Special Issue

Electrochemical CO₂ Reduction at Glassy Carbon Electrodes Functionalized by Mn¹ and Re¹ Organometallic Complexes

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The catalytic activities towards electrochemical CO₂ reduction of two new rhenium and manganese complexes, namely *fac*-Mn(apbpy)(CO)₃Br (1) and *fac*-Re(apbpy)(CO)₃Cl (2) (apbpy = 4-(4-aminophenyl)-2,2'-bipyridine), in both homogeneous and heterogeneous phases are compared. A glassy carbon electrode (**GCE**) surface has been functionalized with complexes 1 and 2 by two approaches: a) direct electrochemical oxidation of the amino group with formation of C–N bonds, and b) electrochemical reduction of the corresponding diazonium salts with formation of C–C bonds. The chemically modified GCEs show efficient conversion of CO_2 into CO, with turnover numbers (TONs) about 60 times higher than those of the corresponding catalysts in homogeneous solutions, and in a much shorter time.

1. Introduction

The catalytic reduction of CO_2 is a great challenge for clean energy and environment. The reduction of greenhouse gas (e.g. CO_2) emissions and the quest for new energy sources are currently among the world's top research priorities.^[1] Therefore, CO_2 reduction by renewable energies (artificial photosynthesis) to useful chemicals and fuels such as CO, HCOOH, CH₃OH, and CH₄ is a perfect combination that would give substantial contributions to both fields.

The selective conversion of CO_2 into CO, catalyzed by Re(bpy)(CO)₃Cl takes place via photochemical activation followed by reductive quenching.^[2] Such a mechanism is very close to the electrochemical one,^[3] since in both cases the active catalyst is the 1 e⁻ reduced species. The direct electrochemical reduction of CO_2 is an interesting, convenient, and clean approach because the role of the sacrificial reagent in the photocatalytic process is replaced by electrons. However, for kinetic reasons, the direct electrochemical reduction of CO_2



is a highly unfavorable process that requires a very negative reduction potential (-1.9 V (vs. the standard hydrogen electrode, SHE) in water^[1,4]); thus, the use of a suitable catalyst is mandatory.^[4]

In this context, organometallic $Re^{[2,5]}$ and $Mn^{[5b-d,6]}$ complexes carrying a bipyridyl ligand have been employed as photo- and electro-active catalysts towards the reduction of CO_2 in homogeneous phase. A promising alternative is the hybrid homogeneous-heterogeneous approach,^[7] consisting in bonding an intact organometallic fragment (the catalysts) onto the electrode surface for electrocatalytic CO_2 reduction. Herein, we extended this method employing organometallic Re and Mn complexes (see Scheme 1). While there are several procedures



Scheme 1. The synthesized complexes.

to obtain electrode functionalization,^[7a] two approaches^[7c] have drawn our attention for functionalizing glassy carbon electrodes by intact organometallic fragments: the first consists in the oxidation of a terminal amino group, leading to the formation of a C–N bond, the second is based on the reduction of a diazonium salt that leads to the formation of a strong C–C bond.^[8] Herein we will compare and discuss the properties of these two kinds of functionalization.



Experimental Section

Materials and Reagents

Reagents were purchased from Alfa Aesar and Aldrich and used without further purification. Acetonitrile was distilled over calcium hydride just before use. Materials for electrochemistry were prepared as described elsewhere.^[9] 4-(4-aminophenyl)-2,2'-bipyridine was synthesized according to published procedures.^[10] Re and Mn carbonyl complexes 1 and 2 were synthesized reacting 4-(4-aminophenyl)-2,2'-bipyridine with the corresponding precursor, Re(CO)₅CI or the Mn(CO)₅Br, following a similar synthetic approach as previously reported.^[5–i,11]

Complex 1: ¹H NMR (200 MHz, [D₆]acetone): δ =9.31 (d, 1 H, J= 4.0 Hz), 9.11 (d, 1 H, J=6.0 Hz), 8.73 \approx 8.79 (m, 2 H), 8.22 (t, 1 H, J= 8.0 Hz), 7.91 \approx 7.70 (m, 4 H), 6.85 (d, 2 H, J=10.0 Hz), 5.31 ppm (s, 2 H). ATR-IR (selected): $\tilde{\nu}$ =3408 m, 3321 m, 3203 w, 2016 s, 1914s, 1895 s, 1593 m, 1479, 1441, 829, 188, 686, 632 cm⁻¹.

