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Electrocatalytic reduction of CO_2 gas at Sn based gas diffusion electrode

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ABSTRACT

The tin (Sn) based gas diffusion electrode was fabricated and applied for CO_2 electroreduction in a zero gap cell. The fabrication was done by electrodeposition from a simple citrate–chloride plating solution by chronoamperometric method. The electrode showed good stability during CO_2 reduction even though the conversion of CO_2 into formate reached only 18% faradaic efficiency during the initial 5 min and maintained about 12% until the end of the reduction time of 1 h.

1. Introduction

Technologies to reduce greenhouse gas emisions especially the CO_2 gas has been carried out through a variety of methods. One of such methods is electroreduction which has been carried out in different media such as aqueous [1] and gaseous phase [2]. The reduction process necessitates the use of specific metal catalysts due to their product selectivity [3]. To improve the reduction process, gas diffusion electrodes has been previously reported to alleviate mass transport limitations across the gas liquid interface and to the catalyst surface [4]. In addition, the gas diffusion electrodes has been reported to allow good distribution of the gaseous reactants over the surfaces of the catalyst while providing low current density with high current efficiency for the formation of desired products [5,6]. Therefore, there is a potential of using the gas diffusion electrodes in Zero gap cell configuration due to its attractiveness in terms of its compactness, scalable and potential for onsite application [6].

The CO_2 gas has been reported to be electroreduced into formic acid in aqueous solutions on metal electrodes such as Sn and Pb [7–10]. The Sn [10] electrodeposited on copper mesh has been recently applied in a pilot scale for CO_2 electroreduction into formic acid. However, Sn electrodeposited on carbon substrates for application as gas diffusion electrodes for gaseous CO_2 reduction has been hardly reported.

Sn has been commonly electrodeposited from complicated solutions with one or several additives [11,12]. We aimed at fabricating the Sn electrode (GDE) using carbon paper as a gas diffusion media. However, the growth process of crystallites has been previously reported to depend on the nature of additive, substrate, experimental conditions such as initial additive/metallic ion concentration ratios and applied overpotential [12–14]. In order to monitor the process effectively, the simple electrodeposition was done from a solution containing a single additive of citrate ion.

The work described below is one of our ongoing activities aimed at applying gas diffusion electrodes for gaseous CO_2 conversion into valuable chemicals and fuels. This contribution is focused on applying the Sn based gas diffusion electrode, able to realize the low temperature reduction of the gaseous CO_2 into formic acid in a zero gap cell. In this configuration, the CO_2 gas was saturated with water vapor that acted as both a catholyte and participant for the hydrogenation.

2. Experimental

The plating solution was freshly prepared from 0.036 M $SnCl_2.2H_2O$ (Sigma Aldrich) and 0.05 M $Na_3C_6H_5O_7$ (Sigma Aldrich). The plating solution was degassed by applying N_2 gas for 15 min. The working electrode was a carbon paper (9 cm^2, Toray 170, E-TEK)

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mounted on the Pt current collector. The Ag/AgCl and Pt coil was used as reference and counter electrodes, respectively.

The electrochemical deposition experiments were carried out in a conventional three-electrode cell connected to a potentiostat (PGSTAT 302N). The electrodeposition was done under a constant potential mode of −0.85 V. The morphology and phase of the crystallites were examined by Field Scanning Electron Microscope (FE-SEM, Hitachi, S-4700) and X-ray diffraction (XRD, Rigaku Miniflex II).

The cell configuration was CO_2 (50 ml/min)/Sn/Nafion 117/Pt/H_2 (10 ml/min) + N_2 (90 ml/min), operated at a potential of −1.6 V at 40 °C for 1 h. The gas flow and operational temperature was monitored during the reduction reaction. The CO_2 gas was supersaturated with water vapor (the catholyte in this reduction process). The reduction product was collected at intervals and samples analyzed at 210 nm absorbance using a UV–Vis spectrophotometer (UV-1800 Shimadzu).

3. Results and discussion

Our goal was to fabricate an Sn based gas diffusion electrode and consequently apply it for the CO_2 electroreduction. As a first step, the electrodeposition potential was to be identified by voltammetry of the carbon paper in a plating solution. The electrodeposition potential was identified to be −0.55 V and could be done also with more negative values. In this experiment, we carried out the electrodeposition at −0.85 V.

