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Electrolyte Dependence of CO_2 Electroreduction: Tetraalkylammonium Ions Are Not Electrocatalysts

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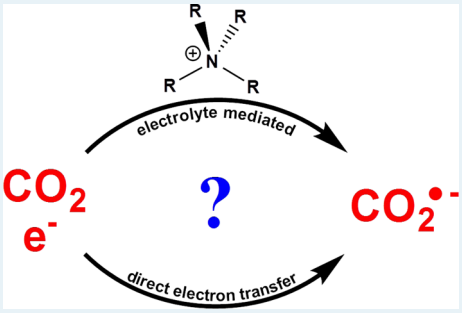
Supporting Information

ABSTRACT: The ability of tetraalkylammonium ions (NR_4^+) to facilitate CO_2 electroreduction at various electrode surfaces has been investigated. Scan rate dependence shows this process to be diffusion-controlled and largely independent of working electrode material. Variation of the R groups on NR_4^+ is shown to have little effect on the reduction potential, indicating that catalysis via reduced $NR_4^{\bullet}$ species, as previously proposed in the literature, is not a viable mechanism for CO_2 electroreduction. Rather, CO_2 is reduced via outer-sphere electron transfer according to the mechanism put forth by Savéant and co-workers [Lamy, E.; Nadjo, L.; Savéant, J.-M. *J. Electroanal. Chem.* **1977**, *78*, 403−407]. This view is supported by a full analysis of the reaction products, which consist exclusively of CO and CO_3^{2-}, as well as solvent decomposition products formed at the counter electrode. No degradation of NR_4^+ ions is observed, which rules out the transient formation of $NR_4^{\bullet}$ radical species during electroreduction. However, Li^+ ions are definitively shown to inhibit CO_2 reduction, even in the presence of NR_4^+ ions. This inhibition likely occurs via surface adsorption of the Li^+ ions.



KEYWORDS: *carbon dioxide, electrochemistry, tetraalkylammonium, boron-doped diamond*

INTRODUCTION

A large body of current research is devoted to the discovery of alternative fuel sources and the mitigation of greenhouse gas emissions.[1,2] In particular, electrochemically driven CO_2 reduction to give useful industrial feedstocks provides an attractive blueprint for recycling carbon-based emissions. In this way, CO_2 can be converted to a variety of compounds including carbon monoxide, formaldehyde, methanol, and others. A number of transition-metal-containing catalysts for these reactions have been developed in recent years,[1−6] with rates of up to 1000−10 000 M^{-1} s^{-1} for conversion of CO_2 to CO having been achieved.[5,7,8] However, it is important to note that CO_2 can be electrochemically or photoelectrochemically reduced to CO in the presence of tetraalkylammonium (NR_4^+) cations,[9,10] which are very commonly used as supporting electrolytes and widely believed to be chemically inert. Under proton-limited conditions, these systems typically produce CO with carbonate presumed to be the byproduct via eq. 1:[11,12]

$$2CO_2 + 2e^- \rightarrow CO + CO_3^{2-} \quad \text{(eq. 1)}$$

Tetraalkylammonium salts have been described as CO_2 reduction "catalysts" even though they are always employed in large excess relative to CO_2.[13,14] The typical mechanism invoked for the observed reactivity involves reduction of NR_4^+ to give the corresponding neutral radical, which then transfers an electron to CO_2.[13] However, experimental evidence supporting such a mechanism is lacking. In protic solvents, a mixture of several CO_2 reduction products is formed,[15,16] but in aprotic solvents, the reaction is claimed to be selective for the production of CO.[12] In order to clarify the mechanistic role of NR_4^+ species, we explore here electrochemical CO_2 reduction in aprotic solvents under a broad range of conditions with NR_4^+ cations of variable alkyl chain length as well as complementary experiments utilizing Li^+ and Cs^+. Several working electrode materials are tested, including inexpensive boron-doped diamond. Labeling experiments with $^{13}CO_2$ were also performed to assess unambiguously the product distribution of the reactions.

