



# Electrochemical carboxylation of titanium to generate versatile new interfaces

Jacques Simonet

MACSE, UMR 6226, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France

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## ABSTRACT

Titanium covered with a thin layer of titanium dioxide was reduced in aprotic polar solvents (dimethylformamide or acetonitrile) saturated with carbon dioxide in the presence of tetraalkylammonium salts (TAAX). When using tetramethylammonium salts CO<sub>2</sub> is irreversibly reduced at potentials < -1.6 V vs. Ag/AgCl/KCl<sub>sat</sub>, generating an inactive surface down to -3.2 V. Anodic oxidation of the modified surface in the same solvent led to regeneration of a titanium interface free of oxide. Employing other TAAX salts permits reversible reduction of CO<sub>2</sub> ( $E_{p/2} = -2.21$  V in the presence of TBuABF<sub>4</sub>). Under conditions of total passivation of the Ti surface followed by sonication, stable electrode surfaces inactive in organic polar solvents between -3 V and +2 V were obtained. Within the cathodic range, several organic  $\pi$ -acceptors were reversibly reduced down to -3 V, which shows the potential of such “Ti-CO<sub>2</sub>” surfaces as new working electrodes.

## 1. Introduction

Carbon dioxide is known to be electroactive at a number of metallic cathodes. In particular, it can be quite easily reduced in aqueous electrolytes and several attempts have been made to develop a process for the selective cathodic conversion of CO<sub>2</sub>. The electrochemical valorization of carbon dioxide is emerging as a real challenge at the present time, principally because carbon dioxide is being produced in huge amounts by industry and a constantly growing world population. Owing to the specific electrophilicity of the carbon atom and its cathodic activity, carbon dioxide could be viewed as a reactive species at electro-generated materials (like poly-anions derived from electroactive carbons and polymers). Specifically, the cathodic charge of allotropic forms of carbon such as graphite, fullerenes, and carbon tissues [1–3] leads to functionalized carboniferous materials. Additionally, CO<sub>2</sub> may be transformed via reduction into valuable products under protic (buffered or unbuffered) conditions. CO<sub>2</sub> can also be chemically converted at various polarized metallic surfaces, optimizing the reduction potential for product selectivity. In particular, CO<sub>2</sub> valorization through cathodic reduction at different catalysts has been recently discussed [4]. This area of study has been well documented [5–12]. However, the cathodic reductions considered are often poorly selective, yielding mainly oxalate, methanol, carbon monoxide and methane.

The catalytic reactivity of CO<sub>2</sub> at cathodically polarized metals like gold, silver, copper, platinum, and palladium has also been reported [13–16]. The cathodic carboxylation of some metal surfaces under specific experimental conditions (aprotic polar solvents containing

tetraalkylammonium salts (TAA<sup>+</sup>X<sup>-</sup>) as electrolytes) allows the reversible formation of thick carboxylated deposits which may be removed by oxidation at very anodic potentials. Carbon dioxide is regenerated and the overall process constitutes a versatile and convenient way to reversibly store this polluting gas. In addition, this simple carboxylation method could also be useful for protecting transition metals (such as Cu, Ni and Fe) against moisture and atmospheric corrosion.

Titanium is a metal of significant industrial interest, principally due to its exceptional resistance to corrosion and excellent biocompatibility (equivalent to that of platinum and gold). Upon contact with air, Ti is spontaneously covered by a protective layer of titanium dioxide (TiO<sub>2</sub>). Efficient anodizing procedures have been used to produce thicker TiO<sub>2</sub> layers [17–18]. In the reverse process, pure titanium can be generated by electrolysis or photochemical methods from TiO<sub>2</sub>, generally in a mixture of molten salts or reducing metals [19–23]. Additionally, the generation of a high conductivity titanium sub-oxide coated electrode has been reported [24]. In analytical electrochemistry, carbon dioxide coverage strongly affects the use of titanium as an electrode material, especially within the cathodic range. Consequently, it would be of great interest to generate a modified oxide-free Ti surface through chemical or electrochemical formation of a layer free of oxides, while ensuring protection against Ti oxidation since, under specific conditions, ‘naked’ Ti still remains reactive toward dioxygen.