Complex 2: ¹H NMR (400 MHz, $[D_6]DMSO$): $\delta = 9.02 \approx 9.00$ (m, 2 H), 8.84 (d, 1 H, J = 1.6 Hz), 8.78 (d, 1 H, J = 6.2 Hz), 8.34 (td, 1 H, J =7.9 Hz, J = 1.4 Hz), 7.91 \approx 7.86 (m, 3 H), 7.75 (t, 1 H, J = 6.9 Hz), 6.73 (d, 2 H, J = 8.6 Hz), 5.93 ppm (s, 2 H). ATR-IR (selected): $\tilde{\nu} = 3423$ m, 3320 m, 3201 w, 2015 s, 1892 s, 1596 m, 1442, 1253, 1200, 828, 188, 482 cm⁻¹.

The corresponding diazonium salt chlorides of 1 and 2 were synthesized by an ordinary procedure. The appropriate complex was solubilized into a 37% HCl solution, cooled at -5 °C by salt ice bath, and an aqueous solution of NaNO₂ (1.01 molar ratio) was added over 40 min to the mixture, with a continuous vigorous stirring for further 5 h. The starting yellow color changed to brown and the resulting solid was washed twice with 37% HCl, then with ethanol and diethyl ether, and finally dried under vacuum.

Diazonium salt of complex 1 ATR-IR (selected): $\tilde{\nu} = 3350$ plateau, 2264 m, 2024 s, 1907s, 1612 m, 1581 m, 1476, 1440, 1396, 826, 789, 680, 628 cm⁻¹.

Diazonium salt of complex 2 ATR-IR (selected): $\tilde{\nu}$ = 3386 plateau, 2272 m, 2294 m, 2014 s, 188 3 s, 1604, 1475, 1441, 191, 167 cm⁻¹.

Electrochemistry

Electrochemical experiments were carried out in freshly distilled acetonitrile 0.1 m TBAPF₆ solutions, in the usual conditions^[9] employing an Autolab PGSTAT302N electrochemical analyzer. Glassy Carbon Electrode (GCE) was used as working electrode, Ag wire as pseudo reference and Pt wire as counter electrode; all the potentials are reported against ferrocene/ferrocinium (Fc/Fc⁺) redox couple.

General Procedure for Electrode Functionalization

Two approaches were adopted for electrode functionalization: the first one is based on the oxidation of the amino moiety to get a C-N bond, the second consists in the reduction of the diazonium salt to get a C-C bond. Before every experiment, the working electrode was polished on alumina nano-powder suspended in deionised water, and rinsed with water and acetone. Background current was registered in a solution containing only the supporting electrolyte. The functionalization was accomplished by cyclic voltammetry (CV) in a 1 mm acetonitrile solution of the selected complex,

using TBAPF₆ 0.1 M as supporting electrolyte. For amino-containing complexes (1 and 2) the switching potential was selected to be more positive than the oxidation peak of the amino group. On the contrary, functionalizations leading to the formation of C--C bonds on the electrode surface were obtained by selecting a switching potential more negative than the reduction of the corresponding diazonium salts. The formation of C-N bond via oxidative pathway was obtained from solutions containing collidine (2,4,6-trimethylpyridine), which helps the functionalization by favouring the radical cation deprotonation, as previously described. $^{[7c,12]}\xspace$ After each functionalization cycle the electrode was rinsed with solvent and sonicated for 2 min in distilled acetonitrile, to remove physisorbed molecules. The presence of the covalently bound complexes was evaluated electrochemically in a solution containing the supporting electrolyte only, which generated reversible redox signals characteristic of the chemically bonded species. Electrodes area were assessed by chronoamperometric measurements of a ferrocene solution at a known concentration, in a similar way as previously described.^[7c]

2. Results and Discussion

Figure 1 shows the CVs of complexes 1 and 2 in acetonitrile solution under Ar. The electrochemical behavior of 1 and 2 is



Figure 1. a) CVs of a 1 mm solution of 1 in acetonitrile (GCE \emptyset 3 mm), and b) CVs of a 1 mm solution of 2 in acetonitrile (GCE \emptyset 1 mm) at a scan rate of 0.2 V s⁻¹.



