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# Cathodic Carboxylation of Gold in Thick $\{\text{Au-CO}_2\}_n$ Layers. A Model for Reversible Electrochemical Sequestration of $\text{CO}_2$ .

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## Abstract

Catalytic reduction of  $\text{CO}_2$  (saturated in organic polar solvents, e.g. *N,N*-dimethylformamide, containing  $\text{Me}_4\text{NX}$  or  $\text{NaBF}_4$ ) was achieved at smooth gold electrodes and at glassy carbon electrodes galvanostatically capped with a thin layer of gold. Under these quite explicit conditions, very sharp reduction steps were observed near  $-1.5$  V vs.  $\text{Ag}/\text{AgCl}$ . With small cations listed above, an unexpected behaviour was observed, a progressive electrode inhibition occurring upon several scans or after a fixed-potential electrolysis at  $E < -1.7$  V. This phenomenon could be attributed to the insertion of  $\text{CO}_2$  into gold, leading to the formation of a thick iono-metallic multi-strata layer (less conducting than pure metal) that grows with the electrode charge. The formation of this new interface is due to the concur of three elements: transient  $\text{CO}_2$  anion radical, the metal, and rather small-sized cations ( $\text{M}^+ = \text{Na}^+$  or  $\text{TMA}^+$ ), the three possibly associated in a form  $\{\text{Au-CO}_2^-, \text{M}^+\}$  apparently very reactive with oxygen, moisture, and with some organic  $\pi$ -acceptors. Upon multi-scans up to  $-2.2$  V, the thickness of formed layer progressively increases reaching more than  $10^{-7}$  to  $10^{-6}$  mol  $\text{cm}^{-2}$ . Such multi-layers undergo decomposition in the anodic domain at about  $+1.7$  V liberating  $\text{CO}_2$  beforehand trapped in Au. Coulometric analyses demonstrated that insertion (cathodic) and release (anodic) steps are quite equivalent, which permits to consider this process as chemically reversible sequestration of carbon dioxide.

**Keywords:** Gold electrodes; modified electrodes; carboxylation of conducting solids; Au- $\text{CO}_2$  grafting; fixation of  $\text{CO}_2$

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## 1. Introduction

Electrochemistry is a valuable technique for the insertion of free organic radicals and ions into carbon and metallic matrixes. Alternatively, it is also an interesting way for generating new interfaces, allowing the building of new catalytic electrodes. Among the possibilities for transforming the structure of conductive materials (in particular, carbons and different

graphites using electrogenerated organic radicals [1]), the reactivity of gold with free radicals [2], that of mercury via tetraalkylammonium ( $\text{TAA}^+$ ) amalgams [3], and also the unexpected insertion of salts or cations into platinum and palladium within the cathodic range [4] permit to think that all these cases have the same general phenomenon in common, which is worth to be carefully considered for electrochemistry in the future. Thus, cathodic reactivity of  $\text{TAA}^+$  cations with post-transition metals (antimony, tin, lead) remains of high interest [5]. Generally, such reactions lead to the formation of new materials, possessing reducing abilities as electron transfer agents [6], and should be carried out under inert atmosphere.

On the other hand, catalytic capacities of gold were considerably developed in organic chemistry [7] but much less in electrochemistry: for some reasons, platinum is preferred in analytical electrochemistry, possibly because of its long use. So far, gold essentially remains an excellent tool for fixing thiolates [8]. However, reduction of aryl-diazonium salts on gold results in primary immobilized layer that could further be functionalized via click chemistry permitting attachment of organic groups onto Au NPs [9,10].

Small-size electroactive molecules could—after electron transfer at a metallic interface—act as vectors penetrating and diffusing into metals. The nature of metal and ion-pairs formed with the counter-ion of supporting electrolyte should be considered here. We might expect that carbon dioxide is scheming in this context because its apparent reduction potential is very dependant on the electrode material and on the supporting electrolyte; it certainly obeys catalytic rules already observed with many solid conducting materials such as glassy carbon [11], graphite [12], graphene [13], and lead [14,15].

With this in mind, gold is now used as a catalytic material for the reduction of  $\text{CO}_2$  in the presence of  $\text{Na}^+$  and of some  $\text{TAA}^+$  salts in polar aprotic solvents. It is presented here a very simple scheme where the reduced form of  $\text{CO}_2$  (presumably, its anion radical) may induce—under very specific conditions—a paired formation-insertion of an ion/gold intermediate leading to a drastic drop of conductivity of the electrode.

