available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Review (Special Issue on Electrocatalysis Transformation)

Catalytic conversion of CO₂ to value added fuels: Current status, challenges, and future directions

Jingjie Wu, Xiao-Dong Zhou *,

Department of Chemical Engineering, University of South Carolina, 301 Main Street, Columbia, SC 29208, USA

ARTICLE INFO

Article history:

Received 25 April 2016

Accepted 16 May 2016

Published 5 July 2016

Keywords:

Value added fuels

Electrocatalysts

Catalytic conversion

Carbon dioxide

Durability

ABSTRACT

The electrochemical reduction of CO₂ into liquid fuels especially coupling with the intermittent renewable electricity offers a promising means of storing electricity in chemical form, which reduces the dependence on fossil fuels and mitigates the negative impact of anthropogenic CO₂ emissions on the planet. Although converting CO₂ to fuels is not in itself a new concept, the field has not substantially advanced in the last 30 years primarily because of the challenge of discovery of structural electrocatalysts and the development of membrane architectures for efficient collection of reactants and separation of products. This overview summarizes recent advances in catalytic conversion of CO₂ and presents the challenges and future directions in producing value-added fuels.

© 2016, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Energy and climate change

An abundant supply of clean and affordable energy is vital to the economic growth, quality of life, and security of the human kind. There are two aspects of the energy problem. World demand for energy is projected to more than double by 2050 (from 12 to 30 terawatts) and more than triple by the end of the century. The increasing demand will create a fierce worldwide competition for the gradually depleting fossil fuel reserves, putting in danger our quality of life that depends on a supply of energy at a low cost. On the other hand, increasing greenhouse emission is mostly likely linked to global warming. Indeed, the concentration of CO₂—the key contributor to global climate change in the atmosphere, is at the highest recorded level since records began; and it is set to further increase.

A report released by an international team led by Pierre Friedlingstein [1] showed that the global greenhouse gas would

continuously rise in 2014 to a level of ~65% above emissions in 1990—the benchmark year when Kyoto Protocol was adopted. Meanwhile, the daily mean concentration of CO₂ in the atmosphere measured at the Mauna Loa Observatory in Hawaii was recorded above 400 ppm for the first time on May 9th, 2013, as shown in Fig. 1. In 2015, the amount of emissions was primarily coming from China (25%), US (16%), EU (11%), and India (6%), where manufacturing and traveling accelerated the use of fossil fuels (e.g. coal and petroleum). The rapid increase level of CO₂ in ambient air may build up an irreversible and uninhabitable planet for our future generations. The need to simultaneously increase our energy supply while reducing CO₂ emissions is one of the major challenges facing our global society today. In order to control the global mean temperature increase by 2.0–2.4 °C, the global CO₂ emission would have to be reduced by 50%–80% by 2050 (based on the emission level in 2000) [2].

* Corresponding author. Tel: +803-777-7540; Fax: +803-777-0973; E-mail: zhou.teaching@gmail.com

DOI: 10.1016/S1872-2067(16)62455-5 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 37, No. 7, July 2016

Fig. 1. Keeling curve of the atmospheric CO₂ recorded at the Mauna Loa Observatory, Hawaii.

2. CO₂ properties and management

The total amount of CO₂ in earth's atmosphere is enormous. In 2013, the global CO₂ emission from the use of fossil fuels and cement production was 36 billion tones. As a result, the technologies for CO₂ capture, storage and utilization are needed at a large scale [3–5]. CO₂ utilization efforts focus on developing beneficial uses of the CO₂ where geologic storage may not be a desirable solution. Currently, there are essentially three pathways for CO₂ conversion and utilization as shown in Fig. 2 [4]: utilizing CO₂ as a medium for energy recovery, heat transfer and solvent; converting CO₂ for fuel synthesis via renewable energy sources for sustainable development; and using CO₂ as a feedstock to produce industrially useful chemicals and materials, which adds value to the process. The conversion of CO₂ to useful fuels using non-carbon based energy sources (such as solar, wind, nuclear, or geothermal), although highly challenging, is expected to be a truly sustainable alternative to reduce CO₂ emission [6]. The approaches to convert CO₂ to fuels include electrochemical conversion, solar driven photochemical reduction, biological fixation, and thermal catalytic conversion (e.g. hydrogenation) [5,7–9]. Both the storage and utilization rely on the understanding of the physical and chemical proper-

ties of CO₂, which will be discussed as follows.

