



Selective electroreduction of CO₂ to formate on Bi and oxide-derived Bi films



Erwan Bertin^a, Sébastien Garbarino^a, Claudie Roy^a, Sona Kazemi^b, Daniel Guay^{a,*}

^a INRS-Énergie, Matériaux Télécommunications, 1650 Lionel-Boulet Boulevard, P.O. 1020, Varennes, QC, J3X 1S2, Canada

^b BC Research, 12920 Mitchell Road, Richmond, British Columbia, V6V 1M7, Canada

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ABSTRACT

Bi and oxide-derived Bi films were prepared through potentiostatic electrodeposition on titanium substrates, and subsequent electrochemical and thermal oxidation. The morphology of the films was studied through scanning electron microscopy (SEM), and their structure was analyzed via x-ray photoelectron spectroscopy (XPS) and x-ray diffraction (XRD). The electrocatalytic activity and stability of these films with regard to CO₂ electroreduction in aqueous solution was then assessed.

As-deposited Bi films exhibited a high activity ($j_{\text{HCOOH}} = 1.6 \text{ mA cm}_{\text{geo}}^{-2}$ at -0.82 V vs RHE , which corresponds to an overpotential of 800 mV) and stability for CO₂ conversion to formate. The activity of electrochemically oxide-derived Bi films, however, was significantly higher ($j_{\text{HCOOH}} = 8.3 \text{ mA cm}_{\text{geo}}^{-2}$) at only a slightly larger overpotential (900 mV). The formate faradic efficiency vs potential curve of both types of films were almost identical, although the Bi electrochemically active surface area was increased by a factor of four. This is believed to reflect the fact that both the hydrogen evolution and the CO₂ electrochemical reduction reactions are occurring on the same site, or on two different sites affected in identical ways by the treatment.

1. Introduction

The rise in atmospheric CO₂ concentration since the beginning of the Industrial Age has raised concerns on its potential effect on global temperatures [1]. While several factors such as natural climate changes, variations in solar activity, and volcanic eruptions may also contribute to observed variations in CO₂ concentrations, it has been well established that anthropogenic emissions contribute to the annual emission of over 30 billion tonnes of CO₂, only about half of which is recycled through natural pathways [2].

Carbon dioxide is used in industry – as a cryogenic fluid for example – as well as in packaging and beverage carbonation; however, these applications remain limited to roughly 0.5% of total anthropogenic emissions [3,4]. Consequently, in the past twenty years several methods have been developed to capture and store CO₂, or convert it to value-added products.

Currently, CO₂ sequestration methods – such as its use in enhanced oil recovery (EOR) technology – are frequently used by industry [4,5]. Other sequestration methods have also been proposed, such as mineralization or biological fixation. However, the effectiveness of these storage methods in fixing CO₂ over significant time periods remains unclear [4]. Moreover, it is now well-established that photosynthesis has a very low conversion yield of approximately 1%; consequently, the amount of land and water required for large-scale capture would be

extremely high [6].

CO₂ conversion into value-added products is another avenue explored to mitigate environmental issues. Conversion methods appear promising, as they offer the potential to produce liquid and gaseous fuels for use either in the aeronautics industry, or as a chemical storage method for the intermittent energy produced by windmills and photovoltaic panels [7,8]. Fuel synthesis may be achieved via either the production of a syngas mixture (H₂ and CO) through the water gas shift reaction and subsequent conversion into hydrocarbon fuel through processes such as Fisher-Tropsch, or by direct electrochemical reduction of CO₂ [3,7]. While all methods may result in similar conversion yields, depending on the catalyst used [1,9], direct electrochemical conversion of CO₂ into value-added products is a low-temperature process, with the further advantage of requiring relatively simple equipment [3,7].

Copper is unequivocally the most studied catalyst for CO₂ electroreduction, as it is the only metal with significant hydrocarbon yield at low current densities [10–14]. However, copper has low selectivity and tends to simultaneously form carbon monoxide, methane, ethylene, and methanol, among other products [10].

