

Organic molecules as mediators and catalysts for photocatalytic and electrocatalytic CO₂ reduction†

Cite this: *Chem. Soc. Rev.*, 2013, **42**, 2253

Yeonji Oh and Xile Hu*

Reduction of CO₂ by electrochemical and photoelectrochemical methods to produce carbon-rich fuels is a heavily pursued research theme. Most of the current efforts are focused on the development of transition-metal-based catalysts. In this tutorial review, we present an overview of the development of organic molecules as mediators and catalysts for CO₂ reduction. Four classes of organic molecules are discussed: tetraalkylammonium salts, aromatic esters and nitriles, ionic liquids, and pyridinium derivatives. It is shown that reactions mediated or catalyzed by these organic molecules can be competitive compared to their metal-catalyzed counterparts, both in terms of product selectivity and energy efficiency.

Received 23rd July 2012

DOI: 10.1039/c2cs35276a

www.rsc.org/csr

1. Introduction

Considering the Earth's abundance of fossil fuels, particularly coal, the world's energy problem is essentially related to the problem of carbon dioxide (CO₂).^{1,2} The excessive anthropogenic

emission of CO₂ resulting from the combustion of fossil fuels has caused and will continue to cause climate change. The idea that CO₂ might be reduced to chemical fuels using renewable energies sounds like chemists' perfect revenge to the CO₂ problem.³ Selective and energy-efficient reduction of CO₂, however, is a chemical challenge that remains unsolved.

The development of electrochemical and photochemical CO₂ reduction catalysts is a recurring research theme. The majority of work has been focused on the catalytic properties of metal electrodes and transition metal complexes. Several excellent reviews are available on this topic.^{4–8} As pointed out in

Laboratory of Inorganic Synthesis and Catalysis, Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne (EPFL), EPFL-ISIS-LSCI, BCH 3305, Lausanne, CH 1015, Switzerland. E-mail: xile.hu@epfl.ch;

Fax: +41 216939305; Tel: +41 216939781

† Part of the solar fuels themed issue.



Yeonji Oh

Yeonji Oh obtained her BS (2009) and MS (2011) degrees from the Department of Chemistry and Nano Science, Ewha Womans University (South Korea). She is currently a PhD student under the direction of Prof. Xile Hu at the Ecole Polytechnique Fédérale de Lausanne (EPFL) in Switzerland. She is working on the development of electrochemical and photochemical CO₂ reduction catalysts.

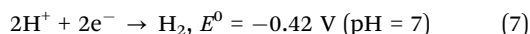
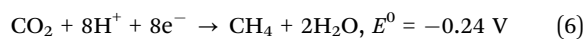
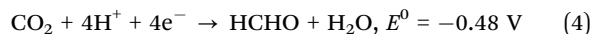
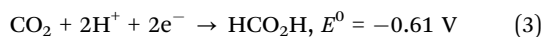
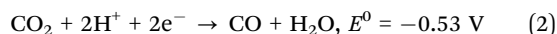
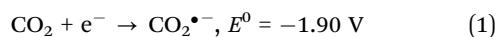


Xile Hu

Xile Hu was born in 1978 in Putian, China. He received a BS degree from Peking University (2000) and a PhD degree from the University of California, San Diego (2004; advisor: Prof. Karsten Meyer). He then carried out a postdoctoral study at the California Institute of Technology (advisor: Prof. Jonas Peters) before joining the faculty of the Ecole Polytechnique Fédérale de Lausanne (EPFL) as a tenure-track assistant professor in

2007. His research interests span from organometallic chemistry, synthetic methodology, and asymmetric catalysis to bio-mimetic and bio-specified coordination chemistry to electrocatalysis and artificial photosynthesis.

these reviews, a principal difficulty in CO₂ reduction is the kinetic inertness of CO₂. The one-electron reduction of CO₂ to CO₂^{•-} has an E^0 of -1.90 V vs. NHE (normal hydrogen electrode) at pH = 7 (eqn (1)). Thus, even though multiple proton-coupled electron transfers to CO₂ are thermodynamically facile (eqn (2)–(6)), these reactions require large overpotentials to take place even with the help of catalysts. A second major difficulty in CO₂ reduction is the selectivity. Reduction of CO₂ may lead to CO, HCOOH, HCOH, CH₃OH, CH₄, or higher hydrocarbons. Furthermore, in protic solvents, hydrogen evolution (eqn (7)) is often favored over CO₂ reduction.

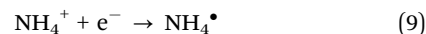
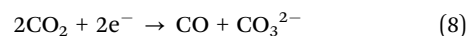


This review presents the studies of organic molecules as mediators and catalysts for electrochemical and photochemical CO₂ reduction. Four classes of organic molecules are discussed: tetraalkylammonium salts, aromatic esters and nitriles, ionic liquids, and pyridinium derivatives. While the development of metal-free catalysts and cocatalysts is not yet in the main-stream of current research in CO₂ reduction, we believe that this alternative approach might lead to interesting discoveries and creative ideas in catalyst design.

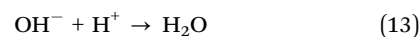
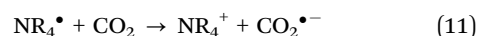
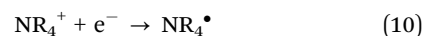
2. Tetraalkylammonium salts as mediators

In 1983, Bockris and co-workers discovered the important role of electrolyte in electrochemical reduction of CO₂ at a p-type CdTe photocathode.⁹ In a 0.1 M solution of tetrabutylammonium perchlorate (TBAP) in DMF containing 0.1% to 10% water, CO₂ could be reduced starting at $E = -1$ V vs. SCE under 600 nm illumination. Electrolysis at -1.6 V vs. SCE gave CO as the main reduction product in a 70% current efficiency. The quantum efficiency was close to unity. The results from two different supporting electrolytes, TBAP and lithium perchlorate (LiClO₄), were then compared. The photocurrent for CO₂ reduction when LiClO₄ was used as the supporting electrolyte was unstable and was less than 1/10 of the current observed with TBAP. It was proposed that tetrabutylammonium (TBA) ions provided a more hydrophobic environment at the electrode, which was beneficial for CO formation. Because there was a small change in the onset potential for CO₂ reduction when the water content was changed from 0.2–10%, two reactions were considered to occur (eqn (2) and eqn (8)). Without water, CO₂ reduction was not observed at the same potential. It was soon found that several other tetraalkylammonium perchlorates (C₂–C₈, *i.e.*, tetraethyl to tetraoctyl) and even NH₄ClO₄ also promoted the photoelectrochemical CO₂

reduction.¹⁰ The particular photoelectrochemical behavior in the presence of NH₄ClO₄ led to the consideration that NH₄⁺ might serve as a redox mediator according to eqn (9).