2.1. Physical and chemical properties of CO₂

CO₂ is a colorless and odorless gas. The molecule is linear with a double bond between the carbon and oxygen atoms (O=C=O). The two C–O bonds are equivalent and are short (116.3 pm). The molecular orbital (MO) diagram of CO₂ is based on a C atom and an O–O ligand fragment. Carbon 1s and oxygen 2s are assumed to be nonbonding. Carbon 2s and 2p_z orbitals are hybridized to form sp orbitals. The σ-bonding interacts between oxygen 2p_z and carbon sp orbital, while π-bonding is formed between oxygen 2p_x or 2p_y orbitals with “empty” orbitals of the same kind on the central carbon. The carbon atom in a CO₂ molecule is electrophilic and therefore, can interact via chemisorption with an electron-rich surface (typically metals) resulting in the bending of the bonds in a CO₂ molecule. The oxygen atom in a bent CO₂ molecule can be easily attacked by protons, while the C atom is prone to the reaction with the adsorbed H atoms that often requires a higher activation energy though. Since CO₂ is centrosymmetric, the molecule has no net electric dipole. Consistent with this fact, only two vibrational bands are observed in the IR spectrum: an anti-symmetric stretching mode at 2349 cm⁻¹ and a bending mode near 666 cm⁻¹. A symmetric stretching mode at 1388 cm⁻¹ is only observed in the Raman spectrum.

Table 1 provides a summary of the physical and chemical properties of CO₂ [4]. At an atmospheric pressure and 0 °C, the gas CO₂ density is 1.976 g/L, 1.5 times heavier than air. Fig. 3 shows the phase diagrams of CO₂ [3]. CO₂ can be liquefied by

Table 1
Physical and chemical properties of CO₂ [4].

Property	Value and unit
Molecular weight	44.01 g/mol
Sublimation point at 1 atm (101.3 kPa)	−78.5 °C
Triple point at 5.1 atm (518 kPa)	−56.5 °C
Triple point pressure	5.185 bar
Critical temperature (<i>T</i> _c)	31.04 °C
Critical pressure (<i>P</i> _c)	7383 kPa
Critical density (<i>ρ</i> _c)	0.468 g/L
Gas density at 0 °C and 1 atm	1.976 g/L
Liquid density at 0 °C and 1 atm	928 g/L
Solid density	1560 g/L
Specific volume at 1 atm and 21 °C	0.546 m ³ /kg
Latent heat of vaporization at the triple point (−78.5 °C)	353.4 J/g
at 0 °C	231.3 J/g
Viscosity at 25 °C and 1 atm CO ₂	0.015 cP
Solubility in water at 0 °C and 1 atm	0.3346 g/100g-H ₂ O
25 °C and 1 atm	0.1449 g/100g-H ₂ O
Heat of formation at 25 °C	−393.5 kJ/mol
Entropy of formation at 25 °C	213.6 kJ/mol
Gibbs free energy of formation at 25 °C	−394.3 kJ/mol
Heat capacity under constant pressure at 25 °C	37.1 J/(mol K)
Heat capacity under constant volume at 25 °C	28.1 J/(mol K)
Thermal conductivity	14.65 mW/(m K)

Fig. 2. Different pathways of utilizing CO₂ [4].