Our strategy is based on evidence that TiO<sub>2</sub> layers can be efficiently reduced using specific liquid electrolytes. The procedure consists in reducing, at room temperature, smooth titanium covered by oxide in an aprotic polar medium to produce a pure ‘Ti metal surface’ which would

E-mail address: [jacques.simonet@univ-rennes1.fr](mailto:jacques.simonet@univ-rennes1.fr).

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then react with reagents present in the bulk solution. Clearly, short-lived intermediates produced in situ (such as free radicals) are candidates to react with native Ti. In the present contribution, we focus on the addition of CO<sub>2</sub> reduced form(s) to generate poly-carboxylated titanium interfaces, taking advantage of the fact that they are electrochemically and chemically stable over a large potential range.

## 2. Experimental conditions

As stressed above, the cathodic conversion of CO<sub>2</sub> in aqueous solutions or in organic polar solvents mixed with convenient proton donors has generally been carried out at smooth transition metal electrodes [4]. By contrast, the present study uses only polar aprotic solvents containing exclusively tetramethylammonium TMeA<sup>+</sup> salts (essentially associated with tetrafluoroborate and perchlorate). Importantly, TMeA<sup>+</sup> salts are selected because they are not subject to Hofmann elimination (instability of onium salts [25] that become an efficient source of protons in the presence of bases, here essentially electrogenerated at the cathode surface). Therefore, preventing protonation of the CO<sub>2</sub> anion radical is regarded as key to metal carboxylation. Other TAA<sup>+</sup> salts (such as TBuA<sup>+</sup>BF<sub>4</sub><sup>-</sup>) were also tested in the present study but do not produce any carboxylation of the Ti surface.

Making the titanium electrodes is quite simple: sealing a metal wire (1 mm diameter) in an appropriate glass tube. The electrodes were polished with silicon carbide paper (Struers 500 and 1200) before use and rinsed with water, then alcohol and finally with acetone. High grade dimethylformamide (DMF) and acetonitrile (ACN) were used. The carboxylation method has been previously reported for other metals (Au, Pd, and Pt) [13–16]. Initially, contact of the liquid electrolyte with freshly activated neutral alumina was used, but it was found that simply storing the liquid electrolyte under Al<sub>2</sub>O<sub>3</sub> was sufficient to instigate a solid and stable Ti carboxylation process under good conditions. (In concrete terms, the moisture level of the liquid electrolyte has to be less than 800–1000 ppm to permit an efficient heterogeneous carboxylation process). Thus, the observed fast decay of the CO<sub>2</sub> reduction step upon repetitive scans at > -2.5 V can be seen as a sign of the polycarboxylation of the Ti interface. Solutions of CO<sub>2</sub> were simply obtained by gentle bubbling to obtain a saturated solution of carbon dioxide (at 25 °C, CO<sub>2</sub> concentration is about 0.2 M L<sup>-1</sup> in DMF). After the carboxylation processes described above, the modified titanium plates and disk electrodes were sonicated, rinsed with water and acetone and dried. The modified Ti surfaces showed good stability to the atmosphere and to moisture.

## 3. Immobilization of carbon dioxide at the titanium interface

Before carboxylation, the voltammetry of the smooth Ti surface was recorded in aprotic DMF containing only TMeABF<sub>4</sub> (Fig. 1, curve A). In the cathodic branch, the main reduction wave is observed at about -0.8 V and can be assigned to the reduction of superficial titanium oxides. After several scans, the progressive disappearance of the cathodic waves assigned to different Ti sub-oxides can be observed. Under conditions where there is not too much moisture in the solution (see above) and TMeA<sup>+</sup>BF<sub>4</sub><sup>-</sup> is used as electrolyte, the presence of CO<sub>2</sub> (here saturated in DMF) leads, beyond -1.5 V, to a reduction step which gradually decreases upon repetitive scans due to the loss of surface activity (Fig. 1, curves B). This is attributable to an efficient carboxylation process at a quasi-pure Ti surface. This “native” Ti surface can be successively recarboxylated by reduction (step B), then regenerated by oxidation (step C) without any loss of activity.

