

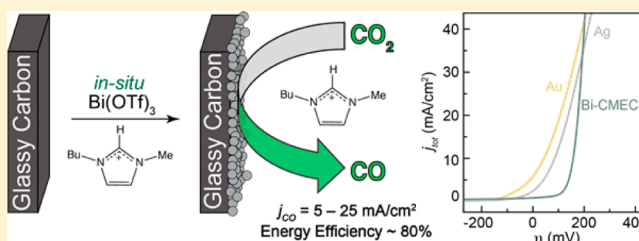
Efficient Reduction of CO₂ to CO with High Current Density Using in Situ or ex Situ Prepared Bi-Based Materials

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S Supporting Information

ABSTRACT: The development of inexpensive electrocatalysts that can promote the reduction of CO₂ to CO with high selectivity, efficiency, and large current densities is an important step on the path to renewable production of liquid carbon-based fuels. While precious metals such as gold and silver have historically been the most active cathode materials for CO₂ reduction, the price of these materials precludes their use on the scale required for fuel production. Bismuth, by comparison, is an affordable and environmentally benign metal that shows promise for CO₂ conversion applications. In this work, we show that a bismuth–carbon monoxide evolving catalyst (Bi-CMEC) can be formed under either aqueous or nonaqueous conditions using versatile electrodeposition methods. In situ formation of this thin-film catalyst on an inexpensive carbon electrode using an organic soluble Bi³⁺ precursor streamlines preparation of this material and generates a robust catalyst for CO₂ reduction. In the presence of appropriate imidazolium based ionic liquid promoters, the Bi-CMEC platform can selectively catalyze conversion of CO₂ to CO without the need for a costly supporting electrolyte. This inexpensive system can catalyze evolution of CO with current densities as high as $j_{\text{CO}} = 25\text{--}30\text{ mA/cm}^2$ and attendant energy efficiencies of $\Phi_{\text{CO}} \approx 80\%$ for the cathodic half reaction. These metrics highlight the efficiency of Bi-CMEC, since only noble metals have been previously shown to promote this fuel forming half reaction with such high energy efficiency. Moreover, the rate of CO production by Bi-CMEC ranges from approximately $0.1\text{--}0.5\text{ mmol}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$ at an applied overpotential of $\eta \approx 250\text{ mV}$ for a cathode with surface area equal to 1.0 cm^2 . This CO evolution activity is much higher than that afforded by other non-noble metal cathode materials and distinguishes Bi-CMEC as a superior and inexpensive platform for electrochemical conversion of CO₂ to fuel.



INTRODUCTION

The renewable production of CO via the $2\text{e}^-/2\text{H}^+$ reduction of CO₂ is an energy conversion half reaction of prime importance for the sustainable production of carbon-based fuels. Reaction of CO with water via the water–gas shift (WGS) reaction produces H₂, and this CO/H₂ mixture (syngas) can be used to generate synthetic petroleum and other liquid fuels using conventional Fischer–Tropsch (FT) methods.^{1–3} Accordingly, the use of renewable sources of electricity to drive the electrolytic generation of CO at ambient temperatures and pressures provides an attractive route to the renewable production of liquid fuels.⁴

Over the past several decades, fervent effort has been aimed at the study of molecular electrocatalysts for reduction of CO₂ to CO.^{5–7} In recent years, extensive work has shown that properly designed *fac*-tricarbonyl complexes of rhenium^{8–10} and manganese^{11–13} can catalyze this electrochemical reaction with good selectivity and reasonable kinetics. Additionally, Costentin and Savéant have shown that iron porphyrins containing pendent proton donors can promote conversion of CO₂ to CO with remarkably high selectivity and excellent current densities at low overpotentials.^{14,15}

Although these molecular systems can be proficient CO evolution electrocatalysts, in order to incorporate such species

into electrolytic devices, it is necessary to tether these systems to conducting solid supports, which is a nontrivial undertaking.^{16–18} Although recent work has shown that immobilization of a cobalt porphyrin onto conducting diamond¹⁹ or nickel cyclam onto a conducting poly(allylamine) support²⁰ can promote the electrocatalytic production of CO, these heterogeneous architectures do not currently display technologically relevant current densities (fast kinetics) for CO₂ conversion applications.