EXPERIMENTAL SECTION

Research grade CO_2 gas (99.999%) was purchased from Airgas Specialty Gases (Chicago, IL) and was used without further purification. Anhydrous solvents were prepared either by distillation over CaH_2 or via a Vacuum Atmospheres solvent purification system. Anhydrous $LiClO_4$ and tetrabutylammonium hexafluorophosphate were purchased from Fisher Scientific (Pittsburgh, PA); the latter was dried under vacuum prior to use. All other tetraalkylammonium salts were purchased from GFS Chemical and used without further purification. Boron-doped polycrystalline CVD diamond surfaces were purchased from Element Six and then heated at 800 °C in a 13.56 MHz inductively coupled hydrogen plasma

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(50 Torr H_2) for 1 h prior to use. Thin-layer diamond on Mo was prepared according to literature methods.[17]

Electrochemical measurements were performed using a BAS Epsilon potentiostat connected to a N_2-flushed cell containing 0.25 cm^2 of exposed surface (working) along with Pt (counter) and Ag (reference) wire electrodes. When necessary, the counter electrode was isolated from the bulk solution via a fine glass frit. Data were not corrected for ohmic drop as the reference electrode was positioned within 1 cm of the working electrode and the electrolyte solutions employed display sufficiently low resistance. FT-IR gas analysis was performed using a 20 cm cell fit with CaF_2 windows mounted in a Bruker Vertex 70 spectrometer. ^{1}H NMR data were collected on a Bruker 400 MHz Avance spectrometer.

RESULTS AND DISCUSSION

Benchmarking with the Tetrabutylammonium Ion. In order to investigate claims that NR_4^+ ions catalyze CO_2 reduction, the tetrabutylammonium (NBu_4^+) ion was used as a benchmark. Here, a 0.25 cm^2 working electrode was exposed to CO_2-saturated solutions containing 0.1 M NBu_4^+ as either the hexafluorophosphate or perchlorate salt in an air-free electrochemical cell. It is important to note that the anion present was not found to have any noticeable effect on any electrochemical results. A variety of working electrodes and solvents were also employed under these conditions, as discussed below. Importantly, solution FT-IR data show no interaction between dissolved CO_2 and any NR_4^+ ions in CH_3CN. For example, Figure S1 shows that the CO_2 stretching vibration remains unchanged in the presence or absence of 0.1 M NMe_4^+.

Voltammetric analysis in the presence of NBu_4^+ clearly shows a large current increase beginning at −1.8 V vs Ag/Ag^+ for CO_2-saturated solutions as compared to a N_2 background (see Figure 1, top). Notably, there are no signals present under N_2 that can be construed as reduction of NBu_4^+ to $NBu_4^\bullet$ radical. Under CO_2-limited conditions (2 mL gas injection to 30 mL solvent), an irreversible reductive feature is observed at approximately −2.6 V vs Ag/Ag^+ during cyclic voltammetry in dry CH_3CN containing NBu_4^+. This feature is assigned as the formation of $CO_2^{\bullet-}$ according to eq. 2.[18]

$$CO_2 + e^- \rightarrow CO_2^{\bullet-} \quad E^0 = -1.97 \text{ V vs SHE in DMF} \qquad \text{(eq. 2)}$$

A plot of the peak current versus (scan rate)$^{1/2}$ shows a linear response for this feature, indicating a diffusion-controlled process (see Figure 1, bottom).

In a further attempt to probe for surface adsorption and adhesion effects, the working electrode material was varied under CO_2-reducing conditions in the presence of NBu_4^+. Four electrode materials were chosen including platinum, boron-doped conductive diamond, thin-layer diamond on molybdenum, and glassy carbon. As shown in Figure S2, no substantial difference is present in the CO_2 reduction data for each surface. This result is consistent with an outer-sphere electron transfer to CO_2, which does not involve the formation of any strongly surface-bound species.