The electrodeposition was done at a constant voltage mode for 1200 s and the resultant electroredeposits were characterized by SEM as shown in Fig. 1. The electrodeposits comprised of tetragonal shapes with large free areas of carbon surfaces of the gas diffusion media. This observation is in good agreement with the tendency of Sn electrodeposition on other carbon surfaces such as glassy carbon reported elsewhere [15]. In addition, a general pattern reported elsewhere of electrodeposists having a decay profile towards the interior of the electrode was also observed [13].

The composition and phase purity of the Sn gas diffusion electrode before and after the CO_2 electroreduction were examined by the X-ray diffraction as shown in Fig. 2(a) and (b) respectively. All the diffraction can be indexed to a tetragonal phase with a body centered lattice, having lattice constants of $a = 3.811$ A° and $c = 3.483$ A°, respectively. The orientations of this phase corresponded to ● (110), ▼ (101) and ■ (200). The intensity of these

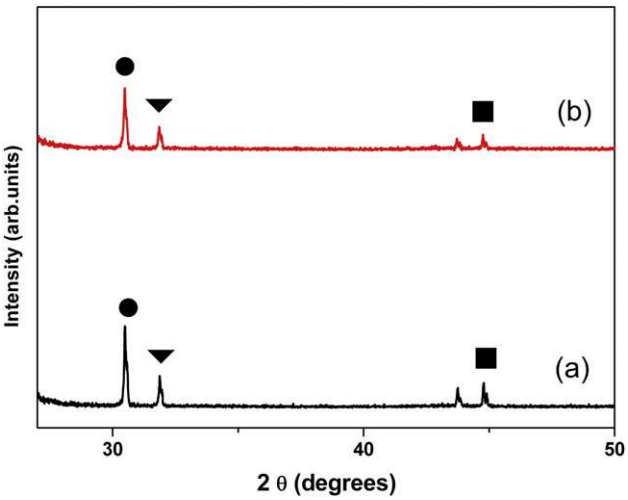

Fig. 2. XRD data of Sn electrode before (a) and after (b) the CO_2 electroreduction in a zero gap cell. The Sn tetragonal phase with their corresponding orientations in brackets are ● (110), ▼ (101) and ■ (200).

peaks before and after the electroreduction was almost same reflecting little changes in weights that occurred.

The CO_2 electroreduction was carried out in a zero gap cell at −1.6 V for 1 h. The resultant reduction current profile is as shown in Fig. 3. Initial reduction current of about −5 mA/cm^2 decreased to about −2 mA/cm^2 at the first 10 s and maintained this level until the end of the experiment. Similar reduction current has been reported to support the CO_2 electroreductions, such as that with a faradaic efficiency of 70% obtained when the applied potential was −1.6 V in 2 h [16].

The CO_2 gas was reduced over Sn GDE and gave the formate amounts as shown in Fig. 4. The production rate was high in the first 500 s that gave about 0.09 mg/s (equivalent to 45 mg/L) and reached a faradaic efficiency of 18%. However, the rate decreased for the next 500 s to about 0.05 mg/l and maintained this value until the end of the experiment with a faradaic efficiency of 12%. The lower efficiency obtained might be attributed to the number of reasons such as the amount of the catalyst electrodeposited on the gas diffusion media, and probably some side reactions and deactivation of the catalyst due to prolonged CO_2 reduction. This reaction

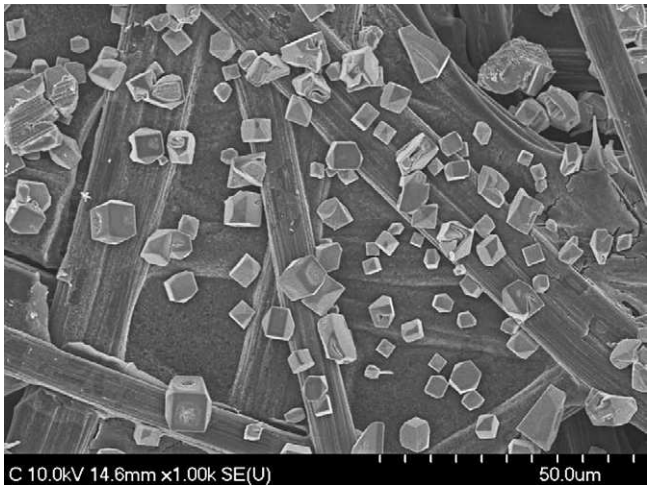

Fig. 1. SEM images of an Sn gas diffusion electrode prepared from 0.036 M $SnCl_2.2H_2O$ + 0.05 M $Na_3C_6H_5O_7$ solution for 1200 s at −0.85 V.