Several heterogeneous cathode materials have been shown to promote the rapid conversion of CO₂ to CO;^{21,22} however, only precious metals such as Ag^{23–25} and Au^{26–29} can catalyze this reaction with faradaic efficiencies (FEs) that are in excess of 80% while operating with appreciable current density (competent rate) at modest overpotentials (reasonable cathodic half reaction energy efficiency).³⁰ Although less expensive materials such as those based on Cu³¹ and Sn^{32,33} that are more economically suited for renewable fuel synthesis show promise for reduction of CO₂ to formic acid, these systems generally do not show high activities (i.e., appreciable current density/fast kinetics) or selectivities for CO produc-

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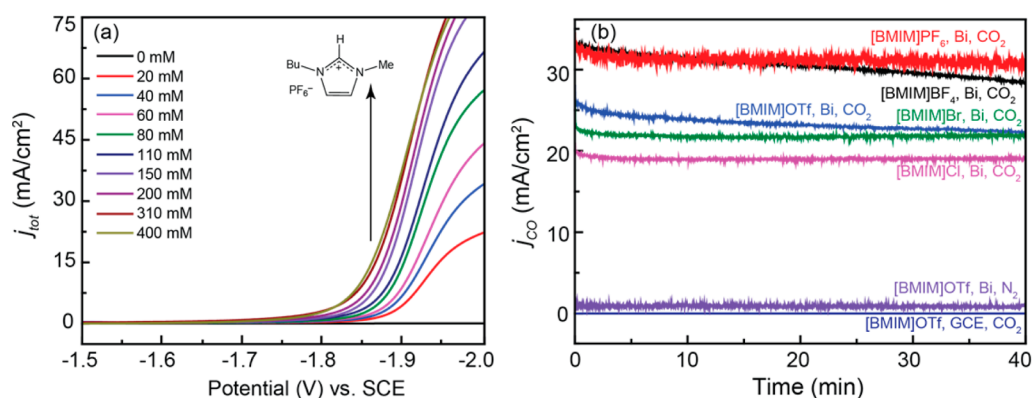


Figure 1. (a) LSV traces recorded for a GCE covered by Bi-CMEC in CO₂ saturated MeCN containing varying amounts of [BMIM]PF₆. (b) Partial current density profiles for CO production (j_{CO}) by Bi-CMEC and GCE at -2.0 V in MeCN in the presence of various imidazolium based ILs.

tion.^{34–36} Moreover, inexpensive metallic cathodes typically only activate CO₂ upon application of very large overpotentials,³⁷ which has been a significant barrier to implementation of such systems for the production of renewable liquid fuels.

Given the above considerations, the development of a robust and inexpensive material that can promote the rapid and selective reduction of CO₂ to CO under ambient conditions is a key milestone to the economically viable production of carbon-based fuels from renewables. Bismuth is an attractive material for heterogeneous catalyst development, as this metal has a negligible environmental impact and few significant commercial applications, which sustains low and stable pricing for this element.³⁸ Against this backdrop, our group recently developed the first bismuth-based catalyst for the electrochemical conversion of CO₂ to CO. This inexpensive and easily prepared material was studied in MeCN containing 0.1 M TBAPF₆ as a supporting electrolyte, since this solvent/electrolyte combination supports a large electrochemical window and is commonly employed for CO₂ electrocatalysis.^{37,39} Efficient CO production was realized with this system upon addition of a 1,3-dialkyl substituted imidazolium based ionic liquid (IL) promoter such as 1-ethyl-3-methylimidazolium hexafluorophosphate ([EMIM]PF₆) or 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF₆) to the catholyte solution.⁴⁰ Since this bismuth–carbon monoxide evolving catalyst (Bi-CMEC) operates in a catholyte solution of low proton availability (the pK_a of the IL promoter is ~ 32)⁴¹ and the position of $E^{\circ}_{\text{CO}_2/\text{CO}}$ is dependent on the proton donating ability of the electrolyte,¹⁴ the equilibrium potential for the $2e^-/2H^+$ conversion of CO₂ to CO under these conditions is $E^{\circ}_{\text{CO}_2/\text{CO}} = -1.78$ V versus SCE.⁴² Previous work showed that this system is highly active, as Bi-CMEC promotes CO production with exceptional cathodic half reaction energy efficiency ($\Phi_{\text{CO}} \approx 85\%$)⁴² and a FE over 90% at an applied overpotential of less than $\eta = 200$ mV.⁴⁰

Although the efficiency of Bi-CMEC rivals the best noble-metal cathodes described to date, our initial studies of this system relied on electrodeposition of this Bi material from concentrated aqueous acid.⁴⁰ Since such solutions are incompatible with CO₂ electrocatalysis, it was necessary to form Bi-CMEC ex situ prior to studying the catalyst's CO₂ reduction activity in MeCN. Accordingly, we rationalized that it would be highly beneficial to develop a method to electrodeposit Bi-CMEC directly from the organic catholyte employed

for CO₂ reduction experiments. Prior to pursuing the in situ formation of Bi-CMEC, however, we first sought to optimize the activity of this electrocatalyst by varying the composition of the catholyte solution and determining the extent to which the catholyte anion impacted CO₂ activation. We also wondered whether the expensive and frequently used supporting tetraalkylammonium electrolyte (TBAPF₆) could be eliminated from the catholyte solution while maintaining efficient CO₂ catalysis with the Bi-CMEC system.