This process is interestingly related to a coupled anodic step (equivalent in terms of charge to the cathodic step) which is attributed to the release of also permit their carboxylation (superficial and massive). Thus, the process described here could be considered as a reversible sequestration of  $\text{CO}_2$  and be seen as a model for the carboxylation of a wide series of non-corrodible metals (from palladium to rhodium).

## 2. Experimental section

### 2.1. Salts and solvents

In the present work, essentially 0.1 M solutions of tetramethylammonium and sodium tetrafluoroborates in dimethylformamide (DMF) were used. Salts and solvents were purchased from Aldrich (quality for syntheses). The procedures given hereafter can be performed even in reasonably dry commercial solvents, used as received (water content >800 ppm). For excluding oxygen, all electrochemical experiments were performed under inert atmosphere bubbling argon through the solution. Alternatively, corresponding to the aim of this study, liquid electrolytes were saturated with CO<sub>2</sub> (from Air Liquide) bubbling it for 5 min at room temperature.

All potentials are referred to aqueous Ag/AgCl/KCl<sub>sat</sub> electrode. The electrochemical instrumentation has been previously described [11,12].

## 2.2. Working electrodes

Gold and glassy carbon (GC) electrodes used for voltammetry had an apparent surface area of 0.8 mm<sup>2</sup>. Before using, their surfaces were carefully polished with silicon carbide paper (Struers 500 and 1200) or with Norton polishing paper (type 02 and 03) and rinsed with water, alcohol and at last with acetone. After recurrent scans or fixed potential electrolyses, gold electrodes were eventually sonicated for two minutes. Finally, the electrodes were dried with a hot air flow for 30 s. Coulometry and electrolyses reported in this work were carried out using three-electrode two-compartment cells with a total catholyte volume of about 5 mL.

## 2.3. Organic materials

All organic compounds used for testing gold materials, modified by insertion of CO<sub>2</sub>, were purchased from Merck and Aldrich.

# 3. Results

## 3.1. Reactivity of CO<sub>2</sub> at a negatively polarized gold electrode.

Obviously, the experiments described hereafter might appear to a general reader as quite unusual. When polarized gold ( $E < -1.5$  V) and carbon dioxide meet under specific conditions (in the presence of small-sized cations of supporting electrolyte), a spectacularly sharp reduction peak is observed (Figure 1), in contrast to the usual reduction step obtained when using large-sized Bu<sub>4</sub>N<sup>+</sup> cations (Figure 1, A), and which stems from a strongly inhibiting process certainly due to the formation of an organometallic species at gold interface. More specifically, as is featured in Scheme 1, the electrochemical technique may provide a very

easy way to form an intermediate, allying Au and CO<sub>2</sub> (tentatively written as {Ag-CO<sub>2</sub><sup>-</sup>,M<sup>+</sup>} with M<sup>+</sup> representing the cation of the electrolyte). In these experiments, we essentially used the solutions of (TMA<sup>+</sup>BF<sub>4</sub><sup>-</sup>) in DMF saturated with CO<sub>2</sub> (to 0.2 mol L<sup>-1</sup> at RT [16,17]), in contact with the polarized smooth gold electrode. Linear voltammetry reveals a strong increase of intensity at E ≤ -1.4 V (sharp peak (I), Figure 1, B) followed by a quite fast decay until very small currents at E < -2.4 V. Progressive decrease of electron exchange efficiency can be seen through the voltammetry at different scan rates, which suggests the formation of a thick poorly conductive layer of {Ag-CO<sub>2</sub>-M}. Now, resting thus modified electrode under the flow of argon (at 0 V) permits replacing CO<sub>2</sub> with Ar in the cell atmosphere and in the solution. Surprisingly, the response of the gold electrode indicates that it still reacts with some residual CO<sub>2</sub> (Figure 1, C, step (I) slightly shifted relative to the initial step (I), Figure 1, B). It suggests that even under Ar atmosphere, gold still contains quite appreciable amounts of CO<sub>2</sub> probably stockpiled in the metal matrix. The observed potential shift of step (I) could be due to the TMA<sup>+</sup> diffusion inside the metal matrix.