In 1989, Bockris and Wass studied the efficiency, kinetics, and mechanism of the photoelectrochemical reduction of CO₂ in DMF (5% water) solutions containing tetraalkylammonium cations.¹¹ On a bare p-CdTe illuminated at 560 nm, the onset potential for CO₂ reduction was -0.70 V vs. NHE with 0.1 M tetraethylammonium perchlorate (TEAP) as the electrolyte. This was a 700 mV improvement over the best metal electrode (In) at that time. The limiting photocurrent was 2.7 mA cm⁻² at -1.5 V vs. NHE. The Faradaic yield for CO production was about 90%, while small amounts of formaldehyde and formic acid were also detected. Based on the kinetic data, the following mechanism was proposed, showing the catalytic role of tetraalkylammonium cations (NR₄⁺) (eqn (10)–(13)).



An ammonium cation is first reduced by one-electron to form a radical (eqn (10)). The radical reacts with CO₂ to give the CO₂^{•-} anion and to regenerate the ammonium cation (eqn (11)). The CO₂^{•-} anion reacts further with a proton and an electron to give CO (eqn (12)). The reactions were proposed to occur on two reactive sites which have different adsorption energies for NR₄⁺ (Fig. 1). NR₄⁺ is adsorbed at site A, but not at site B. At site A, reactions (10) and (11) occur, and these reactions are light-insensitive. At site B, CO₂^{•-} is reduced to CO, and this step requires light energy. The catalytic effect of tetraalkylammonium cations is to provide CO₂^{•-} which is further reduced photoelectrochemically.

The photocatalytic activity of this system could be further enhanced using additives, and crown ethers were found to be the best additives. The photocurrents were positively shifted in the presence of crown ethers. The maximum promotional effect was observed when the size of the ring of the crown ether matched with the size of the NR₄⁺ ion (Fig. 2). Thus, when TEAP was used as the mediator and the electrolyte, the effect of crown ethers increased in the order of 24-crown-8 < 15-crown-5 < 18-crown-6. With 18-crown-6, a positive shift of 410 mV was

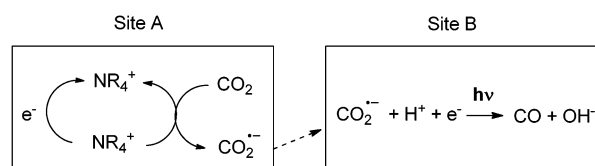


Fig. 1 CO reduction at two sites on a p-CdTe electrode.

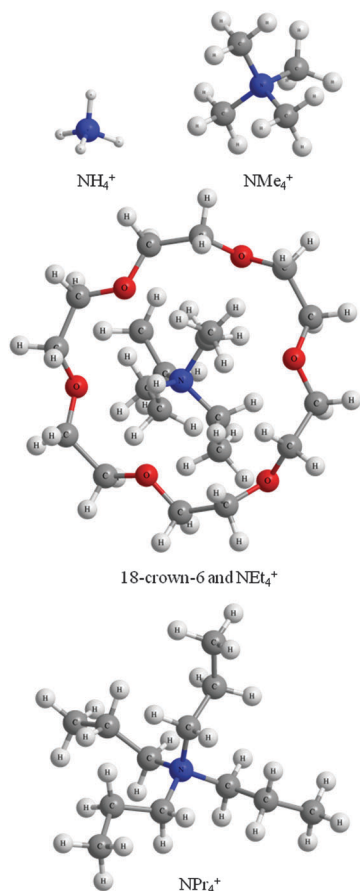


Fig. 2 Molecular drawings depicting the sizes of 18-crown-6 and tetraethylammonium cations.

achieved, equivalent to 10^2 – 10^3 times increase in rate constant. The crown ethers were proposed to be adsorbed on the electrode surface. In the absence of crown ethers, the NR_4^+ cation is adsorbed on the outer Helmholtz plane ($d \approx 8 \text{ \AA}$). In the presence of crown ethers, NR_4^+ is brought onto the inner Helmholtz plane ($d \approx 3 \text{ \AA}$). The electron transfer to NR_4^+ is then significantly faster. It was also proposed that in the presence of crown ethers, the reactions at sites A and B were coupled. It is interesting to note that methanol was produced in about 10% Faradaic efficiency when 18-crown-6 and 15-crown-5 were used as additives. No explanation was given for their formation.

In 1995, the group of Fujishima also reported the influence of supporting electrolytes in the selectivity of CO_2 reduction at a Cu electrode in a methanol + CO_2 system.¹² CO was the main product when TBA salts were used as the supporting electrolytes. However, methyl formate (the electrolysis gave HCOOH as the CO_2 reduction product, and under the reaction conditions, HCOOH reacted with the CH_3OH solvent to give methyl formate), was the major product of CO_2 reduction when lithium salts were used as the electrolytes (Table 1). At the same time, hydrogen production became significant. Anions such as BF_4^- or ClO_4^- had little influence on the product distribution. The results were consistent with the notion that the hydrophobic environment at the electrode provided by TBA^+ ions was important for the selective reduction of CO_2 to CO. A more hydrophilic environment provided by the Li^+ ions would give rise to more other products such as CH_3COOH and H_2 . Besides poorer selectivity, Li^+ ions also caused a larger overpotential for CO_2 reduction.

These studies suggest that tetraalkylammonium ions can promote CO_2 reduction in two ways: (1) the ions can create a hydrophobic micro environment at the electrode, which will lead to a more selective reduction to CO; (2) the ions can mediate the reduction through 1e reduced radical intermediates. Strictly speaking, these ions are not catalysts because they are in excess with regard to the quantity of the substrate (CO_2). It will be interesting to design systems in which the tetraalkylammonium ions are used in catalytic amounts.

