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Achieving both High Selectivity and Current Density for CO₂ Reduction to Formate on Nanoporous Tin Foam Electrocatalysts

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Abstract: Currently, low catalytic activity, selectivity and stability are the biggest challenges which restrict the large scale applications of CO₂ electrochemical reduction. Formic acid, one of the highest value-added products from electrochemical reduction of CO₂, has gathered much interest. Here, we develop nanoporous tin foam catalysts which exhibit significantly high selectivity and faster production rate to formate. In a 0.1 M NaHCO₃ solution, the maximum Faradaic efficiency for formate production reaches above 90% with a current density over 23 mA cm⁻², which are among the highest reported value to date under ambient conditions. The improved production rate can be attributed to the high surface area and porous structure. Moreover, the electrocatalysts are quite stable, namely, the Faradaic efficiency remains unchanged during 16 hour electrolysis. This is a promising technology to convert CO₂ into useful hydrocarbons.

Introduction

It is generally believed that the rising CO₂ in the atmosphere is the key factor for climate change because of its greenhouse effects.^[1] It has been reported that the concentration of CO₂ has increased from 278 ppm before the industrial revolution to around 400 ppm at present. The reduction of CO₂ released and the conversion of CO₂ to useful chemicals have become a significant challenge and many countries are expanding financial investment in this field.

Generally, CO₂ conversion can be grouped into four categories, namely, chemical methods,^[2] photocatalytic reduction,^[3] biotransformation^[4] and electrocatalytic reduction^[5]. Energy generated from carbon-free sources such as renewable energy (e.g., solar, wind, geothermal, wave etc.) and nuclear energy are generally in the form of electricity. The places where these sources are sufficient are usually far away from the places where there is a high energy demand.^[6] Storing the redundant electric energy in the chemical form would be a good way to solve this energy imbalance issue. From this point of view, CO₂

would be an ideal feedstock to store the energy in chemical form by converting it into fuels. It is easy then to transport these synthesized fuels to the user sites. As a result, electrocatalysis of CO₂ has aroused great attention among the many CO₂ conversion methods. Extensive studies have been reported for electrochemical reduction of CO₂, among which the metals and their related compounds are frequently used as electrocatalysts.^[7]

Among all the available products from CO₂ electroreduction, formic acid/formate is one of the highest value-added chemicals.^[8] The demand of formic acid is dramatically expanding year by year due to its various applications, e.g., silage for animal, production of leather, and manufacturing of rubber. Recently formic acid has been proposed as a promising hydrogen carrier.^[9] Tin is one of the most common catalysts with high selectivity for electrochemical reduction of CO₂ to formic acid/formate. Lv *et al.* studied the catalytic properties of commercial tin foil for the electroreduction of CO₂ to formate.^[10] The optimal conditions were 0.1 M KHCO₃ at -1.8 V vs. Ag/AgCl, under which the Faradaic efficiency was up to 91% however, the current density was only 2.5 mA cm⁻². Zhang *et al.* prepared high surface area tin oxide nanocrystals by a facile hydrothermal method and investigated its capability for CO₂ reduction to formate in 0.1 M NaHCO₃ solution.^[11] Wu *et al.* concluded the change of morphological and the corresponding Faradaic efficiencies on Sn particles gas diffusion electrode (GDE) during the electrolysis.^[12] At -2.0 V vs. Ag/AgCl, the Faradaic efficiencies toward formate formation degraded to 56% after long term electrolysis. Using the similar cell system, Prakash *et al.* found that Nafion coated Sn powder GDL electrode achieved a high current density and Faradaic efficiency for the electroconversion of CO₂ to formate.^[13] A current density of 27 mA cm⁻² with faradaic efficiency of 70% was reached at -1.6 V vs. NHE. These studies reveal that the selectivity and activity of the tin catalysts are greatly affected by the microstructure and preparation conditions.