Fig. 3. Relevant characteristics of CO₂. (a) Phase diagram; (b) Adsorption on coal; (c) Solubility in fresh water; (d) Decrease in solubility with increasing water salinity [3].

compressing to 2 MPa and cooling to -18.8°C , or by compressing to a higher pressure of 5.78 MPa at 21.8°C . At the triple point of -56.6°C and 0.518 MPa, three phases of gas, liquid and solid co-exist. The solid CO₂ can sublime directly into gas without going through the liquid phase upon absorbing heat, and thus it is called dry ice. If the pressure on dry ice is reduced to the atmospheric pressure, the temperature of dry ice drops to -78.5°C . When the temperature and pressure are above the critical point of 31.8°C (T_c) and 7.38 MPa (P_c), CO₂ becomes a supercritical fluid, which is widely used as a solvent in chemical extraction industry. The characteristic of a great CO₂-coal affinity of adsorption enables the sequestration of CO₂ in coal seams or the enhancement of methane recovery (Fig. 3(b)). The solubility of CO₂ in water is 0.033 mol/L at 25°C and 1 atm [10]. The solubility in water (Fig. 3(c)) increases with an increase in pressure or a decrease in temperature and water salinity (Fig. 3(d)).

2.2. Thermodynamics of CO₂ conversion reactions

In order to chemically convert CO₂ to chemicals or fuels, a

substantial input of energy and an active catalyst are required due to its stable molecule involving rather low energy content ($\Delta G^0 = -394$ kJ/mol in gas phase). The Gibbs-Helmholtz relationship describes the change of Gibbs energy of a system as a function of temperature (Eq. (1)). The entropy contribution through the term $(-T\Delta S)$ is negligible to the thermodynamic driving force for the reaction at room temperature, so the value of the enthalpy change ΔH is a good guide to thermodynamic feasibility.

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

The reaction involving CO₂ as a single reactant is indeed energy-demanding. For example, in Eq. (2), the cleavage of C-O bond in CO₂ to form CO and O₂ associates a large positive ΔH^0 (293 kJ/mol). However, a more favorable enthalpy of reaction under standard state conditions (1 atm pressure for each product or reactant at 25°C) can be achieved if less stable reactants and more stable products are involved [11]. For example, hydrocarbons can be used as reductants in a CO₂ reforming reaction as shown in Eq. (3), requiring a less energy ($\Delta H^0 = 247.3$ kJ/mol). The reverse water gas-shift reaction, (Eq. (4)) also known as the hydrogenation of CO₂, is more thermody-

$$2\text{CO}_2 = 2\text{CO} + \text{O}_2 \quad \Delta H^0 = 293 \text{ kJ/mol CO}_2 \quad (2)$$

Fig. 4. Chemical processes of converting CO₂ to useful chemicals and fuels [4,6].

C1 hydrocarbons from a syngas at a temperature between 150–300 °C (Eq. (7)). The FT catalysts are transition metals like Co, Fe, and Ru, along with a number of promoters (e.g. K and Cu). The direct reaction is similar to FT synthesis, but using a CO₂/H₂ feed. The direct reaction is implemented via a single-stage approach, using a bifunctional catalyst that combines RWGS and FT chain growth activity. Short-chain olefins (ethylene and propylene) could be directly produced from syngas using modified FT catalysts, for instance Fe/Mn/K or Fe/Cu/Al/K, or indirectly, via the formation of methanol following a consecutive conversion to short-chain olefins on small-pore zeolites.

CO₂ hydrogenation to methane, known as the Sabatier reaction (Eq. (8)), can be achieved over common Ni-based catalysts (e.g. 10 wt% Ni/CeO₂). But this process is not suitable for the conversion of CO₂ to fuels using H₂ due to the enormous consumption of H₂ and a low energy per volume.

Besides the conversion of CO₂ to fuels, CO₂ is a raw material for the synthesis of useful chemicals in chemical industry. These processes include: the synthesis of urea from ammonia and CO₂ (Eq. (9)) and the production of salicylic acid from phenol and CO₂ (Eq. (10)). Urea is extensively used to make various polymer materials and to produce fertilizers, while the acetyl salicylic acid is used to make Aspirin, a widely used common medicine.

2.5. Photochemical and photo-electrochemical reduction of CO₂

Mimicking nature's photosynthesis process, photoreduction of CO₂ is one of the most promising routes for CO₂ conversion due to the abundance and free access of sunlight [8,9]. Photon-assisted reduction of CO₂ can be divided into four major categories[22]: (1) homogeneous photochemical reduction by a molecular catalyst, (2) direct heterogeneous CO₂ reduction by a biased semiconductor photocathode, (3) heterogeneous CO₂ reduction by metal particles anchored on a biased semiconductor photocathode, and (4) homogeneous photo-electrochemical CO₂ reduction by a molecular catalyst through a semiconductor/molecular catalyst junction.