Analysis of reaction products was performed using a combination of NMR and IR spectroscopy, as well as a $PdCl_2$ assay that is selective for the presence of CO.[19] Due to the significantly lower amount of product formation during shorter time frame experiments, $^{13}CO_2$ gas was used to enable efficient NMR analysis of the nonvolatile electrolysis products.

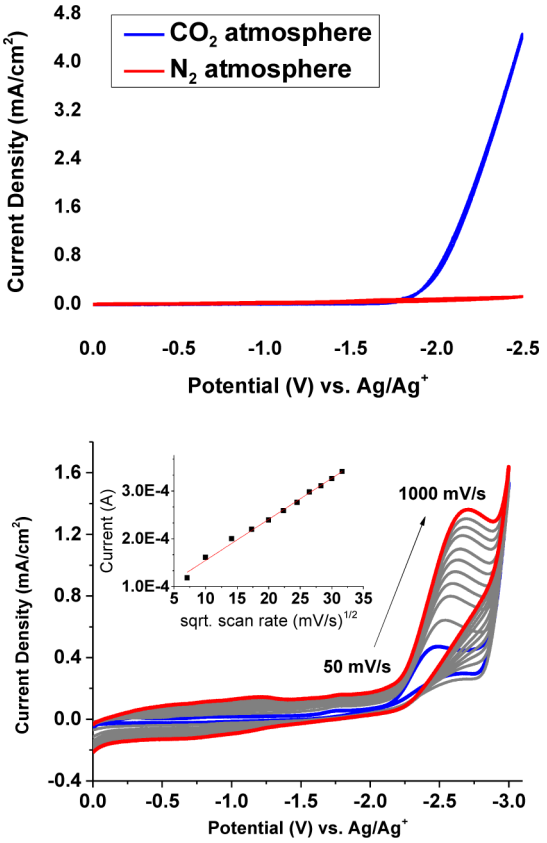
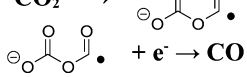


Figure 1. (Top) Cyclic voltammetry recorded at 100 mV/s of CO_2-saturated CH_3CN with 0.1 M NBu_4^+ as compared to the same solution under N_2. (Bottom) Cyclic voltammetry under CO_2-limited conditions along with a correlation plot showing current vs (scan rate)$^{1/2}$. All data recorded with a boron-doped diamond working electrode.

When NBu_4^+ ions were employed during CO_2 reduction in CH_3CN, headspace analysis by $PdCl_2$ assay reveals production of CO at or near 100% Faradaic efficiency after controlled potential electrolysis (CPE) between −2.1 and −2.6 V. Isotope experiments employing $^{13}CO_2$ gas lead exclusively to formation of ^{13}CO after CPE as evidenced by IR gas analysis (see Figure S3). These results are consistent with a reduction mechanism in which dimerization of the $CO_2^{\bullet-}$ (which would form oxalate as in eq. 3) is suppressed due to high concentrations of neutral CO_2 molecules within the outer Helmholtz plane of the electrode surface. In this way, any $CO_2^{\bullet-}$ produced reacts with neutral CO_2 before it is able to diffuse away from the surface as in eq. 4 and eq. 5.[6,11,12]

$$2\,CO_2^{\bullet-} \rightarrow C_2O_4^{2-} \qquad \text{(eq. 3)}$$

$$CO_2^{\bullet-} + CO_2 \rightarrow \qquad \text{(eq. 4)}$$



$$+ e^- \rightarrow CO + CO_3^{2-} \qquad \text{(eq. 5)}$$

In addition, after long time frame electrolysis (10−24 h) under the above conditions, a yellow/brown precipitate appears at the counter electrode, which is likely NBu_4^+ cyanoacetate judging by ^{13}C NMR and ^{1}H NMR spectroscopy (see Figures S4 and S5). This side product likely occurs via coupling between $NCCH_2^\bullet$ produced at the anode via eq. 6 and CO_2 and is only seen upon mixing across the counter electrode frit (see eq. 7 and eq. 8 for the propagation steps of this radical