Electrodeposition is an excellent method for the preparation of nano-structured materials. It has been reported that nanoporous 3D metallic copper and tin have been successfully prepared by an electrodeposition method.^[14] In a previous paper, it has been reported that the Faradaic efficiency and distribution of products formed from electrodeposited nanoporous copper differ significantly from those obtained at smooth electropolished copper electrodes.^[15] In a recent report, a tin dendrite electrode has been prepared by an electrodeposition method and then it was pre-heated in air at 180 °C for 3 hours.^[16] A current density of 17.1 mA cm⁻² with Faradaic efficiency of 71.6% towards formate has been achieved when applied -1.36V RHE. In this study, nanoporous tin foam was also prepared by an electrodeposition method as described in a previous report.^[14] The results show that the porous structure of the tin foams is highly depends on the electrodeposition time. The high surface area of the foam structure promotes the formate yield. At the

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optimal potential, the Faradaic efficiency achieved 90% with current density over 23 mA cm^{-2} on the deposited cathode.

Results and Discussion

Characterization of tin foam electrodes

Figure 1a shows the X-ray Diffraction (XRD) pattern of the electrodeposited tin foam on a tin substrate (90 s). The pattern matches well with the Sn in database (ICCD 04-013-6163) which indicates that pure tin foam electrode has been prepared. To eliminate the effects of tin substrate, electrodeposition of tin foam on a copper substrate was prepared using the same method (Figure S1). It can be seen that the patterns are totally the same as they on a tin substrate except for the (111), (210) and (222) peaks of Cu substrate. This indicates that tin was deposited on the copper foil. It can be reasonably deduced that tin was also deposited on tin foil under similar conditions.

During the electrodeposition, the evolution of hydrogen is extreme because of the high current density applied. The hydrogen bubbles prevent the formation of a compact tin film on the substrate, leaving a porous foam structure. Figure 2 shows the typical SEM images of tin foams electrodeposited at different deposition times. Apparently, the foam structure significantly depends on the electrodeposition time. Foam structure is not formed after 30 s deposition (Figure 2a), and as the time increases to 60 s (Figure 2b) and 90 s (Figure 2c), the porous structure becomes more obvious. However, too many tin foams accumulate together when the deposition time was 120 s (Figure 2d), leading to an uneven surface and unstable deposited layer. Under higher magnification, it is found that the foams are composed of small tin dendrites (Figure 2e) with diameter of $0.5 - 1 \mu\text{m}$ (Figure 2f).

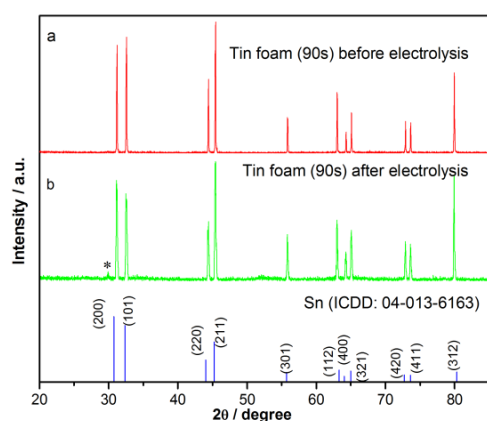


Figure 1. XRD pattern of tin foam on a tin substrate (90 s). a) before and b) after controlled potential electrolysis (* corresponds to the (111) peak of SnO_2).