3. Aromatic nitriles and esters as catalysts

The groups of Saveant and Vianello had studied the catalytic properties of radical anions for CO_2 reduction in an aprotic medium such as DMF.^{13,14} They observed a marked difference in the product distribution between direct electrolysis on Hg and electrolysis catalyzed by radical anions. Various mixtures of CO and oxalate were produced in direct electrolysis. In contrast, oxalate was the sole product if the reduction was catalyzed by radical anions of aromatic esters and nitriles (Fig. 3).

The mechanism of direct electrolysis at an inert electrode, such as mercury, was proposed to be a sequence of eqn (14)–(19).

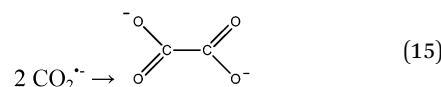


Table 1 Effect of the supporting electrolytes on the products in the electrochemical reduction of CO_2 in a CO_2 + methanol medium (ref. 12)

Salt	Current density (mA cm^{-2})	Potential (V vs. Ag QRE)	Current efficiency (%)					
			H_2	CO	CH_4	C_2H_4	CH_3COOH	Total
TBABF_4	200 ^a	−2.1	3.5	76.0	2.6	1.1	23.4	106.6
	333 ^b	−2.3	5.4	86.6	Not detected	Not detected	9.0	101.0
TBAClO_4	200 ^a	Not measured	9.7	48.1	7.6	5.2	25.4	96.0
LiBF_4	200 ^a	−3.8	33.3	8.6	7.2	0.0	54.5	103.6
LiClO_4	333 ^b	−4.1	58.9	5.9	6.7	Not detected	46.7	118.2
NH_4ClO_4	200 ^a	Not measured	84.6	7.9	5.3	0.4	Trace	98.3

^a Electrolyses were performed at 40 atm at 20 °C. ^b Electrolyses were performed at 40 atm at 25 °C.

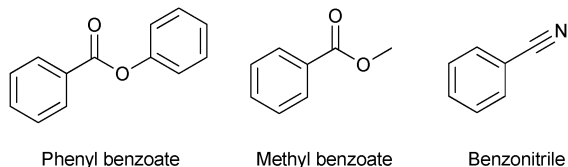
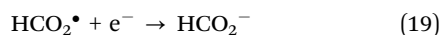
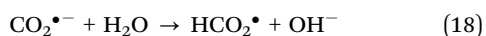
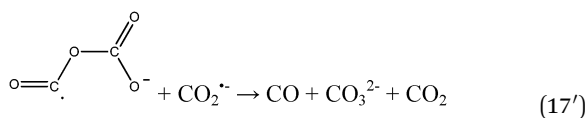
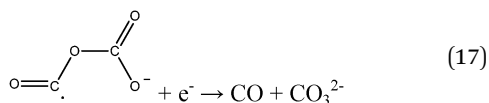
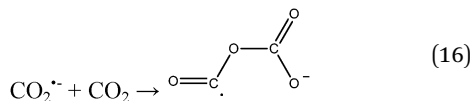
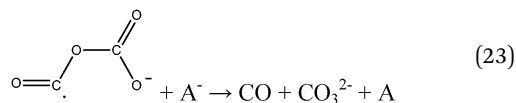
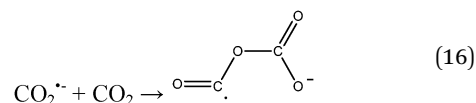
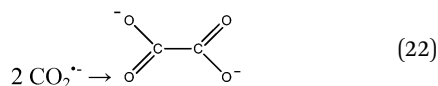
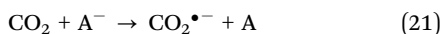


Fig. 3 Representative aromatic esters and nitriles investigated as catalysts for CO₂ reduction at a Hg electrode.



CO₂ is first reduced at the electrode to form a CO₂^{•−} anion (eqn (14)). Then two CO₂^{•−} anion radicals recombine to form oxalate (eqn (15)). But the CO₂^{•−} anion can also react with CO₂ to form an adduct (eqn (16)). Reduction of this adduct gives CO and carbonate (eqn (17)). Alternatively, reaction of this adduct with another molecule of CO₂^{•−} anion also leads to the formation of CO and carbonate (eqn (17')). If water is present in the reaction medium, the CO₂^{•−} anion can be protonated to form HCO₂[•] (eqn (18)), which after an additional electron transfer step (eqn (19) or (19')), produces formate. The effect of CO₂ concentration and temperature was also investigated. It was shown that the yields of CO increased not only when the concentrations of CO₂ increased, but also when the temperature decreased.

In the reactions catalyzed by aromatic ester and nitrile compounds, the first step is the reduction of ester or nitrile to an aromatic radical anion (eqn (20)). The radical anion then transfers the electron to CO₂ to form a CO₂^{•−} anion (eqn (21)), which dimerizes to give oxalate (eqn (22)). The path to the formation of CO (eqn (16) and (23)) is not favorable compared to the path to oxalate under these homogeneously catalyzed conditions.



In addition to esters and nitriles, chrysene and picene were also employed as catalysts for electrochemical CO₂ reduction.^{15,16} The products derived from CO₂ were not identified. A small extent of photocatalytic CO₂ reduction was reported to occur with anthracene, pyrene, and oligo (*p*-phenylenes).^{17,18} The main product was formate, and the proton likely came from the C–H bond of the sacrificial electron donor (amine).

The aromatic nitriles and esters can be considered as real electro-catalysts in these reactions because they are regenerated after transferring electrons to CO₂. A major drawback of these catalysts is the very negative potential that is required for their reduction. As a result, the overpotential is large. The high selectivity for oxalate formation is however attractive. It remains to be seen if CO₂ reduction might be mediated by more easily accessible aromatic radicals.

4. Ionic liquids as mediators

Electrochemical fixation and reduction of CO₂ in ionic liquids have drawn some attention recently.¹⁹ Ionic liquids are organic salts that exist in the liquid state at near room temperature. They are considered as green reaction media thanks to several characteristics, including high thermal and chemical stability, high viscosity, extremely low vapor pressure, and good solvating ability for organic and inorganic compounds.^{20–27} Moreover, ionic liquids exhibit high intrinsic conductivity and wide electrochemical potential windows.^{20,21,23,25,26} A number of reports show the electrochemically assisted reaction of CO₂ with amine to form carbamate in ionic liquid.^{28,29} While this reaction is strictly speaking not a net reduction of CO₂, it occurs *via* a one-electron reduction of CO₂ at first. Therefore these reports are described here as possible precedents that ionic liquids are used as redox mediators for CO₂ reduction. There are also examples where net reduction of CO₂ is conducted in ionic liquids on metal electrodes. The structures and notation of some representative ionic liquids are given in Fig. 4.

