



Fabrication of Ag₂S electrode for CO₂ reduction in organic media

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Abstract

Electro-reduction of carbon dioxide (CO₂) to carbon monoxide (CO) has been extensively studied on metal and alloy electrodes for many decades. However, owing to their disadvantages of low current density and high over-potential, the practical application of these electrodes has been limited. Hence, it is highly desirable to explore new and high efficient electrode for CO₂ reduction to CO. Ag₂S has been widely studied as electrode material in electrochemistry due to its unique properties, such as high conductivity, chemical stability, and easy to be prepared. In this work, we have fabricated an Ag₂S electrode via electro-oxidation of Ag in aqueous solution. X-ray diffraction (XRD) and scanning electron microscope (SEM) confirm that Ag₂S has been modified on Ag foil, which made the electrode surface roughness. And then, we have evaluated the performance of Ag₂S electrode as the cathode for CO₂ reduction in propylene carbonate/tetrabutylammonium perchlorate. The cathodic current density reaches to 9.85 mA/cm², with the faradic efficiency for CO formation remaining stable at 92% during 4 h long-term electrolysis.

Keywords CO₂ electro-reduction · Organic electrolyte · Ag₂S electrode

Introduction

Electrochemical reduction of CO₂ to CO is the first step in the synthesis of more complex carbonaceous products [1–4]. In the past decades, numerous works have been done to explore an efficient electrode to convert CO₂ into CO with high efficiency. Most of the works focused on metal and alloy electrodes. However, owing to their disadvantages of low current density and high over-potential, the practical application has been limited. Hence, it is highly desirable to develop new electrode to improve the efficiency of CO₂ reduction [5–10].

Silver sulfide (Ag₂S) has been widely used as electrode materials in electrochemistry, because it possesses many unique properties such as high conductivity, low price, and anti-poisonous characteristics [11–15]. In recent years, it was found that Ag₂S has high catalytic effects towards hydrogen evolution [16, 17]. But little attention has been given to investigate electro-reduction CO₂ on Ag₂S. In present work, we intend to study the electrochemical property of Ag₂S towards CO₂ reduction.

CO₂ is a non-polar molecule and is highly soluble in organic electrolyte. Therefore, it would be beneficial to conduct the electrochemical reduction of CO₂ in an organic electrolyte. Selection of suitable supporting electrolyte and organic solvent is essential to CO₂ reduction. Because CO₂ is a non-polar molecule and has high solubility in organic solution, it would be beneficial to conduct CO₂ reduction in organic media. Among the commonly used organic solvents (AN, DMF, DMSO, and PC), acetonitrile (AN) is not suitable for practical application, because it is toxic and easily volatilize at ambient condition, it would result in hazardous effect to human health and environment. *N,N*-Dimethylformamide (DMF) is not suitable for practical application also, because it is poisonous and readily hydrolysis. Towards dimethyl sulfoxide (DMSO), because its melting point is 18 °C, CO₂ reduction cannot be conducted at ambient condition below 18 °C. Propylene

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carbonate (PC) [18] is normally used as CO₂ absorber in industry, and also, it is a widely used medium in organic electrochemical, which has many advantages, such as non-toxicity, wide electrochemical window, low volatility, high CO₂ solubility, high boiling point, and high dielectric constant [19]. Thereby, we select PC as the organic solvent. Imidazolium ionic liquids (ILs) has been extensively studied as a novel support electrolyte for CO₂ reduction [20–22], owing to that they have some unique properties, such as negligible vapor pressure, wide electrochemical window, low volatility, and adjustable physical and chemical properties. Nevertheless, due to their disadvantages of high cost and readily decomposition at very negative potential (electro-reduction of CO₂ requires large negative potential) [23], it is not ideal for industry application. Tetrabutylammonium perchlorate (TBAP) [24, 25] is a commonly used supporting electrolyte in the organic electrochemistry, which possesses many outstanding advantages, such as low cost, easily to be prepared, and wide electrochemical windows. Hence, in this work, we select TBAP as the supporting electrolyte.