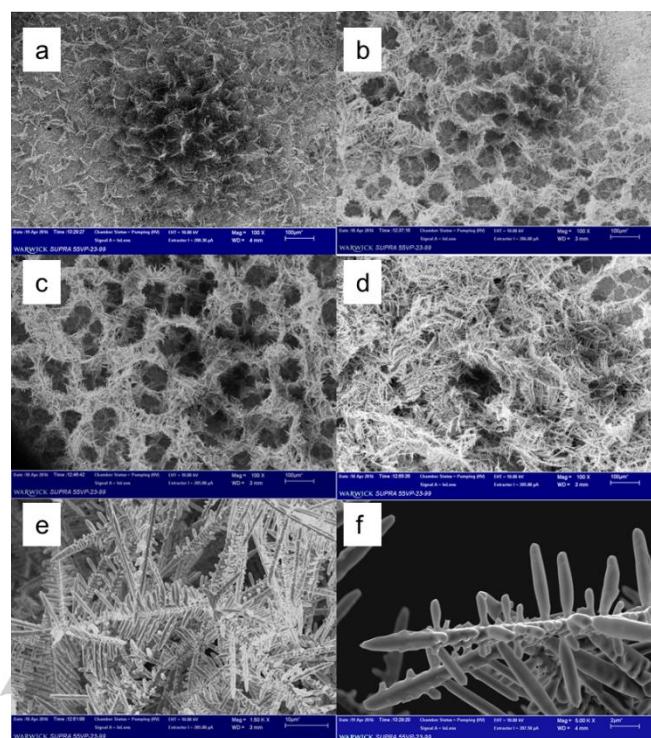


Figure 2. SEM images of electrodeposited tin foams on a tin substrate for a) 30 s, b) 60 s, c) 90 s and d) 120 s; e, f) enlarged images of tin foam (90 s).

Faradaic efficiencies for different applied potentials and electrodeposition time

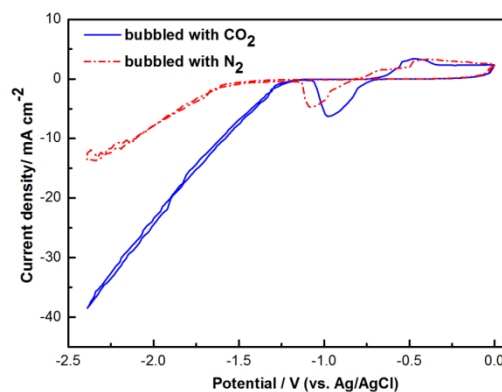


Figure 3. Cyclic voltammograms of a tin foam electrode (90s) in 0.1 M NaHCO_3 solution after being bubbled with CO_2 (solid line) or N_2 (dash line) for 60 minutes. The scan rate was 50 mV s^{-1} .

Figure 3 shows the CV of the tin foam electrodes in 0.1 M NaHCO_3 solution after purging CO_2 or N_2 for 60 minutes. The pH values were 8.65 and 7.04 after bubbling N_2 and CO_2 for 60 min (see details from Tables S1 and S2). The anodic peaks around -

0.5 V vs. Ag/AgCl can be attributed to the oxidation of tin while the cathodic peaks between -0.9 and -1.1 V should be caused by the reduction of the tin oxides. At the more negative potential, the current density sharply increases which is due to the massive reduction of water (N_2 saturated), or CO_2 and water (CO_2 saturated). It can be seen that at -2.4 V vs. Ag/AgCl, the current density under CO_2 saturated condition achieved 40 mA cm^{-2} , nearly three times of the current density under N_2 saturated condition.

Table 1. Summary of tin electrocatalysts for CO_2 reduction.

Material	Potential	Electrolyte	Formate Faradaic efficiencies (%)	Current density (mA cm^{-2})	Reference
Tin foil	-1.75 V vs. SCE	0.1 M $KHCO_3$	91	2.5	[10]
Tin foil	-2.0 vs. SCE	0.5 M $KHCO_3$	63.49	28	[17]
Tin gas diffusion electrode (GDE)	-1.75 V vs. SCE	0.5 M $KHCO_3$	72.99	13.45	[18]
Reduced nano- SnO_2 /graphene	-1.8 V vs. SCE	0.1 M $NaHCO_3$	93.6	10.2	[11]
Tin dendrite	-2.0 vs. SCE	0.1 M $KHCO_3$	71.6	17.1	[16]
Tin foam electrode	-1.95 V vs. SEC	0.1 M $NaHCO_3$	90	23.5	This work

The value of potential is converted to SCE based on information from the articles.

