Origin of the Performance Degradation and Implementation of Stable Tin Electrodes for the Conversion of CO₂ to Fuels

Jingjie Wu,¹ Shi-Gang Sun,² and Xiao-Dong Zhou^{1*}

¹ Department of Chemical Engineering, University of South Carolina, Columbia, SC 29208, USA

² State Key Laboratory of Physical chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, P. R. China

Submitted to

Nano Energy

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Abstract

Mastery of the electrochemical conversion of carbon dioxide and water to fuels using renewable electricity can shed light on understanding the nature of artificial photosynthesis and offer an approach to mitigate the negative impact of anthropogenic carbon dioxide emissions on the planet. Presently, copper, silver and tin are the most extensively scrutinized electrocatalysts, which can primarily convert CO₂ to CH₄, C₂H₄ and alcohols, CO, and carbolic acid in aqueous electrolytes, respectively. A long-lasting challenge in the electrosynthesis of fuels from CO₂ is to achieve durable electrochemical performance, an equally important characteristic of an electrode as the activity and selectivity, but it has not yet been tackled in open literature. Here, we describe the origin of degradation of an active electrode for the electrochemical reduction of CO₂ to liquid fuels and an approach to implement stable and active electrode materials. Pulverization was observed in tin-based electrocatalyst particles, resulting in an increase in cell Ohmic resistance and subsequently decreasing the apparent potential at the cathode. As a consequence, the selectivity towards the formation of formate was decreased during a long-term operation. The pulverization was attributed to hydrogen diffusion-induced stress with a calculated critical size of ~3 nm. Nanosized particles below this size were capable of suppressing pulverization in electrocatalysts and resulted in a stable and active performance.

Introduction

The activity and selectivity of the electrocatalysts for the conversion of CO₂ have been subject to intensive investigations, aiming at the electrosynthesis of C1 or C2 fuels on metallic electrodes.^{1,}

^{2, 3, 4} A generic electroreduction of CO₂ is a proton-coupled electron transfer reaction,⁵ $\text{CO}_2 + \text{H}^+ + \text{e}^- \rightarrow \text{fuels}$, which competes with the hydrogen evolution reaction, $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$. The evolution of hydrogen via electrolysis is known to generally occur at a low overpotential.⁶ Hence, an effective electrocatalyst for CO₂ conversion must be sluggish towards hydrogen evolution while exhibiting a low overpotential for CO₂ reduction in order to suppress hydrogen evolution and promote carbon dioxide reduction reaction. Copper (Cu) and tin (Sn) are known non-precious metallic catalysts which can meet the aforementioned requirements. Copper was found to be active towards the formation of hydrogen carbons and alcohols.^{1, 2, 5, 7} Tin exhibits a superior selectivity towards the formation of formate (HCOO^-) with a Faradaic efficiency up to 98%.⁸ A rapid performance degradation was observed in both Sn- and Cu-based electrodes after approximately 30 minutes from the start of CO₂ electrolysis.^{9, 10, 11, 12} Hypotheses for the origin of the deactivation of CO₂ reduction electrode included the formation of intermediates like oxide, hydroxide^{1, 13} and carbon species^{2, 3}, as well as the accumulation of a soluble CO₂ reduction product in the electrolyte causing a remarkable decrease in the selectivity¹⁴. Hori et al.¹⁵ examined the deactivation of Cu electrode and postulated that the degradation of cell performance was originated from the deposition of iron and zinc contaminants in the electrolyte on the active surface of the catalyst.

Results and discussion

We found that impurity alone could not explain the degradation of the electrode performance. **Figure 1a** shows the Faradaic efficiency towards the formation of CO, HCOO^- , and H₂ as a function of time with **Sn electrodes in a pre-purified electrolyte** in a full electrochemical cell (**Figure S1**). The selectivity of Sn electrode towards the formation of HCOO^- was found to decrease from 90% to 50% during a 60-hour operation, regardless of the purity of the electrolyte (**Figure S2**). **The total current density preserved with 17 mA cm⁻² at applied cell potential of -2 V over the long-term running (Figure 1b).** Initial research focused on the identification of the origin of selectivity degradation by examining the evolution of the electrode microstructures. During long-term operation, Sn catalytic particles were observed to undergo changes in both morphology and size. **Figure 2** are transmission electron microscopy (TEM) images illustrating the temporal evolution of the size and shape of Sn catalysts. Pulverization of catalyst particles was observed in the electrode operated for 3-hour electrolysis, during which the originally spherical Sn particles (~100 nm) evolved into smaller particles with irregular shapes. The size of Sn-catalyst particles

