



Short communication

Porous indium electrode with large surface area for effective electroreduction of N₂O

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ABSTRACT

Increasing the electrochemical surface area of electrocatalyst is important for achieving high Faradaic efficiency with rapid reaction rate in bulk electrolysis of gaseous reagents. Hence, we fabricated efficient and cost-effective porous indium foam for the electrochemical reduction of nitrous oxide by using electrodeposited copper foam as the template. Indium grew on the surface of copper foam, preserving the original porous foam structure. The electrochemical investigation on indium revealed a high selectivity and a fast reaction rate of indium foam electrode towards nitrous oxide electroreduction.

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1. Introduction

As a greenhouse effect gas, N₂O has a 310 times greater ability to trap the atmospheric heat than CO₂ [1–4]. Although the volumetric portion of N₂O among the greenhouse effect gases is merely 6%, the potential of N₂O for greenhouse effect is equivalent to 3 billion tons of CO₂, which is similar to 50% of the total car emissions worldwide [2,5]. Therefore, various chemical processes have been developed for the decomposition of N₂O [1–3,6]. Most of these processes are applicable for industrial fields because they usually require a heat source for the temperature elevation to the point where N₂O decomposition can occur. However, such high-temperature processes are inadequate for the decomposition of N₂O generated at room temperature in the biological and medical fields [7–11]. Considering these facts, extensive research for alternative approaches, especially those involving electrochemical N₂O reduction, have been studied [8–11].

Electrochemical N₂O reduction reaction (NRR) is thermodynamically favorable with high standard reduction potential value ($E^\circ = 1.76$ V vs. SHE at 298 K) [8–11]. Nevertheless, the rate of NRR depends on the concentration and mass transfer rate of N₂O in the electrolyte, adsorption of N₂O, and desorption of the produced N₂ (or H₂, evolved by water electrolysis) [8–10]. Because the latter two factors are affected by the electrode material and structure, the development of effective catalyst for NRR with increased surface area is essential.

Among various metallic catalysts applicable for NRR, Pd is known to exhibit ~100% Faradaic efficiency for the NRR [8,9]. Unfortunately, it is improper to use Pd in practice because of its extremely high cost.

One possible replacement candidate for Pd can be In because In also completely converts N₂O to N₂ [8]. Moreover, as In and its alloys are stable in alkaline condition [12,13], applications of In for the cathode material of NRR are promising because NRR is more favored than H₂ evolution in alkaline condition [9,14]. Therefore, nanoporous three-dimensional (3D) In foam was formed by the electrodeposition method, motivated by the fact that a nanoporous 3D foam structure has great potential for rapid electrochemical reactions with excellent stability [15–23]. Instead of direct In foam fabrication, however, 3D Cu foam was introduced as the template for In electrodeposition to minimize the loading amount of In.

Simple and well-developed hydrogen bubble template electrodeposition methods have been utilized for the 3D metal foam formation [16, 17,21–23]. Despite various studies having successfully prepared single [16,19] or alloy [17,20] metal foams by using the method, functional material decoration on the foam template has not yet been much investigated. The surface modification of the foam template with noble metals such as Ag, Pd [18], and Pt [21–23] have been attempted using spontaneous galvanic replacement procedure. However, because the galvanic replacement has limitations about material selection and concerns for substrate deterioration during the replacement [24], the electrodeposition method was used for the coating of the foam template with less noble but more precious metal. Herraiz-Cardona et al. reported a covering of Cu foam with Ni by electrodeposition method [25]. Although they reported pronounced performance of fabricated foam over the hydrogen evolution reaction, lack of Ni loading amount control and Ni coverage estimation resulted in the partial blockage of the original nanopores and even the macropores after Ni electrodeposition.

In this study, the original nano- and macroporous structure of Cu foam template was conserved despite complete In coating without

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forming any pinhole, by means of systematically controlled electrodeposition method. The deposition amount of precious In metal was minimized, accomplishing the main purpose of the fabrication of economic and effective catalyst for NRR.

