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Article

Efficient electrocatalytic reduction of carbon dioxide to ethylene on copper–antimony bimetallic alloy catalyst

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ABSTRACT

The exploration of efficient electrocatalysts for the reduction of CO₂ to C₂H₄ is of significant importance but is also a challenging subject. Cu-based bimetallic catalysts are extremely promising for efficient CO₂ reduction. In this work, we synthesize a series of porous bimetallic Cu–Sb alloys with different compositions for the catalytic reduction of CO₂ to C₂H₄. It is demonstrated that the alloy catalysts are much more efficient than the pure Cu catalyst. The performance of the alloy catalysts depended strongly on the composition. Further, the alloy with a Cu:Sb ratio of 10:1 yielded the best results; it exhibited a high C₂H₄ Faradaic efficiency of 49.7% and a high current density of 28.5 mA cm⁻² at -1.19 V vs. a reversible hydrogen electrode (RHE) in 0.1 M KCl solution. To the best of our knowledge, the electrocatalytic reduction of CO₂ to C₂H₄ using Cu–Sb alloys as catalysts has not been reported. The excellent performance of the porous alloy catalyst is attributed to its favorable electronic configuration, large surface area, high CO₂ adsorption rate, and fast charge transfer rate.

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1. Introduction

The transformation of greenhouse gas carbon dioxide (CO₂) to useful chemicals and fuels is an appealing approach to reducing CO₂ emission, but is difficult because CO₂ is thermodynamically stable and kinetically inert [1–3]. Electrocatalytic reduction is a very promising approach for converting CO₂ to chemicals and fuels, especially with the use of intermittent renewable energy [4–7]. At present, many electrocatalysts are used for the reduction of CO₂ to different products, such as CO, formic acid, methanol, and C₂ compounds [8–11].

Ethylene (C₂H₄) is an important building block for the chemical industry, especially for producing polymers [12,13], which are produced using fossil carbon resources. C₂H₄ possesses energy densities of higher economic value than its C₁ counterparts. Some excellent studies have been carried out for the electrochemical reduction of CO₂ into C₂H₄ using different kinds of electrocatalysts, such as surface-modified Cu [14,15], Cu-based supported catalysts [16,17], oxide-derived Cu catalysts [18–20], and nitrogen-doped carbon materials [21]. For example, a carbon-supported Cu catalyst was reported for the selective electroreduction of CO₂ to C₂H₄ with a Faradaic effi-

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ciency (FE) of 45%, which was 2.3-fold the FE of electrodeposited smooth Cu film [16]. Furthermore, a nanometer-sized N-doped graphene quantum dot (NGQD) catalyst showed a C_2H_4 selectivity of 30% [21]. Although progress is impressive, it is still quite desirable to design highly active and robust electrocatalysts that generate C_2H_4 with high current density and selectivity.

Recently, Cu-based binary alloys have attracted great attention for their CO_2 reduction reaction (CO_2RR), as their electronic structure and binding energy can be easily modified by adding a second metal. This leads to a remarkable enhancement in catalytic activity with respect to different products [22,23]. Some excellent studies have also been carried out on this topic. For example, it was reported that CO_2 could be reduced to C_2H_4 on Ag/Cu nanocrystals [24], with a selectivity of 40% in contrast to the 12% selectivity obtained on a bulk Cu catalyst. In another study, a CuZn bimetallic catalyst was shown to reduce CO_2 to C_2H_4 with an FE as high as 33.3% at -1.1 V vs. a reversible hydrogen electrode (RHE) [25]. Furthermore, oxide-derived Cu_xZn catalysts have also been used to convert CO_2 to C_2H_5OH with an FE of 29.1% [26]. These studies suggest that Cu-based binary alloys are promising catalysts for enhancing the selectivity of CO_2RR toward multi-carbon products.

In this work, we synthesized a range of bimetallic Cu–Sb alloys with different compositions and porous morphology through a facile one-step process. The resulting Cu–Sb bimetallic alloy exhibited high selectivity toward C_2H_4 (~50%) production at a relatively low applied potential (-1.19 V vs. RHE) with a high current density (28.5 mA cm^{-2}). By combining material characterizations and a series of control experiments, we further confirmed that the enhanced selectivity toward C_2H_4 could be attributed to the synergistic effect of Cu and Sb, which produced a higher CO_2 adsorption rate and a larger surface area, and facilitated charge and mass transfer. As far as we know, this is the first work to use Cu–Sb alloys for the electrocatalytic reduction of CO_2 to produce C_2H_4 .