A homogeneous CO₂ photochemical reduction system consists of a molecular catalyst, photosensitizer (light absorber), sacrificial electron donor, and/or electron relay. The generic mechanism of the photocatalytic reduction of CO₂ consists of a photosensitizer (P) capable of absorbing radiation in the ultraviolet or visible region and generating an excited state (P*) [23,24]. The excited state is quenched by a sacrificial donor (D) generating a singly reduced photosensitizer (P⁻) and an oxidized donor (D⁺). The choice of photosensitizer must be such that P⁻ is able to transfer an electron efficiently to the catalyst species (cat) to generate a reduced catalyst species (cat⁻). In some cases the photosensitizer and the catalyst are the same species. The cat⁻ then binds CO₂ and proceeds with a catalytic mechanism to release the intended products and regenerate

catalyst. Common photosensitizers used in these systems include aromatics (e.g. p-terphenyl), phenazine and polypyridine-coordinated transition metal complexes. Ruthenium(II) trisbipyridine ([Ru(bipy)₃]²⁺) is the most often employed transition metal complex due to its strong visible-light absorption and high photo-stability [25]. The macrocycle complexes of Ni, Co and Fe, and Re(CO)₃bpyX (X=Cl⁻ or Br⁻) based complexes are the most efficient catalysts [26–29]. The homogeneous system with a macrocycle, however, suffers from a low quantum efficiency, a low selectivity, and a low turnover frequency due to the significant production of H₂. Although Re(CO)₃bpyX catalysts improve the quantum efficiency and turnover frequency, they lack extended absorption in the visible region.

There are several semiconductors that can serve as photocathode materials with a suitable band gap and conduction band potential capable of CO₂ reduction, for example p-GaP (2.3 eV), p-CdSe (1.7 eV), p-Si (1.1 eV), p-GaAs (1.4 eV), and p-InP (1.3 eV) [22]. Heterogeneous photo-electrochemical reduction of CO₂ on semiconductor surfaces has been achieved with a satisfactory selectivity towards the formation of formate or formic acid and CO [30–34]. The p-type GaAs has been used for the direct photo-electrochemical reduction of CO₂ to produce methanol [35]. But the mechanism for methanol production is still obscure. The electrolyte, either aqueous or non-aqueous, has a significant impact on the efficiency of the photo-electrochemical reduction, which mainly results from the great difference in CO₂ solubility. Non-aqueous solvents such as acetonitrile, dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and methanol have a higher solubility of CO₂ than water. In a truly photoelectrocatalytic system, when a photoelectrode coupled with a catalyst (metal particles, like Cu, Au, Ag, Pd and Ru) is operated under illumination, apart from a positive shift in the onset voltage called the photovoltage shift, the dependency of the productivity on the applied potential has a similar behavior as the catalyst alone [36,37]. Besides the p-type semiconductor, some other oxides with a suitable negative and positive redox potential in the conductance-band and valence-band edge, respectively, have been under study for CO₂ reduction, for example, ZnO (3.2 eV), V₂O₅ (2.7 eV), WO₃ (2.8 eV), TiO₂ rutile (3.0 eV) and TiO₂ anatase (3.2 eV) [38]. However, these oxides have a large band gap which requires a high energy input to allow the electron excitation. For example, the anatase TiO₂, a stable photocatalyst with a large band-gap energy (3.2 eV), only utilize a small fraction of UV, ~ 2%–3% solar light. The approaches using photosensitizing dyes and doping transition metals by an ion-implantation technique have been developed to improve the visible light response [39,40]. The nanostructure TiO₂ has an improvement of photoreduction activity compared to bulk materials [41]. The highly dispersed TiO₂ on a zeolite cavity and framework has a unique local structure and improves the reaction rate and selectivity for the formation of CH₃OH and CH₄.