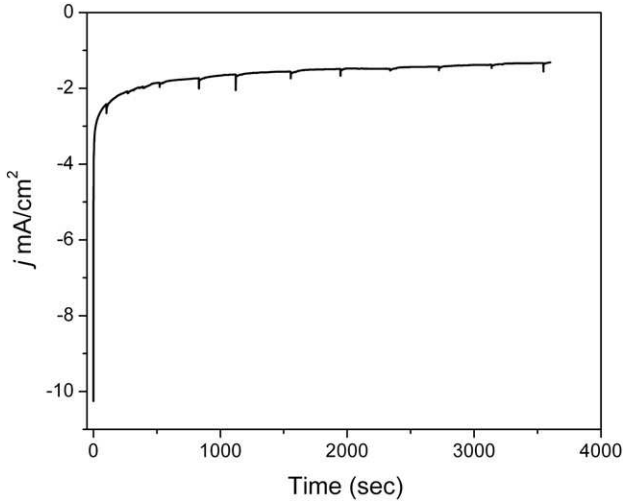

Fig. 3. The current profile obtained during CO_2 electroreduction at −1.6 V for 1 h.

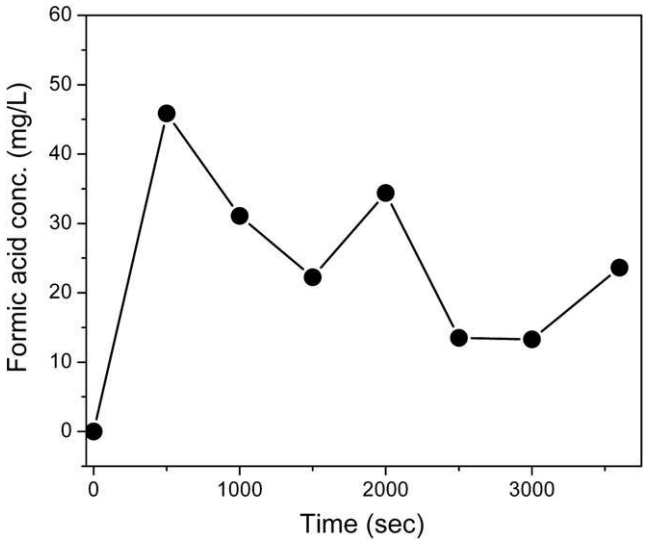

Fig. 4. Formic acid production rate on Sn based gas diffusion electrode applying −1.6 V for 1 h in a supersaturated water vapor catholyte.

was done at low operational temperature which might not have promoted much of the side reactions. Similar decreasing tendency have been reported previously by Hui and Oloman [10], who observed a decrease from 70 to 39% of faradaic efficiency in 100 min and attributed the results to several reasons such as washing away of the Sn electrodeposits on the Cu mesh, competitive hydrogen evolution reaction and deactivation of the catalysts due to exposure to concentrated CO_2 gas and prolonged electroreduction.

From the results in Fig. 4, we can see that the Sn initially showed better and stable production of formate than that of the Pb GDE [14]. This may be attributed to the stability of the electrodeposited Sn catalyst on the carbon paper. As shown in Fig. 2(b), the crystallite orientations and intensities remained almost the same before and after the reduction experiment. This is different to some of the previous work on Pb [17] and Sn [10] gas diffusion electrodes. In order to promote and increase the performance of the electrode, more efforts to make a uniformly distributed Sn catalysts on the carbon paper are needed. This might have a profound effect on the conversion efficiency and also stability.

4. Conclusion

We successfully prepared an Sn based gas diffusion electrode for CO_2 electroreduction. The faradaic efficiency was about 18%. Even though the formate production was relatively low, the electrode was stable as supported by the XRD analysis and production rate. Therefore to improve the catalytic reaction rates, uniformly distributed catalysts on the electrodes might be beneficial. We also hope that, alloying of Sn with a uniformly electrodeposited metal on carbon paper such as Pb, that gives the same reduction products in the same media is important and might be a viable alternative to undertake.

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