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chain reaction process). Interestingly, CPE performed under identical conditions at 2−3 h time frames shows no indication of cyanoacetate via ^{1}H or ^{13}C NMR. However, a clear signal for carbonate formation is observed at 168 ppm in the ^{13}C NMR spectrum. Upon continued electrolysis up to 65 h, additional unknown peaks appear in the ^{13}C NMR spectrum at 165 and 155 ppm. Interestingly, these peaks do not show coupling to any signals in the corresponding ^{1}H NMR spectrum. In fact, no new proton signals are observed at all. Moving away from acetonitrile into DMF solutions greatly clarifies the NMR analysis. Here, only CO is detected as the gaseous product, and only HCO_3^- is observed by ^{13}C NMR. The additional peaks observed when using acetonitrile are therefore attributable to solvent decomposition rather than CO_2 reduction byproducts. The relevant ^{1}H and ^{13}C NMR spectra are shown in Figures S4−S10.

$$CH_3CN \rightarrow \bullet CH_2CN + H^+ + e^- \quad \text{(eq. 6)}$$

$$\bullet CH_2CN + CO_2^{\bullet -} \rightarrow NCCH_2COO^- \quad \text{(eq. 7)}$$

$$NCCH_2COO\bullet + CH_3CN \rightarrow NCCH_2COOH + \bullet CH_2CN \quad \text{(eq. 8)}$$

Finally, to test the hypothesis of diffusion-controlled outer-sphere CO_2 reduction in the presence of NBu_4^+ ions, we decided to investigate the influence of various solvents. For an outer-sphere electron transfer process, the reaction rate (and thus the measured current density) should strongly depend on the properties of the solvent. Due to the large negative potentials required for CO_2 reduction in aprotic media, there are only a handful of solvents that can accommodate the required reaction conditions. For this reason, we chose to use CH_3CN, THF, DMF, and propylene carbonate (PC) to assess the solvent dependence of this reaction. Figure 2 shows cyclic voltammograms obtained with H-terminated boron-doped diamond and Pt electrodes in the aforementioned solvents saturated with CO_2 in the presence of 0.1 M NBu_4^+ hexafluorophosphate. These data show acetonitrile to be the optimal solvent choice, giving the largest current at the smallest required potential. THF did not perform well in comparison to the other solvent choices, potentially due to its much lower dielectric constant of 7.58 compared to 36.7 for DMF, 37.5 for CH_3CN, and 64.9 for PC. However, DMF (which has a dielectric very close to CH_3CN) and PC (which has a much larger dielectric) also performed poorly in relation to CH_3CN.

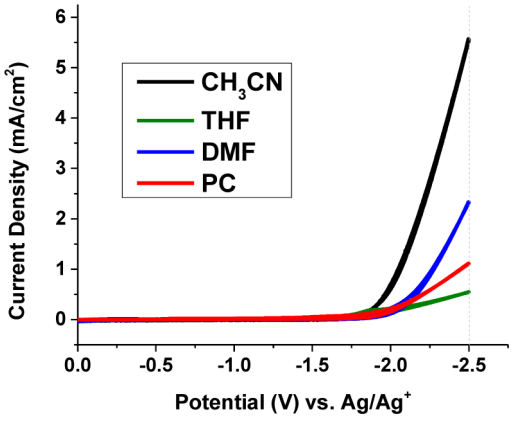

Figure 2. Solvent dependence on CO_2 reduction in the presence of NBu_4^+. Data recorded at 100 mV/s using a boron-doped diamond working electrode.