rapidly decreased to 20-30 nm after 7 hours and 4-5 nm after 15-hour electrolysis. Afterwards, the rate of pulverization became slow, and the size of Sn-particles evolved to ~ 3.5 nm after 30 hours. The particles were further pulverized into ones with average size of ~3 nm beyond the 30-hour electrolysis. This morphological and size evolution as shown in the TEM images is consistent with the observations by using scanning electron microscopy (**Figure S3**), which show the agglomeration of nanoparticles in the electrode after 60-hour electrolysis. The pulverized Sn nanoparticles are more easily to be oxidized when exposed to the air as revealed by the high resolution TEM and X-ray photon spectroscopy results (**Figure S4 and S5**).

The close relationship between the pulverization of catalyst particles and the degradation of electrode performance manifests the structural origin for the decrease of the Faradaic efficiency of HCOO^- . The chemical origin, however, still remains unclear and requires further studies. In order to unravel the chemical origin of the degradation of Faradaic efficiency, we measured the impedance response of the full electrochemical cell. The pulverization was observed to play a significant role on the Ohmic impedance. During the long term operation, an increase in Ohmic area specific resistance (ASR) of the full electrochemical cell was observed (**Figure 3a**). The Ohmic ASR increased by 49% from an initial value of $22.7 \Omega \text{ cm}^2$ to $33.7 \Omega \text{ cm}^2$ after 60 hours. The increase in Ohmic ASR resulted in the decrease of cathodic potential because a constant cell potential was applied on the full electrolysis cell. **Figure 3b** shows the measured cathodic potential as a function of time. The decrease of the cathodic potential value was observed to accompany with a decrease in the Faradaic efficiency towards the formation of HCOO^- ⁸. When the initial Ohmic ASR was $22.7 \Omega \text{ cm}^2$, the cathodic potential was -1.4 V vs. Ag/AgCl and the Faradaic efficiency for HCOO^- was 90%, consistent with the results observed in a three-electrode cell⁸. At the end of the operation, the Ohmic ASR of $33.7 \Omega \text{ cm}^2$ resulted in a cathodic potential of -1.0 V vs. Ag/AgCl and 50% Faradaic efficiency, which also agree with our previous observations⁸.

A pulverization-induced increase in Ohmic resistance has been reported in the electrodes for lithium ion batteries due to the cyclic insertion and extraction of lithium ions^{16, 17, 18, 19}. The pulverization process continues until the particle reaches a critical size, at which the stress due to ion insertion is compensated by an increasing surface free energy of the smaller particles^{20, 21, 22}. The selectivity degradation due to electrode pulverization in fuel cells or electrolyzers has not yet

been reported in literature, even though hydrogen diffusion into metallic particles is a ubiquitous phenomenon. The diffusion process of hydrogen into Sn electrode can be expressed as follows.²³ Hydrogen ion initially adsorbs on the electrode surface to generate hydrogen ad-atom during the initial charge transfer step (Eq. [1]). Due to a sluggish kinetics for the hydrogen evolution (Eqs. [4] and [5]) on Sn electrode, the hydrogen ad-atoms diffuse into the bulk of solid phase, forming a solid solution in the host lattice (Eqs. [2] and [3]). This hydrogen insertion creates stress and subsequently results the fracture of Sn particles.

1. Electrosorption-desorption of hydrogen at Sn surfaces:

2. Hydriding-dehydriding of the solid-phase (solid state transfer of hydrogen):

3. Evolution of molecular hydrogen:

Theoretical calculation was carried out by computing the bulk strain energy per unit surface area total bulk strain energy and compare it with the surface energy, $\gamma(r)$ ^{22, 24}. The bulk strain energy density is accumulated as a result of the elastic deformation for the isotropically deformed sphere as²⁴

$$e(r) = \frac{1}{2E} (\sigma_r^2 + 2\sigma_{\theta}^2) - \frac{\nu}{E} (2\sigma_r\sigma_{\theta} + \sigma_{\theta}^2) \quad [6]$$