2. Experimental

2.1. Materials

Copper(II) chloride ($CuCl_2 \cdot 2H_2O$, Sinopharm Chemical Reagent Co., Ltd.), antimony trichloride ($SbCl_3$, Shanghai Aladdin Biochemical Technology Co., Ltd.), sodium borohydride, sodium borohydride ($NaBH_4$) (98%, Sinopharm Chemical Reagent Co., Ltd.), Toray Carbon Paper (CP, TGP-H-60, $19\text{ cm} \times 19\text{ cm}$), Nafion D-521 dispersion (5% w/w in water and 1-propanol, $\geq 0.92\text{ meg/g}$ exchange capacity), and Nafion N-117 membrane (0.180 mm thick, $\geq 0.90\text{ meg/g}$ exchange capacity) were purchased from Alfa Aesar China Co., Ltd. Both CO_2 and N_2 had a purity of 99.999%, and were provided by Shanghai Chemistry Industrial Zone Pujiang Special Type Gas Co., Ltd.

2.2. Synthetic procedures for Cu–Sb alloys

Cu–Sb alloys were synthesized via the co-reduction of metal precursors through a facile one-step process using $CuCl_2 \cdot 2H_2O$,

$SbCl_3$, and $NaBH_4$ as precursors [27,28]. In a typical preparation, 3.5 mmol $CuCl_2 \cdot 2H_2O$ and 0.35 mmol $SbCl_3$ were dissolved in 14 mL distilled water. The above solutions were injected into the $NaBH_4$ solution (2.0 M, 20 mL) using the ethanol and H_2O mixed solution, and the resulting mixture was stirred in an ice bath. After 4 h, the precipitate was obtained via centrifugation, and washed with 50 mL of water six times. It was then washed with 50 mL of acetone to remove the unreacted precursors and other possible byproducts. The powder was then dried at $60\text{ }^\circ\text{C}$ overnight in a vacuum oven. The final product was obtained after cooling to room temperature. The powder was labeled Cu_xSb_y , where x and y represent the relative moles of $CuCl_2$ and $SbCl_3$.

Alloys with different molar ratios of Cu to Sb, i.e., the Cu_6Sb_1 , Cu_8Sb_1 , $Cu_{10}Sb_1$, $Cu_{12}Sb_1$, and $Cu_{15}Sb_1$ alloys, were prepared by adjusting the amount of precursor.

2.3. Characterization

The morphology of the samples was characterized using a Hitachi S4800 scanning electron microscope (SEM) at 3 kV, and a FEI Tecnai G2 F30 transmission electron microscope (TEM) operated at 300 kV. A Rigaku Ultima VI X-ray diffractometer was employed to record the X-ray diffraction (XRD) patterns with a scanning speed of $5^\circ/\text{min}$ between 10° and 90° . The diffractometer was operated at 35 kV and 40 mA with Cu K_α radiation. X-ray photoelectron spectroscopy (XPS) data were obtained using an AXIS Supra (XPS) surface analysis instrument with an X-ray monochromatic source (combined Al/Ag anode, energy 1486.6/2984.2 eV). The adsorption isotherms of CO_2 were determined at $25\text{ }^\circ\text{C}$ in the pressure range of 0–1 atm on BELSORP-max II equipment.

2.4. Electrode preparation

The method for preparing the electrodes using a Cu–Sb alloy as the catalyst was similar to that used in previous reports [29,30]. Briefly, 6 mg catalyst was dispersed in 350 μL isopropyl alcohol and 30 μL Nafion solution (5 wt%) and was sonicated for 30 min to obtain a homogenous catalyst ink. Then, 64 μL ink was dropped onto a carbon paper ($1 \times 1\text{ cm}^2$) surface using a micropipette. The electrode was then dried under room temperature. The amount of Cu–Sb catalyst on the electrode was 1 mg cm^{-2} .

2.5. Linear sweep voltammetry (LSV) and electrolysis

Electrochemical measurements were performed in a gas-tight two-compartment H-cell separated by an ion exchange membrane (Nafion117) in a three-electrode system on a potentiostat (CHI 660E, Shanghai CH Instruments Co., China). 0.1 M KCl solution and 0.1 M $KHCO_3$ solution were utilized as the cathodic and anodic electrolytes, respectively. LSV scans were conducted within a single compartment batch cell with a three-electrode configuration, which consisted of a working electrode, platinum gauze as the counter electrode, and Ag/AgCl (saturated KCl solution) as the reference electrode.