After repeated cathodic scans down to -2.4 V, a Ti-CO<sub>2</sub> layer will form and grow over time (see Scheme 1, reactions 1 and 2). Fig. 2A shows the EDX analysis of a carboxylated Ti surface (electrolysis at -2 V of a smooth Ti sample), and Fig. 2B and C show SEM images of the smooth Ti surface and the carboxylated surface, respectively. These analyses confirm the presence of carbon at the Ti surface. The amount

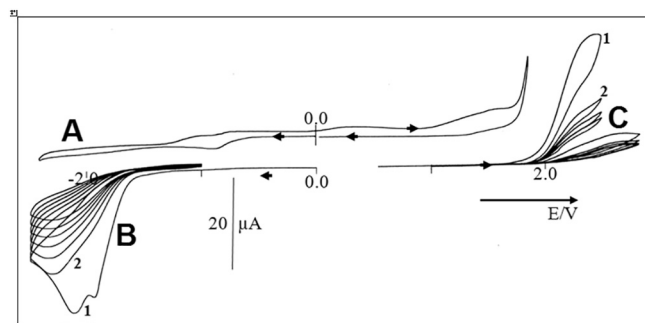
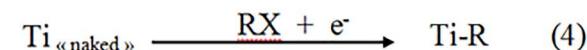
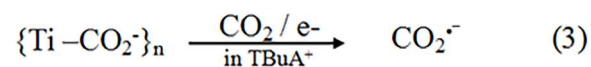
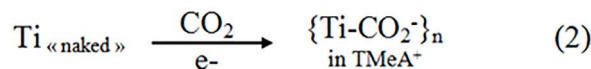
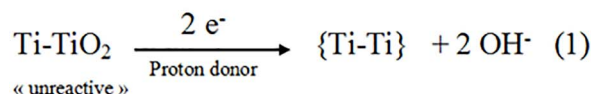
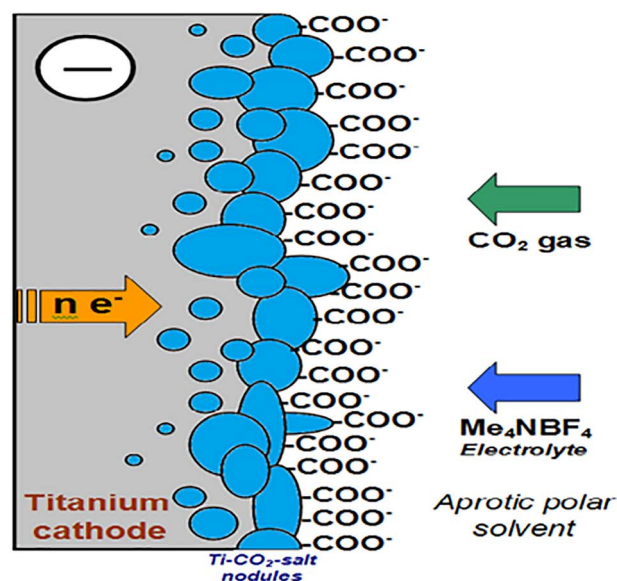


Fig. 1. Voltammetry at Ti electrodes (surface area: 0.8 mm<sup>2</sup>, electrolyte: TAA<sup>+</sup>X<sup>-</sup> in DMF, concentration: 0.1 M). Reference electrode: Ag/AgCl. A: Response of Ti surface alone (modified by TiO<sub>2</sub>) in the presence of Me<sub>4</sub>NBF<sub>4</sub> 0.1 M. Scans from 0 V down to -2.3 V and then one sweep to +2.2 V. Scan rate: 50 mV s<sup>-1</sup>. 1B: Under the same conditions, carboxylation of Ti polarized in the presence of a saturated solution of CO<sub>2</sub> (0.2 M L<sup>-1</sup> at room temperature). C: Oxidation of the carboxylated Ti surface obtained after repetitive scans up to +2.8 V (8 cycles, see Panel B) until a flat response is obtained.



Scheme 1. Schematic representation of the growth of the carboxylated layer according to reactions (1) and (2). There is no carboxylation when using TBuABF<sub>4</sub> as electrolyte. The sole reaction occurring is the reversible reduction of CO<sub>2</sub> (reaction (3)). Lastly, reaction (4) suggests addition of alkyl halides (RX) at  $E < -1.2$  V via free radicals electro-generated in situ.

of electricity required for the complete reductive potentiostatic carboxylation at -2.0 V (reduction peak B of Fig. 1) is equal to the amount used for the complete decarboxylation by potentiostatic oxidation at +2.1 V (oxidation peak C) under a dioxygen-free atmosphere.

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