2. Experimental

All the electrochemical experiments were performed at 25 °C with saturated calomel reference and Pt wire counter electrodes. However, the potentials reported in the manuscript are converted with respect to the reversible hydrogen electrode (RHE), represented by the following equation:

$$E_{\text{RHE}} = E_{\text{SCE}} + 0.059\text{pH} + 0.241$$

A Si wafer covered with 50 nm of Cu film was used as the substrate for the experiment and cut into $1.5 \times 1.5 \text{ cm}^2$ pieces, and loaded to a homemade electrochemical cell which enclosed the substrate. The exposure area of the specimen to the electrolyte was 1 cm^2 . Before the electrodeposition of Cu foam or In, the native oxides of substrate were removed by the cathodic polarization process (5 mA cm^{-2} , 5 min) in 0.1 M H_2SO_4 solution.

A Cu foam template was fabricated via the hydrogen bubble template electrodeposition method. Cu foam was deposited by applying 3 A cm^{-2} of cathodic current for 7 s in electrolyte consisting of 0.4 M $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 0.6 M $(\text{NH}_4)_2\text{SO}_4$, and 0.7 M H_2SO_4 . During the formation of the Cu foam, the electrolyte was continuously agitated by a centrifugal stirrer to inhibit the growth of long metallic dendrites [17,18]. The In electrodeposition was conducted on the Cu substrate using an electrolyte containing 0.5 M HClO_4 and 0.05 M InCl_3 . From the preliminary experiments, potentiostatic In electrodeposition was optimized by varying the applied potential and charge by observing surface roughness and uniformity, which was set as -0.5 V and 30 mC cm^{-2} (corresponding to 15 nm cm^{-2} thick In deposits on a flat Cu substrate), respectively.

Cyclic voltammetry (CV) experiments were conducted at a scan rate of 50 mV s^{-1} to verify the coverage of the electrodeposited In and to investigate the electrochemical activity of In towards NRR. Moreover, potentiostatic electrolysis was carried out to evaluate the long-term stability of In electrodes. Both experiments were performed in an electrolyte containing 0.5 M NaOH. For the verification of In coverage, the electrolyte was deaerated by N_2 purging. In contrast, during the NRR activity and long-term stability tests, the solution was saturated with N_2O by continuous N_2O purging.

The surface analysis of the specimen was conducted by field-emission scanning electron microscopy (FESEM; S-4800, Hitachi). The composition of the deposit was evaluated by energy-dispersive X-ray spectrometry (EDS, INCA Energy, Oxford Instruments Analytical Ltd.). A potentiostat (VersaStatII, EG&G) was used for the electrochemical measurement and deposition.

3. Results and discussion

In is liable to diffuse into Cu and forms intermetallic Cu–In compound even at room temperature [26,27]. Because the intermetallic Cu–In compound reduces the Faradaic efficiency of NRR [8], the substrate surface should be completely covered by metallic In. Hence, the surface morphology and coverage of Cu film and In-deposited Cu film (In/Cu film) were analyzed by FESEM and CV. The comparison of the FESEM analyses results shown in Fig. 1(a) and (b) show that both surfaces are distinct but uniform change in the morphology was observed after performing the potentiostatic In deposition on Cu. Moreover, the In/Cu film did not show corresponding peaks relevant to Cu oxides reduction (0.4 V and 0.12 V with a shoulder) and formation (1.0 V with a shoulder) during the CV analysis as in Fig. 1(c). Instead, the reduction of In hydroxide and oxide (cathodic scan, -0.33 V and -0.46 V) and an oxidation peak attributed to the dissolution of In (anodic scan, -0.14 V) were observed on the In/Cu film [12,13,26]. Any current peak related to the dissolution of In from Cu–In intermetallic