Prior to the experiment, the electrolyte was purged with N₂ or CO₂ for at least 30 min, and then the LSV measurement was carried out in the potential range of 0.0 V to −1.19 V vs. RHE at a scan rate of 20 mV s^{−1} [31]. In all measurements, we used Ag/AgCl as the reference electrode, and the potential (vs. Ag/AgCl) was converted to RHE using the following equation [32]:

$$E(\text{RHE}) = E(\text{Ag/AgCl}) + 0.197 + 0.059 \times \text{pH}$$

In the electrolysis experiment, the amount of electrolyte was 30 mL, and the electrolytes were bubbled with N₂ or CO₂ for at least 30 min to form an N₂- or CO₂-saturated solution. The reaction was performed at a constant potential. First, the cathode side was electrochemically reduced using cyclic voltammetry (CV), which ranged from 0 to −1.39 V vs. RHE at a rate of 0.1 V s^{−1} for five cycles to completely reduce the possible oxidized species [33].

2.6. Product analysis

The gaseous product was detected by a gas chromatograph (GC; Agilent-7890A) using a flame ionization detector (FID) for hydrocarbons and a thermal conductivity detector (TCD) for H₂ and CO. The liquid product was quantified using a nuclear magnetic resonance (NMR) spectrometer (Bruker; Ascend 400–400 MHz) in DMSO-d₆ with phenol as an internal standard. The gaseous product FE was calculated using:

$$\text{FE} = nFA\alpha v t / Q_{\text{total}} \times 100\%$$

where n is the number of electrons involved in the electrode reaction, F is the Faraday constant, A is the integral area of the gaseous product peak in GC, α is the conversion factor determined from the calibration of the GC with standard samples, v is the CO₂ inflow rate, t is the electrolytic time, and Q_{total} is the total quantity of electric charge.

2.7. Electrochemical active surface area (ECSA) measurement

The ECSA was determined from the capacitive current, which was measured with a double-layer (C_{dl}) charging of the scan-rate dependence of CV (the potential windows were between −0.78 V and −0.88 V vs. RHE). The C_{dl} was estimated by plotting the Δj ($j_a - j_c$) at −0.83 V vs. RHE (0.1 M KCl solution) against the scan rates, where j_a and j_c were the anodic and cathodic current densities, respectively. The scan rates were 20, 40, 60, 80, 100, 120, 140, and 160 mV s^{−1}. Briefly, the double-layer capacitance was measured by conducting CV in a potential range where no Faradaic processes occur, and hence the measured current was due to the non-Faradaic process of charging the electrochemical double layer. During the CV scans, the charging current j was linear to the scan rate v , and the slope of the line was equal to the double-layer capacitance (C_{dl}): $C_{\text{dl}} = \Delta j / v$, where the measuring unit of C_{dl} was mF cm^{−2} [24].

2.8. Electrochemical impedance spectroscopy (EIS)

The experimental apparatus was the same as that used for the LSV measurements. The EIS measurement was carried out in CO₂-saturated 0.1 M KCl solution at an open circuit potential

(OCP) with frequencies that ranged from 0.01 Hz to 100 kHz, and the amplitude of the applied voltage was 5 mV. The data obtained from the EIS measurements were fitted by ZView® software (Version 2.9c, Scribner Associates, USA).

3. Results and discussion

3.1. Catalyst characterization

The synthesis procedure for Cu–Sb alloys is schematically shown in Fig. 1a. Briefly, the Cu–Sb alloys were prepared through a facile one-step process using copper(II) chloride, antimony trichloride, and sodium borohydride as precursors. The Cu–Sb alloys were obtained after centrifuging and vacuum drying. In this study, we prepared Cu_{*x*}–Sb_{*y*} alloys with different Cu and Sb compositions, in which x and y represent the relative atomic numbers of Cu and Sb. The detailed discussion of the procedures for the alloy preparation is given in the experimental section.