### 3.2. Evidence for electrochemically driven insertion/desorption of CO<sub>2</sub>.

At smooth gold, the solution CO<sub>2</sub>/DMF/TMA<sup>+</sup> does not show any oxidation step up to +2.0 V. Gold electrode, preliminarily carboxylated between -1.1 V and -1.9 V under conditions of Figure 1D (e.g., three consecutive scans, leading to the cathodic insertion of CO<sub>2</sub>, correspond to 4.5 × 10<sup>-7</sup> mol cm<sup>-2</sup>), shows quite different response: large irreversible step (II) at E<sub>p</sub> = +1.76 V. A neat pre-peak is tentatively assigned to the oxidation of the superficial carboxylated layer. Current integration of peak (II)—attributable to the emission of CO<sub>2</sub> through the anodic scission of Au-CO<sub>2</sub> bond—suggests that the initial content of CO<sub>2</sub> in the multilayer amounts to 4.0 × 10<sup>-7</sup> mol cm<sup>-2</sup>. This value is astonishingly close to that obtained during total cathodic charge (leading to complete passivation of the electrode) at the level of step (I). Several experiments matching charge/discharge processes revealed a rather good parity between cathodic and anodic coulometric values. Furthermore, anodic discharge permits to check the emission of CO<sub>2</sub> by the gold electrode: see curve 2 (red), Figure 1D; an additional charge—on the condition of weak diffusion of released CO<sub>2</sub>—allows observing a *new* current increase of peak (I). Similarly, discharge of a carboxylated gold plate (≈ 1 cm<sup>2</sup>) near a smooth gold electrode permits demonstrating the local evolution of carbon dioxide under the conditions of formation of step (I).

### 3.3. Some additional remarks on the charge of gold with CO<sub>2</sub>.

A SEM image (Figure 2) of Au interface after reduction (Step (I)) unravels superficial change of the pristine gold sample. In our sense, the morphology of the surface looks compatible with insertion of CO<sub>2</sub> (formation of {Au-CO<sub>2</sub><sup>-</sup>,M<sup>+</sup>} phase) followed by desorption with large flat deposits. EDS (B) and FTIR (C) confirm surface carboxylation, remaining after sonication. Some traces of fluorine revealed by EDS are thought to arise from the co-insertion of some amount of BF<sub>4</sub><sup>-</sup> anion that is partly involved in the interface structure for compensating the charge of inserted TMA<sup>+</sup> cations left without a counter charge when the carboxylated interface partly decomposes and entrapped CO<sub>2</sub> partly leaves the modified zone.

Finally, Nyquist plots (D) indicate a large increase of the interface impedance.

### 3.4. What about glassy carbon covered with a thin gold layer?

Cathodic behavior of smooth gold in the presence of CO<sub>2</sub> was compared to that of a GC-Au electrode (see Figure 2, E and F). Curve E shows four scans almost limited to the step (I). On the anodic branch (1a) we note, as expected, an anodic peak that corresponds to the evolution of CO<sub>2</sub> along with a reversible pre-peak specifically assignable to surface decarboxylation. Contrariwise, in F (GC-Au electrode), the insertion (first scan) occurs in *two* consecutive steps assigned to the insertion into gold with following carboxylation of GC [8]. Quite amazingly, these two processes merge from the second scan to a single step located between them, which could correspond to the insertion into an intimately mixed material {GC + Metal}. Now the emission of CO<sub>2</sub> occurs according to a sole huge peak ( $4 \times 10^{-7}$  mol cm<sup>-2</sup>) clearly shifted toward less anodic potentials. Therefore, it is expected that dual solid materials used for the insertion of CO<sub>2</sub> may possess peculiar properties. This behavior is confirmed with several mixed metals and alloys (Cu-Pd and Ag-Pd).

## 4. Conclusion

The insertion of CO<sub>2</sub> into gold and GC-Au electrodes under described conditions is apparently limited to small-size electrolyte cations: TMA<sup>+</sup> and Na<sup>+</sup>. The process occurring at about -1.4 V vs. Ag/AgCl is apparently of catalytic nature due to gold. The present contribution reveals a fundamental difference of insertion of CO<sub>2</sub> into gold compared to the process with silver [18], due to the oxidation of Ag<sup>+</sup> in the over-process. Preliminary experiments suggest the carboxylation of metal surface to occur through the inclusion of {Au-CO<sub>2</sub><sup>-</sup>,TMA<sup>+</sup>} layers whose thickness progressively increases with the amount of electricity injected in this process. The cathodic insertion was found to be related to anodic release of CO<sub>2</sub> (around +1.8 V). The whole process thus corresponds to a simple reversible

insertion/emission of CO<sub>2</sub> into gold and it certainly deserves to be considered for other metals as well as for numerous applications at the micrometric scale.