Herein, for the first time, we have reported CO₂ reduction on Ag₂S in PC/TBAP using two-compartment cell. Since electro-reduction of CO₂ to CO naturally generates H₂O, the presence of water in PC/TBAP is inevitable, and water plays in crucial role during CO₂ reduction process. Thereby, we have also discussed water effects on CO₂ reduction on Ag₂S.

Experimental section

Materials

Propylene carbonate (PC, analytical grade) was purchased from Meryer Chemicals and distilled before use. Tetrabutylammonium perchlorate (TBAP, analytical grade) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). Ethanol absolute (AR, analytical grade), sulfuric acid (H₂SO₄, 98.08%), and sodium sulfide (Na₂S, 99.99%) were used as received from Aladdin Ltd. (Shanghai, China) without further purification. Ion-exchange membrane (Nafion 117) was purchased from DuPont Company. CO₂ and Ar (99.99%, purity) were purchased from Messer Company (Hainan, China). All the water in the experiment is double distilled.

Preparation of Ag₂S electrode

The Ag electrode was polished with 0.05 μm alumina slurry and then sonicated in double-distilled water for 3 min, subsequently pretreated by degreasing in acetone, immersed in 10% nitric acid 3 min, and rinsed with a copious amount of doubly distilled water. Ag₂S was prepared by anodic oxidation method in 0.1 M Na₂S solution. During this process, Ag⁺ resolved in Na₂S

solution via anodization of Ag electrode at 0.9 V (NHE). It reacts with S²⁻ and formed a film of Ag₂S, which was deposited on Ag electrode. The electrode reaction is as follows:



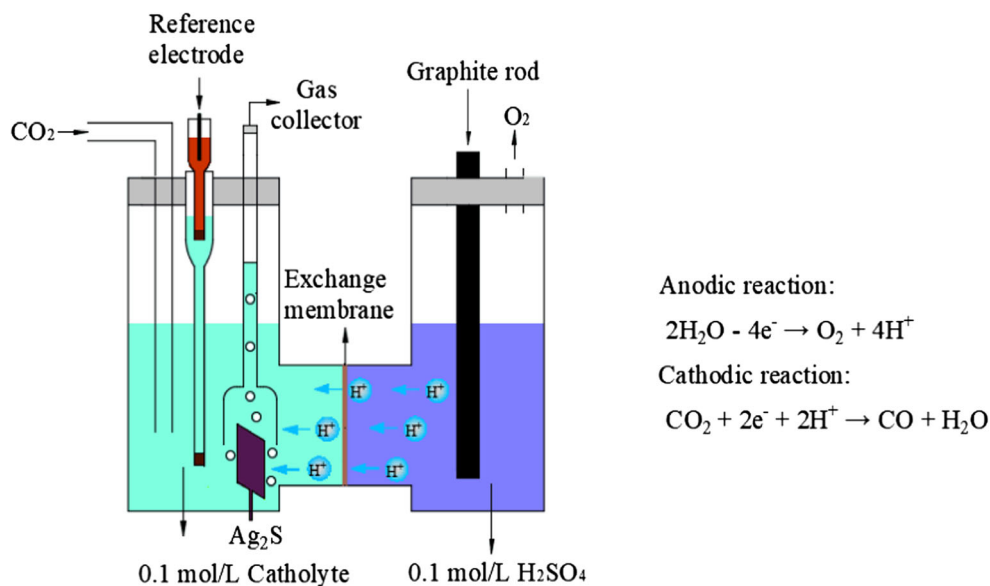
Electrochemical experiments

A two-compartment electrolysis cell [26] has been designed for CO₂ reduction in propylene carbonate (PC)/tetrabutylammonium perchlorate (TBAP) electrolyte. The electrolysis cell is separated into two compartments by an ion-exchange membrane (Fig. 1). In this cell, CO₂-saturated organic electrolyte was used as the catholyte, and 0.1 M H₂SO₄ aqueous solution was used as the anolyte. The required proton and electrons for CO₂ reduction through from the anolyte, the reaction can be carried out more easily. Ag₂S modified Ag electrode (99.99%, 2 mm × 2 mm) was used as the cathode. A graphite rod (99.99%, 5 mm in diameter and 15 cm in length) was used as the anode [27]. An I₃⁻/I⁻ electrode was used as the reference electrode [28]. This reference electrode was constructed by immersing a Pt wire in a 0.1-M PC/TBAP solution containing 0.05 M I₂ and 0.1 M Bu₄NI. The I₃⁻/I⁻ reference electrode was end with a porous Teflon cylinder and isolated from the cathode compartment by a salt bridge. The salt bridge contained the same solution as the catholyte. The salt bridge was separated from the catholyte by an ultra-fine glass frit. The tip of the salt bridge was placed 3 mm away from the cathode. The graphite rod was polished with 1200 grid sandpaper, and then, the Ag₂S electrode and graphite rod are cleaned using ultrasonication in distilled water and rinsed thoroughly with double-distilled water. During the electrolysis process, the generated protons from H₂O oxidized transfer through the proton-exchange membrane and diffuse to the cathode. On the cathode, CO₂ is reduced to CO with the participation of proton. The half reactions of anodic and cathodic are as follows in Fig. 1.

Measurements

All the electrochemical experiments are performed on CHI660D electrochemical working station at room temperature. PT-101 ultrasonic cleaner was purchased (Germany Branson Company, China). During the electrolysis process, the cathodic gas products are collected in a gas collector and analyzed by a gas chromatograph (Agilent-7890B, Westeas Analytical Instruments, China). The temperatures of the injector, the oven, and the detector are maintained at 130 °C, 120 °C, and 110 °C. X-ray diffraction (XRD) analysis of the

Fig. 1 Schematic of the two-compartment electrolysis cell for CO₂ reduction



samples was performed on the X-ray diffractometer (Model D/MAX2500, Rigaka Denki Co., Ltd., Japan) with Cu-K_α radiation ($\lambda = 1.54184 \text{ \AA}$) at a voltage/current of 40 kV/40 mA, and the scan speed was 2°min^{-1} and a step size of 0.02° . Variable temperature XRD data were collected using a Shimadzu XRD-7000 with Cu-K_α radiation ($\lambda = 1.54184 \text{ \AA}$). The morphologies of Ag₂S electrode was characterized by a HITACHI S-4800 scanning electron microscope (SEM) (Hitachi, S-4800, Tokyo, Japan) with a magnification of 100 k and emission voltage of 10 kV.

Results and discussion

XRD analysis

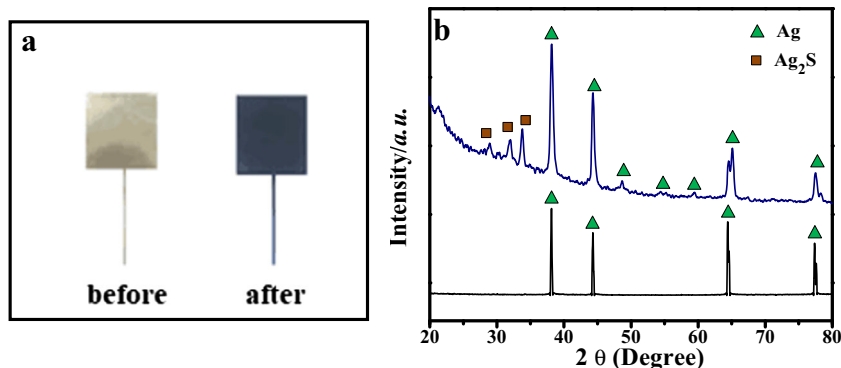
Figure 2a shows the pictures of Ag electrode which were taken before and after the electro-oxidation of Ag electrode in Na₂S solution. Before the electro-oxidation, Ag electrode displayed mirror-like surface. After the electro-oxidation, a film of black

substance was formed and deposited on the surface of Ag electrode. To determine the ingredient of the black adsorbates, X-ray diffraction (XRD) was performed (Fig. 2b). Comparing with the pure Ag, several characteristic monoclinic planes of Ag₂S have been observed, which located at 28.1° , 34.3° , and 36.4° , corresponding to 200, -121 , and 022. These results demonstrated that Ag₂S was formed and deposited on Ag foil. The formation process of Ag₂S should be explained as follows: when the Ag electrode was electro-oxidation in Na₂S aqueous solution, Ag⁺ was generated and entered into the aqueous solution, which further reacted with S²⁻, resulting in the formation of Ag₂S. Because the solubility of the Ag₂S is very low, it was crystallized on Ag foil and formed a film. Thus, Ag₂S-modified Ag electrode was obtained.