The characterization results of Cu–Sb alloys are shown in Fig. 1b–1e. The SEM images (Fig. 1b and 1c) of Cu and the Cu₁₀–Sb₁ alloy reveal that porous nanoparticles on a scale of approximately 60 nm were formed. The higher magnification image (the inset) indicates that the particles were composed of small domains of about 5 nm, with numerous interfaces and junctions between them. The results also show that the surface of the Cu₁₀–Sb₁ alloy (Fig. 1c) was much rougher than that of pure Cu (Fig. 1b). The high-resolution TEM (HRTEM) images show a polycrystalline structure in such Cu–Sb alloys (Fig. 1d

Fig. 1. (a) Schematic illustration of the procedure for preparing Cu–Sb alloys; (b, c) SEM images of pure Cu and Cu₁₀–Sb₁, and (d, e) TEM images of pure Cu and Cu₁₀–Sb₁; the inset images show pure Cu and the Cu₁₀–Sb₁ alloys at high magnification.

Fig. 2. XRD patterns of pure Cu and $\text{Cu}_{10}\text{-Sb}_1$ alloys.

and 1e), demonstrating that grain boundaries existed at the interface of the alloy [34–36]. The HRTEM image of the representative particle further shows spacings of 0.205 and 0.245 nm, corresponding to (110) plane of cubic Cu(I) oxide and the (111) plane of Cu(0) [37].

The XRD patterns of Cu and $\text{Cu}_{10}\text{-Sb}_1$ are shown in Fig. 2. The results show that the Cu diffraction peaks of the (111), (200), and (220) facets and the Cu_2O diffraction peaks of the (110), (111), and (220) facets were present in the alloy samples, indicating the formation of segregated pure metallic Cu and Cu_2O phase in the pure Cu and $\text{Cu}_{10}\text{-Sb}_1$ alloy. The XRD pattern of the $\text{Cu}_{10}\text{-Sb}_1$ alloy showed two distinct sets of diffraction peaks arising from the alloy structure of Sb and Cu, indicating the formation of $\text{Cu}_{10}\text{-Sb}_1$ alloy [38].

XPS identified the valence states of Cu and Sb in the alloy. The peaks in the spectra indicate chemical binding energies of approximately 932.4, 531.3, and 530.5 eV, corresponding to Cu 2p, Sb 3d, and O 1s, respectively (Fig. 3a). The XPS spectra for Cu $2p_{3/2}$, and for Sb $3d_{5/2}$ and $3d_{3/2}$ (Fig. 3b and Fig. S4) indicate the reduction to the Cu^0 and Sb^0 metallic states. The Cu LMM XAES characterization results of 913.7 eV with respect to Cu^+ while those reduced at 917.6 are donated by Cu^0 sites (Fig. 3b). The results are consistent with that of the XRD study [39–41]. Previous work has shown that the selectivity in CO_2 catalysis can be affected by the oxidized phase concentration in the sur-

face region. With an increasing relative ratio of Cu^+ to Cu^0 , the higher productivity of C_2^+ species indicates that Cu^+ is needed to produce C_2^+ products. Furthermore, other elements such as boron were not detected (Fig. 3c), suggesting that the reductant was not incorporated into the Cu–Sb alloys during the synthesis.

The above results suggest the successful synthesis of Cu–Sb alloys with a porous morphology and nanostructured features. Notably, it can be seen in Fig. S4 that blue-shift occurred in the Cu–Sb alloys, which affected the charge transfer and interatomic interaction of the catalyst. Such a phenomenon allows the transformation of a local effect to a global effect, and thus impacts the catalytic behavior of the entire Cu domain when interfaced with the Sb domain by enhancing its intrinsic activity. The metallic Sb component of the Cu–Sb alloys resulted in changes in, and possibly the strengthening of the electronic interactions in the Cu–Sb alloys. Changes in electronic configurations may improve electrocatalytic performance [42].

3.2. CO_2RR performances of Cu–Sb alloys

An LSV study was conducted to investigate the performances of the Cu–Sb alloys in the potential range from 0.0 V to -1.19 V vs. RHE, and the results are shown in Fig. 4a. The current density over $\text{Cu}_{10}\text{-Sb}_1$ reached a high value of approximately 35.86 mA cm^{-2} at -1.19 V vs. RHE in CO_2 -saturated 0.1 M KCl solution, and was higher than that over the pure Cu electrode, indicating higher activity for the $\text{Cu}_{10}\text{-Sb}_1$ alloy. In addition, the LSV curves using pure Cu and the $\text{Cu}_{10}\text{-Sb}_1$ alloy in N_2 -saturated 0.1 M KCl solution were also determined, and the current density was much lower, demonstrating the reduction of CO_2 over the pure Cu and $\text{Cu}_{10}\text{-Sb}_1$ alloy electrodes, and the $\text{Cu}_{10}\text{-Sb}_1$ alloy electrode exhibited better performance for CO_2RR .