CO_2 Reduction in the Presence of a Series of NR_4^+ Ions. Given the moderate current densities observed in the presence of NBu_4^+ during CO_2 electroreduction, the investigation of other NR_4^+ salts is warranted. Thus, we chose to look at the effect of varying the alkyl chains between methyl and decyl via addition of the corresponding NR_4^+ salts during electroreduction of CO_2. As shown in Figure 3, all of the NR_4^+ salts tested show reductive current in the presence of CO_2. Most interestingly, all of the trials, with the exception of NMe_4^+, show surprisingly similar electrochemical signatures. This is also evident from CPE experiments, although the data are not as straightforward to interpret. Here, CPE data were collected at −2.2 V vs Ag/Ag^+ (Figure S11). However, standardization of the reference potential to ferrocene reveals that the electrolytes with longer alkyl chains appear to alter the Ag wire reference electrode, effectively increasing the "real" applied potential. While the data shown in Figure 3 have been corrected for this discrepancy, indicating no significant difference in the onset of CO_2 reduction with respect to NR_4^+ ion choice, it was not possible to perform such a normalization of the CPE data. Also, due to the incompatibility of an internal ferrocene standard with CO_2-saturated solutions, all reactions had to be referenced externally to ferrocene, which likely accounts for the small observed spread in onset potentials in Figure 3 due to the reference media not matching exactly that used during CO_2 reduction. We note that NMe_4^+ shows somewhat different behavior from the other electrolytes, showing wave-like behavior in the cyclic voltammogram and a rapid loss of current during CPE. These features are likely due to decomposition of the NMe_4^+ ion during electrolysis.

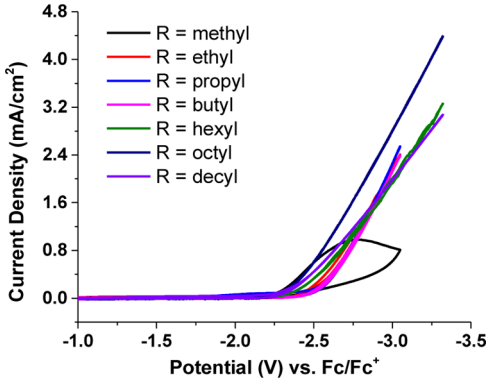

Figure 3. Cyclic voltammetry corrected vs Fc/Fc^+ for CO_2-saturated solutions containing various NR_4^+ salts at 0.05 M. Data recorded at 100 mV/s using a boron-doped diamond working electrode.

The series of NR_4^+ ions was also used to allow us to assess the role of the purported $NR_4^{\bullet}$ radical species as suggested in the literature.[13,14] Relatively little information is available on the electrochemical reduction of NR_4^+ salt solutions. However, reduction of NR_4^+ salts have been shown to give the corresponding NR_3 amine along with either R_{alkane} or R_{alkene}.[20,21] The ratio of alkane/alkene formation depends on the nature of the alkyl substituents and the availability of proton donors in solution. Adventitious water and substituents such as ethyl that are more susceptible to Hoffman elimination will favor the alkene. Alternatively, N−C bond cleavage of $NR_4^{\bullet}$ followed by reduction to give the corresponding carbanion will

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favor alkane products. Dahm and Peters have shown that the electrochemical reduction of NEt_4^+ and NBu_4^+ occurs at similar potentials to CO_2 reduction in our system, although we see no evidence to support this under our experimental conditions.[20] Not only do we see no electrochemical reduction waves in an atmosphere of N_2, but no signs of the expected $NR_4^{\bullet}$ decomposition products have been observed in our NMR studies. Even after more than 100 C of charge has been passed under a constant potential of −2.2 V vs Ag/Ag^+ in CO_2-saturated solution, NMR spectra show no indication of either the alkane/alkene or trialkylamine decomposition products of $NBu_4^{\bullet}$, both of which would be expected to form in some quantity after such a long time frame reduction. All told, these data do not support the role of NR_4^+ as a catalyst or even mediator for CO_2 reduction. Only outer-sphere CO_2 electroreduction is observed as has been previously investigated in great detail.[10,12,18,22]

Inhibition of CO_2 Reduction by Li^+ Ions. In acetonitrile solution, one of the only cation options other than NR_4^+ that is stable under highly reducing conditions is Li^+. Importantly, essentially no current density is seen under CO_2-saturated conditions when Li^+ ions are present (0.1 M) in the supporting electrolyte. This is a general trend observed on all working electrode materials tested: glassy carbon, platinum, and boron-doped diamond. These observations have been explained by Li^+ ions inhibiting CO_2 reduction via formation of a hydrophilic layer at the working electrode.[13,14] Our results are not inconsistent with such an interpretation. Figure 4 shows a comparison of the CO_2 reduction current in the presence of NBu_4^+ ions and lithium ions.