Table 1. Half-wave and peak potentials for 1 and 2 and for similar complexes (in V vs. Fc/Fc $^{\rm +}$).					
Complex	E _{1/2} (0/1 ⁻)	E _p (1 ⁻ /2 ⁻)	E _p (1 ⁻ /0)	E _p (0/1 ⁺)	Ref.
1 2 Mn(bpy)(CO) ₃ Br Mn(dmbpy)(CO) ₃ Br Mn(bpy- ^t Bu)(CO) ₃ Br Re(bpy)(CO) ₃ Cl Re(dmbpy)(CO) ₃ Cl	$\begin{array}{c} -1.52^{[a]}\\ -1.70\\ -1.64^{[a]}\\ -1.72^{[a]}\\ -1.77^{[a]}\\ -1.72\\ -1.81\\ -1.83\end{array}$	-1.76 -2.12 -1.88 ^[a] -1.97 -1.95 -2.11 -2.15 -2.21	-1.42 -1.57 -1.47 -1.56 -0.68	-0.61 -0.49 -0.59 -0.63	This work This work [5b] [5b] [6b] [14] [14a] [14a]
[a] E_p for irreversible processes. [b] Two-electron reduction.					

similar to that of analogue derivatives extensively investigated.^[6b, 10a, 13] Details are listed and compared in Table 1.

The electrochemical behavior of complex **1** is similar to that of the parent compound $Mn(bpy)(CO)_3Br.^{[5b]}$ After the first irreversible reduction ($E_p = -1.52$ V) the Br⁻ is quickly released. The remaining fragment dimerizes, forming the neutral Mn dimer that is reduced at -1.76 V vs. Fc/Fc⁺. The reoxidation of the radical anion and the dimer can be observed at -1.42 V and -0.61 V, respectively.

The CV of complex **2** shows the classical first reversible or quasi-reversible reduction $(E_{1/2} = -1.70 \text{ V vs. Fc/Fc}^+)$ and a second irreversible reduction at more negative potential $(E_p = -2.12 \text{ V vs. Fc/Fc}^+)$ followed by the release of Cl⁻.^[15] Although the radical anions of bipyridyl Re analogues are generally stable at low temperatures, they could still lose Cl⁻ at r.t., ^[13b] whereas in the absence of a coordinating solvent they can dimerize.^[14b] The peaks at -1.57 and -0.49 V are due to the reoxidation of **2** (where Cl⁻ is replaced by the solvent) and of the dimer, respectively.^[16] Complexes **1** and **2** show a further reduction process at more negative potential that will not be discussed here. The Randles-Sevčik analysis (plot of peak currents vs. square root of the scan rate) is linear, indicating that the electrochemical behavior of these complexes is diffusion-controlled (Figure S1).

Since the Mn complex 1 does not have local proton sources, under CO₂-saturated solution ($\approx 0.28 \text{ m}^{[6b, 17]}$) it does not show any catalytic activity (Figure 2 a).^[5b,c] The progressive addition of a Brønsted acid (water or methanol) results in a dramatic increase of current after the second reduction. The maximum peak current was obtained with the addition of 8% (v/v) water or 4% (v/v) methanol (Figure 2 and Table 2). Higher quantities had limited effects on the observed catalytic current peak.

Complex **2** shows an evident catalytic reduction of CO₂ already after the second reduction process (with $E_p = -2.15$ V, see Figure 3), even in the absence of Brønsted acids.

Usually, the addition of Brønsted acids increases the catalytic current observed employing rhenium bipyridyl derivatives.^[6b,18] However, in the case of **2**, a small addition of methanol (0.5% v/v) did not alter significantly the catalytic current (Figure 3 b), while higher quantities (up to 12.5% v/v) had the effect of increasing the catalytic current in CV, and eventually exceeds the value in the absence of acid.

