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Recent Advances on Catalytic CO2 Reduction by Organometal Complexes Anchored on Modified Electrodes

Cunfa Sun, Roberto Gobetto and Carlo Nervi

Critical overview of the very recent literature on heterogeneous electrochemical catalysis of CO2 reduction with organic metal modified electrodes is summarized. Five methods for electrode functionalization are discussed and compared in terms of efficiency and selectivity: adsorption, by using membranes, adopting an “hybrid” covalent organic framework approach, performing electropolymerization directly on the electrode surface, and exploiting the formation of strong covalent chemical bonds between the surface and the desired catalyst. Cells dedicated to CO2 reduction, currently one of the most popular tasks,6 PEC cell design is a complex matter and involves simultaneous managing of a multitude of processes related to solar excitation, charge separation, electrical conduction, molecular transport, catalytic chemistry, and reaction product recovery. Progress in this field has been made, especially for H2O reduction,6,9 but PECs for CO2 reduction are still in their infancy. An interesting review on modified electrodes by anchoring transition metal complexes as catalyst for CO2 reduction has been published some years ago by Vos and coworkers.10 Nevertheless the field is so rapidly growing both in interest and importance that a critical overview of the recent results is desirable. In this focus we present a brief overview of the most important recent results of such modified electrodes as electrocatalysts for CO2 reduction by different methods of anchoring transition metal complexes on the electrodes.

Electrode functionalization by adsorption

Among the different techniques for immobilizing the catalysts onto the electrode surface, chemisorption certainly represents one of the most convenient methods.11-13 Catalyst molecules bearing special moieties such as aromatic group or double bonds, etc. show chemical affinity to form spontaneously non-covalent modification of electrode surfaces enough stable for long periods in solvents where they are insoluble. Meshitsuka and coworkers14 in 1974 published the first attempt to perform heterogeneous CO2 electrocatalysis by phthalocyanine (Pc) metal (Mn, Pd, Cu, Fe, Co, Ni) complexes (MPC) adsorbed on graphite electrode surface; Co(Pc) proved to be one of the most reactive catalysts for CO2 electroreduction. After the seminal work of Leh and coworkers15 that introduced bipyridyl Re complex into CO2 electrocatalysis, many efforts have been performed with these complexes due to their higher selectivity compared with other catalysts. However the first paper of non-covalent surface attachment of a bipyridyl Re mo-

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Introduction

The catalytic conversion of the extremely stable CO2 molecule to usable fuels or chemical products is a critical goal that would positively impact the global environment and hopefully helping in overcoming some of the problems of energy crisis.1-6 Valuable products, such as carbon monoxide, formic acid and high-molecular-weight polymers, obtained from the electrochemical conversion of CO2, have been indicated as chemicals that can store intermittent energy sources, thus balancing power supply and energy demand and environmental concerns of greenhouse gas emissions. A possible approach to reduce the large overpotentials required for this multi-electron process is the use of organometal molecular compounds, able to catalyze CO2 reduction through proton-assisted processes.4,7 Most electrocatalytic studies in this field focus primarily on the catalyst/substrate interaction in homogeneous solution. Relatively few works were focused on the heterogeneous electrochemical catalysis despite the large number of potential advantages such as easier recovery of products and catalyst, small amounts of catalyst necessary for efficient electrolysis, deactivation pathways often hindered or suppressed and elimination of solubility problems. Furthermore, in heterogeneous system the electron transfer will be more efficient to the attached or bonded catalyst compared with that in solution, lowering the limitation of the electron transfer in the catalytic cycle. Transition metal complexes immobilized on electrode surfaces can represent promising catalysts to be utilized on a large-scale process for CO2 reduction, particularly if non-precious metals like cobalt, iron, nickel, copper, and zinc are involved. Although the interest in this area began several decades ago, it has drawn substantial attention only in the recent years, due to the development of photoelectrochemical (PEC)
lucular complex for catalytic CO$_2$ reduction appeared only in 2013.$^{18}$ A graphite electrode was modified with a Re complex containing pyrene groups that sticks on the graphite electrode through a π−π stacking interaction. At a rather negative applied potential, -1.67 V vs NHE (Normal Hydrogen Electrode), in acetonitrile, the modified electrode shows CO faradaic efficiency ($\eta_{co}$, defined as the moles of electrons consumed to get the desired reaction product divided by the total moles of electrons transferred from anode to cathode) = 70% and TON$_{CO} = 58$ with no H$_2$ formation (TON= Turn Over Number, defined as the moles of intended reaction product formed divided by the moles of catalytic sites). Functionalized surface lost its activity after 1 h due to the reduction of the pyrenyl moieties at the very negative potentials, probably due to electrostatic repulsion with the surface and consequent loss of planarity and surface binding.