RESULTS AND DISCUSSION

Since imidazolium based ILs can interact with CO₂ and have found application for gas separation/carbon sequestration^{43–45} and can serve as robust electrolytes for a variety of electrochemical^{46–49} and energy conversion applications,^{50–52} we hypothesized that imidazolium salts such as [BMIM]PF₆ could serve as both a promoter for CO₂ activation at Bi-CMEC and the supporting electrolyte in the catholyte solution. Linear sweep voltammograms (LSVs) recorded in CO₂ saturated MeCN using a glassy carbon electrode (GCE) onto which a film of Bi-CMEC had first been electrodeposited (Figure 1) showed that the addition of small aliquots of [BMIM]PF₆ results in polarization curves that are nearly identical to those recorded in the presence of TBAPF₆. This current response cannot simply be attributed to reduction of [BMIM]⁺ at the electrode surface, as analogous cyclic voltammograms recorded under an atmosphere of N₂ did not show a reduction wave at potentials less negative than -2.1 V versus SCE (all potentials in this manuscript are reported with respect to this reference). Moreover, CV experiments conducted using the GCE substrate for 300 mM solutions of [BMIM]PF₆ in MeCN under N₂ show that the imidazolium is only reduced at potentials more negative than -2.2 V versus SCE (Figure S1 in Supporting Information). When taken together, these voltammetry experiments suggest that the cathodic feature observed in Figure 1 corresponds directly to the IL promoted reduction of CO₂ by the Bi-CMEC covered electrode.

Upon establishing that Bi-CMEC could promote reduction of CO₂ to CO in the presence of [BMIM]PF₆ without supporting electrolyte, we sought to identify if other [BMIM]⁺ salts displayed comparable activities. In particular, we were curious to see if [BMIM]⁺ salts comprising anions less expensive than PF₆[−] could be tolerated during electrocatalysis. Moreover, given that anions such as BF₄[−] and PF₆[−] can slowly hydrolyze,⁵³ we were eager to identify if more robust [BMIM]⁺ salts would also be good promoters of CO₂ reduction by Bi-

CMEC. As such, [BMIM]⁺ salts of BF₄[−], Cl[−], Br[−], and OTf[−] were titrated into CO₂ saturated solutions of MeCN and LSVs were recorded with a Bi-CMEC coated GCE. Each of these ILs produces virtually identical polarization curves with an onset potential for CO₂ reduction at approximately −1.8 V versus SCE (polarization curves for [BMIM]BF₄ and [BMIM]OTf are shown in Figure S2). We note that this onset potential is nearly coincident with the equilibrium $E^{\circ}_{\text{CO}_2/\text{CO}}$ potential (−1.78 V) under these conditions.⁴² As was observed for [BMIM]PF₆ (vide supra), as the concentration of any of the [BMIM]⁺ salts increases, the CO₂ reduction onset shifts to slightly more positive potential and the cathodic response increases in magnitude. This current response plateaus at an IL concentration of ~300 mM in the catholyte solution. Further increasing the concentration of any of the [BMIM]⁺ salts past this point did not yield larger gains in current density.

Upon establishing that each of the [BMIM]⁺ salts that we had screened could promote CO₂ activation by Bi-CMEC in the absence of supporting electrolyte at an applied overpotential (η) of less than 250 mV past $E^{\circ}_{\text{CO}_2/\text{CO}} = -1.78$ V, the stability and efficiencies of these systems were assessed by controlled potential electrolysis (CPE) experiments. These experiments were performed for CO₂ saturated solutions of MeCN containing each of the [BMIM]⁺ salts listed in Table 1

Table 1. Faradaic Efficiencies (FE) and Current Densities for Electrocatalytic Reduction of CO₂ to CO at an Applied Potential of −2.0 V vs SCE in the Presence of 300 mM IL

electrode	ionic liquid	solvent	CO FE (%)	Φ_{CO} (%)	j_{CO} (mA/cm ²)
Bi-CMEC	[BMIM]PF ₆	MeCN	82 ± 12	73	31 ± 2
Bi-CMEC	[BMIM]BF ₄	MeCN	82 ± 11	73	26 ± 4
Bi-CMEC	[BMIM]Cl	MeCN	79 ± 12	70	17 ± 2
Bi-CMEC	[BMIM]Br	MeCN	74 ± 4	65	20 ± 1
Bi-CMEC	[BMIM]OTf	MeCN	87 ± 8	77	25 ± 2
GCE	[BMIM]OTf	MeCN	none		0.4 ^a

^aTotal current density.