Apart from Cu, the remaining catalysts studied for CO₂ electroreduction may be separated into three groups. The first group, which includes gold, silver, zinc, and to a lesser extent, copper, produces CO with a high faradic efficiency [9,15,16]. The second group, composed

* Corresponding author.

E-mail address: guay@emt.inrs.ca (D. Guay).

of metals such as Pt, Ni, Fe, Ti and Al, mostly form hydrogen [4,13] although Pt is also able to form hydrocarbons with up to nine carbon atoms, but at an extremely low yield [17]. Finally, the third group is composed of metals such as Hg, Cd, Pb, In and Sn with high hydrogen overpotential, which reduce CO₂ primarily to formic acid and formate salts.

Formic acid, or formate salts, are used in a variety of chemical processes such as electrowinning [18], leather tanning, and aircraft de-icing [19]. Alternatively, formic acid and formate salts may be considered a hydrogen storage medium [20]. Direct formic acid [21], and more recently, direct formate [22] fuel cells, have been investigated in the literature as they demonstrate significant benefits over methanol fuel cells, including higher open circuit voltage and lower crossover.

The main advantage of the third group of catalysts is their high selectivity, as they mainly produce aqueous formate and hydrogen gas. According to Oloman and Li, they may represent the cornerstone for commercial formate production, through the direct electroreduction of CO₂ [23]. In this respect, lead and tin have been extensively studied; however, their stability during sustained electrolysis remains limited [24,25].

In H-type cells, Kwon and Lee reported approximately 25% deactivation on Pb, and attributed it to the dissolution of nanoparticles of some specific shapes [25]. On the other hand, Li and Oloman reported that deactivation of tin after 2–3 h of operation in a continuous “trickle bed” reactor was caused by metallic impurities (Sb, As, Cu and Fe), but with significant variability between catalyst batches [24]. In another study, Argawal et al. reported that the activity of tin and tin alloys in a flow-through reactor was stable for up to 20 h, after which rapid catalyst deactivation was observed and associated with the formation of a graphitic carbon layer loosely attached to the electrode [20]. Clearly, there is a pressing need for more efficient and stable catalysts for the conversion of CO₂ to formate.

Recently, several reports in the literature have described how the activity and selectivity of materials used in the electrochemical conversion of CO₂ to value-added products can be altered (and usually increased) after oxide formation. These materials are termed oxide-derived (OD) materials, and enhanced activity for CO₂ reduction has been observed for OD-Cu [26,27], OD-Au [28], and OD-Pb [29] compared to their metallic surfaces. These OD materials were obtained after formation (and subsequent reduction) of a thick oxide layer, formed through thermal annealing (OD-Cu [27]), reactive sputtering [30], or electrochemical oxidation (OD-Au [28] and OD-Pb [29]). The enhancements in activity and selectivity were attributed to the formation of a greater number of highly-active grain boundaries. Clearly, OD catalysts behave differently from their parent metals for CO₂ electroreduction.

Although far less studied than lead and tin, one promising catalyst for the electroreduction of CO₂ is bismuth (Bi), which is non-toxic and has negligible environmental impact. It has few commercial applications, and its price has been low and relatively stable in recent years. Bismuth was investigated as a catalyst for CO₂ reduction in ionic liquid, achieving a faradic efficiency of up to 87 ± 8% toward the production of carbon monoxide [31]. In aqueous media, a faradic efficiency as high as 82% was reported toward formate production at high pressure (30 atm) from commercial Bi shots, but no sustainability experiments were performed [32].

More recently, metallic Bi formed through the reduction of BiOCl was investigated as a catalyst for CO₂ electroreduction in aqueous electrolytes [33]. A faradic efficiency as high as 92% for formate production was obtained and maintained for over six hours of electrolysis. In that study, the bismuth catalyst was derived from the reduction of BiOCl, and then compared to a polished Bi electrode and Bi powder, with both of the latter electrodes having lower surface areas. It turns out that the oxychloride-derived Bi films' activity and selectivity for formate were enhanced.