Compared to CO$_2$ reduction by one-electron process, proton coupled multi-electron reduction requires less potential.$^{10,15}$ An ITO/multilayer electrode$^{18}$ was modified by the Layer-by-Layer method (LBL) with corresponding multimetallic complex, Mn(III)/Ni(II)/Zn(II) μ-(meso-5,10,15,20-tetrapiridil)porphin) tetrakis [bis (bipyridine) chloride ruthenium(II)] [(MTRP)$^{5+}$ (Fig. 1; M = Mn(III), Ni(II) and Zn(II), n = 5, 4, 4 respectively), and polyoxotungstate ([SiW$_{12}$O$_{40}$]$^{3−}$). By performing electrolysis at -0.8 V vs. Ag/AgCl for 6 h in aqueous solution, CO was the only product on [ZnTRP]$^{6+}$/[SiW$_{12}$O$_{40}$]$^{3−}$ multilayer electrode with TON$_{CO} = 3850$, while the analogues [NiTRP]$^{6+}$/[SiW$_{12}$O$_{40}$]$^{3−}$ and [MnTRP]$^{5+}$/[SiW$_{12}$O$_{40}$]$^{3−}$ produced methanol (TON$_{MeOH} = 1.76 \times 10^5$) and formic acid (TON$_{HCOOH} = 1.06 \times 10^5$), respectively. It is worth noting in the energy transfer of the TRP that extra irradiation altered the catalysis pathway and lowered the potential, enhancing the catalytic efficiency. At -0.6 V vs. Ag/AgCl under irradiation, [MnTRP]$^{5+}$/[SiW$_{12}$O$_{40}$]$^{3−}$ produced formaldehyde only with TON$_{CHO} = 1.8 \times 10^5$.

With the help of polyethyleneimine and high surface area multi-walled carbon nanotubes (MWCNT), Zhao and coworkers$^{19}$ were able to produce cobalt tetra-amo-no-phthalocyanine (CoTApC) modified electrodes with multilayers by using LBL self-assembly technique. The new electrodes significantly decreased the overpotential of the CO$_2$ reduction, and the cathode successfully reduced CO$_2$ to formic acid. MWCNT/CoTApC modified electrode produced twice number of moles of formic acid than the electrode without MWCNT. Later, they reported a glassy carbon (GC) or carbon felt electrode functionalized with MWCNT/FeTApC, showing catalysis at less negative potential and higher reaction rate than the electrode with only MWCNT or FeTApC.$^{20}$

Electrode functionalization by membrane

Polymeric matrices which could confine the catalyst in a membrane attached onto the electrode surface provides another convenient way for electrode modification. The electrochemical reaction takes place in the membrane–electrode–catalyst layers and requires high proton and electron conductivity, and effective access of reactants to the catalyst. Preliminary inves-

tigation in this field have been reported by Yoshida and coworkers$^{21}$ that studied the catalytic activity towards CO$_2$ reduction in aqueous solution of [Co(tpy)$_2$]$^{3+}$ (tpy = 2,2′:6′,2″-terpyridine) on Nafion coated carbon electrodes. Re(bpy)(CO)$_2$Br and Re(tpy)(CO)$_2$Br (bpy = 2,2′-bipyridine, tpy = 2,2′:6,2″-terpyridine) coated on Nafion membranes in aqueous solution showed higher selectivity,$^{12}$ but strongly dependent on the applied potentials. In particular Re(tpy)(CO)$_2$Br complex produces mainly formic acid and requires larger overpotential than the bpy analogous.