Where E is Young's modulus, ν is Poisson's ratio, and σ_r and σ_{θ} are the radial and tangential components of the stress tensor, respectively. The total bulk strain energy (G) could be obtained by integrating the bulk strain energy density over the whole sphere:

$$G = \frac{2\pi R^3}{E} \int_0^1 [(\sigma_r^2 + 2\sigma_{\theta}^2) - 2\nu(2\sigma_r\sigma_{\theta} + \sigma_{\theta}^2)] x^2 dx \quad [7]$$

To calculate the critical particle size, the bulk strain energy per unit surface area is calculated based on the bulk strain energy density and equals to the surface energy:

$$\gamma(r) = \frac{R}{2E} \int_0^1 [(\sigma_r^2 + 2\sigma_{\theta}^2) - 2\nu(2\sigma_r\sigma_{\theta} + \sigma_{\theta}^2)] dx \quad [8]$$

The calculation shows the maximum strain energy per unit surface area drops to close to zero when the particle size reaches ~3 nm so that the pulverization of Sn particles stops (**Figure S6**). The congruence between calculation and experimental observation in critical size shows that nanosized Sn catalysts (e.g. ~3 nm) can provide a stable performance due to the lack of particle disintegration. Unfortunately, Sn possesses a thin protective oxide layer at the surface to prevent further oxidation even though Sn is considered as a poor metal because of its higher electronegativity than most transition metals. Our previous work showed that Sn particles of 100 nm had a ~3.5 nm oxide scale. Therefore Sn nanoparticles with an average size of 3 nm may not be stable in air, nor during the subsequent electrode fabrication processes. As a result, SnO₂ nanoparticles (~3 nm) were chosen. Detailed characterization of nanometer SnO₂ can be found from the supplemental materials (**Figure S7**).

The Faradaic efficiencies of CO and HCOO⁻ for nanosized SnO₂-electrode were monitored periodically during the long-term test. Three independent electrodes were measured with their data matching with each other, showing highly reproducibility of the cell components in our research.²⁵ The initial increase in Faradaic efficiencies of CO and HCOO⁻ may be attributed to the gradually SnO₂ reduction to Sn accompanying the CO₂ reduction, but requires further study. The Faradaic efficiencies of CO and HCOO⁻ stabilized at 6% and 70%, respectively (**Figure 4a**). The current density was nearly constant at ~12 mA cm⁻² over 174 hours (**Figure 4b**). The improved stability of performance for nanosized catalysts was attributed to the reduction of pulverization (**Figure S7**). Consequently, the cell Ohmic resistance increased slightly from an initial value of 22.5 Ω cm² to 25.2 Ω cm² after 174-hour electrolyte, as shown in **Figure S8**.

Conclusion

In summary, the degradation of selectivity of Sn particles towards CO₂ reduction is accompanied with pulverization. The decrease of the selectivity towards CO₂ reduction, especially for the HCOO⁻ production, is attributed to the decrease of the cathode potential resulted from an increase in Ohmic resistance during pulverization process. These results have two consequences. First, the successful understanding of the performance degradation will enable the design of electrodes for the electrochemical conversion of CO₂ over long durations, during which the hydrogen diffusion induced stress plays a key role in the catalyst structural evolution. This is especially important in light of the fact that our understanding of artificial photoelectrosynthesis needs to advance. Second,

the use of nanosized catalysts can suppress the pulverization and thus enables a stable and active performance of the electrode for the electrochemical conversion of CO₂ to fuels.

Methods

The CO₂ reduction was operated in a custom-designed full electrochemical cell which featured a circulating liquid-phase buffer layer residing between an ion exchange membrane (Nafion[®] 212, Dupont) and the cathode Sn GDE. The detailed cell configuration and electrode preparation were reported as previously⁸. The Sn catalyst layer is made up of 100 nm Sn particles (Alfa Aesar) with Sn loading of ~2 mg cm⁻². The stability of Sn GDE for CO₂ reduction in the full electrochemical cell was tested at a constant cell potential of -2.0 V controlled by a Solartron 1470E potentiostat/galvanostat. The SnO₂ GDE is comprised of 3 nm SnO₂ nanoparticles (Nano Oxides Inc.) and tested under the identical experimental conditions. The individual electrode potential was monitored periodically with respect to the reference electrode Ag/AgCl in the buffer layer during cell operation. An impedance test was initiated before the stability test then again periodically throughout the stability tests to monitor the Ohmic resistance of the full electrochemical cell. The impedance measurement was performed at a constant cell potential of -0.8 V within the frequency range of 100 kHz-0.1 Hz by a Solartron 1255B frequency response analyzer connected to the Solartron 1470E potentiostat/galvanostat. The amplitude was set at 5% of the cell potential.