using a Bi-CMEC modified GCE. After initiation of the electrolyses at −2.0 V ($\eta \approx 220$ mV), the reaction headspace was periodically analyzed by gas chromatography. For each of the [BMIM]⁺ salts surveyed, CO was the only gaseous product formed during the CPE experiments. Quantification of the CO produced during these electrolyses afforded the faradaic efficiencies (FEs) for the 2e[−]/2H⁺ reduction of CO₂ to CO. These values are listed in Table 1 along with the calculated current densities associated with CO generation (j_{CO}). Each of the ILs surveyed displays excellent selectivities for CO production and j_{CO} values that range from 17 to 30 mA/cm². As shown in Figure 1b, current densities for CO formation were quite steady during a 40 min CPE experiment for each IL probed, suggesting that Bi-CMEC is neither passivated nor degraded by any of the anions that were surveyed. Importantly, control CPE experiments conducted in the absence of either Bi-CMEC or CO₂ show negligible total current densities (j_{tot}) and do not produce appreciable amounts of CO (Figure 1b).

Analysis of the FE and j_{CO} values in Table 1 and Figure 1b shows that CPE of CO₂ saturated solutions containing the [BMIM]⁺ halides resulted in conversion of CO₂ to CO with the lowest efficiencies and slowest kinetics of the ILs surveyed. This may be due to the fact that [BMIM]Br and [BMIM]Cl are more hygroscopic than the other ILs studied, as the presence of

water in the electrolyte solution may lead to the formation of other CO₂ reduction products such as formate, as has been shown previously.⁵⁴ By contrast, electrolyses conducted for the BF₄[−], PF₆[−], and OTf[−] salts of [BMIM]⁺ resulted in FEs for CO production of ~85% with impressive kinetics as demonstrated by the high current densities for CO generation of $j_{\text{CO}} \geq 25$ mA/cm².

While selectivity and current density are important metrics by which any electrocatalyst is judged, energy conversion efficiency is also a critical parameter in benchmarking electrocatalyst platforms for renewable energy storage and/or fuel synthesis. The cathodic half reaction energy efficiency with which Bi-CMEC promotes the electrocatalytic production of CO from CO₂ (Φ_{CO}) can be determined by considering the FE for CO formation, the equilibrium potential of the CO₂/CO redox couple under the CPE conditions ($E^{\circ}_{\text{CO}_2/\text{CO}}$), and calculation of the overpotential (η) at which CPE is carried out.^{55–57} With these values in hand, the cathodic half reaction energy efficiency of electrocatalytic CO production by Bi-CMEC in the presence of each of the imidazolium promoters listed in Table 1 was calculated using eq 1.

$$\Phi_{\text{CO}} = \frac{\text{FE} \times E^{\circ}_{\text{CO}_2/\text{CO}}}{E} \quad (1)$$

Except for the case of [BMIM]Br, which shows the lowest FE for CO production, each of the ILs studied promotes the conversion of CO₂ to fuel with energy efficiencies that are above 70% and the value for Φ_{CO} approaches 80% for [BMIM]OTf.

That [BMIM]OTf promotes the reduction of CO₂ to CO with such impressive efficiency and kinetics is notable, as this is one of the least expensive commercially available [BMIM]⁺ salts with a current price of ~\$2/g. The theoretical maximum for CO₂ reduction current density under aqueous conditions is limited to ~10 mA/cm² by the relatively low solubility of CO₂ (~38 mM) in water under ambient conditions.⁵⁸ That the inexpensive Bi-CMEC platform in conjunction with a [BMIM]⁺/MeCN catholyte gives rise to current densities for CO production of $j_{\text{CO}} = 25\text{--}30$ mA/cm² with attendant energy efficiencies that approach $\Phi_{\text{CO}} \approx 80\%$ is a significant achievement, as there are virtually no materials other than precious metals that excel in both these regards.⁵⁷

Although the Bi-CMEC platform that is deposited ex situ from concentrated HCl is an excellent platform for electrocatalytic CO production, the in situ formation of this system from an MeCN catholyte would simplify preparation of this electrocatalyst and allow Bi-CMEC to be deposited on substrates that are too delicate or reactive to tolerate the highly acidic conditions required to electrodeposit Bi-CMEC from aqueous solutions. The in situ induced deposition of a Bi-based material for CO₂ electrocatalysis may be accomplished if reduction of an organic soluble bismuth complex can be carried out at a potential more positive than the onset potential for CO₂ reduction and leads to precipitation of Bi-CMEC at the electrode surface. Although most Bi³⁺ salts can be reduced at potentials that are more positive than the −1.8 V required for CO₂ catalysis, the majority of such species are completely insoluble in the MeCN based catholyte required for CO production.