Constant-potential electrolysis of CO_2 over Cu–Sb alloys was conducted at different applied potentials. After electrolysis at a controlled potential of -1.19 V vs. RHE for 3 h, the gas and liquid products were quantified using GC and ^1H NMR, respectively. Fig. 4b shows the distribution of major CO_2RR products over $\text{Cu}_{10}\text{-Sb}_1$ at different potentials vs. RHE. H_2 , CO, and C_2H_4 are the only gaseous products monitored by GC, and no liquid product was detected by NMR. As expected, C_2H_4 was the major

Fig. 3. (a) XPS survey spectrum; (b) Sb 3d XPS spectrum and Cu LMM Auger spectra; (c) B 1s XPS spectrum of $\text{Cu}_{10}\text{-Sb}_1$ alloys.

Fig. 4. Electrochemical performances of the Cu-Sb alloy catalysts. (a) LSV curves for pure Cu and Cu₁₀Sb₁ electrodes in CO₂ and N₂-saturated 0.1 M KCl electrolyte; (b) FE of the major products and total current densities over Cu₁₀Sb₁ at different applied potentials; (c) FE for C₂H₄ over various electrocatalysts at -1.19 V vs. RHE; (d) Partial current densities of C₂H₄ at various applied potentials over various electrocatalysts; (e) FE and current densities for C₂H₄ production over Cu₁₀Sb₁ electrode at -1.19 V vs. RHE within 4 h.

product at the optimal potential. As the electrolytic potential increased, the FE of C₂H₄ first increased and then decreased. The FE of C₂H₄ reach 49.7% with a partial current density of 28.5 mA cm⁻² at -1.19 V vs. RHE (Fig. 4b). The decrease in the FE of C₂H₄ at a high applied potential resulted from the enhancement in the production rate of H₂ and CO. Fig. 4c and Fig. 4d show the FE and partial current density over the Cu-Sb alloys with different compositions at the optimal applied potentials, respectively. It is evident that both the FE and the partial current density over the alloys were higher than that over the pure Cu and Sb catalysts. For pure Cu, the highest FE for C₂H₄ was only 15.8% (Fig. 4c). For pure Sb, the CO₂RR products were H₂ and CO (Fig. S2), a finding that was similar to that previously reported [43]. Fig. 4c shows that the FE was significantly influenced by the composition of the alloys. The Cu₁₀Sb₁ alloy exhibited the best performance of all the catalysts, and showed a 3.3-fold FE enhancement for C₂H₄ compared with pure Cu of a similar size and shape.

When the Sb content was small, the FE of C₂H₄ increased with the content of Sb. When the Sb content was larger than that in Cu₁₀Sb₁, the FE decreased with further increases in the Sb content. At the same potential of -1.19 V vs. RHE, the partial current density of C₂H₄ over the other alloy catalysts was also lower than that over the Cu₁₀Sb₁ alloy catalyst. These results indicate that the performance of the alloy catalysts could be tuned effectively by the atomic ratios of Cu and Sb in the alloys, suggesting a synergistic effect of Cu and Sb in catalyzing the CO₂ reduction. The surfaces of the Cu-Sb alloys give rise to steps

and edges with low-coordinate metal atoms, which promote the adsorption of CO intermediates and facilitate their dimerization to form C₂ products. The review of the literature that concerns C₂H₄ production is illustrated in Table S1. It shows that the Cu₁₀Sb₁ alloy is among the most effective catalysts for C₂H₄ production.

In addition, long-term electrolysis shows that the FE and current density showed no obvious change during the reduction process (Fig. 4e). From the XRD spectra of Cu₁₀Sb₁ after electrolysis (Fig. S1), it can be observed that the composition and structure of Cu₁₀Sb₁ show no change. All these results illustrate the stability of Cu₁₀Sb₁ under the reaction conditions.