The conventional stability test was conducted with an electrolyte of 0.1 M KHCO₃ (Sigma Aldrich, ACS grade) circulating within the buffer layer at 7 ml min⁻¹. As a control, the full electrochemical cell was also tested with a pre-electrolyzed 0.1 M KHCO₃ which was purified by a Pt foil (Alfa Aesar, 4×4 cm²) working electrode at -2.5 V vs. Ag/AgCl in a traditional three-electrode cell. For both tests, the electrolyte was withdrawn for nuclear magnetic resonance (NMR) analysis and periodically replaced with a fresh one. The gas-phase product was quantified by a gas chromatograph (GC) (Inficon Micro 3000 GC) as described previously. A GC run was initiated every 3 minutes in the first 10 min and then every 15 minutes during the rest of the stability test. The quantification of liquid-phase product in the electrolyte was accomplished periodically using a Varian Mercury/VX 400 MHz NMR spectrometer.

Transmission electron microscopy (TEM) images were taken in an H-9500 300 kV transmission electron microscope (Hitachi, Japan). Scanning electron microscopy (SEM) images and energy-dispersive X-ray spectra (EDS) were acquired with a Zeiss ultra plus thermal field emission SEM instrument (Carl Zeiss SMT AG, Germany). Powder X-ray diffraction (XRD) patterns were obtained with a Rigaku D/MAX2500 X-ray diffractometer. X-ray photoelectron spectra (XPS) were obtained with a Kratos AXIS Ultra DLD XPS microprobe equipped with a hemispherical energy analyzer and a monochromatic Al K α source.

Acknowledgements

The authors would like to thank NSF-SSMC program and US Department of Energy for supporting this program. Dr. Haijun Qian in the Electron Microscope Facility at the Clemson University helped us with TEM measurements and analysis.

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Figure 1. Sn-based gas diffusion electrode performance over 60-hour operation in a full electrochemical cell with a high purity 0.1 M KHCO₃ at -2 V cell potential, room temperature and ambient pressure. (a) Faradaic efficiency towards the formation of HCOO⁻, CO and H₂. (b) Recorded total current density. The cathode and anode compartment was supplied with CO₂ at 45 ml min⁻¹ and H₂ at 150 ml min⁻¹, respectively. The 0.1 M KHCO₃ solution was pumped to the buffer layer at 7 ml min⁻¹.

Figure 2. TEM image of morphology and size evolution of 100 nm Sn particles during a long-term operation.

Figure 3. (a) Electrochemical impedance spectra of the full electrochemical cell measured as a function of time, and (b) measured cathode potential during the long-term operation.

Figure 4. Nanoized SnO₂-based gas diffusion electrode performance over long-term operation. (a) Faradaic efficiencies towards the formation of CO, HCOO⁻ and H₂ as a function of time. (b) Representative total cell current density. Three full cells were operated to investigate the reproducibility. The cell was operated at -2 V with as-received 0.1 M KHCO₃.

Dr. Jingjie Wu received his Ph.D from the University of South Carolina in Chemical Engineering. Currently, he is a Postdoctoral Fellow at Rice University in the Department of Materials Science and NanoEngineering. His research interest is in materials synthesis in atomic/nano-scale and catalysis for green energy conversion.

Dr. Shi-Gang Sun received Doctorat d'Etat (Docteur ès Sciences) in 1986 from Université Pierre et Marie Curie (ParisVI), and then carried out one year post-doctoral research at the Laboratoire d'Electrochimie Interfaciale du CNRS, France. He is a professor at the State Key Laboratory of Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Xiamen University, China, a Fellow of the Royal Society of Chemistry, UK, and a Fellow of the International Society of Electrochemistry. His research interests include electrocatalysis, electrochemical surface science, spectroelectrochemistry, and electrochemical energy conversion and storage.

Dr. Xiao-Dong Zhou received his Ph.D. from the University of Missouri-Rolla in Ceramic Engineering. Currently, he is an Associate Professor in the Department of Chemical Engineering at the University of South Carolina. His research interests focus on synthesis, characterization and theoretical understanding of materials and interfaces for batteries, fuel cells, and thermoelectrics devices.

Graphical Abstract

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