The electrochemistry in CO₂-containing ionic liquids needs to be treated with caution because CO₂ can influence the electrochemical potential window, viscosity, and conductivity of ionic liquids. In this sense, CO₂ might be treated as a non-innocent solute like water or halide ions. For example, it was previously shown that water decreases and halide ions increase the viscosity of ionic liquids.^{26,30} In 2009, Compton and co-workers studied the effect of CO₂ on the redox couple ferrocene/ferrocenium (Fc/Fc⁺) in the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethane-sulfonyl)imide (C₂MIM-NTf₂).³¹ In CO₂-saturated C₂MIM-NTf₂, significant increases in both the limiting current

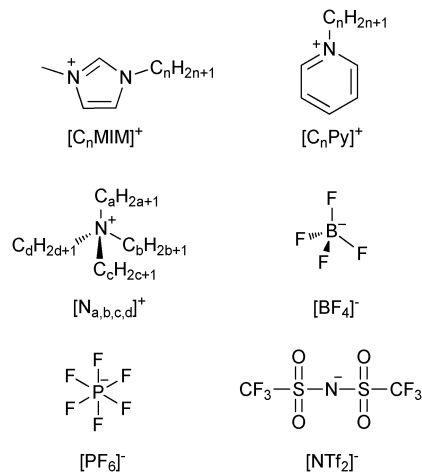
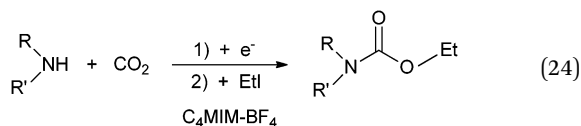


Fig. 4 The molecular structures of common cations and anions in representative ionic liquids.

and the diffusion coefficient of Fc were observed. This work shows the non-innocent character of CO₂ in electrochemistry in ionic liquids even if the apparent redox chemistry does not involve CO₂. Very often, the physical parameters in ionic liquids are not independent of solutes like CO₂, therefore skilled and precise sample preparation is important when working with ionic liquids.

In 2007, the groups of Feroci and Inesi reported an electrochemical method for the synthesis of carbamate from amines and carbon dioxide in a CO₂-saturated solution of ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate (C₄MIM-BF₄), with ethyl iodide as the alkylating reagent (eqn (24)).²⁹



The cathodic reduction of CO₂ to CO₂^{•-} was the first step in this reaction. The CO₂^{•-} anion was proposed to yield carbonate anions (CO₃²⁻) in the ionic liquid, and the carbonate anion could react with amine to give carbamate anions, which further reacted with EtI to give ethyl carbamate as the final product (Fig. 5). The reactions were efficient with Pt and Cu as cathodes, at $E = -2.4$ V vs. Ag electrode, $P(\text{CO}_2) = 1.0$ atm, and $T = 55$ °C. It was proposed that in C₄MIM-BF₄, the interaction of carbamate anions with C₄MIM cations was weak, leading to an increased

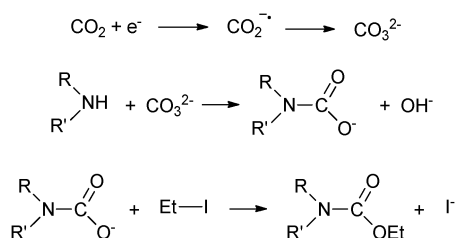


Fig. 5 Proposed mechanism for the electrosynthesis of organic carbamates from amines and carbon dioxide.

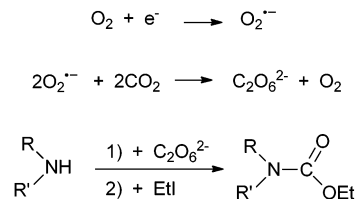
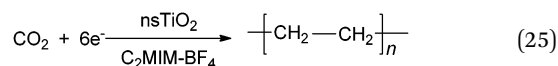


Fig. 6 Proposed electrochemical procedure to synthesize organic carbamates from amines and activated carbon dioxide via superoxide ion (O₂^{•-}).

nucleophilicity of the oxygen of the carbamate anion. Consequently, O-alkylation was favored against N-alkylation.

The same groups studied the same reactions, but in O₂/CO₂ saturated ionic liquids.²⁸ O₂ was first reduced to superoxide (O₂^{•-}), which reacted with CO₂ to give the peroxydicarbonate ion C₂O₆²⁻. The latter then reacted with amine and alkyl halide to give carbamates (Fig. 6). Because O₂^{•-} can be generated in ionic liquids at a less negative potential (-1.4 V vs. Ag) than that of direct reduction of CO₂ (-2.4 V vs. Ag) at a Pt or Cu electrode, this system appears advantageous than the O₂-free system.

In 2008, Chu and coworkers studied the electrocatalytic reduction of CO₂ on a nanostructured TiO₂ film electrode to give low-density polyethylene (LDPE) (eqn (25)).³²



The reaction was conducted in a mixture of ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate (C₂MIM-BF₄) and H₂O (1:1 v/v). The current efficiency of LDPE was about 8–14% at -1.50 V vs. SCE, but the turnover number was not reported. The overall reaction was proposed as shown in Fig. 7. First, Ti(III) species were produced by reduction of Ti(IV) at the TiO₂ electrode. The Ti(III) species then reduced CO₂ to CO₂^{•-} radical anions which were adsorbed on the surface. The CO₂^{•-} anion then reacted with a proton and an electron to give surface-adsorbed CO, which was proposed to take 4 protons and 4 electrons to give surface-adsorbed CH₂ species. Polymerization of CH₂ species then gave polyethylene. There was however no direct evidence for the proposed surface-adsorbed species. It was also proposed that the role of the ionic liquid was to provide a high concentration of CO₂ at the electrode surface. Thus, the ionic liquid was not recognized as a redox mediator in this study.

