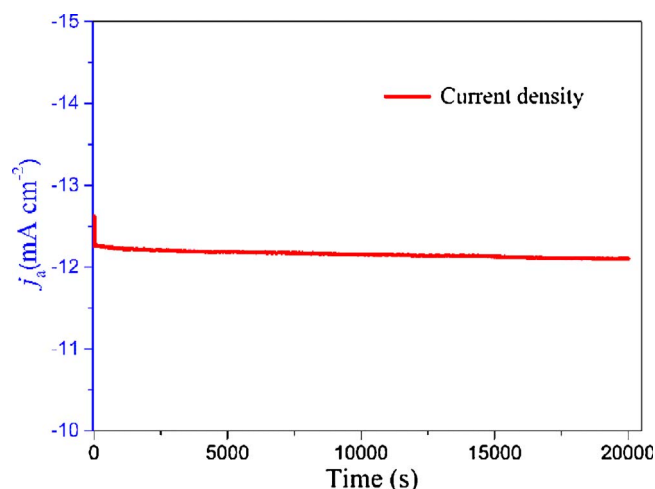


Fig. 9. Chronoamperograms of a Cu/Cd composite electrode in 0.5 M aqueous KHCO₃ purged with CO₂ at the -1.8 V.

Further electrolysis experiments were carried out on the pure Cu electrode and the Fig. 8a shows the product distribution on the Cu, G-P/Cd and Cu/Cd electrodes at the electrolysis potential of -1.8 V. Comparing Cu/Cd to Cu electrodes, it can be seen that the Cd film which is deposited on Cu substrate inhibits the production of CH₄ and H₂ on the Cu electrode and the Faradaic efficiency of formate production on Cu/Cd composite electrode was significantly improved; Comparing Cu/Cd to G-P/Cd electrodes, the results reveal that the Cu substrate promotes the efficiency of CO and formate production on the Cd film. Consequently, Cu substrate and Cd film play a synergistic role in promoting the production of formate in the composite electrode. The comparison of the Cu, G-P/Cd and Cu/Cd electrodes on average current density, Faraday efficiency and production rate of formate are shown in Fig. 8b. For the Cu plate, G-P/Cd and Cu/Cd electrodes, the average current densities are 17.3, 6.6 and 10.6 mA cm⁻², respectively; the Faradaic efficiencies are 36.1%, 62.0% and 76.2%, respectively; the production rates are 5.1, 3.4 and 6.7 g L⁻¹ day⁻¹, respectively. The Cu plate electrode exhibits the highest current density, whereas the Faradaic efficiency is great lower than the other two electrodes. As previously reported that the Cu electrodes showed low Faradaic efficiency of formate production toward CO₂ reduction [28,37]. The Faradic efficiency and production rate on Cu/Cd composite electrode is higher than that on the Cu plate and G-P/Cd electrodes. Together, these results indicate that depositing a layer of Cd film on the Cu plate substrate can enhance electrocatalytic activity of Cu plate electrode for producing formate.

Shown in Fig. 9 is the chronoamperogram of the Cu/Cd composite electrode with 300 nm thick Cd film in 0.5 M aqueous KHCO₃ purged with CO₂ at the -1.8 V. The current density only decreases from

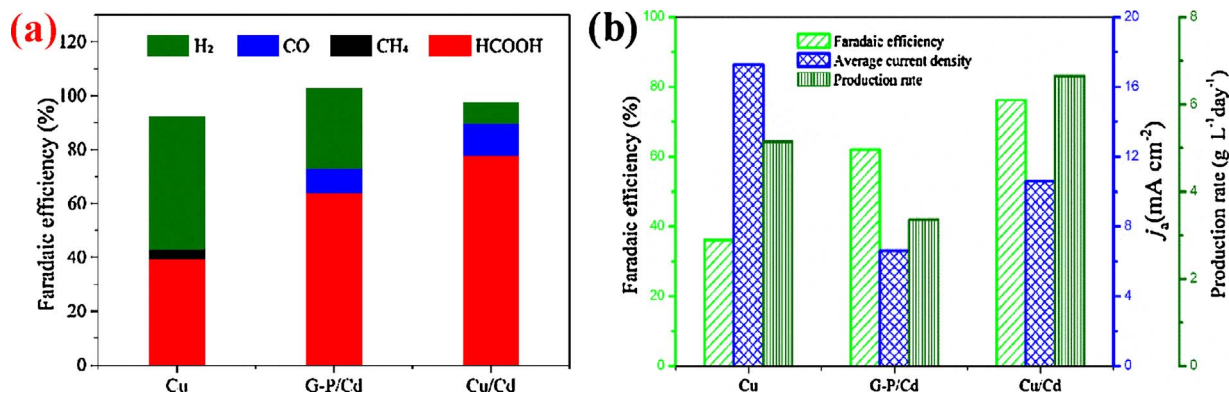


Fig. 8. (a) Product distribution on the Cu, G-P/Cd and Cu/Cd electrodes at -1.8 V. (b) Comparison of average current density, Faraday efficiency and production rate of formate on the Cu, G-P/Cd and Cu/Cd electrodes at -1.8 V.

12.3 mA cm⁻² to 12.1 mA cm⁻² after continuous electrolysis for 20,000 s. The result indicates that the attenuation of current density on Cu/Cd composite electrode is negligible during the long time process of CO₂ reduction. This suggests the Cu/Cd composite electrode which is prepared by vacuum evaporation coating Cd film on the Cu plate substrate has excellent stability.

4. Conclusions

The Cu/Cd composite electrode was prepared by vacuum evaporation coating Cd film on the Cu plate substrate. The SEM, AFM and XRD results reveal that the Cd film was deposited on the Cu plate substrate successfully with novel flaky shape and the crystal forms of Cu and Cd has not been destroyed in the process of preparing the Cu/Cd composite electrode. The performance of CO₂ reduction on the Cu/Cd composite electrode has been studied by controlled potential electrolysis and cyclic voltammetry in 0.5 M KHCO₃. The results indicate that the Faradaic efficiency of formate production is related to the applied potential and the thickness of Cd film. The appropriate potential for producing formate efficiently should be around -1.8 V and the optimal thickness of the Cd film is around 300 nm in this experiment. The maximum Faradaic efficiency of 76.2% for formate production was achieved with high stability and current densities of 10.6 mA cm⁻² on the Cu/Cd composite electrode. Furthermore, the electrocatalytic activity of the Cu/Cd composite electrode for CO₂ reduction have been enhanced compared with the pure Cu plate electrode and G-P/Cd composite electrode. Together, it can be concluded that the preparation method used in this experiment is a simple and cost effective way of manufacturing composite electrodes and the Cu/Cd composite electrode exhibits excellent performance on CO₂ reduction.

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