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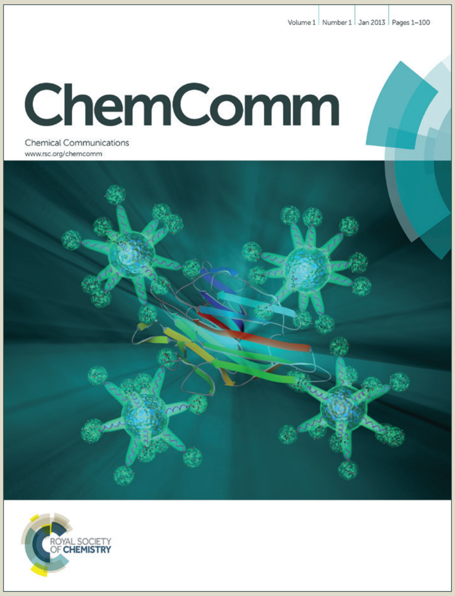

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Selective reduction of carbon dioxide to formate through bicarbonate reduction on metal electrodes: New insights gained from substrate-generation/tip-collection mode of scanning electrochemical microscopy

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We discovered in SECM of electro-reduction of CO_2 at Au in CO_2-saturated $KHCO_3$ solutions that (i) formate comes solely from direct reduction of bicarbonate; and (ii) CO forms only from CO_2 reduction (under low pH conditions) and at higher applied potentials. Results point to the possibility of selective reduction of CO_2 to formate product.

Converting carbon dioxide to useful chemicals in a selective and efficient manner remains a major challenge in renewable and sustainable energy research.[1] Among the several approaches for carbon dioxide fixation[2], its cathodic reduction is one of the promising steps in the total process of carbon dioxide conversion. [1,3] While molecular level understanding of the reduction process has paved way for the discovery of different molecular catalysts,[4-6]electrochemical reduction of CO_2 at metal electrodes[7] in aqueous solutions leads to products like CO, $HCOO^-$, CH_4, C_2H_4 and alcohols in addition to H_2.[8–10]Recently, Compton et al[11] reviewed the work on the use of room temperature ionic liquids for the electro-reduction of CO_2 and in one of the communications[12] formic acid electro-synthesis was studied in acidified ethylmethylimidazolium bis(trifluoromethylsulfonyl)imide. However, there is a need to evolve electrocatalysts that are effective in the aqueous environment. Though the metals with high hydrogen overpotential give highest faradaic efficiencies, only those with low hydrogen overpotentials offer higher energy efficiency. Hence, obtainment of a balance of faradaic vs. energy efficiency with minimum hydrogen evolution requires better understanding of CO_2 reduction on various surfaces vis-à-vis the product distribution. Nanoparticle variants of many metals[13] have also been the subject of exciting recent research activity in the area of carbon dioxide conversion. Gold and silver are interesting electrocatalysts owing to their ability to convert carbon dioxide to carbon monoxide selectively in aqueous solutions at room temperature. [8]

According to Hori and later workers, CO_2 electro-reduction on Au and Ag in 0.1M $KHCO_3$ solution produce CO as the major product with a small percentage of formate ions.[8,9]The proximity of the potentials at which both CO_2 reduction and hydrogen evolution reaction (HER) take place, precludes the possibility of observing current-potential features in aqueous voltammetry. This is made further difficult as the presence of CO_2 moves the solution pH into the acidic region, and thus HER becomes a significant interference. As the current-potential plots are invariably featureless, preliminary identification of the nature of products poses a challenge. Hence, other ways of detecting the reduction products online are to be resorted to. In the bulk electrolysis, the reduction is usually carried out at a fixed potential and the products analyzed by titration methods[14], GC-MS[15], NMR[16] and differential electrochemical mass spectrometry.[17] However, simpler and faster methods of preliminary screening of catalytic surfaces prior to undertaking bulk electrolysis are preferred. To our great advantage, formate/formic acid, alcohols and CO, invariably found in the analysis of CO_2 reduction products are electroactive and hence amenable to electrochemical detection. Earlier work on the use of rotating ring-disk electrode set-up for analyzing the products formed an interesting part of electrochemical studies on CO_2reduction.[18] In comparing SECM and RRDE[19], the former is preferred as its collection efficiency is larger than that of RRDEs (improving the precision of the measurement) and is more convenient, since it allows variation of the substrate-tip distance (d) (compared to the fixed ring-disk spacing) and simple replacement of the substrate (compared to replacement of the disk material). In this work, we employ the substrate-generation/tip-collection (SG-TC) mode of the scanning electrochemical microscopy (SECM) to sense the products of the reduction of CO_2/HCO_3^- at Au substrate (and Ag) using a platinum ultramicroelectrode (tip). In SG-TC experiments the tip travels within a thick diffusion layer produced by the large substrate.[19]