Organometallic Bi(III) complexes such as [Bi^{III}(Ph)₃] can be supported by the organic electrolyte employed in the CO₂ reduction studies highlighted above; however, this neutral

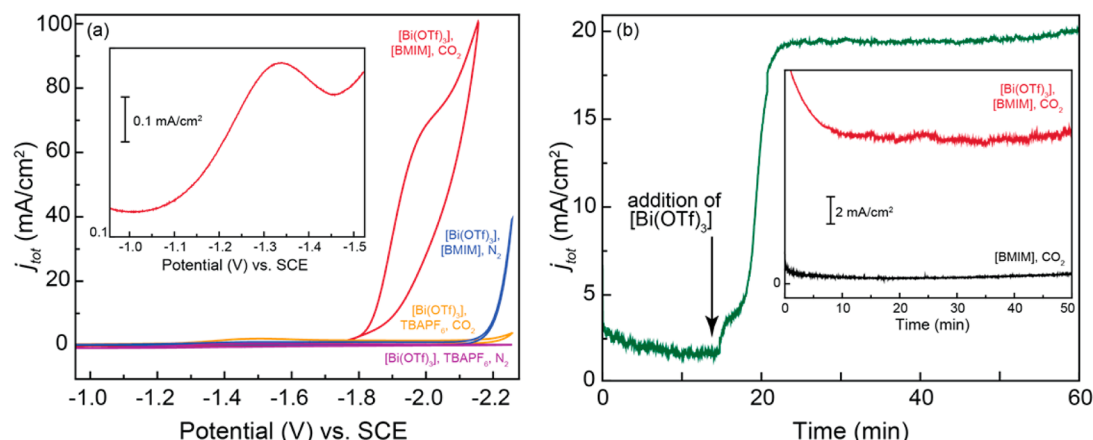


Figure 2. (a) CV traces recorded at a GCE in MeCN solutions containing 1.0 mM [Bi(OTf)₃] under an atmosphere of either CO₂ or N₂. Inset: LSV trace obtained upon reduction of a 1.0 mM [Bi(OTf)₃] solution in MeCN at a GCE. (b) Total current density trace recorded for a Ni disk electrode at -2.0 V in MeCN containing 300 mM [BMIM]OTf before and after addition of 1 mM [Bi(OTf)₃]. Inset: Partial current density profiles for CO production (j_{CO}) at GCE in MeCN containing 300 mM [BMIM]OTf in the presence (red) and absence (black) of [Bi(OTf)₃].

Bi(III) derivative is only reduced at potentials that are more negative than the onset potential for CO generation by Bi-CMEC (Figure S3), thereby precluding its use as an in situ precursor of Bi-CMEC. Bismuth triflate ([Bi(OTf)₃]) represents a rare example of a Bi³⁺ salt that is soluble in MeCN. Having established that triflate salts do not interfere with the electrocatalytic conversion of CO₂ to CO at Bi-based cathodes (vide supra), we rationalized that [Bi(OTf)₃] would be an attractive precursor for in situ Bi-CMEC electrodeposition. To explore the possibility of CO production by an in situ generated Bi-based electrocatalyst, we examined the electrochemical reduction of MeCN solutions containing Bi³⁺ and ionic liquid. Cyclic voltammograms recorded for 1.0 mM [Bi(OTf)₃] and 300 mM [BMIM]OTf in CO₂ saturated MeCN exhibit a cathodic feature at $E = -1.2$ V, followed by the onset of an intense catalytic wave at -1.8 V (Figure 2a). This sharp rise in current is reminiscent of the polarization curve observed for CO₂ electrocatalysis using an ex situ generated Bi-CMEC modified GCE (Figure 1), suggesting that cathodic polarization of the MeCN solution containing [Bi(OTf)₃] leads to electrodeposition of a Bi-based material that can electrochemically activate CO₂. Polarization experiments conducted for MeCN solutions containing 1.0 mM [Bi(OTf)₃] and 300 mM [BMIM]OTf under an atmosphere of N₂ are consistent with this analysis. As shown by the blue trace in Figure 2a, in the absence of CO₂ a large increase in current is not observed in the region from -1.8 to -2.1 V. Similarly, voltammograms recorded in the absence of [BMIM]OTf show no catalysis, indicating that as was true for ex situ prepared Bi-CMEC, Bi, CO₂, and IL are all integral to the observed catalysis.

The strong catalytic wave observed under CO₂ at potentials more negative than -1.8 V in Figure 2a prompted us to examine the activity of the in situ generated Bi material during a CPE experiment. We employed a glassy carbon or nickel working electrode to ensure negligible background activity for CO₂ catalysis. As shown by the green trace in Figure 2b, electrolysis of a CO₂ saturated solution of MeCN containing 300 mM [BMIM]OTf at -2.0 V at a Ni cathode showed low current densities of $j_{\text{tot}} \approx 1$ mA/cm² with no detectible CO production. Upon addition of [Bi(OTf)₃] to the electrolysis solution, a sharp rise in current density was observed, ultimately leading to a steady state value of ~ 20 mA/cm². This rise in current was accompanied by formation of a dark electro-

deposited coating on the working electrode surface. Similar results were obtained upon electrolysis of a CO₂ saturated solution of MeCN containing 1.0 mM [Bi(OTf)₃] and 300 mM [BMIM]OTf at -2.0 V at a GCE (Figure 2b red trace), indicating that in situ formation of the electrodeposited Bi catalyst can be accomplished using a variety of conducting substrates.