The photoelectrochemical reduction of CO₂ through a p-type semiconductor/molecular catalyst junction involves three steps [22]: (a) charge carrier generation and separation in the semiconductor, (b) heterogeneous charge transfer to the molecular electrocatalyst, and (c) homogeneous catalysis. In a

given p-type semiconductor/ molecular electrocatalyst junction, the molecular catalyst must be chosen to match the catalytic current density with the photocurrent density corresponding to the illumination intensity used and the catalyst's turnover frequency. CO₂ reduction has been studied on p-GaAs and p-GaP photocathodes with Ni(cyclam)²⁺ (cyclam = 1,4,8,11-tetraazacyclotetradecane) as the molecular catalyst. A Faradaic efficiency of CO of 80%–100% has been achieved on p-GaP, which is 5 times higher than on p-GaAs due to the inherent surface chemistry characteristics [42,43]. Methanol production from CO₂ with a Faradaic efficiency of 63%–100% was obtained on the electrode consisting of a p-GaP (111) photocathode and a soluble pyridinium molecular catalyst [44].

Considering the distinct advantages of homogeneous catalysts (e.g. selectivity and tunability) and heterogeneous catalysts (e.g. robustness and easy separation of products from catalysts), there is a considerable interest in “heterogenizing” the homogeneous catalysts by covalently linking them to surfaces. But the reported selectivity of this system is low [45,46]. As a result, more efforts are needed to covalently bind the molecular catalyst to the surface to prevent it from loosening on the semiconductors.

Solar photocatalytic reactors for CO₂ reduction have been designed including a two-phase reaction packed bed, a three-phase reaction fixed-bed, and a suspended reactor. A more promising reactor is a photoelectrochemical cell which integrates the photochemical oxidation of water, electrochemical reduction of CO₂, and membrane processes (Fig. 5) [47,48]. One half-cell of this reactor is a photoanode consisting of photocatalysts to split water into one proton plus oxygen. Electrons transfer directly to another half-cell, whereas protons are transported through a Nafion membrane. The photons, electrons, and CO₂ molecules meet at the cathode and react at the electrocatalysts to form new products. The implementation of the cathode reaction requires an understanding of the electrochemistry of CO₂ reduction on the electrocatalysts.

2.6. Solid oxide electrolysis for CO₂ conversion

The electrochemical reduction of CO₂ using electricity from

Fig. 5. A schematic of a CO₂ photo-reduction reactor [47,48].

renewable sources of is an alternative approach to produce fuels, akin to photosynthesis, thus potentially reducing the dependence on foreign fuels as well as mitigating the concentration of CO₂ in the atmosphere. The electrochemical reduction process, a.k.a. electrolysis, can take place over a wide range of temperatures, from room temperature to over 1000 °C. High temperature electrolysis supplies enough energy to overcome the activation energy barrier for C–O bond cleavage in CO₂. Moreover, the high temperature reaction favors the formation of carbon monoxide and hinders the formation of longer chain molecules [49]. Solid oxide electrolysis cells (SOECs) are used for the electrochemical conversion of CO₂ into CO or co-electrolysis of H₂O and CO₂ to form syngas (CO and H₂) at temperature between 600 and 1000 °C over Ni/YSZ (yttria stabilized zirconia) electrode. SOEC is a reverse version of solid oxide fuel cells (SOFC). The basic principle for an SOEC and SOFC operating on H₂O/H₂ and CO₂/CO is shown in Fig. 6. In general, SOECs exhibit a low overpotential, superior selectivity, and high current density towards CO formation [50–52]. The overarching challenges facing prolonged SOEC operation include the electrode degradation largely due to the formation of coke, sulfur contamination, and volatile nickel-carbonyls [53–55].

In order to produce long-chain products, it is imperative to develop electrocatalysts and reactors for CO₂ electrolysis at low temperatures (usually room temperature). To design electrocatalysts requires an understanding of the characteristics of CO₂ adsorption, the interactions with catalyst surface and reductants, and the molecular energetic. The catalyst surface morphology including defects/kinks/steps and composition potentially influence the catalytic CO₂ reduction. The electrolyte property of dielectric constant and polarity as well as type (aqueous or non-aqueous solution) are also the important parameters that can affect catalysis of CO₂ reduction. In terms of reactor design, the effort in developing a bench-scale full electrochemical cell allowing direct gas-phase CO₂ reduction is the priority. The status and prospect of the electrochemical reduction of CO₂ are reviewed in details in the next section.