Based on the CV curves, the electrolysis experiments were carried out in a 0.1 M $NaHCO_3$ solution with constant potential ranging from -1.4 to -2.4 V vs. Ag/AgCl at 0.2 V intervals. The electrolyte was saturated with CO_2 before the electrolysis, and the results for 60 s tin foam electrode are presented in Figure 4a. It demonstrates that the total current density increases with increasing cathodic potential. The Faradaic efficiencies for formate at -1.4 and -1.6 V are below 65% while from -1.8 to -2.4 V, the values increase to over 85%. The maximum current densities reach 90% at -2.0 V with a current density of 23.5 mA cm^{-2} , which is one of the best performances on tin related catalysts for CO_2 electroconversion to formate (Table 1). According to many works carried out with tin related electrocatalysts for CO_2 reduction,^[16, 19] the remaining current efficiencies is supposed to the evolution of hydrogen or carbon monoxide, which was indirectly evidenced by the bubbles at the cathode. At more negative potentials, more bubbles were produced which is due to the enhancement of gas evolution.^[11] The SEM images in Figure 2 indicate that the surface area of tin foams increases as the increasing deposition time, which may lead to a higher CO_2 catalytic property. The results shown in Figure 4b also provide evidence for this. Faradaic efficiencies and current density of formate as a function of the electrodeposition time at the optimal potential of -2.0 V vs. Ag/AgCl (Figure 4b) were measured. The highest Faradaic efficiency and current density reach 91% and 29 mA cm^{-2} at a

120 s electrodeposited tin foam electrode. Although higher current density and Faradaic efficiency were observed for the tin cathode deposited for 120 seconds (Figure 4), the tin foam deposited for 120 s tends to fall off while the 90 s electrode is more mechanically robust.

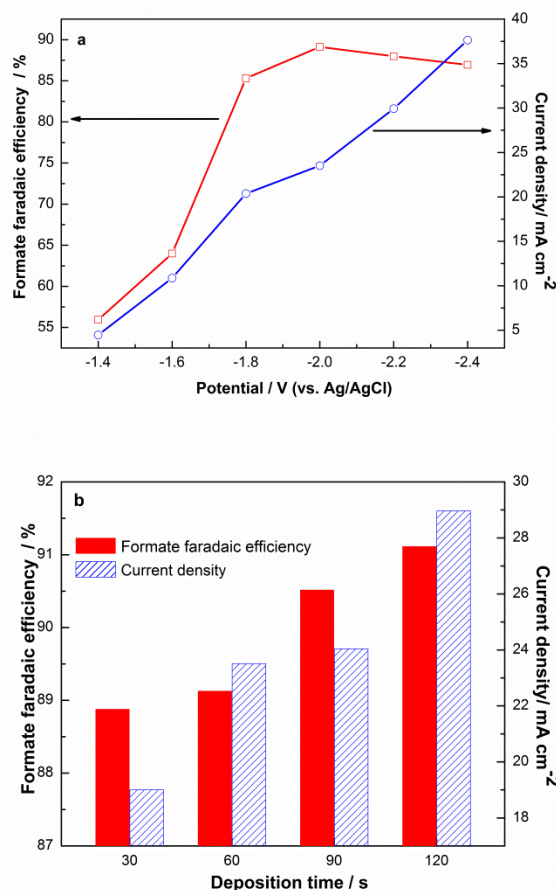
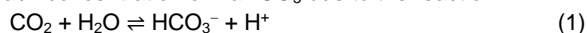


Figure 4. a) Comparison of total current density (blue circles) and Faradaic efficiencies (red squares) for formate production on tin foam electrodes (60 s) at different potentials; b) Faradaic efficiencies of formate as a function of the electrodeposition time at -2.0 V vs. Ag/AgCl.

