Pulse Plating of Copper onto Gas Diffusion Layers for the Electroreduction of Carbon Dioxide

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ABSTRACT

This paper discusses a pulse electroplating method for preparing copper (Cu)-coated gas diffusion electrodes (GDEs) for the electrochemical conversion of carbon dioxide (CO_2) to hydrocarbons such as ethylene. Ionomer coating and air-plasma surface pre-treatments were explored as means of hydrophilizing the carbon surface to enable adhesion of electrodeposited material. The pulsed-current electrodeposition method used successfully generated copper and copper oxide micro- and nano-particles on the prepared surfaces. Copper(I) species identified on the ionomer-treated GDEs are presumed to be highly active for the selective generation of ethylene as compared to other gaseous byproducts of CO_2 reduction. Conversely, copper catalysts deposited onto plasma-treated GDEs were found to have poor activity for hydrocarbon production, likely due to substantial metallic character. Of note, plasma treatment of an ionomer-treated GDE after copper plating yielded further improvements in catalytic activity and durability towards ethylene production.

INTRODUCTION

Utilizing carbon dioxide (CO_2) as a chemical feedstock has been identified as a means of reducing greenhouse gas emissions and moving towards a carbon neutral energy cycle [1]. A promising approach for CO_2 conversion is electrocatalytic reduction to selectively generate hydrocarbons such as ethylene and propylene that are the primary building blocks of the petrochemical industry. The production of these precursors by conventional means from petroleum feedstocks is energy intensive, requiring high temperatures and pressures [1]. Hence, electrochemical methods, which can operate at milder conditions, represent a potentially less expensive and sustainable alternative, provided key performance metrics are realized [2]. Prior reports have demonstrated electroreduction of CO_2 to hydrocarbons on copper (Cu)-coated gas diffusion electrodes (GDEs) to obtain ethylene (C_2H_4). For example, Ma *et al.* reported a partial current density of 140 mA/cm^2 to C_2H_4 at a potential of -0.8 V versus the reversible hydrogen electrode (RHE) [3]. These studies have typically used Cu nanoparticles (NPs) that are mixed with an ionomer and spray-coated onto a microporous carbon layer (MPL)

supported by a carbon fiber substrate (CFS), to form a GDE; the composite substrate prior to catalyzation is termed the gas-diffusion layer (GDL). This approach limits the electroreduction process due to 1) low catalyst specific surface area of the relatively large Cu NPs (20-100 nm) [3], and 2) poor utilization of the Cu NPs, as not all particles are in electronic and ionic contact. Previous work directed towards platinum (Pt) catalyst utilization in polymer electrolyte fuel cell GDEs demonstrated an "electrocatalyzation" (EC) approach to obtain highly dispersed ~5 nm Pt NPs using pulse-reverse electrodeposition [4]. Additionally, since the Pt was electrodeposited through an ionomer that was pre-coated on the MPL surface, the resulting NPs were inherently in electronic and ionic contact within the GDE and the electrolyte respectively, thus improving material utilization. Such an EC approach has also been applied to tin-based GDEs for the electroreduction of CO_2 to formate, leading to a near two-fold increase in current density at about half the catalyst loading as compared to state of the art tin catalysts deposited via conventional means [5].

Herein the electrocatalytic performance of Cu-coated GDEs prepared by pulse-reverse electrodeposition of Cu onto commercial carbon paper GDLs was examined. The goal was to improve the Cu catalyst utilization by eliminating particles not in electronic contact with the GDL, as well as to explore methods to maximize selectivity for C_2H_4. Ionomer application and plasma treatment of the GDL substrate were explored as means to facilitate electrodeposition of Cu onto these highly textured surfaces via hydrophilization of the MPL. The effect of these pre-deposition GDL modifications as well as post-deposition plasma treatment on the magnitude and durability of C_2H_4 selectivity was examined, and correlated with observed differences in the resulting oxidation state of Cu. The EC samples were compared against commercial Cu NP catalysts prepared by conventional spray-painting methods (*vide infra*).