As a substitute of Re, bipyridyl Mn complexes shows excellent selectivity in CO$_2$ with$^{23}$ and without$^{24}$ added Brønsted acid. In 2014 Cowan’s group$^{25}$ embedded [Mn(bpy)(CO)$_2$Br] in a Nafion membrane as an active heterogeneous electrocatalyst for CO$_2$ reduction in neutral aqueous electrolyte at less negative potential compared with the homogeneous solution. Although the number of active catalytic molecules were rather limited in the membrane, TON reached 471 (“36 fold higher than the homogeneous counterpart$^{19}$), η$_{co} = 51%$ and η$_{H2} = 24%$ after 4 hours at -1.5 V vs. Ag/AgCl. The [Mn(bpy)(CO)$_2$Br]/MWCNT/-Nafion electrode leads to a 10 fold current enhancement, but with lower TON value (101) and lower selectivity (η$_{CO} = 22%$, η$_{H2} = 47%$). Very recently, they immobilized [Mn(bpy)$_4$Br$_2$](-CO$_2$)Br$_2$, [bpy(Bu)$_2$ = 4,4′-di-tert-butyl-2,2′-bipyridine) on GC by Nafion/MWCNT. This film improved the selectivity towards CO$_2$ at -1.4 V vs. SCE (η$_{CO} = 44%$, η$_{H2} = 46%$), exceeding that of the previously reported [Mn(bpy)(CO)$_2$Br]/MWCNT/Nafion electrode. The catalysts obtained by replacing bpy with 4,4′-dicarbonyl acid bpy or with 4,4′-diol bpy were found to be active towards CO$_2$ in acetonitrile solutions, but not in Nafion membranes. Aoi and coworkers$^{26}$ studied the CO$_2$ reduction with a GC electrode modified by a CoCl$_2$ complex, Co$_2$(CH)$_3$ adsorbed on MWCNT confined in Nafion (Fig. 2). At -1.1 V vs. NHE in aqueous solution in pH 4.6 buffer, the system yielded CO and H$_2$ as major products with TON = 1100 (with a Turn Over Frequency, TOF, defined as TON divided by the reaction time, equal to 140 h$^{-1}$) η$_{CO} = 89%$, η$_{H2} = 11%$. 

Figure 1. Structural representation of [MTRP]$^{5+}$ (M = Mn(III), Ni(II) and Zn(II), n = 5, 4, 4 respectively)$^{18}$.
Gas diffusion electrode (GDE) promotes catalytic CO₂ reduction in solution at gas-liquid interface. Meyer’s group reported GDE/MWCNT/Ir/PEG system (Ir = iridium catalyst, see Fig. 3, PEG = polyethylene glycol) for CO₂ reduction, where the catalyst was non-covalently adsorbed on the MWCNT, and covered by PEG on the top of the surface. Also, the GC and the fluorine-doped tin oxide (FTO) electrodes were investigated for comparison. The GDE system showed a little better TON than others, while the GC system exhibited \( \eta_{\text{GC}} = 93\% \), TON = 5300 in 2 h at -1.4 V vs. NHE in aqueous solution with \( \eta_{\text{Ni}} = 7\% \), and TON = 203000 in 8 h, which is about four orders of magnitude higher than homogeneous solution. By using a membrane, anchoring the catalyst becomes easier, and the catalysis can be directly tested. Singh and coworkers tested the CO₂ reduction catalytic activity of Ni and Cu salen ligand complexes directly applied with Nafion coated on GDE. These salen ligand complexes showed long stability and produced more quantity of hydrocarbons and CO at a 10-25% less overpotential than their respective metals, with total \( \eta \) of 74% for Ni complex and 25% for Cu complex at -1.5 V and -1.8 V vs. Ag/AgCl, respectively. The catalyst (N,N-Bis(salicyldehyde)-ethylenediamine-Co) was dispersed in carbon black, and the mixture was covered with Nafion over GDE. The electrode with 60wt% exhibited the best activity for CO₂ reduction in aqueous solution, due to the right balance of porosity and conductivity of the carbon black mixture.