3. Electrochemical CO₂ conversion

3.1. Molecular catalysts for the electrochemical reduction of CO₂

Molecular complexes can be directly used in a solution or be immobilized at an electrode surface. The insight gained from molecular electrocatalysts can be translated to the development of heterogeneous electrocatalysts [56]. Promising exam-

Fig. 6. A schematic of the operational principle for a solid oxide electrolysis cell and a solid oxide fuel cell [51,52].

ples of molecular electrocatalysts include late transition metal macrocyclic complexes, rhenium bipyridine complexes, palladium triphosphine complexes and bimetallic copper complexes [57–61].

The metal macrocycles have been extensively studied, including Ni^{I} and Ni^{II} macrocycles [57], Co^{I} tetraazamacrocycles [62], Pd complexes [63,64], Ru^{II} complexes [65] and Cu^{II} complexes [66]. $[\text{Ni}^{\text{II}}(\text{cyclam})]^{2+}$ complex (structure 1, Fig. 7) is a very efficient and selective catalyst in the reduction of CO_2 to form CO in the aqueous solution only [67]. The proposed mechanism assumes that the $[\text{Ni}^{\text{I}}(\text{cyclam})]^+$ complex plays a crucial role. In particular, a $[\text{Ni}^{\text{I}}(\text{cyclam})(\text{CO})]^+$ intermediate species has been detected in the course of the electrolysis experiment. Systems favoring the formation of the Ni^{I} state are expected to be an efficient electrocatalyst. In general, the Ni^{II} complexes in some fluorinated cyclams, which exhibit a $\text{Ni}^{\text{II}}/\text{Ni}^{\text{I}}$ potential less negative than $[\text{Ni}^{\text{II}}(\text{cyclam})]^{2+}$, work well for CO_2 reduction [68]. Ni^{II} azacyclam shows a comparable reduction current to that of $[\text{Ni}^{\text{II}}(\text{cyclam})]^{2+}$ under the same complex concentration [57]. Fourteen-membered cyclam framework is a crucial pre-requisite for the encircled nickel center to act as catalyst in the CO_2 electroreduction.

$[\text{Pd}(\text{triphosphine})(\text{CH}_3\text{CN})]^{2+}$ complexes (structure 2, Fig. 7) are also active catalysts for the electrochemical reduction of CO_2 to CO [58]. In this structure, the dissociation of a weakly coordinating solvent molecule, acetonitrile in structure 2, favors the formation of M–O bond during a catalytic cycle. In addition, electron-donating substituents on the triphosphine ligand result in increased catalytic rates. The rate constant is between 5 and 300 $(\text{mol/L})^{-1} \text{s}^{-1}$. Inspired by the CO dehydro-

genase enzymes, the binuclear palladium complexes (structure 3) in which the two $\text{Pd}(\text{P}3)$ compartments are separated by a methylene spacer were used for CO_2 reduction [69]. This complex binds CO_2 through two Pd sites, with one metal interacting with C and the other with O. The binuclear palladium complexes show a very high catalytic rate for CO_2 reduction, $>10^4 (\text{mol/L})^{-1} \text{s}^{-1}$, but exhibit a turnover number of ca. 10. The $\text{Re}(\text{bipy-tBu})(\text{CO})_3\text{Cl}$ ($\text{bipy-tBu}=4,4'$ -di-*tert*-butyl-2,2'-bipyridine) complexes (structure 4) also have been reported to rapidly convert CO_2 to CO with a Faradaic efficiency $\sim 100\%$ in the acetonitrile electrolyte [59]. The complex of $\text{Re}(\text{bipy-tBu})(\text{CO})_3\text{Cl}$ forms a stable $\text{Re}(0)$ radical and significantly less dimers during the electrolysis than its $\text{Re}(\text{bipy})(\text{CO})_3\text{Cl}$ counterpart, which is attributed to the enhanced catalytic activity.