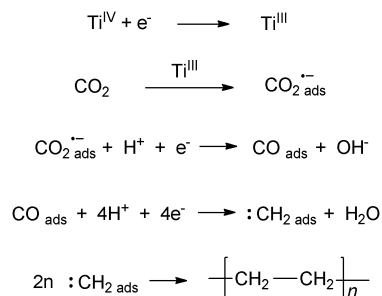
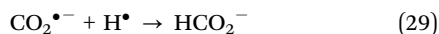


Fig. 7 The overall reaction for electrochemical reduction and polymerization of CO₂ on a nsTiO₂ film.

Barrosse-Antle and Compton reported the electrochemical reduction of CO₂ in 1-butyl-3-methylimidazolium acetate (C₄MIM-Ac) at a Pt electrode.³³ They chose C₄MIM-Ac because it could interact with CO₂ chemically, which was different from other ionic liquids which absorbed gaseous CO₂ physically.^{34,35} The solubility of CO₂ in C₄MIM-Ac at 25 °C is as high as 1520 ± 50 mM, and the chemical adsorption of CO₂ was nearly irreversible. It was found that CO₂ could be reduced at *ca.* -1.3 V *vs.* cobaltocenium/cobaltocene couple, or -1.8 V *vs.* Ag wire in this ionic liquid. The diffusion coefficient of CO₂ in C₄MIM-Ac was also determined electrochemically. A very low value of 2.6 × 10⁻¹² m² s⁻¹ was found. Nevertheless, the reduction of CO₂ was found to be sustainable for 15 minutes, although the products were not determined.

Compton and Martindale then showed that formic acid could be produced by electrochemical reduction of CO₂ in a protic medium at a pre-anodised platinum electrode in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C₂mim]-[NTf₂]).³⁶ A strong acid, H[NTf₂], was used as the proton source. In the absence of CO₂, hydrogen evolution started at -1.3 V *vs.* Pt wire. When CO₂ was introduced to the reaction medium, an additional reduction feature corresponding to CO₂ reduction was observed at -3.3 V *vs.* Pt wire. Formic acid was identified as one product by electrochemistry. The following reactions were proposed to occur on Pt: (eqn (26)–(30))



In 2011, Yu and coworkers synthesized an ionic liquid 1-ethyl-3-methylimidazolium chlorotrifluoroborate (C₂MIM-BF₃Cl) which can be used as an electrolyte, a solvent, and at the same time, a catalyst for electrochemical reduction of CO₂.³⁷ The ionic conductivity of dry C₂MIM-BF₃Cl was 19.0 mS cm⁻¹ at room temperature, and the CO₂ solubility was 0.52 ± 0.25 mass% at 1 atm and room temperature. It was suggested that the anion of C₂MIM-BF₃Cl might catalyze CO₂ reduction through an interaction with CO₂ as shown in Fig. 8. The B–Cl bond (1.73 Å) is longer and weaker than the B–F bond (1.30 Å). The dissociation of BF₃Cl⁻ yields BF₃, which is an oxophilic Lewis acid. BF₃ can form a BF₃–CO₂ adduct through an oxygen atom of CO₂. In BF₃–CO₂, the C=O bond was proposed to be 1.18 Å, slightly longer than that in CO₂ gas (1.16 Å). The interaction of CO₂ with BF₃ makes it possible to reduce CO₂ at a less negative potential. Indeed, CO₂ reduction on Pt in this ionic liquid has a current density of

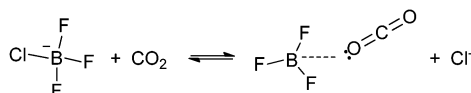


Fig. 8 Proposed interaction of BF₃Cl⁻ with CO₂.

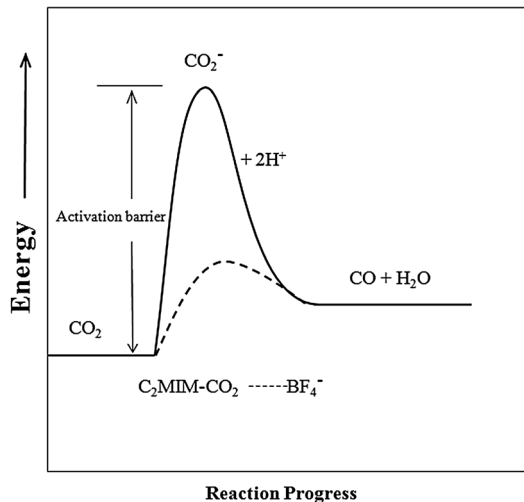
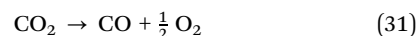


Fig. 9 A schematic diagram of the free energy system for the reaction CO₂ + 2H⁺ + 2e⁻ → CO + H₂O in water or acetonitrile (solid line) or in 18 mol% C₂MIM-BF₄/water (dashed line). Redrawn according to ref. 38.

5.7 mA cm⁻² at -1.8 V *vs.* Ag wire. No significant CO₂ reduction was observed at this potential in other ionic liquids such as 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF₄) and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMIM-NTf₂). A potential drawback of the system is the low thermal stability of the BF₃Cl anion, which decomposes at around 200 °C. Normally ionic liquids are thermally stable until 300 °C.

In 2011, Masel and coworkers reported an important progress in the reduction of CO₂ in ionic liquids.³⁸ The one electron reduction of CO₂ to CO₂^{•-} has a very negative equilibrium potential in almost all solvents, leading to a high overpotential. They thought ionic liquid C₂MIM-BF₄ could complex CO₂ in a way that the formation of CO₂^{•-} was also facilitated (Fig. 9). A silver cathode was used as the catalyst for the reduction of CO₂ to CO, but C₂MIM-BF₄ was an indispensable mediator (a small amount of water was also present). The equilibrium potential for the reaction is 1.33 V.