Linear sweep voltammetry

Figure 3 shows linear sweep voltammetry (LSV) measured on Ag₂S. In Ar-saturated PC/TBAP, the negative limiting potential was detected as -2.35 V (Fig. 3a). After purged

Fig. 2 **a** Photographs of Ag electrodes before and after deposition of Ag₂S; **b** XRD patterns of Ag and Ag₂S



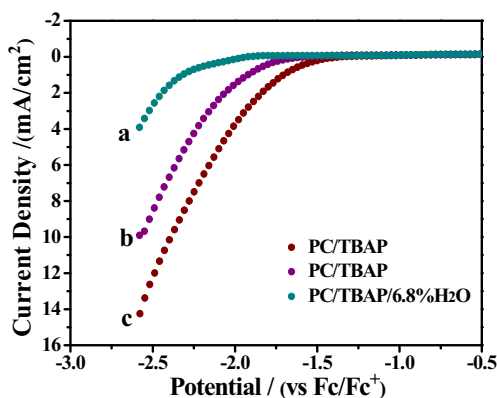


Fig. 3 Linear sweep voltammetry on Ag_2S in 0.1 M **a** PC/TBAP with Ar; **b** CO_2 -saturated PC/TBAP solution; **c** CO_2 -saturated PC/TBAP/ + 6.8 wt% H_2O solution

with CO_2 , the onset potential shifted positively to -1.70 V (vs. Fc/Fc^+), and the current density increased obviously (Fig. 3b), indicating that CO_2 electro-reduction took place on Ag_2S -modified electrode. Because electro-reduction of CO_2 to CO naturally produces H_2O , the accumulation of H_2O in PC/TBAP is inevitable [29]. When the content of H_2O exceeds saturation level, it would separate from PC/TBAP due to the hydrophobic nature of PC/TBAP. The saturation content of H_2O in PC/TBAP is 6.8 wt% (measured via Karl Fisher titration) [29]. We have also conducted LSV measurements in the PC/TBAP + 6.8 wt% H_2O . The results are shown in Fig. 3c. As can be seen, the current density detected on Ag_2S increased sharply up to 14.18 mA/cm^2 , and the onset potential shifted positively to -1.50 V (vs. Fc/Fc^+). These results verified that H_2O has catalytic effects on CO_2 reduction.

Kinetic analysis

Tafel curves have been measured on Ag_2S in PC/TBAP. Since CO_2 is a thermodynamically stable molecule, electrochemical reduction CO_2 needs high over-potential. Hence, the equilibrium potential of CO_2 reduction was -1.72 V (Fig. 4a). After adding 6.8 wt% of H_2O in 0.1 M PC/TBAP, the onset potential shifted positively to -1.50 V (Fig. 4b). These results further demonstrated that H_2O has catalytic effects on CO_2 reduction.

The dynamic parameters of CO_2 reduction were calculated according to Eqs. (3)–(5) [30]. The results are listed in Table 1.

$$\eta = a + b \log|i| \quad (3)$$

$$a = \frac{RT}{n\alpha F} \ln i_0, b = \frac{2.3RT}{n\alpha F} \quad (4)$$

$$R_{ct} = \frac{RT}{nF i_0} \quad (5)$$

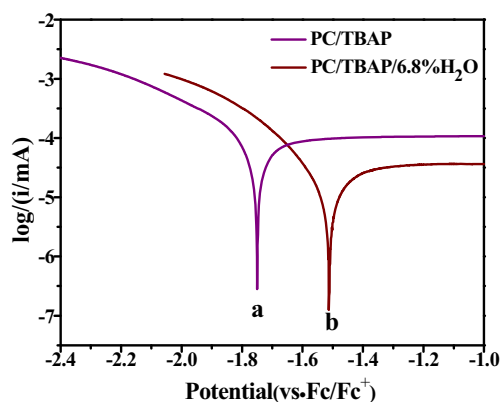


Fig. 4 Tafel curves for CO_2 reduction to CO on Ag_2S in 0.1 M **a** PC/TBAP; **b** PC/TBAP/ + 6.8 wt% H_2O (condition same as Fig. 3)

Where η is the activation over-potential, a and b are Tafel constant, α is the charge transfer coefficient, n is the number of electron transfer, i_0 is the exchange current density, F is Faraday's constant, R is universal gas constant, T is the absolute temperature, and R_{ct} is the polarization resistance.