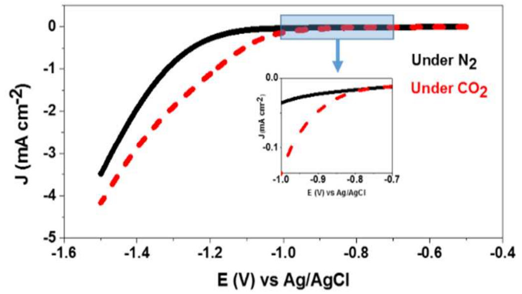

Figure 1. Linear sweep voltammetry of CO_2 reduction on Au in 0.1M $KHCO_3$ solution at a scan rate of $0.05Vs^{-1}$

In the course of investigations on CO_2 reduction at Au electrodes in 0.1M $KHCO_3$ solutions, we observed featureless voltammograms only marked by an infinite current increase at the extreme cathodic potentials both in the absence and presence of CO_2 [Figure 1]. However, interestingly when a Pt ultramicroelectrode (Pt-UME probe) tip is placed close to the Au substrate (cathode) in the SG-TC mode of SECM [Scheme in Figure 2c] voltammetric features typical of formic acid oxidation on Pt appeared in the tip voltammograms. In addition, voltammetric features displaying oxidation of both formic acid and CO appear when $KHCO_3$ is saturated with CO_2, to a varying extent depending on the pH of the electrolyte and the applied substrate potential. We present in this communication (a) the possibility of generation of formate by *direct reduction of bicarbonate* alone; and (b) bring out the fact that CO forms only under low pH conditions (subsequent to the formation of formate) taking advantage ofthe SG-TC mode for determine the exact potentials at which the onset of product generation (here, formate and CO) occurs.

To ensure approach of the tip to the substrate in the SG-TC mode of SECM, a standard probe-approach curve [Figure 2 (a) and (b)] was constructed using ferrocenemethanol probe (1 mM in 0.2M KCl) and brought the probe ≈ 20 µm (*d/a* = 4) (where '*a*' is the tip radius) close to the substrate (as it is appropriate to maintain d/a >> 1 in order to avoid problems due to interference between diffusion layers of the substrate and the tip[20]) before each series of experiments on bicarbonate or CO_2 reduction. A set of cyclic voltammograms at a Pt UME tip (10 µm) for the oxidation of products of bicarbonate reduction at Au substrate in 0.1M $KHCO_3$ solution are shown in Figure 1 C. The responses were acquired at the Pt UME tip kept at a distance *(d)* of approx. 20 µm above the Au substrate that is biased at various cathodic potentials. As can be seen from the CV panel in Figure 2d, at a potential of -0.85V, features of oxidation of small organic molecules[21] start emerging to assume full-fledged characteristics of formic acid oxidation [Figure 1 of Ref. 22(b)] under lower alkaline conditions (the current characteristic of the Pt UME tip in the region of -0.3 to -0.6 V (Figure 2) is likely to arise from the oxidation of molecular hydrogen[22]). ^{13}C nmr spectroscopy confirms formation of formic acid as the main product, ESI, Figure S11.

The scenario totally changes when the bicarbonate solution is saturated with CO_2, with associated change in pH from 8.3 to 6.8. Depending on the substrate potential, a sharp voltammetric peak at 0.6V vs Ag/AgCl emerges to grow in its magnitude at the expense of the response of formic acid oxidation [Figure 3a]. It is easy to understand the origin of this sharp feature, by recalling the conventional knowledge of CO-oxidation on Pt surface.[23] To prove that this is due to the oxidation of CO, the following control experiments were carried out. Tip responses were acquired for the reduction of species produced at the Au substrate from (a) the bicarbonate solution acidified by using a phosphate-buffer of pH 6.8 (equivalent to CO_2-saturated bicarbonate solution) in the SG-TC mode; (b) CO-oxidation at Pt UME in bicarbonate solutions bubbled with carbon monoxide. The similarities in the shape and position of the anodic peak pattern in Figure 3b and 3c confirm that the product of the reaction mixtures (a) and (b) is indeed carbon monoxide, arising from CO_2 reduction on Au surface. Whereas, the solutions of (i) CO_2 + KOH, and (ii) carbonate buffer (1:1 mol % K_2CO_3:$KHCO_3$) yield formate as the product [Figure 4]. That is, when electroreduction is performed in CO_2 + 0.5M KOH solutions (pH = 8.3), only formate ion is formed. However, when the pH was changed to 6.5, CO is obtained as a major product with minor quantities of formate. The following simple equilibria are of relevance to the situation that we are describing:

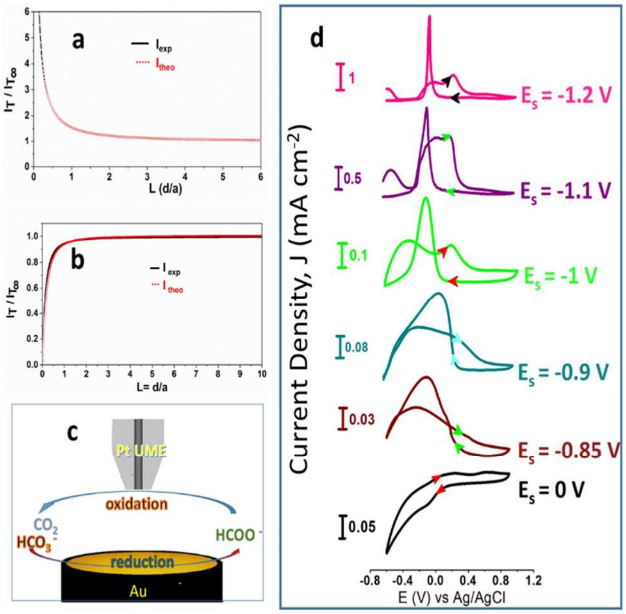

Figure 2: (a) Positive and (b) Negative approach curves of SECM using Pt 10µmUME; (c) Schematic of SG-TC mode for bicarbonate reduction-formate oxidation (d). Cyclic voltammetric responses of Pt UME (10 µm) -tip probe to the products ($HCOO^-$) generated at Au substrate in 0.1M $KHCO_3$.Tip scan rate: $0.05Vs^{-1}$.

$$CO_2 + OH^- \rightleftharpoons HCO_3^- \qquad \text{Equation (1)}$$

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+ \qquad \text{Equation (2)}$$

Similar results were obtained in the case of Ag with inherent differences in the position of the potentials. In spite of the reported similarities in catalytic behavior of Ag with Au, according to the Hori's classification of metals with CO as the major product, the (substrate) potentials are significantly more cathodic than those observed with Au (ESI, Figures S1 and S2). The SG-TC mode is also unique in that it enables identification of the exact substrate potential [e.g., Figure 2 and Figure 3] at which the useful products are formed (formate/formic acid, CO) with total control over the potential needed for the avoidance of hydrogen evolution.

A few control experiments involving other metal surfaces that are electrocatalytic to the reduction of (i) bicarbonate to formate; and (ii) CO_2 to formate, are in order here. Direct reduction of bicarbonate to formate at a palladium electrode was established by Andre and Wrighton[24], Spichiger-Ulmann and Augustynsky.[25] Thus, Pd can serve as a good *benchmark* for quantitative comparison of our result with Au substrate. In accordance with the results reported in ref.25, we notice current peaks corresponding to the direct reduction of bicarbonate in our studies too [ESI, Figure S3 and Figure S4] and identify the peaks are due to the formation of formate ion, with the aid of SG-TC mode. Based on the magnitude of Pt UME tip currents recorded, it may be stated that Au surface is more favorable than Pd in producing formate ion from bicarbonate.

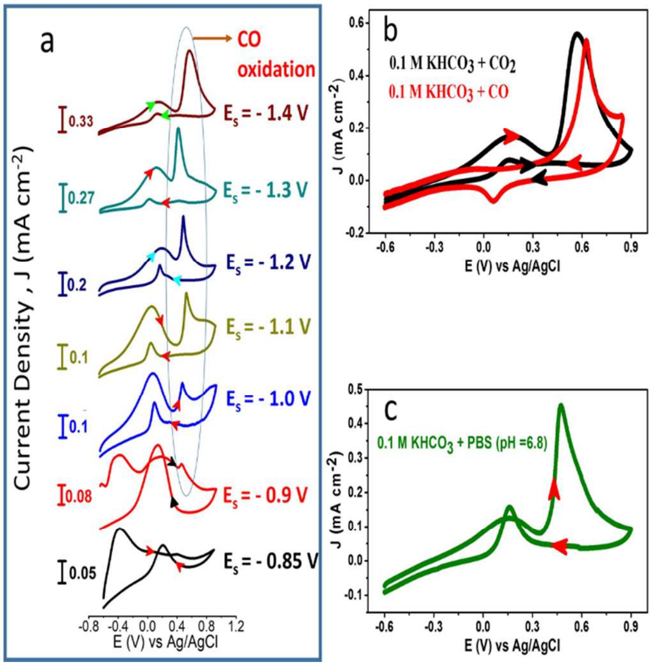

Figure 3. (a) Cyclic voltammetric responses of Pt UME (10 µm)-tip probe to the products ($HCOO^-$ and CO) generated at Au substrate in 0.1M $KHCO_3$ solution saturated with CO_2; Tip scan rate: 0.05Vs^{-1}. (b) Responses of Pt UME (10 µm)-tip probe to the oxidation of CO (red) in CO bubbled 0.1 M $KHCO_3$ (black) CO generated from Au substrate in 0.1M $KHCO_3$ solution saturated with CO_2; (red). (c) 0.1M $KHCO_3$ + PBS solution of pH = 6.8.