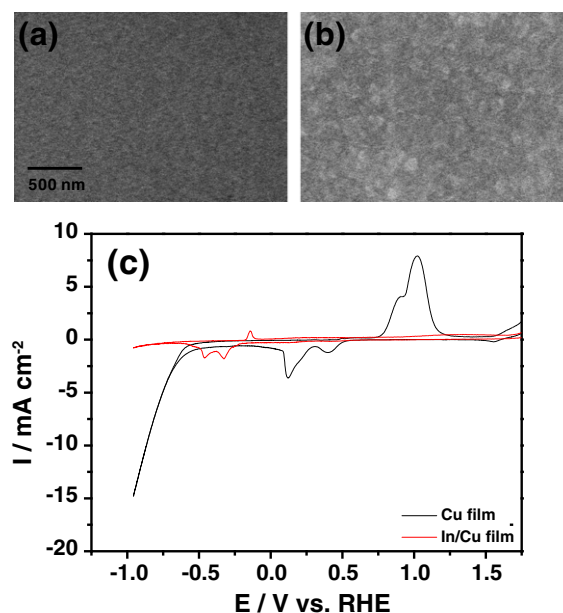


Fig. 1. (a, b) FESEM surface analyses of (a) Cu and (b) In/Cu films and (c) CV analyses on the Cu and In/Cu films. For the CV experiments, the 0.5 M NaOH electrolyte was purged with N_2 .

compound was not detected near 0 V during the anodic scanning [26], indicating that the surface of the In/Cu film exposes only metallic In.

Subsequently, a porous In foam was fabricated via the electrodeposition of In onto a Cu foam template. Regular Cu foam template was well formed on the Cu film substrate as shown in Fig. 2(a–c). Prior to the electrodeposition of In on a Cu foam, however, the deposition amount should be adjusted considering the roughness factor (R_f). The R_f of a foam electrode was evaluated by comparing the double-layer capacitance with that of a film ($25.7 \mu\text{F cm}^{-2}$ for Cu and $31.6 \mu\text{F cm}^{-2}$ for In/Cu) electrode. To measure the double-layer capacitance of the electrode, CV was performed in a 0.1 M HClO_4 electrolyte in a potential range where no Faraday reaction occurred. The averaged current density was plotted against the scan rate, and the slope of the linear regression gave the double-layer capacitance of the foam electrode [19,28]. Consequently, the deposition amount of In was adjusted to 6 C cm^{-2} , because the R_f of the Cu foam template was measured as 216.

The surface morphology and composition were compared between Cu foam and In-deposited Cu foam (In/Cu foam). As shown in Fig. 2(d) and (e), the morphology of Cu foam was retained after the In electrodeposition. Moreover, the EDS mapping result indicated that In distributed on the specimen resembling the foam structure (Fig. 2(f)). The additional roughening of the surface by In electrodeposition increased the R_f of In/Cu foam to 242.

Complete exposure of In was also observed on the In/Cu foam. The coverage of In on In/Cu foam was also determined by CV. Unfortunately, large current related to the surface oxide formation and reduction prohibited accurate surface analysis, especially when the Cu foam was evaluated (Fig. 3, inset). Therefore, the starting point of CV analysis was set to the open circuit potential (OCP) of the specimen, and a potentiostatic surface oxide reduction was conducted at a potential of -0.05 V (vs. OCP of specimen) for 15 min prior to the measurement. Consequently, similar polarization behavior was observed on Cu foam as on a Cu film substrate; residual oxides reduction progressed at 0.5 V and H_2 started to evolve at -0.25 V (Fig. 3, black line). In contrast, OCP of foam template shifted to $\sim 0.2 \text{ V}$ after In electrodeposition and the current related to the Cu oxides reduction was not observed on the In/Cu foam, irrespective of the starting point of CV scanning (Fig. 3, red and blue line). Instead, In hydroxides or oxide reduction currents appeared from -0.1 V , as on the In/Cu film.

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