EXPERIMENTAL DETAILS

Materials and analysis

Sodium hydroxide (99.999%, Sigma Aldrich), LIQUion® 1100 EW (Ion Power Inc., 15% w/w), copper nanoparticles (70 nm, U.S. Research Nanomaterials), hydrochloric acid (37%, balance H_2O, Sigma Aldrich), copper sulfate pentahydrate (> 98%, Sigma Aldrich), sulfuric acid (95-98%, Chemical Services, Inc.), isopropyl alcohol (ACS reagent grade, Sigma Aldrich), H_2 (99.9%, Ultra High Purity 5.0, Airgas), CO_2 (99.99%, Research Grade 5.0, Airgas), platinum on Vulcan XC-72 (20 wt.%, Fuel Cell Store, College Station, TX), and gas diffusion layers (Sigracet GDL 39BC, Fuel Cell Store) were used as received. A mixed metal oxide (MMO) anode (Republic Anode, Valley City, OH) was used as the counter-electrode for electrodeposition of Cu catalyst layers. Electrolyte solutions were prepared using deionized water (>18 MΩ-cm). Scanning electron microscope (SEM) images were acquired using a Zeiss Merlin High Resolution microscope. X-ray diffractograms (XRD) were obtained using a Rigaku Smartlab instrument.

Preparation of conventional gas diffusion electrodes

Sigracet 39 BC GDLs were used as the substrate in this study. The baseline cathodes were spray-painted whereas the anode (Pt on Vulcan) was hand-painted; the catalysts for both were applied onto the MPL side of the GDL as per previously reported procedures [5, 6]. Typical loadings of the cathodes and anodes were ca. 0.35 ± 0.07

mg/cm^2 and 1 ± 0.15 mg/cm^2, respectively, as determined by weighing the samples before and after deposition.

Surface treatment of gas diffusion layers

Two pre-treatment methods were tested to hydrophilize the MPL surface before electrodeposition, buoyant floating on ionomer dispersion as per previously reported procedures [5] and treatment with air plasma. For air plasma treatment, the GDL samples were processed in a PDC-001 plasma cleaner (Harrick Plasma, Ithaca, NY) immediately prior to electrodeposition. The effect of different RF power settings and durations of plasma treatment was found to be negligible. Enhancements in catalytic activity towards hydrocarbon products have been recently reported at plasma-treated Cu nanomaterials [7, 8], where the role of copper (I) oxide was investigated and demonstrated to be critical for the production of hydrocarbons such as ethylene; hence, the effect on catalytic activity of plasma modification of an ionomer-treated GDL after electrodeposition was also studied.

Pulsed electrodeposition of copper onto pre-treated gas diffusion layers

Copper plating directly onto untreated MPL surfaces led to poor adhesion of the catalysts and hence pre-treatment (*vide supra*) was necessary. Catalyst electrodeposition was performed in a custom cell equipped with patented flow hardware for enhanced flow uniformity [9-12]. The cell was charged with a copper sulfate electrodeposition bath (5 mM CuSO$_4$ • 5H$_2$O and 100 g/L H$_2$SO$_4$) with continuous circulation at 7.57 L/min as measured by an inline rotameter (McMaster-Carr, Aurora, OH). GDLs were mounted in the custom holder and inserted directly into the electrodeposition cell. A set PR waveform was applied under current control for an identical period of time for all EC samples studied in this work. The waveform was similar to those described previously [13, 14]. The actual voltage and current responses of the cell were measured by oscilloscope (TBS-1052B, Tektronix, Salem, OR) to confirm the fidelity of the applied waveform and to calculate the actual net cathodic charge passed in each test. After plating, the Cu-coated GDEs were removed from the cell, gently rinsed with deionized water, photographed, and left to dry overnight in a fume hood. Catalyst loadings on the GDEs were determined by weighing the sample before and after deposition using an analytical balance (Symmetry PA-224E Analytical balance) with a precision of 0.1 mg. Cu loadings of 0.40 ± 0.04 mg/cm^2 were obtained across the three samples examined herein.