Electrolytes often play an important role in CO₂ electroreduction [23]. Therefore, in addition to KCl aqueous electrolytes, we also used other electrolytes that contained different cations and anions to perform a reaction over the Cu₁₀Sb₁ alloy. To study the effect of cations, chloride salts with different cations such as 0.1 M KCl, 0.1 M NaCl, and 0.1 M CsCl were used, and the results are illustrated in Fig. 5. The FE of the electrolytes followed the order of KCl > NaCl > CsCl. In the 0.1 M CsCl electrolyte, H₂ was the main product compared with KCl electrolyte. To study the effect of anions, potassium salts with different anions were used, and the electrolysis results over the Cu₁₀Sb₁ alloy catalyst are also provided in Fig. 5. 0.1 M K₂HPO₄ also showed excellent performance (40% FE), although it was lower than that of KCl. However, the FE in the 0.1 M KH₂PO₄ electrolyte was very low when hydrogen was the main product. The

Fig. 5. Product distribution of the Cu₁₀-Sb₁ alloy catalyst in different electrolytes at -1.19 V vs. RHE.

above results indicate that both the cation and anion affected the electrochemical reaction, and KCl was the best electrolyte for generating C₂H₄ of all the electrolytes studied in this work. The local buffering capability of cations should increase the rate of any proton-transfer reaction. Therefore, the variation in the activity and selectivity of the CO₂RR reactions with the cation was different. Similarly, the anions influence the reaction. The change in cation size, the pK_a for cation hydrolysis, and the pH near the cathode lead to an increase in the local concentration of dissolved CO₂. The consequences of these changes bring about a change in cathode activity, and a change in the FEs for H₂, CH₄, CO, and C₂H₄, in full agreement with the experimental observations of CO₂ reduction over Cu-Sb alloys [44,45].

To gain further insights into the excellent performance of the catalysts, single-sweep polarography was used to study the electrochemically active surface area (ECSA) of the catalyst [46]. Based on the Randles-Sevcik equation, the reduction current density plotted against the square root of the scan rate is illustrated in Fig. 6a. According to the measured double-layer capacitance, Cu₁₀-Sb₁ has a larger electrochemical active surface area than that of pure Cu, which is beneficial to increasing the reduction rate.

Fig. 6. Characterizations of the electrochemical performance. (a) Charging current density at -1.19 V vs. RHE plotted against the square root of the scan rate over the Cu₁₀-Sb₁ alloy and pure Cu. (b) Nyquist plots of pure Cu and the Cu₁₀-Sb₁ alloy in CO₂-saturated 0.1 M KCl electrolyte; the inset is the electrical equivalent circuit used to simulate the experimental impedance data, and the components are solution resistance (R_s), electron transfer resistance (R_{ct}), double layer capacitance (C_{dl}), and Warburg-type impedance (Z_w). (c) Volumetric CO₂ adsorption-desorption isotherm of pure Cu and Cu₁₀-Sb₁ alloy; solid symbols represent adsorption curve, and hollow symbols represent desorption curve.

Electrochemical impedance spectroscopy (EIS) was also performed to provide the charge transfer rate at the electrode/electrolyte interface. The Nyquist plot was obtained by running the experiment at an OCP (Fig. 6b). A simple equivalent circuit $R(C(RW))$ was then used to fit the high and medium frequency data (Fig. 6b insert). The results indicated that the charge transfer resistance (R_{ct}) of the Cu₁₀Sb₁ alloy was much lower than that of the pure Cu. Therefore, the Sb in the Cu₁₀-Sb₁ alloy can improve CO₂ activation and enhance electron transfer to CO₂ to form a reduced CO₂^{•-} intermediate, which is vital for CO₂RR [47,48].

In addition, the adsorption ability of CO₂ can also influence the performance of the catalysts for CO₂RR. Hence, we studied CO₂ adsorption over pure Cu and Cu₁₀-Sb₁ alloys. As shown in Fig. 6c, the CO₂ adsorption capacity of the Cu₁₀-Sb₁ alloy reached 3.89 cm³ g⁻¹, which was 1.55 times that of the pure Cu. The results indicated that the Cu₁₀-Sb₁ alloy could improve CO₂ adsorption capacity, which is favorable to CO₂ reduction.