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Figure 2. CVs of 1 in acetonitrile solutions (a), with added water (b), and with added methanol (c) at a scan rate of 0.2 V s^{-1} .

Normally, turnover frequency (TOF), turnover numbers (TONs), faradic efficiency (FE), selectivity, and lifetime parameters are used to evaluate the catalytic activity.^[1, 19]

The TOF can be roughly estimated by Equation $(1)^{[6b,20]}$ at catalyst peak potential from a single CV, as proposed by Savéant and co-workers:^[21]

$$\frac{i_{\rm c}}{i_{\rm p}} = \frac{1}{0.4463} \frac{n_{\rm c}}{\sqrt{n_{\rm p}^3}} \sqrt{\frac{RT}{F}} \sqrt{\frac{(TOF)}{v}} \tag{1}$$



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Table 2. Catalysis properties.								
Complexes	$i_{\rm c}/i_{\rm p}^{\rm [a]}$			TOF ^[b] [s	-1]		<i>E</i> _p [V]	Ref.
	CH₃CN	H ₂ O (concentration)	MeOH (concentration)	MeCN	H ₂ O	MeOH		
1	1.0	16 (8%)	6 (4%)	0	99	14	-1.76	This work
2	9.7	11.8(8%)	8.3 (4%)	36	54	27	-2.12	This work
Re(bpy)(CO) ₃ Cl	3.4	-	-	2.2	-	-	-2.11	[14a]
Re(bpy- ^t Bu)(CO)₃Cl	18.4	-	-	65	-	-	-2.21	[14a]
[Re(bpy- ^t Bu)(CO)₃(MeCN)](OTf)	3.3	9.0 (10 м)	42 (9.9 м)	2.1	16	340	-2.21	[6b]
Mn(bpy)(CO)₃Br	1.0	1.6 (2.77 м)	-	0	0.5	-	-1.88	[5b, 22]
Mn(bpy- ^t Bu)(CO)₃Br	1.0	25 (3.1 м)	26 (5.8 м)	0	120	130	-1.95	[6b]
[a] Calculated or obtained from corresponding works. [b] Calculated with Equation (1) or obtained from corresponding works; En: Catalyst reduction peak								



potential. (F=9.648456×10⁴ C/mol, R=8.31441 J/(Kmol), T=298.5 K, F/RT=38.88 V⁻¹, v=0.2 V s⁻¹).



where i_c and i_p are the catalytic and peak current in the presence and absence of catalysis, respectively; n_c (=2) and n_p (=1) are the number of electrons involved in the catalytic and catalyst reduction, respectively, *F* is the Faraday constant and ν is the applied scan rate.

Table 2 reports the ratio between the catalytic current (i_c) and the current peak (i_p) under Ar with 8% (v/v) water or 4% (v/v) MeOH for 1 and 2 together with analogue compounds. Both complexes 1 and 2 show high TOF at less negative potentials than analogue complexes. For instance, 1 displays TOF comparable with Mn(bpy-tBu)(CO)₃Br, but at about 200 mV less negative potentials. The effect could be assigned to the electronic properties of the aminophenyl moiety.^[14a] While the CV is suitable for getting a rough estimation of the catalytic process at the very beginning of the cycle, a better overall picture can be guessed from the longer time control potential electrolysis (CPE) experiments (Table 3 and Figures S2 and S3 in SI). From CPE experiment, complex 1 shows much better selectivity with MeOH than water (Figure S2), and it is more stable under lower potential. Complex 2 exhibits \approx 3 fold TONs of Re(bpy)(CO)₃Cl in dry MeCN (Table 3 and Figure S3).