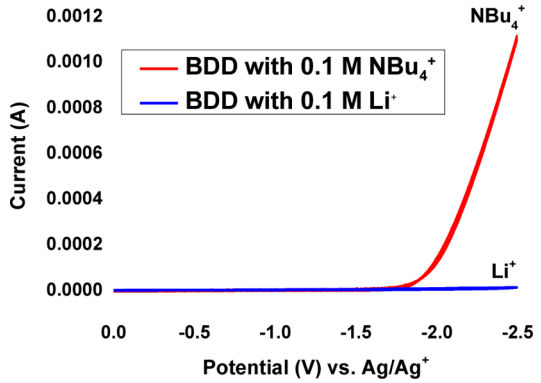

Figure 4. Cyclic voltammetry of CO_2-saturated CH_3CN in the presence of NBu_4^+ and Li^+. Data recorded at 100 mV/s using a boron-doped diamond working electrode.

In the case where Li^+ salts are used as the supporting electrolyte, almost no current increase is observed in the presence of CO_2 as compared to inert N_2 gas. Moreover, Li^+ ions are able to effectively arrest CO_2 reduction even in the presence of NR_4^+ electrolytes. Figure S12 shows that, during CPE, the addition of 2 equiv of $LiClO_4$ (relative to NBu_4^+) to a CO_2-saturated solution with NBu_4^+ rapidly reduces the current to nearly zero. Conversely, even the addition of large amounts of NBu_4^+ to CO_2-saturated solutions containing Li^+ does not result in a noticeable current increase. Thus, it appears as though it is the Li^+ ions, and not the NR_4^+ ions, that interact with the electrode surface. Interestingly, the use of $CsClO_4$ as supporting electrolyte in DMF does show a modest but noteworthy current increase in the presence of CO_2 (see Figure S13).[23] However, CPE experiments at −2.2 V vs Ag/Ag^+ show a rapid drop in current, very similar to what is observed with NMe_4^+ salts (vide infra). The similar ionic radius of Cs^+ and NMe_4^+ potentially allows similar surface interactions with these two supporting electrolytes.

CONCLUSIONS

Based on the available data, the "catalytic" role of NR_4^+ salts in CO_2 electroreduction is non-existent. None of the current data supports a strong electrostatic interaction between either NR_4^+ and CO_2 or NR_4^+ and the electrode surface, and the diffusion-controlled electroreduction best fits a simple direct outer-sphere reduction of dissolved CO_2, the mechanism which was originally put forth by Savéant and co-workers.[18,22] Most importantly, if NR_4^+ ions were involved in catalysis via their corresponding one-electron-reduced radical moiety, the onset of electroreduction should depend greatly on the nature of the R group. This is not the case based on all currently available data. The most likely scenario is therefore that NR_4^+ electrolyte solutions simply do not inhibit outer-sphere CO_2 reduction, whereas Li^+ clearly arrests electroreduction. The observed surface passivation is likely due to either formation of an inhibiting lithium film or to Li^+ adsorption as postulated for photochemical fixation of CO_2 at semiconductor surfaces.[24] Here, Lewis acidic Li^+ ions adsorbed at the electrode surface limit CO_2 adsorption and thus inhibit electron transfer. On the other hand, the diffuse charge density on NR_4^+ ions allows for electrochemical contact between CO_2 and the working electrode surface. At this point, it is clear that carbonate is indeed formed alongside CO but can be lost due to the production of H^+ at the counter electrode.

ASSOCIATED CONTENT

Supporting Information

The following file is available free of charge on the ACS Publications website at DOI: 10.1021/cs501641z.

NMR and FT-IR spectra as well as additional voltammetric data (PDF)

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Notes

The authors declare no competing financial interest.

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