Reaction mechanisms

The Formate Faradaic efficiencies on a tin foam electrode at different concentrations of $NaHCO_3$ from 0.1 to 1.0 M are shown in Figure 5a. The Faradaic efficiencies significantly decline from 90% at 0.1 M to 46% at 1.0 M, which means that more percentage of the current changes to H_2 and CO evolution at high $NaHCO_3$ concentrations.^[16] The results also coincide with the previous work by Wu *et al.*^[17] Figure 5b presents the pH value of different concentration of $NaHCO_3$ before and after

saturating with CO₂. The pH decreases after saturating CO₂ at each concentration of NaHCO₃ due to the reaction:



Obviously, higher concentration of HCO₃⁻ will inhibit the generation of H⁺ during bubbling CO₂, leading to higher pH value. Therefore the pH value of CO₂-saturated NaHCO₃ increases as the increasing concentration. In other words, the H⁺ concentration is higher at a more diluted NaHCO₃ solution. Wu *et al.*^[17] supposed that the H⁺ at the electrode surface [H⁺]_{surface}, played a significant role for production of formate. At a more diluted concentration of electrolyte, more [H⁺] was accumulating at the electrode surface, generating higher [H⁺]_{surface}, and finally promoted the Faradaic efficiencies.

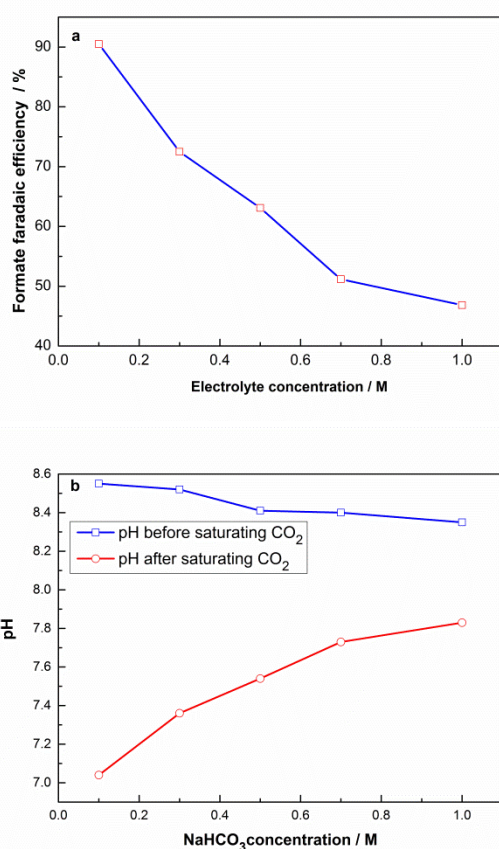
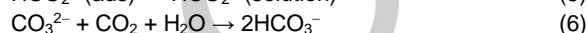
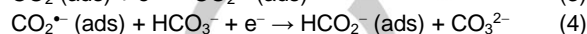
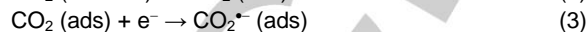
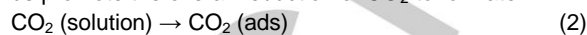


Figure 5. a) Variations in Faradaic efficiencies for formate production on tin foam electrodes (90 s) at -2.0 V vs. Ag/AgCl with concentration of NaHCO₃; b) pH value at different concentration of NaHCO₃ before (blue squares) and after (red circles) saturating with CO₂.

Zhang *et al.* proposed a possible mechanism shown in equations 1-5.^[11] They found that the carbon in formate was derived from CO₂ not the HCO₃⁻, which is consistent with our results, namely, no formate was detected during N₂ purging into NaHCO₃ electrolyte during the electrolysis. From their studies, they also supposed that the rate-determining step for the

reaction was the proton transfer from HCO₃⁻ (equation 3) because the catalytic current densities perform a linear trend with the increasing concentration of NaHCO₃ from 0 to 0.2 M. But in higher concentration of electrolyte, the situation may be different. Won *et al.*^[16] suggested that the rate-determining step was the electron transfer step (equation 3). The tin foam structure prepared here may improve the stabilization of CO₂^{*} thus promote the overall reduction of CO₂ to formate.