Whether the CV or the CPE is considered, the catalysis occurs in the reaction layer, involving only the catalyst present near the electrode surface, that is, a limited quantity if compared with the catalyst present in the bulk of the solution.^[21a] Moreover, electrolysis in homogeneous solution not always gives straightforward real activity and lifetime of a new catalyst, since it can be renewed or consumed by diffusion from the bulk of the solution.^[21] Herein we suggest that one or few molecular layers of catalyst deposited on the electrode surface would offer a faster and reliable way to establish the catalyst properties, overcoming the disadvantages of an homogeneous system. Furthermore, after molecular immobilization, the steric hindrance may only permit the two-electron reduction pathway.^[24]

2.1. Oxidative Functionalization to Form C-N Bonds

The first approach adopted to functionalize glassy carbon electrodes consists in the oxidation of a terminal amino group, leading to the formation of a C–N bond in the presence of collidine. Figure 4 shows the oxidation process carried out at a scan rate of 0.2 V s^{-1} .



Complex	Acid in MeCN	Potential [V]	Time [min]	TON _{CO}	FE _{CO} [%]	Ref.
1	No Acid	-1.85	-	-	-	This wor
	4 % H ₂ O	-1.73	90	12	93	This wor
		-1.85	120	10.9	56.5	This wor
	8% MeOH	-1.85	120	3.6	96.0	This wor
2	No Acid	-2.03	120	7.4	100	This wor
	8% MeOH	-2.0	120	12	96.4	This wor
Mn(CN)(bpy)(CO) ₃	0.5 м Phenol	-2.20	-	4	98	[26]
Mn(bpy)(CO)₃	5% water	-1.78	240	13	100	[5b]
		-1.88	240	13	90	
MnBr(HOPh-bpy)(CO) ₃	5% water	-1.88	240	2.7	76	[22]
Re(bpy)(CO)₃Cl	10% water in DMF	-1.88	180	5.1	98	[13a]
	No acid	-2.02	117	2.8	96	This wor
FC of 1 diazonium salt	4 % H ₂ O	1.75	71	359.6	75	This wor
	8% MeOH	1.95	24	145.2	66.1	This wor
FC of 2 diazonium salt	No Acid	-2.10	29	402.4	100	This wor
FC of 2 oxidation	No Acid	-2.00	20	321.1	100	This wor
Re(bpy)(CO) ₃ Br ^[a]	phosphate buffer (p \approx 7)	-1.98	143	155 134 ^[b]	15.4 ^[c]	[27]
Mn(bpy)(CO) ₃ Br ^[a]	phosphate buffer (pH \approx 7)	-1.92	240	471	51	[28]

Both 1 and 2 behave similarly, displaying an oxidation peak around 0.72 V in the first cycle, due to the oxidation of amino moiety to form the C–N bond.^[7c] After several CV cycles, the current degrades to the background, indicating that the surface has been completely covered with the complexes. The stability of the modified electrodes has been evaluated performing a series of CVs in fresh electrolyte solutions.

The resulting electrode functionalized with **1** proved to be quite instable (Figure 5 a). In the first CV cycle, the first peak corresponds to the reduction of **1** followed by the release of the bromide anion. The side and second peaks are assigned to the formation of the dimer and its reduction, respectively. Unexpectedly, the surface quickly decomposes after the reduction and completely loses its functionalization after four cycles.

Conversely, complex **2** provided a stable functionalized electrode (Figure 5 b), retaining its properties for 24 h in acetonitrile or for one week when exposed to air.

The surface coverage (Γ) has been assessed by means of Equation (2)^[7c, 25]:

$$\Gamma = \frac{Q}{FA} \tag{2}$$

where Q is the charge oxidizing (or reducing) the organometallic complex on the electrode surface evaluated by integration of the background-corrected CVs, F is the Faraday constant and A is the area of the electrode.

In the case of oxidative functionalization with **2**, a value of $\Gamma = 4.3 \times 10^{-10} \text{ mol cm}^{-2}$ has been estimated. Meanwhile, the plot of the peak current versus scan rate reveals a linear dependence (Figure 6), indicating that the redox process is no longer diffusion controlled, and the electrochemical behavior is that of an adsorbed species on the electrode surface. Following the same methodology previously discussed,^[7b] the electrode surface coverage can be estimated from the peak cur-



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Figure 4. Oxidation CVs at 0.2 Vs^{-1} for electrode modification with 1 (a) and 2 (b) in the presence of collidine.