We examined the substrate surfaces belonging to the class of metals (Hg, Bi and Sn) that are classified to yield only formic acid/formate as the product of CO_2 reduction[8,9] viz., Hg and Bi besides Pd that is known to produce formate from the reduction of bicarbonate[26]. We collected the tip responses for the products of reduction at the Hg-, Bi- and Pd-substrates. In the case of Hg substrate, potentials as high as -2.0V vs. Ag/AgCl are required to initiate generation of formate from bicarbonate, while the potential is shifted 0.5V less cathodic when the bicarbonate solution is CO_2-saturated to produce only formate [ESI, figure S5 and S6]. Bismuth-coated glassy carbon substrates also show the same trend but with reduction occurring at much lesser cathodic potentials than on Hg (ESI, figure S7 and S8). These results suggest that (a) formate/formic acid generation at these electrodes from CO_2 is easier than from bicarbonate; and (b) only formate/formic acid are generated until the potential limit of hydrogen evolution reaction.

It is now clear that at Au and Ag surfaces (a) bicarbonate undergoes direct reduction; (b) in CO_2-saturated bicarbonate solutions (pH 6.8), bicarbonate undergoes reduction first to produce formate and at higher applied potentials, CO_2 is reduced to CO; (c) in alkaline solutions (pH 8.5 to 10), CO_2-saturated solutions yield Only formate as the main product; (d) whereas even in slightly acidic solutions (pH 6.5), CO appears to be the major product. More importantly, it is demonstrated here that one can have a control over the nature of the product species by exactly fixing the applied potential. This would suggest the possibility of obtaining selectivity between formate and CO based on the applied potentials. It will be much more advantageous if CO_2 is converted to bicarbonate which in turn undergoes reduction at lower applied potentials. The present results in juxtaposition with the suggestion of Koper et al[26] assume significance when other more catalytic metals or alloys (for example, copper) are used. Incidentally, the local pH measurements made [ESI, Notes in Figure S10] during various time intervals of electrolysis show a pH shift towards more alkalinity, pointing to a plausible reduction mechanism involving reactions [equation 3 and 4].

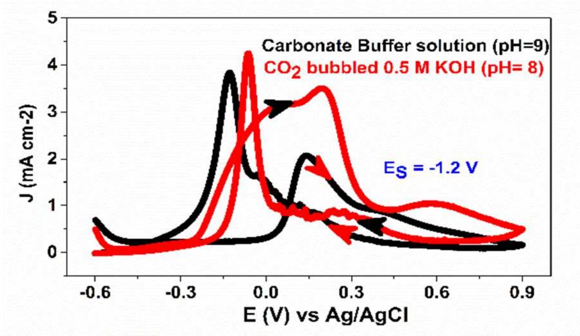

Figure 4. Cyclic voltammetric responses of Pt UME (10 µm)-tip probe the product ($HCOO^-$) generated at Au substrate in0.1M carbonate buffer solution pH = 9 (black) (ii) 0.5M KOH solution saturated with CO_2 pH = 8 (red); Tip scan rate: 0.05Vs^{-1}; Substrate potential E_S fixed at -1.2 V.

$$HCO_3^- + H_2O + 2e^- \longrightarrow HCO_2^- + 2OH^- \quad \text{Equation (3)}$$

$$CO_2 + H_2O + 2e^- \longrightarrow CO + 2OH^- \quad \text{Equation (4)}$$

The present results will eventually lead to the classification of metal surfaces for bicarbonate reduction, as it has been done for CO_2 reduction (ca. work of Hori et al). With a thesis of recent observations on the bicarbonate reduction at copper electrodes[26] and other studies reported on nanostructured electrocatalysts[13,27] it will be possible to design surfaces for selective reduction. We are currently pursuing approaches for electrocatalyst selection that in turn need deployment of product-specific ultramicroelectrode tips for in-situ process monitoring[28] and for mechanistic elucidation that is more involved than the simplistic picture presented in reactions [equation 3 and 4].

Notes and references

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