As can be seen, the exchange current density i_0 measured on Ag_2S in PC/TBAP is 0.6144×10^{-4} $\text{A}\cdot\text{cm}^{-2}$. The polarization resistance R_{ct} is 209.2812 $\Omega\cdot\text{cm}^{-2}$ (Table 1). These results are consistent with LSV (Fig. 3). After adding 6.8 wt% of H_2O in 0.1 M PC/TBAP, i_0 increased to 0.9784×10^{-4} $\text{A}\cdot\text{cm}^{-2}$, and R_{ct} decreased to 98.2960 $\Omega\cdot\text{cm}^{-2}$. The increase of i_0 and decrease of R_{ct} are caused by the catalytic effects of H_2O .

Long-term stability

Long-term potentiostatic electrolysis was carried out on Ag_2S in PC/TBAP. To avoid the decomposition of the electrolyte, the electrode potential was controlled at -2.3 V (vs. Fc/Fc^+). The results are shown in Fig. 5. As can be seen, the cathodic current density kept stable at 6.63 mA/cm^2 (Fig. 5a). After adding 6.8 wt% of H_2O in 0.1 M PC/TBAP, the current density increased significantly. It reached to 9.85 mA/cm^2 and remained stable at this level until the completion of the electrolysis experiment (Fig. 5b).

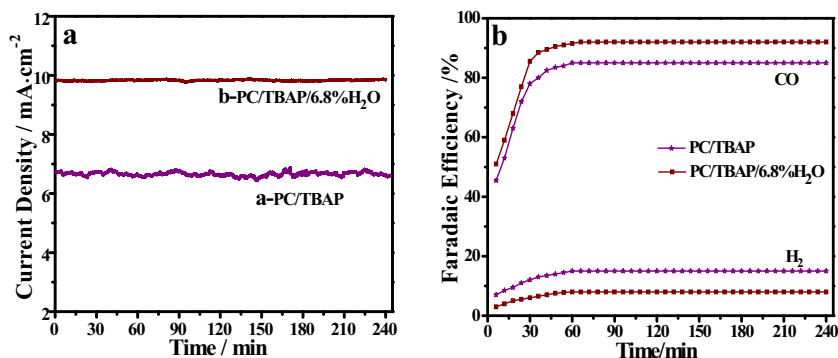
The faradaic efficiency (η) of CO formation had been calculated according to Eq. (6) [31, 32].

$$\eta = 2nF/Q \quad (6)$$

Table 1 Dynamic parameters for CO_2 reduction in PC/TBAP over Ag_2S electrode

Electrolyte	a	b	α	$i_0/(\text{A}\cdot\text{cm}^{-2})$	$R_{ct}/(\Omega\cdot\text{cm}^{-2})$
Blank	0.7180	0.1437	0.2042	0.6144×10^{-4}	209.2812
6.8 wt% H_2O	0.7393	0.1748	0.1511	0.9784×10^{-4}	98.2960

Fig. 5 Potentiostatic electrolysis and faradaic efficiency for CO formation on Ag₂S in 0.1 M **a** PC/TBAP; **b** PC/TBAP/+ 6.8 wt% H₂O