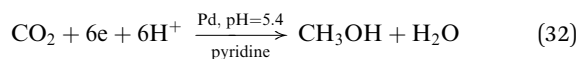
In this Ag–C₂MIM-BF₄ system, CO was produced at an applied voltage of 1.5 V, which indicated that the overpotential was only about 0.17 V. The Faradaic efficiency of CO production was greater than 96%, and only less than 3% of H₂ was formed. Without C₂MIM-BF₄, CO was not produced until a potential of 2.1 V was applied. The turnover frequency (with respect to Ag) varied from 0.8 to 1.4 s⁻¹ when the cell potential was changed from 1.5 to 2.5 V. Thus, the system does not exhibit an ideal Tafel behavior. In an electrolysis experiment, the cell was run at 2.5 V for 7 hours, and 26 000 turnovers were achieved. The system therefore appeared to be robust. Several improvements are still needed before this system can become commercially competitive. The rate of catalysis is still too slow, the electrode surface area is too small, and expensive catalysts (Pt and Ag) and membranes are still required. Nevertheless, this work

represents a breakthrough for electrochemical CO₂ reduction in terms of energy and Faradaic efficiency.

In summary, ionic liquids have started to be used as solvents and mediators for electrochemical CO₂ reduction. Much emphasis is on the “green solvent” and high CO₂ solubility aspects of ionic liquids, but the stabilization of radical species including the CO₂^{•−} radical is being recognized. In the latter aspect, the ionic liquids play a catalytic role. The origin of the stabilization is not fully understood and may become an interesting research topic.

5. Pyridinium derivatives as catalysts

The group of Bocarsly has developed an interesting system for electrocatalytic and photoelectrocatalytic CO₂ reduction using pyridinium as a homogeneous catalyst.^{39–42} Initially they found that CO₂ could be reduced to methanol electrochemically at a hydrogenated Pd electrode in a pH = 5.4 solution, with a Faradaic yield of 30% (eqn (32)).⁴²

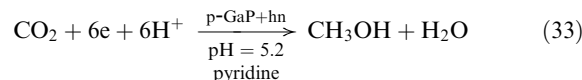


While hydrogen production was a major side reaction, CO₂ reduction could be sustained for 19 h, with a current density of 40 μA cm^{−2} at an overpotential of 200 mV. The pH of the reaction mixture was important. No CO₂ reduction was observed if the pH > 7. This indicated that protonated pyridine, or pyridinium, was the active catalyst. For this reason, the reactions were normally conducted at pH ≈ 5 (pK_a of pyridinium = 5.2). If the pyridinium cation was replaced by the *N*-methyl pyridinium cation, the reduction of CO₂ could not be observed, further confirming the essential role of pyridinium. Because the efficiency of methanol production increased when the Pd electrode was pre-loaded with hydrogen, there was a possibility that Pd catalyzed the transfer of adsorbed hydrogen to CO₂, and the pyridinium cation served as a selective surface poison. This was deemed to be unlikely because earlier experiments showed that at the hydrogenated Pd electrode, CO₂ was reduced to HCOOH or CO, but not to CH₃OH.⁴³

It was later found that Pt could also be used as an electrode, and formic acid and formaldehyde were identified as intermediate products.⁴¹ In Galvanostatic electrolysis experiments at 40 μA cm^{−2} (potential not reported), the Faradaic yields for HCOOH and CH₃OH formation were 11% and 22%, respectively. Because Pd and Pt are very active electrodes for hydrogen evolution, hydrogen evolution always outcompeted CO₂ reduction in the electrocatalysis. On the other hand, no detectable CO₂ reduction was observed when a more inert electrode such as glassy carbon was used. This indicates that the surface-adsorbed hydrogen atom plays an important role. It was also shown that the species being reduced is CO₂ (sol), but not bicarbonate.⁴⁰

The selectivity for pyridinium-catalyzed methanol production increased significantly under photoelectrocatalytic conditions. Bocarsly and coworkers showed that at an illuminated p-GaP electrode, methanol was produced in a nearly 100% Faradaic yield at a potential of −0.22 V vs. SCE, that is, 300 mV more

positive than the dark thermodynamic potential of −0.52 V for this system at pH = 5.2 (eqn (33)).³⁹ The quantum efficiencies for CH₃OH formation under 365 nm illumination were 11% to 44% at *E* = −0.20 to −0.50 V vs. SCE. The efficiencies diminished to 1.3% to 2.6% at *E* = −0.20 to −0.50 V vs. SCE under 465 nm illumination. While solar-to-fuel efficiency is still too low for immediate commercial applications due to the poor overlap between the solar spectrum and the absorption spectrum of p-GaP, this chemistry appears to be the most efficient method for photoelectrochemical methanol formation. It was thought that the higher Faradaic yield for CO₂ reduction was due to the lower activity of p-GaP for hydrogen evolution.



The CO₂ reduction at the p-GaP photoelectrode involves complex photoelectrochemistry at the semiconductor–liquid interface. Therefore, the mechanism of CO₂ reduction was studied under electrocatalytic conditions at a Pt electrode.⁴¹ In the absence of CO₂, a reduction peak was observed at −0.58 V vs. SCE at pH = 5.2. This peak was attributed to the reduction of pyridinium, formed by protonation of pyridine. Based on data from a thorough electrochemical and computational study, Bocarsly and coworkers proposed the following mechanism (Fig. 10).⁴¹ Under the experimental conditions, pyridine (1) accepts a proton to form pyridinium (2). 2 is then reduced to form pyridinyl radical (3), which reacts with CO₂ to form the key carbamate radical intermediate (4). This is the rate determining step of the catalysis.⁴⁰ Further reaction of 4 leads to a surface-adsorbed hydroxyformyl radical (5), possibly with formic acid as an intermediate. The hydroxyformyl radical reacts with surface-bound hydrogen to give a formyl radical (6), which reacts with the pyridinyl anion to give formaldehyde and eventually methanol. For CO₂ reduction at the illuminated p-GaP electrode, because there are no surface-bound hydrogen atoms, the reaction shall proceed through formic acid. Consecutive reduction of formic acid with the pyridinyl radical leads to the formation of methanol (Fig. 10B).