Periodic GC analysis of the reaction headspace during the course of the CPE experiment showed CO to be the sole gaseous product formed during the electrolysis experiment. Furthermore, quantification of the amount of CO produced during the CPE experiment corresponded to a FE of $\sim 75\%$ for the $2e^-/2H^+$ conversion of CO₂ to CO, with an average partial current density of $j_{\text{CO}} = 5.0 \pm 0.9$ mA/cm². This current density was stable for more than 3 h with no appreciable loss in FE during the course of longer electrolysis experiments. We note that this system is extremely selective for CO production, as no CH₄ or H₂ was detected during the CPE experiment. Using a combination of NMR methods, we observed no coproduction of formate, oxalate, or glyoxalate, which is often observed upon electrochemical reduction of CO₂ in organic catholytes.^{59,60} As such, the slightly reduced FE and j_{CO} values observed for the in situ Bi-CMEC system do not necessarily point to an inherent deficiency of the catalyst but rather may be the result of poorer ohmic contact between the electrocatalyst and underlying GCE, compared to when the Bi-containing film is deposited ex situ from aqueous acid. Losses due to resistance may be accompanied by joule heating, as has been observed for Au and Ag catalysts for CO₂ reduction.^{61–63} Additionally, the reduction in FE under these conditions may be due to the small fraction of passed current that is co-opted to drive [Bi(OTf)₃] reduction during the in situ electrodeposition process.

Repetition of this CPE experiment under N₂ leads to little passed charge and no CO production, indicating that the CO formed under an atmosphere of CO₂ is not simply a product of IL or solvent decomposition. Similarly, repeating this CPE experiment under CO₂ but in the absence of [Bi(OTf)₃] leads to low current densities (~ 0.03 mA/cm²) and no CO production (Figure 2b, black trace). Taken together, these control experiments demonstrate that the IL is integral to the observed electrocatalysis, which is distinguished by high current densities for the selective production of CO over other reduced carbon products or H₂. As such, this system represents a rare

example of a CO₂ reduction electrocatalyst that can be easily formed in situ from an inexpensive metal precursor. To the best of our knowledge, it is the first such system that operates in an organic catholyte that supports the high concentrations of dissolved carbon dioxide that are required for electrolytic CO production with j_{CO} values in excess of 10 mA/cm².

The morphology and composition of the in situ generated Bi-CMEC material were probed by a combination of physical methods. Scanning electron microscopy (SEM) revealed that the electrodeposited catalyst consists of submicrometer-sized particles that have coalesced into a film with a spongelike morphology (Figure 3a). The X-ray powder diffraction pattern

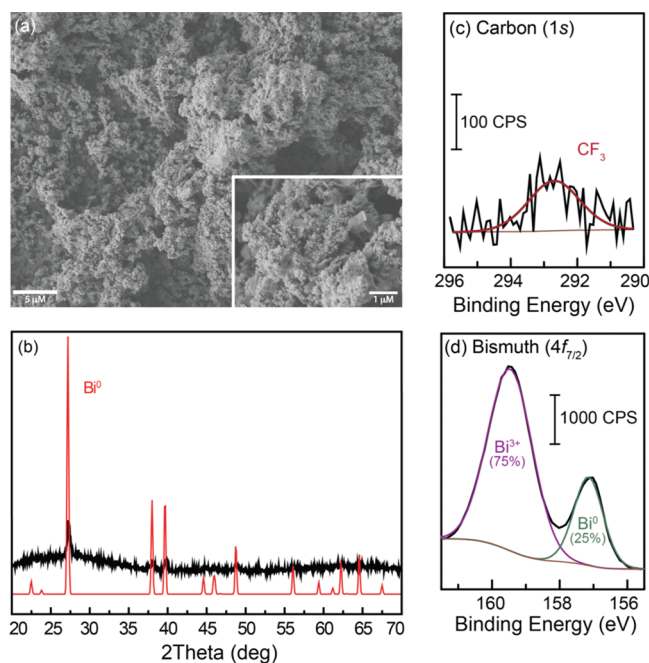


Figure 3. (a) SEM images of Bi-CMEC electrodeposited on a GCE from MeCN containing 300 mM [BMIM]OTf and 1.0 mM [Bi(OTf)₃]. (b) Powder XRD pattern showing the largely amorphous nature of in situ deposited Bi-CMEC. (c) High-resolution C 1s and (d) Bi 4f_{7/2} XPS spectra of in situ deposited Bi-CMEC.