From the results above, we can discuss the main reasons for the excellent electrocatalytic performance of the Cu₁₀-Sb₁ alloy for CO₂ reduction. Firstly, the interaction of Cu and Sb in the Cu-Sb alloys changed the electronic configuration, which may modify the electrocatalytic properties of the catalyst. Secondly, the alloy had the largest electrochemical surface area and the lowest charge transfer resistance (Fig. 6a and 6b), which improves the activity and charge transfer rate [49]. Thirdly, the porous structure of the bimetallic alloy resulted in high accessibility of the active sites, and thus facilitated CO₂ adsorption and efficiency (Fig. 6c). Thus, the porous Cu₁₀-Sb₁ alloy prepared in this work was more efficient than pure Cu.

4. Conclusions

In summary, we have synthesized Cu-Sb alloy electrocatalysts with a porous morphology for the electrochemical reduction of CO₂. Compared with pure Cu catalysts, the Cu-Sb alloys exhibited much higher activity and selectivity for the electroreduction of CO₂ to C₂H₄ using 0.1 M KCl solution as the electrolyte. The Cu₁₀-Sb₁ alloys showed a 3.3-fold FE enhancement for C₂H₄ compared with pure Cu of a similar size and shape, and

the C_2H_4 FE and current density reached 49.7% and 28.5 mA cm^{-2} , respectively. The excellent electrocatalytic performance of the $Cu_{10}Sb_1$ originates mainly from its porous structure, favorable electronic configuration, large electrochemical surface area and low charge transfer resistance. We believe that designing porous alloys with two or more metals is a very promising way to prepare electrocatalysts for efficient transformation of CO_2 into valuable chemicals and fuels.

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Graphical Abstract

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Efficient electrocatalytic reduction of carbon dioxide to ethylene on copper–antimony bimetallic alloy catalyst

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An electrochemical system based on a copper–antimony bimetallic catalyst for reducing CO_2 to C_2H_4 is reported. The excellent electrocatalytic performance originates mainly from its porous structure, favorable electronic configuration, large electrochemical surface area, and low charge transfer resistance.

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铜–锡双金属合金高效电催化还原二氧化碳制乙烯

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摘要: 随着全球工业化进程的快速发展, 日益增多的人类活动不仅加速化石燃料的消耗, 还会导致温室气体二氧化碳(CO₂)的大量排放。同时, CO₂也是廉价、无毒无害、储量丰富的C₁资源, 将其转化为有价值的化学品具有碳资源合理利用和环境保护的双重意义。近年来, 采用电化学方法温和条件下还原CO₂为重要化学品和燃料引起广泛关注。其中, 探索廉价电催化剂, 高效催化还原CO₂为C₂产物仍是一个具有挑战性的课题。铜基催化剂由于自身低成本和可还原CO₂为多种碳氢产物的优点而备受关注。然而, 铜基电催化材料具有选择性差、失活严重和效率低等缺点, 并且在电催化还原CO₂过程中需要较高的过电位, 反应过程中会受到氢气析出副反应的影响。为了得到一种化学性质稳定、高电流密度和高选择性等优点的材料在电催化CO₂还原中得到了广泛的研究。然而, 单纯的铜催化剂对CO₂分子的活化以及反应中间体的吸附能力较低, 导致了铜基材料催化剂电催化CO₂还原活性及选择性较低。因此, 开发出可实际应用的高效率和高选择性的电极材料是当前该技术研究中亟待解决的关键科学问题。

近年来, 铜基二元合金在电催化CO₂还原反应中受到广泛关注。由于二元金属的电子结构和各元素的电子结合能发生变化, 其催化活性明显优于单金属催化剂。因此, 铜基双金属合金在提高CO₂还原产物选择性方面具有广阔的前景。本文采用低温还原的方法制备了一系列不同组成的Cu–Sb双金属合金, 系统研究了一系列不同配比的Cu–Sb双金属合金对电催化还原CO₂为乙烯的影响。研究发现, 当Cu/Sb比例为10/1(Cu₁₀–Sb₁)时, 可有效提高乙烯的法拉第效率及电流密度。当以0.1 M KCl水溶液作为电解液, 电位为–1.19 V vs. RHE时, 乙烯的法拉第效率和电流密度分别为49.73%和28.5 mA cm^{–2}。实验结果表明, Cu–Sb双金属合金催化剂优异的催化性能主要源于适宜的电子态、良好的CO₂吸附性能、较大的电化学比表面积和较高的电子传输速率。迄今, 用Cu–Sb作为催化剂进行电催化还原CO₂制乙烯尚未见报道。

关键词: 二氧化碳还原; 乙烯; 电催化; 铜–锡双金属合金; 协同作用

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