Stability of the electrodes

As 90 s deposited electrode and -2.0 V vs. Ag/AgCl are the appropriate conditions for efficiently producing formate, constant potential electrolysis was conducted under the conditions to investigate the stability. The total current density and Faradaic efficiency during 0 to 16 h are presented (Figure 6). Clearly, the Faradaic efficiencies are relatively stable during the extended time of CO₂ reduction, remaining in the range of 85%-92%. In terms of current density, it exhibited slight decrease during the first 8 h, and then reached a stable level at around 22 mA cm⁻². Additionally, the SEM images in Figure S4 on tin foam electrode after electrolysis demonstrate that the morphology of the tin foams is unchanged. Although there is an extra small peak appearing in the XRD pattern of tin foams after electrolysis (Figure 1b), it is evident that the catalytic properties are not affected during our study. The extra peak might correspond to the strongest (111) face of SnO₂ (ICDD 04-015-3275), but the formation procedures are not clear. Probably, the tin foams become easier to be oxidized in air after electrolysis. It has been reported that partially oxidized tin exhibits better catalytic activity and selectivity to formate production.^[16, 19] The presence of O species could modify the adsorption affinity and thermodynamically stabilize the intermediate during the CO₂ to formate therefore improving the selectivity and catalytic activity.

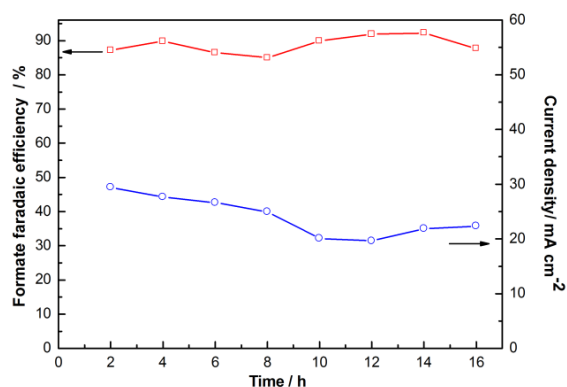


Figure 6. Variations in total current density (blue circles) and Faradaic efficiencies (red squares) for formate production on tin foam electrodes (90 s) at -2.0 V vs. Ag/AgCl over 16 h.

Conclusions

In this work, a tin foam electrode is developed for electroreduction of CO₂, and it exhibits high production rate and selectivity for formate. The electrodes are also stable at -2.0 V vs. Ag/AgCl without degradation during the 16 hour electrolysis. Moreover, the current density could be increased by 1-2 orders of magnitude by applying the catalysts in a flow cell or gas diffusion electrode.^[20] From this point of view, the nanoporous tin foams are potential catalysts for practical application in the electroconversion of CO₂ into formate to be further converted into formic acid at mild conditions therefore this is a promising technology to convert CO₂ into useful hydrocarbons.

Experimental Section

Preparation of tin foam electrodes

The tin foil (0.5 mm thick, 99.9%, Alfa Aesar) was cut into small pieces (2 × 1 cm²) and mechanically polished with 600 and 1200 grade sandpaper. Then they were sonicated with water and isopropyl alcohol. The surface of each tin foil piece was covered with silicone rubber, leaving 1 × 1 cm² active area and small places on the top for the electrode holder. The electrodeposition was conducted by a two electrode system as reported.^[14-15] An appropriate amount of Tin(II) chloride dihydrate (Reagent Grade, Alfa Aesar) was dissolved in water at the concentration of 0.02 M. Two of the as-prepared tin foil electrodes were immersed into the solution as working and counter electrodes. A current of -0.5 A was applied to the working electrode for different time (30, 60, 90 and 120 seconds).