**Electrode functionalization by electropolymerization**

If the catalyst bears a suitable group able to polymerize, the electrode surface can be easily modified by electropolymerization. Portenkircher and coworkers electropolymerized a 5,5′-bisphenylethynyl bipyridyl Re complex on the electrode surface, as a potential catalyst for CO₂ reduction. However, the homogeneous and the heterogeneous catalyst showed in CH₄CN solutions relative low \( \eta_{\text{CO}} \) for CO₂ reduction, 45% and 33% respectively. We very recently exploited the electropolymerization properties of Re(bpy) complexes containing the thiophene moiety, that have the advantage to produce an electron-conducting film, with interesting results.

The electrocatalytic reduction of CO₂ on a ITO electrode covered with cobalt 5,10,15,20-tetrakis(4-aminophenyl)porphyrin (Co-TAPP) polymer in 1-butyl-3-methylimidazolium tetrafluoroborate, BMIMBF₄ as a novel reaction media occurred at a particularly positive potential, -0.8 V vs. Ag/AgCl, which means a significant energy gain in the electrochemical fixation of CO₂. Only CO was detected by gas chromatography, with \( \eta_{\text{CO}} = 64.9\% \) and TON = 69 for 4 h. Later, Zn(II) and Fe(III) were used as catalysts with the same procedure, while but the electropolymerized Fe porphyrin was active toward CO₂ reduction, the corresponding Zn derivative was poorly active.

**Electrode functionalization by chemical bonds**

Formation of covalent chemical bonds between the catalyst and the surface impart particular stability to the modified electrodes. Cobalt porphyrin complexes bearing peripheral acetylene groups were covalently linked to the boron-doped p-type
conductive crystalline diamond electrode surface decorated with alkyl azides.\textsuperscript{42} The modified diamond surface was used as “smart” electrode, exhibiting good stability and electrocatalytic activity for CO\textsubscript{2} reduction to CO in acetonitrile solution.

Very recently, the electrochemical behavior of a GC prepared by simple and direct functionalization of terpyridine containing diazonium salts was explored.\textsuperscript{43} This versatile strategy allows to extend the use of such modified electrodes through the reversible coordination of a variety of metal ions; for example cobalt center have been tested for the CO\textsubscript{2} reduction, with TON\textsubscript{CO} = 70 for 30 min.\textsuperscript{43}

Please Insert Table 1 (that contains Ref. \textsuperscript{44}) around here

Conclusions

Table 1 summarizes the properties of the electrodes herein considered. Often organic metal complexes anchored on modified electrodes exhibit better Turn Over Number, faradic efficiencies, stability, and/or less negative overpotentials compared with the corresponding complexes in homogeneous solution, highlighting the beneficial effect of the immobilization. Physical attachment of catalysts on the surface by Nafion, polymer membrane or nanoparticles etc., would have the drawback of lower number of active sites on the surface (because part of the catalyst embedded in the solid structure may be hidden to the reaction), while monolayer of covalently chemically bonded species or adsorbed polymer, produced also by electropolymerization, have less total amount, but potentially better electron conduction properties. Although no general rule can be suggested at this stage of the research, the best solution appears to adopt electrodes with the largest surface area, in order to maximize the amount of active catalyst in contact with the reactive interface. Hence, the new electrode modification methods by novel hybrid electrode material via covalent organic framework approach seems quite promising. The challenge is to provide an adequate transport of materials (to and from the catalytic center) and electrons (via a conductive material) to the active surface.