### Figure captions

#### Figure 1

(A) Response of an Au electrode in DMF/0.1 M Bu<sub>4</sub>NBF<sub>4</sub>: (1)–baseline, (2)–saturated solution of CO<sub>2</sub>; (3)–saturated solution of CO<sub>2</sub> in DMF / 0.1 M TMABF<sub>4</sub>. (B) Progressive decay of cathodic current of saturated solution of CO<sub>2</sub> (T ≅ 20 °C) in DMF / 0.1 M TMABF<sub>4</sub> at a smooth Au (0.8 mm<sup>2</sup>) during consecutive scans up to its quasi disappearance.  $\nu = 100 \text{ mV s}^{-1}$ . (C) Response of Au electrode charged with CO<sub>2</sub> after replacing CO<sub>2</sub> with Ar in the electrochemical cell (in DMF / 0.1 M TMABF<sub>4</sub>). (D) Cathodic charge (50 mV s<sup>-1</sup>) and progressive carboxylation of Au electrode under CO<sub>2</sub> atmosphere (decay of step I after several cathodic scans), followed by 2 anodic scans (vertex potential 1.9 V). Total decarboxylation of Au is seen in second anodic scan (red) through the total disappearance of II (oxidation of organometallic phase {Au-CO<sub>2</sub><sup>-</sup>, TMA<sup>+</sup>}). Afterwards, another cathodic scan (2), marked in red, shows the beginning of a *new* carboxylation process (whose signal is quasi overlapping with the initial carboxylation process).

#### Figure 2

Carboxylation of gold. (A) SEM of {Au-CO<sub>2</sub><sup>-</sup>, TMA<sup>+</sup>} interface, (B) EDS elemental composition, (C) FTIR, A:  $\nu_{\text{OH}}$ ,  $\nu_{\text{CH}}$ , 3200-2600 cm<sup>-1</sup>; B:  $\nu_{\text{C=O}}$ , 1700-1600 cm<sup>-1</sup>; C:  $\delta_{\text{C-O}}$ ,  $\delta_{\text{CH}}$ , 1440-1230 cm<sup>-1</sup>; D:  $\delta_{\text{OH}}$ , 930 cm<sup>-1</sup>. (D) Nyquist plot (reduction of tetracyanobenzene, 3 mM): (a) at Au-CO<sub>2</sub><sup>-</sup>, TMA<sup>+</sup>, (b) at same interface, after anodic discharge of CO<sub>2</sub>, (c) after mechanical removal of the modified layer. (E) Charge/discharge processes of gold between -1.5 V and +2.0 V under CO<sub>2</sub> atmosphere (DMF + TMAClO<sub>4</sub>). Total amounts of electricity within the cathodic (charge) and the anodic (CO<sub>2</sub> evolution) ranges are equal. (F) Use of a GC electrode electrolytically covered with a thin deposit of gold ( $6 \times 10^{-4} \text{ mol cm}^{-2}$ ). Charge and discharge of the dual electrode by voltammetry (solution of CO<sub>2</sub> in DMF + TMAClO<sub>4</sub>). The charge–huge oxidation peak II–accumulated in the layer is fairly high:  $4 \times 10^{-7} \text{ mol cm}^{-2}$  (corresponding to almost 0.1 mm<sup>3</sup> of CO<sub>2</sub>).

#### Scheme 1

Electrochemical carboxylation-decarboxylation of gold in the presence of TMA<sup>+</sup> cations

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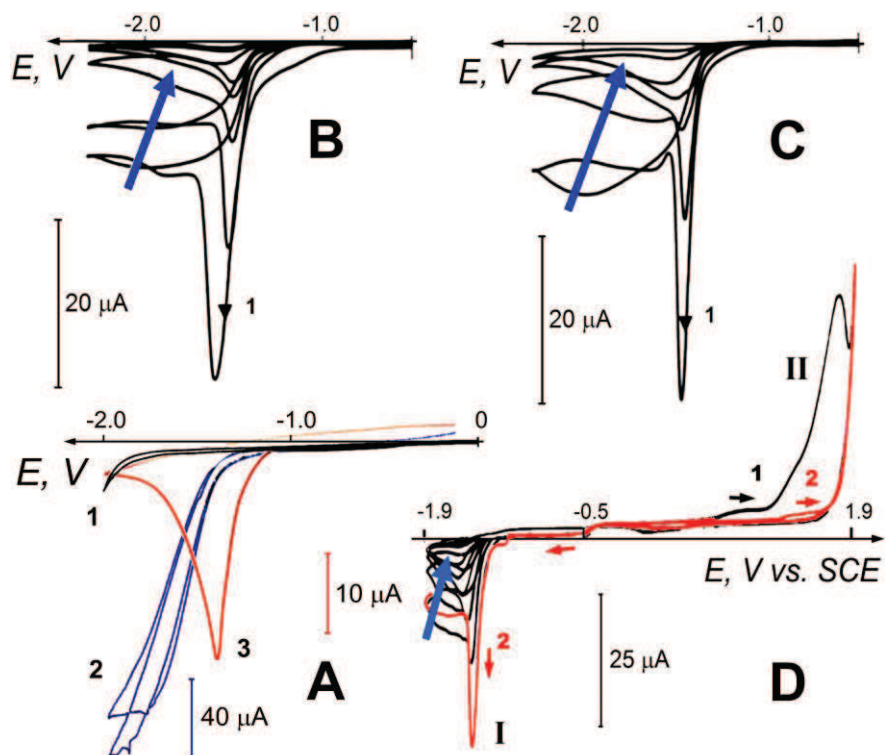