A key intermediate in the mechanism proposed by Bocarsly and coworkers is the pyridinyl radical. While a reduction peak at −0.58 V vs. SCE was attributed to the electrochemical formation of this species under the catalytic conditions, computational studies suggested that the reduction potential of pyridinium was much more negative. For example, Tossell used CBS-QB3 calculation in combination with the CPCM solvation model to calculate the redox potentials and free energies of pyridine, pyridinium, and carbamate radical.⁴⁴ The redox potential of pyridinium was calculated to be −1.44 V vs. SCE, nearly 1 V more negative than the experimentally assigned value. This discrepancy prompted Keith and Carter to investigate further the acidities and redox potential of various proposed intermediate species computationally.⁴⁵ The calculations were based on DFT-B3LYP/aug-cc-pVDZ, and the solvation calculations (CPCM) omitted nonelectrostatic energy contributions, used one explicit water in a cluster-continuum approach, and

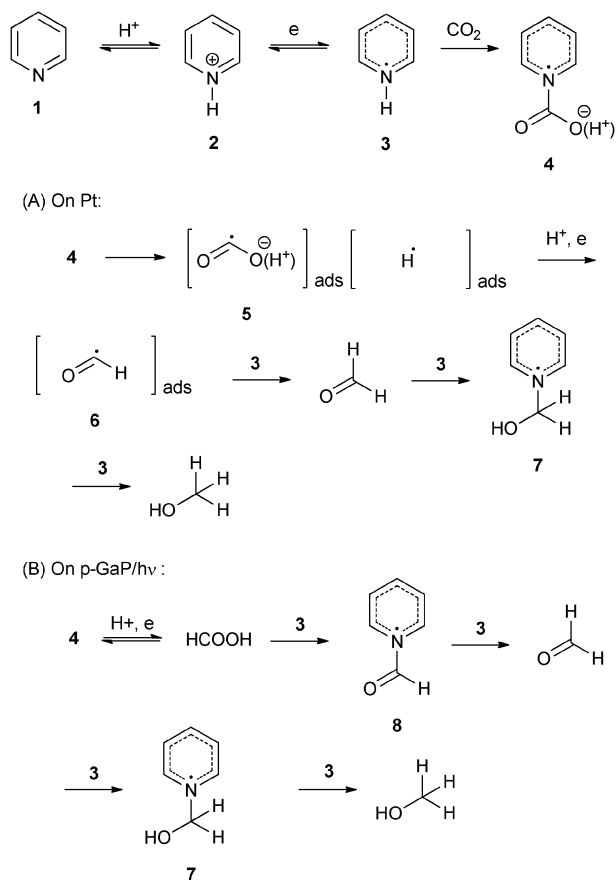


Fig. 10 Proposed mechanism for the pyridinium catalyzed reduction of CO₂ to methanol on (A) Pt electrodes and (B) illuminated p-GaP electrodes.

applied empirical values for the free energies of the proton gas phase and aqueous phase solvation. An extensive benchmarking was conducted to show that the predicted pK_as had a mean unsigned error of 0.9 pK_a unit and a maximum error of 2.1 pK_a unit. The calculated redox potentials for many substituted pyridinium species were within 0.2 V of the experimentally determined values. The calculations predicted a redox potential of -1.45 V vs. SCE for pyridinium, very close to the value predicted by Tossell⁴⁴ despite the different computational approach. The proton-coupled electron transfer redox potential for pyridine was predicted to occur at -1.47 V vs. SCE at pH = 5.3. The large difference between the redox potential of pyridinium and the observed reduction potential suggests that the pyridinyl radical does not play an important role in the catalysis as previously thought. Furthermore, the calculated pK_a of the pyridinyl radical was as high as 27, suggesting that pyridinyl and similar N-protonated pyridinyl species are inactive. These computational results have changed the mechanistic view of pyridinium-catalyzed photoelectrochemical CO₂ reduction. However, it remains unclear what the reduction peak at -0.58 V vs. SCE is due to, and what is the active species in the system.

Despite the mechanistic uncertainty, pyridine or pyridinium is clearly a remarkable catalyst in the electrochemical and photoelectrochemical reduction of CO₂ to methanol. Substituted pyridines could also be used as precatalysts, but with lower

efficiencies than pyridine.⁴¹ The understanding of the role of the surface in this catalytic system will greatly promote the development of ever better catalysts.

6. Conclusions

Simple organic molecules such as tetraalkylammonium salts, aromatic esters and nitriles, ionic liquids, and pyridinium derivatives have been shown as competent mediators and catalysts for photoelectrochemical and electrochemical CO₂ reduction. The products can be CO, oxalate, formic acid, and methanol. It is interesting to note that the product selectivity in these reactions is often high, for example, CO, oxalate, and methanol have been produced exclusively in several systems. Another surprising finding is that CO₂ reduction can take place at low overpotentials using organic mediators and catalysts. For example, with C₂MIM-BF₄ as the mediator, CO is produced at an Ag electrode at an overpotential of less than 170 mV. Likewise, with the pyridinium cation as the catalyst, methanol is produced at a Pt electrode at an overpotential of less than 200 mV. Most of the CO₂ reduction reactions described here seem to involve one-electron charge-transfer mediators or catalysts, and the CO₂^{•-} radical appears to be an intermediate. The results prove that single-electron-transfer catalysts can be efficient for multiple-electron-transfer reactions. While current research in CO₂ reduction is centered on the development of transition-metal-based catalysts, we believe that redox-active organic catalysts should not be overlooked given their diversity and demonstrated efficiency. Furthermore, the combinations of metal-based and organic catalysts might result in superior bifunctional catalysts that would lead to an eventual practical process for the reduction of CO₂ into liquid fuels using renewable energies.

Acknowledgements

This work is supported by a starting grant from the European Research Council under the European Community's Seventh Framework Programme (FP7 2007–2013)/ERC Grant agreement no. 257096.

Notes and references

- 1 K. Caldeira, A. K. Jain and M. I. Hoffert, *Science*, 2003, **299**, 2052–2054.
- 2 M. I. Hoffert, K. Caldeira, A. K. Jain, E. F. Haites, L. D. D. Harvey, S. D. Potter, M. E. Schlesinger, S. H. Schneider, R. G. Watts, T. M. L. Wigley and D. J. Wuebbles, *Nature*, 1998, **395**, 881–884.
- 3 G. M. Whitesides and G. W. Crabtree, *Science*, 2007, **315**, 796–798.
- 4 J. P. Collin and J. P. Sauvage, *Coord. Chem. Rev.*, 1989, **93**, 245–268.
- 5 E. E. Benson, C. P. Kubiak, A. J. Sathrum and J. M. Smieja, *Chem. Soc. Rev.*, 2009, **38**, 89–99.