Electrolysis experiments and product quantification

Carbon dioxide electrolysis experiments were performed in a custom-built small-volume flow cell whose design was adapted from Milshtein *et al.* [15] and controlled by a VSP-300 Biologic multichannel potentiostat (Knoxville, TN). The active area of the working electrode (cathode) was 1 cm^2 with a counter electrode (anode) area of 2.55 cm^2. All potentials were measured relative to a Hg/HgO reference (+140 mV vs. SHE, CH Instruments Inc., Austin, TX) calibrated against a SCE reference (+242 mV vs. SHE, Fisher Scientific), which was placed in the middle of the 1/2-inch thick electrolyte flow compartment (ca. 0.5 cm from the cathode). CO$_2$ and H$_2$ were delivered to the cathode and anode GDEs, respectively, at a constant flow rate of 20 mL/min as determined by mass flow controllers (GF40, Brooks Instruments, Hatfield, PA). The liquid electrolyte (1 M NaOH) was circulated in a closed loop using a peristaltic pump (Masterflex L/S Series, Cole Parmer Inc., IL) between the flow cell and the 25-mL

reservoir at a volumetric flow rate of 2 mL/min. Gaseous products in the effluent gas stream from the cathodic half of the cell were injected via an automated sample loop into a gas chromatograph (GC; Agilent 7890, Foster City, CA). Electrolysis was performed at constant potential of -1.8 V vs. Hg/HgO (ca. -0.7 V vs. RHE) for 1 h, with samples taken for GC analysis at intervals of 12 min after initiating electrolysis. Liquid phase products were not analyzed. Currents reported throughout the manuscript are normalized to the geometric area of the cathode to obtain current densities (mA/cm^2). All experiments were carried out with 85% iR compensation (software controlled) and the remaining 15% was corrected post-run using cell resistance.

DISCUSSION

Physical characterization of copper-loaded gas diffusion electrodes

The aim of this work was to develop an EC technique to selectively deposit Cu catalyst particles onto regions of the electrode with both ionic and electronic accessibility. To ensure deposit adhesion to the carbon surface, hydrophilic character was imparted to the bare MPL of a commercially available gas diffusion layer (GDL) by either ionomer or plasma treatment. Pretreatment was followed by electrodeposition of Cu particles onto the MPL. Figure 1 presents optical images of the electrocatalyzed (EC) and conventional spray-painted (SP) electrocatalysts examined in this work. The spray coated sample (SP, Figure 1a), used as a baseline reference in this study, was visibly uniform, whereas the EC samples (Figure 1 b-d) were more heterogeneous with varying coloration, suggesting different oxidation states of the deposited Cu (i.e., metallic vs. oxide). As noted, the EC samples were prepared with the same electrodeposition parameters, but with different pre- and post-treatment protocols. Samples EC-I and EC-I-P were prepared by treating a bare GDL substrate with ionomer before electrodeposition, with the latter having an additional step of plasma treatment after Cu deposition. Sample EC-P was prepared by treating a GDL substrate with air plasma prior to Cu electrodeposition. Collectively, these four samples (SP, EC-I, EC-I-P, and EC-P) form the basis of comparison for the below preliminary evaluation of the effects of GDL treatment on the composition, morphology, and electrochemical activity of the deposited catalyst layers.
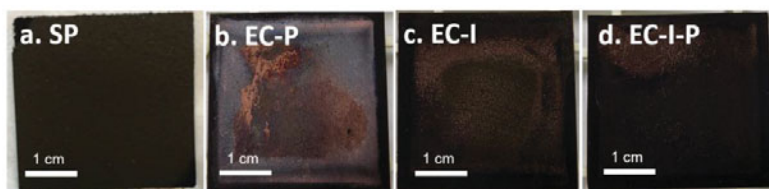

Figure 1. Optical images of Cu-loaded GDEs (a) SP: Spray coated commercial NPs; (b) EC-P: electrocatalyzed on plasma treated substrate (c) EC-I: electrocatalyzed on ionomer treated substrate; (d) EC-I-P: electrocatalyzed on ionomer treated substrate with post-deposition plasma treatment.

Figure 2 shows SEM images of the EC and SP samples at two different magnifications. Irregularly shaped particles with an average size of < 100 nm are visible for sample SP, consistent with the manufacturer specification of 70 nm, with larger micron-sized agglomerates visible at lower magnifications (Figure 2a,b). For samples