The recent works suggested that dispersed catalyst could exhibit much better activity than the concentrated ones, such as the complexes with pores or localized in the porous matrix. That may arise from the more free catalytic environment around the catalyst center, or because reaction products may interfere with the catalytic cycle. The Gas Diffusion Electrode approach that adopt the conductive black carbon is also appealing, due to the gaseous nature of CO\textsubscript{2} that would allow the direct reaction without the need to use an organic solvent for CO\textsubscript{2} solutions. Thus the Covalent Organic Framework and Gas Diffusion Electrode approaches are actually the most efficient ones in term of TON, selectivity, and durability, and appear to be suitable to be embedded in a Photo Electrochemical Cell for CO\textsubscript{2} reduction.

From this point of view the research field appears to be promising and mostly unexplored, when compared to the homogeneous counterpart. The use of intact transition metal complexes anchored to conducting surface appear to be one of the main research fields that would allow a competitive development of Photo Electrochemical solar cell for selective CO\textsubscript{2} conversion, allowing the molecular design of the catalysts. Investigation of proton assisted multi-electron reduction in different solvents, may significantly alter the selectivity, and it seems to be the preferred pathway to follow, due to benefits in decreasing the reduction overpotentials and increasing selectivity.

Although, a lot of efforts have been done in the heterogeneous CO\textsubscript{2} reduction, the elucidation of the mechanism is still obscure compared with the homogeneous, and the catalytic pathways seldom discussed, even there’s some works that mention the use of Infrared\textsuperscript{45} or Electrochemical Impedance Spectroscopy.\textsuperscript{46} The knowledge of the mechanism will certainly help the design of more efficient catalysts and systems. So there are a plenty of research opportunities ranging from molecular or solid state calculations, in \textit{in-situ} spectroscopic techniques, and especially electrochemical techniques that allow to study the chemical reaction at the interfaces.

Notes and references

Table 1. Comparison of modified electrode performances for catalytic CO₂ electrochemical reductions in MeCN solutions (0.1 M TBAPF₆).