- 6 J. Schneider, H. F. Jia, J. T. Muckerman and E. Fujita, *Chem. Soc. Rev.*, 2012, **41**, 2036–2051.
- 7 B. Kumar, M. Llorente, J. Froehlich, T. Dang, A. Sathrum and C. P. Kubiak, in *Annual Review of Physical Chemistry*, editon edn, 2012, vol. 63, pp. 541–569.
- 8 A. J. Morris, G. J. Meyer and E. Fujita, *Acc. Chem. Res.*, 2009, **42**, 1983–1994.
- 9 I. Taniguchi, B. Aurianblajeni and J. O. Bockris, *J. Electroanal. Chem.*, 1983, **157**, 179–182.
- 10 I. Taniguchi, B. Aurianblajeni and J. O. Bockris, *J. Electroanal. Chem.*, 1984, **161**, 385–388.
- 11 J. O. Bockris and J. C. Wass, *J. Electrochem. Soc.*, 1989, **136**, 2521–2528.
- 12 T. Saeki, K. Hashimoto, N. Kimura, K. Omata and A. Fujishima, *J. Electroanal. Chem.*, 1995, **390**, 77–82.
- 13 A. Gennaro, A. A. Isse, M. G. Severin, E. Vianello, I. Bhugun and J. M. Saveant, *J. Chem. Soc. Faraday Trans.*, 1996, **92**, 3963–3968.
- 14 A. Gennaro, A. A. Isse, J. M. Saveant, M. G. Severin and E. Vianello, *J. Am. Chem. Soc.*, 1996, **118**, 7190–7196.
- 15 E. A. Ticianelli, L. A. Avaca and E. R. Gonzalez, *J. Electroanal. Chem.*, 1989, **258**, 379–389.
- 16 H. Lund and J. Simonet, *J. Electroanal. Chem.*, 1975, **65**, 205–218.
- 17 S. Matsuoka, T. Kohzuki, C. Pac, A. Ishida, S. Takamuku, M. Kusaba, N. Nakashima and S. Yanagida, *J. Phys. Chem.*, 1992, **96**, 4437–4442.
- 18 S. Matsuoka, T. Kohzuki, C. J. Pac and S. Yanagida, *Chem. Lett.*, 1990, 2047–2048.
- 19 N. V. Rees and R. G. Compton, *Energy Environ. Sci.*, 2011, **4**, 403–408.
- 20 M. Armand, F. Endres, D. R. MacFarlane, H. Ohno and B. Scrosati, *Nat. Mater.*, 2009, **8**, 621–629.
- 21 P. Hapiot and C. Lagrost, *Chem. Rev.*, 2008, **108**, 2238–2264.
- 22 N. V. Plechkova and K. R. Seddon, *Chem. Soc. Rev.*, 2008, **37**, 123–150.
- 23 D. R. Macfarlane, M. Forsyth, P. C. Howlett, J. M. Pringle, J. Sun, G. Annat, W. Neil and E. I. Izgorodina, *Acc. Chem. Res.*, 2007, **40**, 1165–1173.
- 24 V. I. Parvulescu and C. Hardacre, *Chem. Rev.*, 2007, **107**, 2615–2665.
- 25 M. Galinski, A. Lewandowski and I. Stepniak, *Electrochim. Acta*, 2006, **51**, 5567–5580.
- 26 M. C. Buzzeo, R. G. Evans and R. G. Compton, *ChemPhysChem*, 2004, **5**, 1106–1120.
- 27 T. Welton, *Chem. Rev.*, 1999, **99**, 2071–2083.
- 28 M. Feroci, I. Chiarotto, M. Orsini, G. Sotgiu and A. Inesi, *Electrochim. Acta*, 2011, **56**, 5823–5827.
- 29 M. Feroci, M. Orsini, L. Rossi, G. Sotgiu and A. Inesi, *J. Org. Chem.*, 2007, **72**, 200–203.
- 30 D. S. Silvester and R. G. Compton, *Z. Phys. Chem. (International Journal of Research in Physical Chemistry & Chemical Physics)*, 2006, **220**, 1247–1274.
- 31 L. E. Barrosse-Antle, C. Hardacre and R. G. Compton, *J. Phys. Chem. B*, 2009, **113**, 2805–2809.
- 32 D. Chu, G. X. Qin, X. M. Yuan, M. Xu, P. Zheng and J. Lu, *ChemSusChem*, 2008, **1**, 205–209.
- 33 L. E. Barrosse-Antle and R. G. Compton, *Chem. Commun.*, 2009, 3744–3746.
- 34 A. Yokozeki, M. B. Shiflett, C. P. Junk, L. M. Grieco and T. Foo, *J. Phys. Chem. B*, 2008, **112**, 16654–16663.
- 35 M. B. Shiflett, D. J. Kasprzak, C. P. Junk and A. Yokozeki, *J. Chem. Thermodyn.*, 2008, **40**, 25–31.
- 36 B. C. M. Martindale and R. G. Compton, *Chem. Commun.*, 2012, **48**, 6487–6489.
- 37 L. L. Snuffin, L. W. Whaley and L. Yu, *J. Electrochem. Soc.*, 2011, **158**, F155–F158.
- 38 B. A. Rosen, A. Salehi-Khojin, M. R. Thorson, W. Zhu, D. T. Whipple, P. J. A. Kenis and R. I. Masel, *Science*, 2011, **334**, 643–644.
- 39 E. E. Barton, D. M. Rampulla and A. B. Bocarsly, *J. Am. Chem. Soc.*, 2008, **130**, 6342.
- 40 A. J. Morris, R. T. McGibbon and A. B. Bocarsly, *ChemSusChem*, 2011, **4**, 191–196.
- 41 E. B. Cole, P. S. Lakkaraju, D. M. Rampulla, A. J. Morris, E. Abelev and A. B. Bocarsly, *J. Am. Chem. Soc.*, 2010, **132**, 11539–11551.
- 42 G. Seshadri, C. Lin and A. B. Bocarsly, *J. Electroanal. Chem.*, 1994, **372**, 145–150.
- 43 K. Ohkawa, K. Hashimoto, A. Fujishima, Y. Noguchi and S. Nakayama, *J. Electroanal. Chem.*, 1993, **345**, 445–456.
- 44 J. A. Tossell, *Comput. Theoret. Chem.*, 2011, **977**, 123–127.
- 45 J. A. Keith and E. A. Carter, *J. Am. Chem. Soc.*, 2012, **134**, 7580–7583.