obtained for this material is consistent with this amorphous morphology, largely showing broad features and only small peaks indicative of crystalline Bi⁰ (Figure 3b). In order to gain a greater understanding of the elemental composition of the in

situ generated Bi-containing material, energy-dispersive X-ray (EDX) analysis was performed on 40 × 40 μm² regions of several independently prepared samples of the electrodeposited catalyst (Figure S4). The surface of the material was also analyzed by X-ray photoelectron spectroscopy (XPS). All elements detected by EDX are also accounted for by XPS (Figure S5), which identified Bi, O, S, and F as the principal elemental components and suggests that small amounts of triflate from the Bi³⁺ precursor are incorporated into the electrodeposited material. Consistent with this assignment are the high-resolution XPS spectra of the C 1s, F 1s, S 2s, and O 1s regions (Figures 3c and S5). Integrating the small peak in the C 1s spectrum at 292.7 eV (corresponding to the carbon of a CF₃ group, such as that in triflate), the S 2s peak, the F 1s peak, and a component for the lower binding energy peak in O 1s (530.1 eV), we find the ratio to be approximately 1:3:1:3, respectively. As such, the relative intensities of these components match the ratio of C/F/S/O expected for a triflate anion.⁶⁴ Moreover, XPS analysis of bismuth reveals Bi 4f_{7/2} signals at 157.1 and 159.5 eV, which are values typically observed for Bi⁰ and Bi³⁺, respectively (Figure 3d). On the basis of XPS analysis of the in situ prepared Bi-CMEC material, the ratio of Bi⁰ to Bi³⁺ is ~1:3. We note that electrodeposition of both Bi⁰ and Bi³⁺ ions has been observed for Bi-CMEC films formed from concentrated acidic solutions.⁴⁰ When taken together, the EDX and XPS analyses indicate that in situ reduction of MeCN solutions of [Bi(OTf)₃] containing 300 mM [BMIM]OTf leads to deposition of a largely amorphous material containing metallic Bi⁰ and Bi³⁺ ions that has incorporated a significant amount of oxygen and small amount of triflate.

The variation in partial current density associated with CO generation for an in situ prepared Bi-CMEC on glassy carbon was measured as a function of applied overpotential in CO₂ saturated MeCN containing 300 mM [BMIM]OTf. These data were obtained by performing stepped potential electrolyses between $E = -1.80$ V and $E = -2.3$ V, with commensurate quantification of the gaseous products by GC. The FE for CO production remains high as the applied η is increased; however, the resulting Tafel plot constructed from these data (Figure 4a) begins to deviate from linearity as the applied potential exceeds -2.0 V. This curvature is likely due to uncompensated iR drop caused by the surface resistivity of the GCE along with mass-transport limitations attendant to rapid CO₂ reduction at the Bi-CMEC coated cathode. It is expected that improved mass transport using a flow cell, gas diffusion electrode, or other

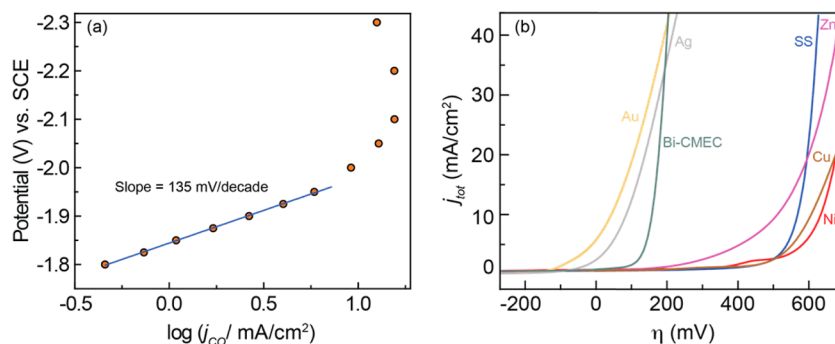


Figure 4. (a) Partial current density for CO production (j_{CO}) Tafel plot for in situ generated Bi-CMEC with 300 mM [BMIM]OTf in CO₂ saturated MeCN. (b) Polarization curves recorded for several cathode materials for carbon dioxide reduction show that under the conditions employed in this work, Bi-CMEC operates with activity that is comparable to that of precious metals.

advanced cell design⁶⁵ would enable even higher current densities (TOFs) for CO production using this system. The Tafel data are linear in the range of $\eta = 0.02$ – 0.17 V, with a slope of 135 mV/decade. This value is close to 118 mV/dec, suggesting that initial electron transfer to generate a surface adsorbed $\text{CO}_2^{\bullet-}$ species is the rate-determining step for CO evolution. This mechanism has been invoked for reduction of CO_2 at many heterogeneous electrodes.⁶⁶ The Tafel slope observed for this material is in the same range as that observed for CO evolution using ex situ prepared Bi-CMEC modified electrodes,⁴⁰ suggesting that both systems operate by analogous mechanisms.