Figure 5. First and steady-state CVs of the electrode modified with complexes 1 (a) and 2 (b) at a scan rate 0.2 V s^{-1} .

can be estimated to be 2.3×10^{-10} and 3.4×10^{-10} mol cm⁻², for the reversible or irreversible cases, respectively. These values are of the same order of magnitude observed for a monolayer of organometallic derivatives of similar dimensions.^[7c]

The electrode functionalized with **2** has been tested in the presence of CO_2 (saturated solutions). The functionalization has a dramatic effect, increasing the current by 86-fold in the first cycle, if compared to the argon saturated solution, indicating a strong catalytic activity for **2** anchored on the electrode surface. However, after only 10 CV cycles the functionalized electrode surface loses completely its catalytic activity towards CO_2 reduction (Figure 7).

In homogeneous solutions the catalyst and substrate are mixed thoroughly, so that a 3D reactivity take place. On the contrary, in heterogeneous condition the catalysis occurs only in 2D and Equation (1) is no longer applicable, even though the ratio of the peak currents is still related to the catalyst activity, and proportional to the TOF.^[22]

The catalytic activity per molecule can be roughly estimated from the CVs via TON', defined as [Eq. (3)]:

$$TON' = \frac{1}{n_s} \frac{\text{moles of catalytic reduction charges}}{\text{moles of catalysts}}$$
(3)

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Figure 6. Plot of current peak versus scan rate for an electrode surface modified after the oxidation of 2.



Figure 7. CVs under CO_2 of the electrode modified by complex 2 at a scan rate of 0.2 Vs⁻¹.

where n_s is the number of electrons needed to reduce one molecule of substrate ($n_s=2$ for producing H₂, CO or HCOOH). The reduction charges under CO₂ were calculated by charge integration of the CV, adopting the CV background as baseline. By this method a **TON**' of 364 can be estimated.



To identify the products, CPE was carried out at -2.03 V under CO₂ with the modified electrode; the amount of catalyst on the surface was calculated by charges integration. Evolution of CO and negligible amounts of H₂ were detected by gas chromatography (GC) within 30 min, when the catalytic current decreased to 10% of the initial value reaching the GC detection limit. By this method a TON value of 321 was obtained (Figure S2 and Table 3).

TON' (obtained by CV) and TON (obtained by CPE) values are in good agreement. Thus we propose to evaluate the catalyst activity simply from the CVs of the surface-modified electrodes, resulting in less complicated, smaller amount and much shorter time experiments.

2.2. Reductive Functionalization to Form C-C Bonds

To increase the stability of the functionalized electrodes, a second approach based on the reduction of diazonium salt was adopted. This method, which employs the diazonium chlorides of complexes **1** and **2**, leads to the formation of strong C–C bonds between the surface and the catalysts. Figure 8 displays the electrode functionalization by CV scans at reduction potentials. During the first cycle there is no evident current peak, but instead a broad plateau. In the following



Figure 8. Electrode functionalization with diazonium salts of: a) 1 and b) 2. Scan rate: 50 mV s⁻¹.

cycles, a more marked peak appears; the shift of peak position indicates multi-layer formation.

Both the resulting functionalized electrodes exhibit an evident and sharp reduction peak in the first CV, which vanish in the following cycles (Figure 9). From the analysis and compari-



Figure 9. First and steady-state CVs of electrodes modified with diazonium salts of 1 (a) and 2 (b).

son of CVs in homogeneous solutions of **1** and **2**, the peaks around -1.36 V and -1.90 V can be directly assigned to the release of Br⁻ and Cl⁻, respectively. Both surfaces show a nondiffusion controlled electrochemical behavior (Figure 11 for **1** and Figure S5 for **2**) and are stable, displaying limited changes after exposure to the air for one week.