EC-I and EC-I-P, low magnification (Figures 2e,g) shows extensive areal coverage of the carbon substrate with catalyst particles both greater than and less than 5 μm in size. The higher magnification of Figures 2f and 2h shows the presence of nanoparticles in both samples (<< 1 μm). While sample EC-I had discrete cube shaped nanoparticles (< 200 nm), sample EC-I-P had a more fused nanostructure, which could be a result of the post-electrodeposition plasma treatment. Energy dispersive X-ray (EDX) analysis of sample EC-I is shown in Figure 3, confirming the co-location of Cu and O, and indicating the likely presence of a copper oxide phase. Sample EC-P (Figures 2c,d) exhibited a large number of micron-sized clusters, which had a fine structure but no discrete nanoparticles. Future efforts will focus on enhancing nucleation versus growth through optimization of the electrodeposition waveforms and thereby further decreasing the Cu catalyst particle size (<< 200 nm), as previously demonstrated for Pt [4, 13, 16].
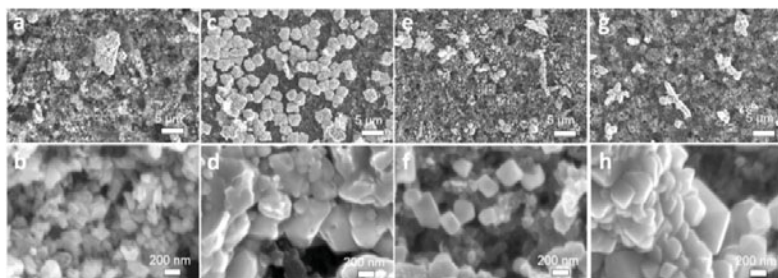

Figure 2. SEM images of Cu-coated GDEs as a function of pretreatments: (a-b) SP; (c-d) EC-P; (e-f) EC-I; (g-h) EC-I-P. Each column represents a different pretreatment, whereas the top and bottom rows show images at low (2500x) and high (60000x) magnification, respectively.
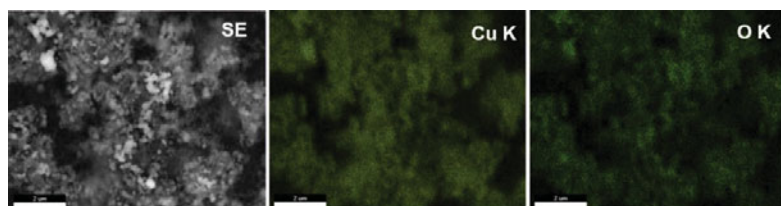

Figure 3. EDX analysis of sample EC-I at the Cu and O K-edges.

X-ray diffraction (XRD) spectra of these Cu-coated GDEs are shown in Figure 4 along with relevant database standards. The baseline sample (SP) shows clear peaks for Cu(II) species in addition to Cu(I) and metallic Cu species, likely due to aerial oxidation of the NPs during the catalyst ink preparation and spraying process. All EC samples showed distinctive peaks for either Cu metal or Cu(I) oxide, but no Cu(II) oxide, revealing a marked difference from the baseline. Sample EC-I showed a distinct peak for Cu(I) oxide, as did its plasma-treated analogue (EC-I-P); the latter exhibited a substantial amount of Cu metal as well. This indication of substantial amounts of both metallic and oxide phases in EC-I-P could be due to the post-deposition plasma treatment. Unlike the

other samples, the plasma pre-treated sample EC-P showed clear peaks for a metallic Cu phase with little oxide content.
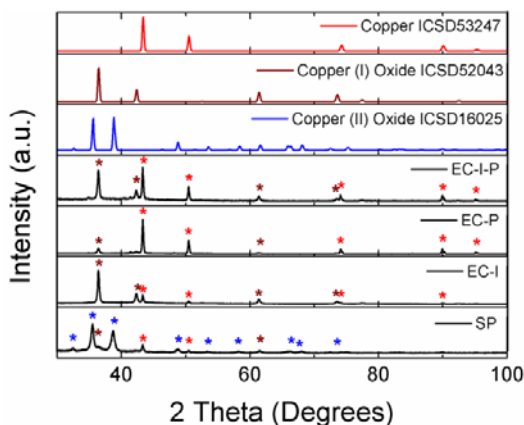
Electrochemical characterization of copper loaded gas diffusion electrodes