<table>
<thead>
<tr>
<th>Method</th>
<th>Electrode/(catalyst)</th>
<th>E (V)</th>
<th>E (V) vs. NHE</th>
<th>ηₐCO (%)</th>
<th>TONₐCO</th>
<th>Time (h)</th>
<th>Solution</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption</td>
<td>graphitic carbon electrode/[[Re(F)]-(CO)₆Cl₂]</td>
<td>-1.67 vs NHE</td>
<td>-1.67</td>
<td>70</td>
<td>58</td>
<td>1</td>
<td>0.1M TBAPF₆ MeCN</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>ITO/[ZNTRP]⁺/[[SiW₁₂O₄₀]⁻(h)]</td>
<td>-0.8 vs Ag/AgCl</td>
<td>-0.51</td>
<td>---</td>
<td>3850</td>
<td>6</td>
<td>0.1 M NaClO₄</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>ITO/[ZNTRP]⁺/[[SiW₁₂O₄₀]⁻(d)]</td>
<td>-0.8 vs Ag/AgCl</td>
<td>-0.51</td>
<td>---</td>
<td>1.76×10⁻¹⁷</td>
<td>6</td>
<td>0.1 M NaClO₄</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>ITO/[MNTRP]⁺/[[SiW₁₂O₄₀]⁻(g)]</td>
<td>-0.8 vs Ag/AgCl</td>
<td>-0.51</td>
<td>---</td>
<td>1.06×10⁻¹⁸</td>
<td>6</td>
<td>0.1 M NaClO₄</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>ITO/[MNTRP]⁺/[[SiW₁₂O₄₀]⁻(f)]</td>
<td>-0.65 vs Ag/AgCl</td>
<td>-0.36</td>
<td>---</td>
<td>1.86×10⁻¹⁸</td>
<td>3</td>
<td>0.1 M NaClO₄</td>
<td>18</td>
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<tr>
<td>Membrane</td>
<td>GCE/[[Mn(bpy)(CO)₃]Br]</td>
<td>-1.50 vs Ag/AgCl</td>
<td>-1.21</td>
<td>51</td>
<td>471</td>
<td>4</td>
<td>phosphate buffer pH=4.7</td>
<td>25</td>
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<tr>
<td></td>
<td>GCE/[[Mn(bpy)(CO)₃]Br]/MWCNT</td>
<td>-1.50 vs Ag/AgCl</td>
<td>-1.21</td>
<td>22</td>
<td>101</td>
<td>4</td>
<td>phosphate buffer pH=7</td>
<td>25</td>
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<td></td>
<td>GCE/[[Mn(bpy)(Bu)c(CO)₃]Br]/MWCNT</td>
<td>-1.40 vs. SCE</td>
<td>-1.07</td>
<td>44</td>
<td>7.3</td>
<td>4</td>
<td>phosphate buffer pH=7</td>
<td>26</td>
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<td></td>
<td>GCE/[[Co₄(Ch)]/MWCNT</td>
<td>-1.10 vs. NHE</td>
<td>-1.10</td>
<td>11</td>
<td>1100</td>
<td>8</td>
<td>5 mM NaClO₄ pH=4.6</td>
<td>27</td>
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<td></td>
<td>GDE/ (Ir/MWCNT)</td>
<td>-1.40 vs. NHE</td>
<td>-1.40</td>
<td>93</td>
<td>5300</td>
<td>2</td>
<td>0.1m NaHCO₃, 0.5m LiClO₄, 1% MeCN v/v</td>
<td>28</td>
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<tr>
<td>COF</td>
<td>carbon fabric/[COF-387-Co]</td>
<td>-1.30 vs. Ag/AgCl</td>
<td>-1.01</td>
<td>83</td>
<td>48000</td>
<td>24</td>
<td>0.5 M KHCO₃ pH=7.3</td>
<td>35</td>
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<tr>
<td>Chemical bond</td>
<td>Potential (V) vs. Ag/AgCl</td>
<td>Current Density (A/cm²)</td>
<td>TP (mA/cm²)</td>
<td>Ce</td>
<td>Electrolyte</td>
<td></td>
<td></td>
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<td>---------------</td>
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<tr>
<td>FTO/(Al₂(OH)₃)₂(TCPP-Co)⁹</td>
<td>-1.33</td>
<td>76</td>
<td>1400</td>
<td>7</td>
<td>0.5 M KHCO₃</td>
<td></td>
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<tr>
<td>Pt-plate /([Re(5,5'-bisphenylethynyl-2,2'-bipyridyl)(CO)₃Cl])</td>
<td>-1.6</td>
<td>33</td>
<td>---</td>
<td>1</td>
<td>0.1 M TBAPF₆ MeCN</td>
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<tr>
<td>ITO/(Co-TAPP)</td>
<td>-0.8</td>
<td>64.9</td>
<td>69</td>
<td>4</td>
<td>BMImBF₄</td>
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<tr>
<td>GCE/Co-tpy</td>
<td>-1.50</td>
<td>70</td>
<td>0.5</td>
<td>0.1 M TBAPF₆ DMF</td>
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</table>

a) TONMeOH; b) TONHCOOH; c) under irradiation; d) TONHCOOH; e) TONNO; f) adjusted by H₂SO₄ aqueous solution; g) formate; h) TCPP-H₂ = 4,4',4,4''-(porphyrin-5,10,15,20-tetrayl)tetrabenzoate. i) the redox potentials are reported against NHE for comparison, using the value in Ref.⁴⁴