If only one or two CV cycles are applied, a very thin and stable film of complex 1 can be obtained after the release of bromine (Figure 10). CV shows three cathodic (at -1.78, -1.45, -1.35 V) and three anodic (at -1.66, -1.44, -0.58 V) peaks in a single CV. The peak at -1.35 V can be assigned to the reduction of 1 in which Br⁻ has been substituted by a single acetonitrile molecule. The peak at -1.45 V is assigned to the one electron reduction of the dimer, which is formed by adjacent monomers. The peak at -1.78 V is the reduction of the dimer to get one electron charged monomer, in a similar fashion as reported in homogeneous solutions.^[6d] Continuous CVs scan from -0.75 to -2.25 V, avoiding the oxidation of the dimer at



Figure 10. a) CVs of an electrode functionalized by a diazonium salt of 1 (black: origin stable CV by full scan; green: first CV by scan start from -0.75 V; red: stable CV by scan start from -0.75 V continuously); b) CV of an electrode functionalized by a diazonium salt of **2** versus ferrocene.

-0.58 V, show that the peak at -1.35 V vanishes (Figure 10a). When the CV scan is performed starting again from-0.4 V (i.e. the dimer is oxidized), the peak at -1.35 V reappears, restoring the original stable CV. All these data suggests that this peak is associated to the reduction of the solvated complex.

According to the stable CVs, the coverage calculated by the charge method [Eq. (2)] is $5.7 \times 10^{-10} \text{ mol cm}^{-2}$. Plotting the peak current versus scan rate, the surface coverage is calculated to be $4.1 \times 10^{-10} \text{ mol cm}^{-2}$ (Figure 11).

Unlike the oxidative functionalization, the reductive approach with diazonium salt provides multilayers by increasing the number of functionalization cycles. For complex **2**, the coverage reached as a function of the number of cycles is listed in Table 4. Thereafter the coverages are evaluated using the charge method [Eq. (2)].

In the case of the electrode functionalized with complex **2**, the stable surface shows three evident reduction peaks (Figure 10b). The small reduction around -1.2 V is attributed to the opposite charges on the layers,^[29] and the following reductions at -1.5 V, -1.7 V, -1.9 V and the corresponding counter peaks are due to the same process observed in the homogeneous solutions (the reversible redox process at $E_{1/2}=0$ V is due



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Figure 11. Plot of the current peak of the first reduction versus the scan rate for a surface functionalized with diazonium salt of **1**.

Table 4. Functionalized electrode properties of complex 2 (currents in μA).						
Cycles	1	5	10	15		
Coverage/ 10^{-10} mol cm ⁻² i_{CO2} i_{Ar} i_{CO2}/i_{Ar}	3.9 30.15 0.318 97.9	17.5 54.66 0.87 63.1	26.5 60.60 1.26 48.4	45.4 84.40 2.05 41.2		

to the ferrocene, added as internal standard). At -0.5 V, the oxidation peak is due to the overlapped oxidations of the dimer and of the derivative coordinating a solvent molecule (Figure 12), similarly to the case of complex 1.

Employing the electrode functionalized with multilayers of 1 (1 mm diameter GCE, 0.72 mm²) with a coverage of 13.5×10^{-10} mol cm⁻² in a solution saturated with CO₂, no significant difference is observed in the first two reduction peaks, while the addition of methanol induces a dramatic change at the second reduction peak. When the volume of methanol reaches



Figure 12. CVs of an electrode functionalized with diazonium salt of 2 after different cycles (black to green are 1, 5, 10, and 15).



Figure 13. CO $_2$ reduction CVs of an electrode functionalized with diazonium salt of 1 in methanol at a scan rate of 0.2 V $s^{-1}.$

20%, the current reaches the maximum value (Figure 13). However, it should be recalled that in the presence of multilayers the current ratio $i_p/i_c = 8.5$ underestimate the real activity of the catalysts on the surface.



Figure 14. Properties of an electrode decorated by a diazonium salt of 1 with 20% methanol: a) decrease of CO_2 reduction; b) fit plot of the decrease of CO_2 reduction and integrate.

Employing the 6.24 mm² electrode with a coverage of 14.3×10^{-10} or of 6.4×10^{-10} mol cm⁻² in a CO₂ saturated solution with 20% methanol, the current ratio is $i_p/i_c = 8.3$ and 24.4, respectively. After addition of the acid, the surface degrades within successive cycles. For the coverage 14.3×10^{-10} mol cm⁻², there is no evidence of residue activity after 60 cycles, when the applied voltage is -2.15 V (Figure 14).