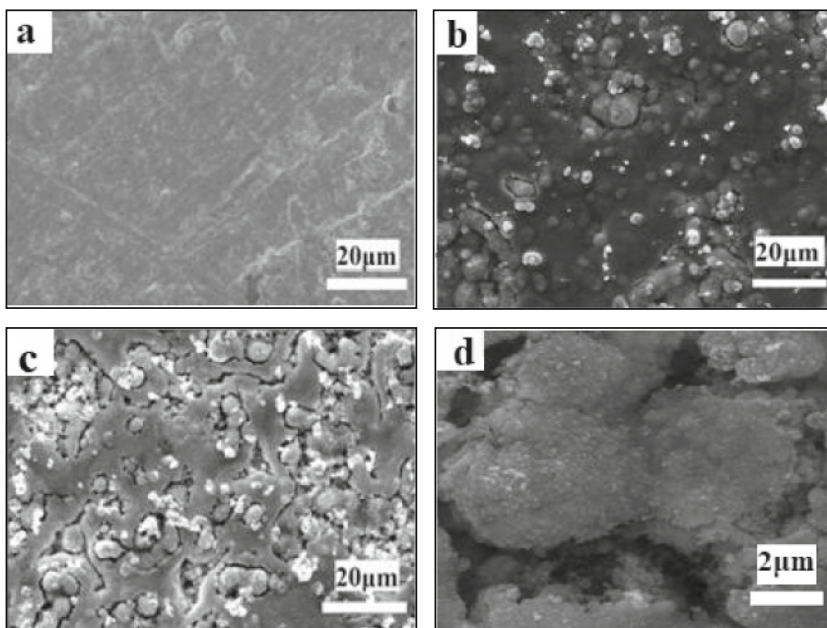
Where n is the amount of substance of CO produced, F is the faradaic constant (96,485 C/mol), and Q is the total charge passed. The results are shown in Fig. 4b. In the initial period, the faradaic efficiency of CO formation is low (both in PC/TBAP and PC/TBAP/+ 6.8 wt% H₂O). This is because a part of CO dissolved in the catholyte [33], which could not be collected for analysis. After 40 min of electrolysis, the faradaic efficiency of CO formation increased significantly and kept stable at high level until the end of the electrolysis. In CO₂-saturated PC/TBAP, the faradaic efficiency of CO formation is high (85%). Owing to the presence of residual water, hydrogen was generated on the cathode, the faradaic efficiency for H₂ formation arrived to 15%. After long-term electrolysis, because CO₂ electro-reduction into CO naturally produces H₂O, the accumulation of H₂O increased. The faradaic efficiency of H₂ formation increased with time. When H₂O content reached to 6.8 wt% (saturated concentration), the faradaic efficiency of CO and H₂ arrived to 92% and 8%, respectively, which remained stable until the end of the electrolysis. Because the electrochemical reduction of CO₂ to CO naturally

produces H₂O, H₂ has been detected on the cathode from water electro-reduction.

SEM observation

To further understand the high performance of Ag₂S electrode for CO₂ reduction, scanning electron microscope (SEM) was employed to observe the morphology of the cathode. Because Ag electrode was polished with aluminum oxide before the tests, it showed mirror surface (Fig. 6a). After deposition of Ag₂S on the Ag electrode by electro-oxidation, the surface of the Ag electrode turned into roughness (Fig. 6b). A layer of black adsorbates adhered to Ag electrode. During the electrolysis process, a part of loosened Ag₂S split away from the cathode. A layer of strongly adsorbed Ag₂S was exposed (Fig. 6c). When the image was enlarged, uniformly distributed Ag₂S nanoparticles could be observed (Fig. 6d). This nano-structure results in a comparatively larger surface area and catalytic effects towards CO₂ reduction. As a consequence,

Fig. 6 **a** SEM image of Ag; **b–d** SEM image of deposition of Ag₂S



the potentiostatic electrolysis current density increased significantly (Fig. 5), and the onset potential shift positively (Fig. 3).

Conclusions

In this work, in order to improve the current density and decreased the onset potential of CO₂ reduction, we have fabricated Ag₂S-modified Ag electrode using the electro-oxidation method. The catalytic performance of the Ag₂S electrode was assessed in 0.1 M PC/TBAP/6.8 wt% H₂O solution. It was found that Ag₂S-modified Ag electrode exhibited high catalytic activity, selectivity towards CO₂ reduction. The faradaic efficiency of CO and the current density reached to 92% and 9.85 mA/cm², respectively. Ag₂S exhibits a promising in CO₂ reduction for practical application.

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