The electrocatalytic reduction of CO_2 to oxalate was recently reported with the use of a binuclear copper complex (structure 5) consisting of a pre-organised, binucleating tetrapodal disulfide ligand [60]. The reduction of the binuclear $\text{Cu}(\text{II})$ complex leads to the formation of $\text{Cu}(\text{I})$ complex, which further forms a new tetranuclear $\text{Cu}(\text{II})$ bis(oxalate) complex (structure 6) with purging CO_2 . The oxalate ligands were found to bridge two adjacent Cu centers. The binuclear oxalate complex was found to react with LiClO_4 to regenerate the starting material and produce insoluble $\text{Li}_2\text{C}_2\text{O}_4$. When tetranuclear $\text{Cu}(\text{II})$ complex was used as an electrocatalyst in the acetonitrile solution containing LiClO_4 , the catalytic turnover started at -0.03 V versus NHE, a potential that is nearly 2 V less negative than that required for the outer-sphere reduction of CO_2 to $\text{CO}_2^{\cdot-}$.

Additionally, non-metal nitrogen-based molecular systems have been investigated, including the pyridinium (structure 7) and its substituted derivatives [44,70,71]. This pyridinium cation acts as one-electron shuttle to perform multiple-electron multiple-proton reduction of CO_2 in an aqueous solution to form products such as formic acid, formaldehyde, and methanol. Using the pyridinium cation as a catalyst on a metal electrode, the Faradaic efficiency of methanol was $\sim 30\%$ at an overpotential of only -0.2 V . When the pyridinium ion catalyst was anchored to a p-GaP electrode, this photochemical system yielded nearly 100% Faradaic efficiency of methanol at a potential of 0.3 V below the thermodynamic potential for the reaction [44]. But the reaction mechanism is unclear and warrants further studies to understand it.

3.2. Heterogeneous catalysts for electrochemical reduction of CO_2

3.2.1. Classification of metal catalysts

Several comprehensive review papers have discussed the heterogeneous metal catalysts for CO_2 reduction. So far, multiple methods have been used to classify a large amount of data in literature on CO_2 reduction [72–74]. Most of these classifications are solely based on the nature of the main product obtained in the electrochemical reduction. Four classes of metallic electrodes in aqueous supporting electrolytes and three classes for nonaqueous media can be distinguished. Thus, in aqueous solution: (1) metallic Cd, In, Sn, Hg, Tl and Pb are selective for the production of formic acid or formate depending on the

Fig. 7. Molecular catalysts of transition metal complexes.

electrolyte pH, (2) metallic Zn, Au and Ag produce carbon monoxide, (3) Cu is the only metal that exhibits the electrocatalytic activity for the formation of hydrocarbons, aldehydes and alcohols, and (4) metallic Al, Ga and Group VIII elements (except Pd) show a low electrocatalytic activity towards CO₂ reduction with the primary product of CO and a low Faradaic efficiency. The CO selectivity which refers to the ratio of the Faradaic efficiency for CO to formic acid/formate on metal catalysts is in the order of: Au > Ag > Cu > Zn >> Cd > Sn > In > Pb > Tl [75]. In an non-aqueous electrolyte [72,76], (1) Pb, Tl and Hg mainly produce oxalic acid; (2) Cu, Ag, Au, In, Zn and Sn form CO and carbonate ions, while Ni, Pd and Pt are selective for CO formation; and (3) Al, Ga and Group VIII elements (except Ni, Pd and Pt) form both CO and oxalic acid.

The metallic catalysts can be classified into two groups according to the electronic configurations in the *d* orbital: *sp* and *d* metal electrodes [72]. The group of *sp* metals is referred to metals with the outermost *d* orbital completely filled with a *d*¹⁰ electronic configuration: Hg, Pd, In, Sn, Cu, Zn, Ag, Au and Cd. This classification enables a better understanding of the electrocatalytic activity associated with the respective electronic characteristics. The trends on the composition and distribution of the reaction products are strongly dependent on the binding energy of intermediates on metals [77]. When used in aqueous supporting electrolytes, *sp* metals, such as Hg, In, Sn and Pb favor the reduction of CO₂ to formic acid or formate. While on *d* metals (e.g., Pd), CO is the main product. However, the same group of metals behaved differently in non-aqueous supporting electrolytes. On *sp* group metals (Tl, Pb and Hg), oxalic acid is selectively produced. On several *d* group metals (Fe, Cr, Mo, Ti and Nb), oxalic acid and CO are the main products. Lastly, CO is mainly formed on several *sp* group metal electrodes (In, Sn, Cd, Zn, Cu, Ag and Au) and *d* group metal electrodes (Pd, Pt and Ni) [78,79]. The various products of CO₂ reduction on *sp* and *d* metals are summarized in Table 3.