Applying a voltage of -1.9 V with a coverage of 6.4×10^{-10} mol cm⁻², the activity is retained for 100 cycles. To roughly estimate the catalytic activity, TON' were calculated (Figure 14) for three different electrode to be 209, 218 and 201 for coverages of 14.3×10^{-10} , 10.1×10^{-10} , and 6.4×10^{-10} mol cm⁻² and applied potentials of -2.15, -2.00 and -1.90 V, respectively. These data suggest that there is no effect of the potential applied in the adopted range, and a mean TON' of 209 can be assumed for **1** with methanol.

Similarly, to evaluate the properties of complex **2**, CVs of the electrode functionalized with **2** [coverage 19.8×10^{-10} mol cm⁻² calculated by Eq. (2)] were recorded under CO₂ atmosphere. The catalytic current decreased progressively cycle after cycle (Figure 15), however the electrode maintained a quite long lifetime if compared with the corresponding electrode modified by oxidative functionalization. The activity lasted for more than 200 cycles when applying a potential of -2.2 V, with a TON' value of 377. TON' of 387 and 384 were obtained for electrodes with Γ equal to 13.2×10^{-10} and 16.7×10^{-10} mol cm⁻², respectively, at -2.0 V and at a scan rate of 0.1 V s⁻¹.



Figure 15. CO_2 reduction CVs of an electrode decorated by a diazonium salt of 2.

To check the TONs, CPE was carried out and the catalytic products were identified by GC (Table 3 and Figure S6–S8). All TON and TON' values are in very good agreement. This once more confirms that TON' is a reliable index to estimate the catalytic activity.

3. Conclusions

Two new rhenium and manganese complexes, containing a substituted bipyridine ligand bearing an amino group, have



been synthesized and their catalytic activities tested towards electrochemical CO_2 reduction.

The behavior of the complexes fac-Mn(apbpy)(CO)₃Br (1) and fac-Re(apbpy)(CO)₃Cl (2) (apbpy = 4-(4-aminophenyl)-2,2'-bipyridine) was investigated in both homogeneous and heterogeneous phases.

Two different electrode modification methods were employed for the functionalization. The complexes with amino terminal group were successfully grafted onto the electrode surface according to an electrochemical oxidation reaction forming C–N bonds. The reduction of the corresponding diazonium salt derivatives provided a grafting based on C–C bonds.

Both complexes exhibit high catalytic activity, reducing CO_2 to CO. The heterogeneous surfaces modified by the catalyst are much more efficient than the corresponding homogeneous solutions. The functionalized electrodes obtained by reducing the diazonium salts display better durability than the ones obtained by oxidizing the amino moiety, this is particularly evident in the case of **1**.

Complex 1, like other typical Mn/Re bipyridyl complexes, accelerates the CO_2 reduction after addition of Brønsted acids. Conversely, complex 2 reveals a hindrance to the catalytic activity for small additions of Brønsted acids, and then increases together with the amount of Brønsted acid.

The functionalization of electrode surface with catalysts by covalent bond could gain most of the advantages of this nonconventional condition. This type of hybrid homogeneous-heterogeneous approach has the advantage of increased performance of the catalysts in terms of TON, durability and by far smaller amounts.

Complex **1** is two times more active in water than in methanol, either in homogeneous solutions or on heterogeneous surfaces. On electrodes functionalized with thin layers of catalyst, complex **1** shows TONs 30–40 fold higher than the homogeneous solution. Although $Mn(bpy)(CO)_3Br$ coated with Nafion membrane showed a slightly higher TON,^[30] this coverage is more expensive than the diazonium salt functionalization.

Complex **2** immobilized on the electrode surface (diazonium salt modification) shows about 60 fold the catalytic activity of homogeneous solution in dry acetonitrile. The catalytic current decreased progressively, however the electrode maintained the activity for more than 200 cycles.

Conflict of interest

The authors declare no conflict of interest.

Keywords: carbon dioxide \cdot electrode functionalization \cdot Mn complexes \cdot Re complexes \cdot reduction

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