Figure 5a plots the partial current densities (PCDs) of the various gaseous products obtained after the first 12 min and at the end of 60 min of electrolysis at a fixed potential of -0.7 V vs. RHE. The baseline sample (SP) provided the largest PCD to C_2H_4 among the four samples tested, with a relatively small amount of H_2 as by-product, which is comparable to the recent literature at -0.7 V vs. RHE [3]. In contrast, the three EC samples generated appreciable amounts of H_2, with varying amounts of C_2H_4. Note that other EC samples than those shown in Figure 5 demonstrated superior performance to the SP baseline, but are not reported here as the focus of this work is the effect of GDL pre-/post-treatment. Sample EC-P generated very little C_2H_4 as compared to the other two EC samples, suggesting that pre-treatment of the carbon substrate with plasma had a distinctive and unfavorable effect on the product selectivity, likely due to the metallic Cu structures obtained, with little or no oxide content (cf. Figure 4). This is consistent with prior literature, which suggests that the Cu oxide phase plays a critical role in the production of C_2H_4 [17, 18]. Figure 5b shows the PCD to C_2H_4 obtained for the four samples as a function of time, with GC sampling performed every 12 min as noted above. While the SP baseline sample exhibited the largest C_2H_4 PCD at the outset, its C_2H_4 production rapidly declined over the course of the hour-long electrolysis (72% decrease). In contrast, samples EC-I and EC-I-P exhibited more modest decreases of 40% and 12%, respectively, over the same period. Interestingly, both samples EC-I and EC-I-P had similar activities at the 12-min sampling point, but the retention of that activity was noticeably superior for the latter. As noted above, enhancements in catalytic activity towards C_2H_4 have been reported at plasma-treated Cu nanomaterials [7, 8], consistent with our observations. Further work is required to develop an explanation for this difference in catalytic behavior.
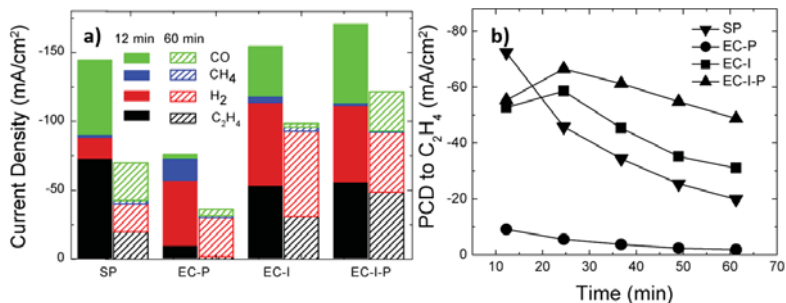
Figure 5. (a) Comparison of total current densities for gaseous products (liquid products omitted) obtained after the first 12 min and at the end of each 60-min electrolysis experiment. (b) Plot of partial current density (PCD) to C_2H_4 over the electrolysis tests of the same GDEs. All tests were conducted at a cathode potential of -0.7 V vs. RHE.

CONCLUSIONS

An EC process based on pulsed waveforms was used to electrodeposit Cu directly onto pre-treated GDLs. Ionomer treatment of the GDLs (EC-I, EC-I-P) allowed the successful deposition of Cu nanoparticles (< 200 nm) with substantial Cu(I) oxide content as determined by XRD measurements. In contrast, while plasma-treated GDLs (EC-P) also supported the deposition of micron-sized particles with a fine nano-structure, the deposits obtained were substantially more metallic in character. These EC electrodes were subsequently tested for their activity in the electroreduction of CO_2, with particular focus towards the generation of C_2H_4, and this performance was compared to that of a conventional spray-painted (SP) baseline GDE. While the ionomer-treated GDE produced amounts of C_2H_4 comparable to literature reports [3], the plasma-treated GDE produced substantially less C_2H_4. We attribute the observed difference in performance due to the presence of Cu(I) species on the ionomer-pretreated GDE, as previously reported for oxide-derived catalysts [18]. Changes in catalytic activities were also studied as a function of electrolysis time, and the electrodeposited GDEs exhibited a significant improvement in durability compared to the baseline. Additional performance enhancement may be attainable by significant reductions of the catalyst particle size, below 10 nm. The authors anticipate optimization of the electrodeposition pulsed waveform conditions will enable reductions on this order of magnitude, based upon prior experience with Pt electrocatalysts [4]. Future studies will focus on tailoring the pretreatment protocols, deposition parameters, and bath conditions (e.g., Cu concentration) to optimize the performance and durability of these electrodes.

ACKNOWLEDGMENTS

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