Physical Characterization

X-ray Diffraction (XRD) was used to determine the crystal structures on a Panalytical X'Pert Pro Multi-Purpose Diffractometer (MPD) with Cu K α 1 radiation working at 45 kV and 40 mA. Scanning electron microscopy (SEM) studies were carried out with ZEISS SUPRA 55-VP operating at 10 kV.

Electrochemical measurements

As Zhang *et al.* reported that the formate would be oxidized on a Pt anode in KHCO₃ solution.^[21] A Nafion 211 membrane (Ion Power) separated two compartments of the H-type cell that was applied in this experiment for CO₂ reduction (Figure S1). Each compartment contained 50 mL of 0.1 M NaHCO₃ solution (99% Alfa Aesar), and the cathode chamber was connected with a gas cylinder which allows N₂ or CO₂ to pass through the electrolyte. A typical three electrode system was applied for the measurements controlled by a Solartron 1287 Electrochemical Interface. A Pt mesh (1 × 1 cm²) and Ag/AgCl electrode (sat. KCl) were used as counter and reference electrodes, respectively, which was determined to be very stable although the potential changed systematically.^[22] The working electrode was the well-prepared tin foam

electrode. All of the experiments were carried out under room temperature and atmospheric pressure.

Cyclic voltammetry (CV) experiment was performed in the above-mentioned system. Prior to the test, N₂ or CO₂ was aerated into the solution at 20 sccm to reach saturated condition. The potential applied was from 0 to -2.4 V vs. Ag/AgCl at a scan rate of 50 mV s⁻¹.

Controlled potential electrolysis was carried out under the same devices. For each electrolysis experiment, the electrolyte was saturated with CO₂ before the experiment started and the CO₂ was continuously bubbled at a flow rate of 20 sccm with vigorous stirring during the electrolysis process. Each electrolysis experiment was terminated when the total charge passed reached 10 C. All the current density recorded here was based on the geometric area of the electrodes.

Product analysis

Following the previous method reported,^[23] 1D ¹H Nuclear Magnetic Resonance (NMR) spectrometer (600 MHz, Bruker Avance) was employed to detect the concentration of formate products in the solution. 4 μ L of dimethyl sulfoxide (DMSO) was dissolved in D₂O forming 5 mL solution, which was used as an internal standard for the test. The NMR sample was prepared by taking 500 μ L of solution from the electrolysis cell and mixing with 100 μ L prepared standard solution. To suppress the water impact, the ¹H spectrum was recorded with presaturation method. Typical ¹H NMR spectra for DMSO and formate is shown in Figure S2.

Quantification of formate and Faradaic efficiency

The Faradaic efficiency for formate can be obtained by the following equation 7:^[10]

$$f = n_{\text{formate}} 2F / Q \quad (7)$$

where *f* is the Faradaic efficiency; *n*_{formate} is the number of moles of formate produced which can be calculated according to NMR data; 2 represents that two electrons are transferred for producing one molecule of formate from CO₂; *F* is the Faradaic constant (96485 C mol⁻¹); and *Q* is the total charge passed during the electrolysis process.

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Keywords: CO₂ • formate • high selectivity • tin foam electrocatalyst

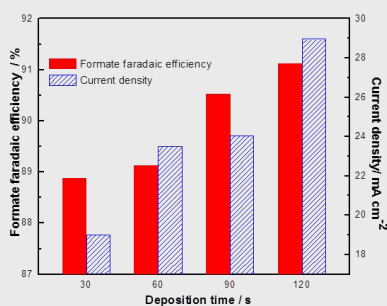
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Layout 2:

FULL PAPER



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Achieving both High Selectivity and Current Density for CO₂ Reduction to Formate on Nanoporous Tin Foam Electrocatalysts