On the basis of these stepped-potential CPE and Tafel results, it is clear that the in situ deposited Bi-CMEC operates with appreciable current densities while maintaining impressive Faradaic and energy efficiencies at $\eta \approx 200$ mV. The j_{CO} values obtained in this potential region correspond to an average sustained activity for CO production of $\sim 100 \mu\text{mol}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$, a value that compares favorably to that observed for conversion of CO_2 to CO using much more expensive Ag based cathode materials.⁶⁷ The efficiency and activity with which Bi-CMEC promotes the electrochemical conversion of CO_2 to CO are highlighted by comparing the polarization curves of several well studied cathode materials for CO_2 reduction using an MeCN/[BMIM]⁺ based catholyte. As shown in Figure 4b, Bi-CMEC can activate CO_2 at significantly lower overpotentials compared to other inexpensive cathode materials such as Cu, Zn, Ni, and stainless steel (SS) and operates with kinetics and a cathodic half reaction energy efficiency that are similar to those of Au and Ag electrodes, which are much more cost prohibitive to prepare.

CONCLUSIONS AND FUTURE DIRECTIONS

The development of efficient and robust cathode materials that can promote the rapid conversion of CO_2 to CO is a key step on the road to the storage and conversion of renewable energy inputs to liquid carbon-based fuels. Although gold and silver catalysts have long been known to be active platforms for this process, the expense associated with use of these materials has precluded their use on the scale required for electrolytic fuel production. By contrast, bismuth represents a poor metal that is environmentally benign and extremely affordable. Both these factors make bismuth well positioned for incorporation into CO_2 conversion and fuel production schemes.

In this work, we have shown that a bismuth based material can be formed under either aqueous or nonaqueous condition using versatile electrodeposition methods. This material can serve as a robust carbon monoxide evolution catalyst and promotes the electrocatalytic reduction of CO_2 to CO in the presence of appropriate imidazolium ionic liquid promoters. This inexpensive Bi-CMEC platform tolerates a variety of different catholyte anions including potentially corrosive anions such as chloride and bromide. Most notably, Bi-CMEC promotes the electrochemical generation of CO from CO_2 with current densities as high as $j_{\text{CO}} = 25$ – $30 \text{ mA}/\text{cm}^2$ and accompanying energy efficiencies for the cathodic half reaction of $\Phi_{\text{CO}} \approx 80\%$. Both these values compare extremely well to those observed using more expensive gold and silver CO_2 reduction electrocatalysts³⁷ and suggest that Bi-CMEC may be incorporated into an energy efficient electrochemical device for fuel production if coupled to an appropriate anodic half reaction. That Bi-CMEC can be easily prepared at a small fraction of the price of these precious metal cathodes, which

have historically been the most efficient platforms for electrolytic production of CO from CO_2 , represents a significant advancement in the field of molecular energy conversion. Moreover, the rate of CO production by Bi-CMEC ranges from approximately 0.1 to $0.5 \text{ mmol}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$ at an applied overpotential of $\eta \approx 250$ mV for a cathode with surface area equal to 1.0 cm^2 . This CO evolution activity is much higher than that afforded by other non-noble metal cathode materials and distinguishes Bi-CMEC as a superior and inexpensive platform for electrochemical conversion of CO_2 to fuel.

In addition to being an inexpensive and efficient platform for CO evolution, Bi-CMEC can also be easily prepared via an in situ electrodeposition pathway. As such, the ease with which Bi-CMEC can be prepared complements other types of CO_2 reduction catalysts that require the presynthesis of metal nanoparticles⁶⁸ or electrode preparation using arc-melting processes.⁶⁹ The ability to electrodeposit the Bi-CMEC catalyst in situ using a Bi^{3+} precursor that is soluble in the CO_2 saturated catholyte solution significantly streamlines preparation of electrode assemblies for CO production. This in situ formation strategy has not commonly been employed for preparation of CO_2 reduction cathodes but offers significant advantages, as it may facilitate catalyst deposition on a variety of substrates that are too fragile to tolerate more traditional catalyst preparation methods. As such, we anticipate that the ability to easily prepare Bi-CMEC via the in situ electrodeposition methods described herein will prove especially beneficial for the construction of advanced energy conversion devices and photoelectrochemical assemblies for the conversion of solar energy to carbon-based fuels.

ASSOCIATED CONTENT

Supporting Information

Experimental methods, surface analysis, and electrochemistry data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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