In this study, we compared the activity and stability for CO₂ electroreduction of high surface area metallic Bi films formed directly on a substrate with those of oxide-derived Bi catalysts. Accordingly, metallic Bi films were prepared through a direct potentiostatic method and both electrochemically and thermally-prepared OD-Bi films were investigated. The Bi films were characterized through SEM, XRD and XPS, and their electrocatalytic activity and stability for CO₂ electroreduction were assessed.

2. Experimental

Bismuth films were electrodeposited on Titanium (Ti) substrates (Alfa Aesar, 99%, 0.2 mm thickness, 1 cm²) pretreated according to a procedure described previously [34]. The electroplating solution consisted of HCl 1 M (Fisher Scientific, ACS), KCl 0.5 M (Acros, ACS Reagent) and 5 mM of Bi₂O₃ (Sigma Aldrich, 99.999%). All depositions were achieved under potentiostatic conditions using a Solartron 1480 A Multipotentiostat, with deposition potentials (E_{dep}) measured toward the standard calomel electrode (SCE). However, all potentials in this study are quoted in accordance with the RHE (Reversible Hydrogen Electrode) scale. After deposition, the samples were rinsed with deionized water (Millipore; specific resistivity > 18.2 MΩ cm).

Two different types of oxide-derived Bi film were prepared. For the first type, Bi films were oxidized by linear sweep voltammetry at 10 mV/s and in 0.5 M CO₂-saturated KHCO₃ to different upper potential limits (E_u), following a procedure reported by Perez et al. [35]. The thickness of the as-grown oxide layer was controlled by varying the upper potential limit (E_u) of the linear voltammetry [35]. Following that, they were reduced at −0.72 V for 30 min in the same electrolyte. For the second type, oxides of Bi were prepared by thermal annealing at 400 °C under Ar/O₂ atmosphere for 30 min, and similarly reduced.

The morphology of the deposits was investigated through scanning electron microscopy (SEM) micrographs (JEOL, JSM-6300F). The deposit's structural characteristics were assessed by x-ray diffraction (XRD) measurements using a Bruker D8 Advanced with Cu K_α radiation at 1.5418 Å, operated at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) studies were performed on a VG Escalab 220i-XL using a polychromatic Mg source and a hemispherical analyzer with a multichannel detector. The baseline was established using a Shirley function. The Bi 4f core level regions were fitted using a symmetric function (GL (70)) using Casa XPS.

Electrochemical characterization was carried out at room temperature in a standard three-compartment cell, using Pt gauze as a counter electrode and a Saturated Calomel Electrode (SCE) as reference. The electrochemically active surface area (EASA) was derived by recording cyclic voltammograms (CVs) at different sweep rates in a 0.5 M KHCO₃ solution to measure variations in the double layer currents, recorded between −0.02 V and 0.23 V. A conversion factor of 28 μF cm_{Bi}^{−2} was used to calculate the EASA [36]. A typical example is given in Fig. S1.

CO₂ electroreduction experiments were performed in a gas-tight cell, using a Nafion 117 membrane to separate the working and counter (a Pt gauze) electrodes. A Luggin capillary was used to minimize the ohmic drop. Experiments were performed in CO₂-saturated (Praxair, 99.99%) 0.5 M KHCO₃ (Fisher Scientific, ACS). The ohmic drop was determined by the current interrupt method (−20 mA applied for 0.05 s, followed by Open circuit Potential (OCP) measurements for 0.05 s, averaged over 25 measurements) and compensated at 85% by the potentiostat (Biologic VSP). Unless otherwise stated, CO₂ electrolyses were performed until a reduction charge of 2C cm^{−2} was reached. Gaseous products (H₂, CO, CH₄, C₂H₆ and C₂H₄) were analyzed using an Agilent 490 micro GC with dual channels (PPQ and MSSA columns). Formate was analyzed using a Dionex ICS-1500 ion chromatograph on an IonPac AS9-HC column. Only formate and hydrogen were detected in quantifiable amounts. CO traces were also observed, but they accounted for less than 0.5%. The total faradic efficiency reached 100 ± 5%, indicating that all major products were quantified.

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