Figure 1

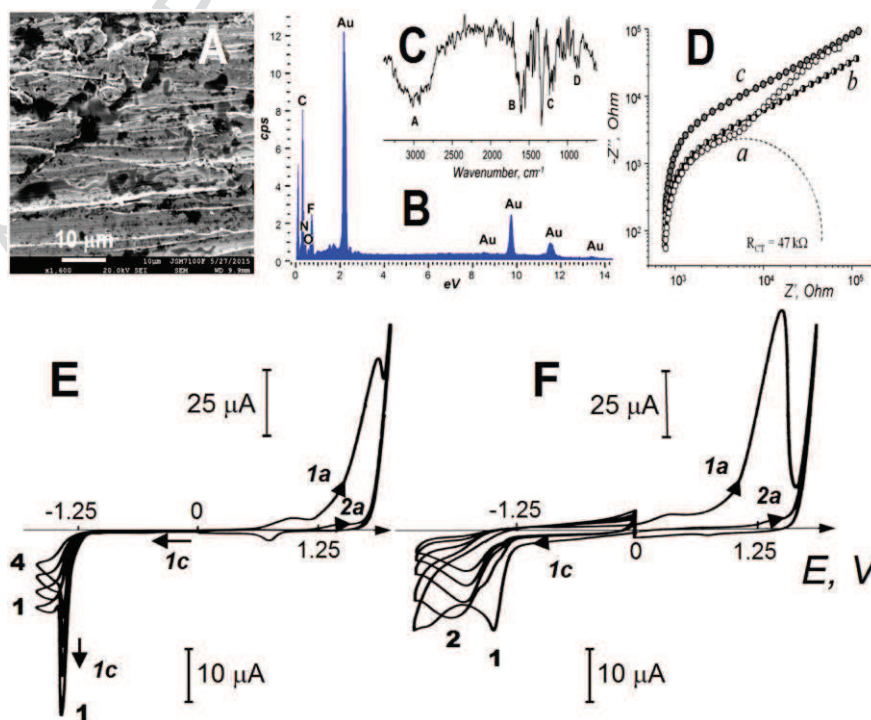
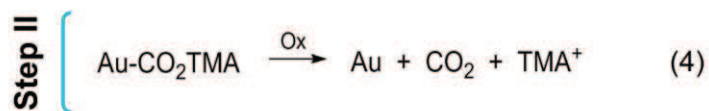
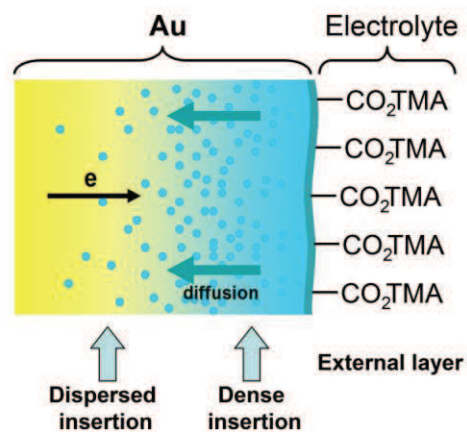
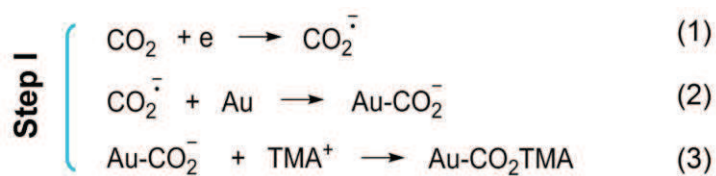


Figure 2



Scheme 1

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**Highlights**

Insertion/desorption of carbon dioxide in gold by cathodic means > Releasing of CO<sub>2</sub> inserted by electrochemical pulse > New 3D modification of gold > A novel process applicable to small size electro-active molecules > A nanometric sequestration of CO<sub>2</sub> in gold > Surface carboxylation of gold.

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