3.2.2. Electrochemical CO₂ reduction on *sp* group metals

Cu is the only known catalyst that produces hydrocarbons, e.g. CH₄, C₂H₄, methanol, ethanol and *n*-C₃H₇OH, from CO₂ reduction [80–84]. Product distribution is strongly dependent on the surface morphology and chemistry [85]. The main hydrocarbons are CH₄ and C₂H₄ with a low Faradaic efficiency on commercial Cu electrodes [82,85–87], and the enhanced yield of CH₄ and C₂H₄ was observed on *in situ* deposited Cu electrodes [88]. CH₄ and C₂H₄ was not observed on the electrode with a heavily oxidized surface, however, the formation of hydrocarbons recovered after the electrode was cleaned by ap-

plying a negative potential [89]. In addition, the pre-electrolyzed electrode from a heavy oxide surface increased the long-term activity compared to a conventional Cu electrode on which the formation of hydrocarbons decayed rapidly. Similarly, anodized or thermal treatment electrodes with a rough surface showed a better durability of the performance than smooth electrodes regarding the production of hydrocarbons [90,91]. Recently, oxide-derived Cu, Au and Co electrodes prepared by reducing a micrometer thick Cu₂O and Au oxide films, respectively, were developed and displayed a great improvement over both selectivity towards the targeted products and stability compared to polycrystalline metals [92–94]. Moreover, oxide-derived electrodes were found to reduce CO₂ at a lower overpotential than the conventional metal electrodes. It is worth noting that Cu electrodes containing a Cu₂O surface layer demonstrated a higher activity towards methanol production [95,96]. The yield of CH₃OH increased with increasing Cu (I) concentration. The Cu-based alloys for CO₂ reduction were also investigated. Only Cu-Ni alloy (Cu/Ni = 90/10) was observed to promote the formation of CH₃OH while the other alloys, e.g. Cu-Sn, Cu-Pb, Cu-Zn, Cu-Cd, tend to form CO and formic acid [97–100].

The CO₂ reduction is sensitive to the surface orientation of Cu electrode. C₂H₄ is promoted on Cu(100), and CH₄ on Cu(111), while Cu(110) showed an intermediate product selectivity [101,102]. The C₂H₄ formation is further promoted by introducing (111) or (110) steps to the (100) basal plane (e.g. Cu(S)-[*n*(100) × (111)] and Cu(S)-[*n*(100) × (110)]), and can also be activated by a certain amount of the step atoms. The highest C₂H₄ selectivity was achieved on the (711) [4(100) × (111)] surface [87]. CH₄ was enhanced by introducing (100) to (111), e.g. the Cu(S)-[*n*(111) × (100)] surfaces [103]. The Cu(S)-[*n*(111) × (111)] surfaces favor the formations of acetic acid, acetaldehyde and ethyl alcohol with an increase of the (111) step atom density. The formation of CH₄ at the Cu(S)-[*n*(111) × (111)] electrodes decreases with increasing the (111) step atom density [87].

Although Cu tends to yield hydrocarbons, the reduction of CO₂ is inefficient, occurring at high overpotentials. The second problem is even more serious, which is the rapid degradation of activity [91,93,104–106]. Several mechanisms, like adsorption of organic intermediate [93,104], black carbon deposition [88,93], poison of copper oxide patina [105], accumulation of an unknown low vapor pressure and soluble CO₂ reduction product [107], contaminants Fe²⁺ and Zn²⁺ deposition [106], have been proposed. However, the real reason behind is still unclear. The pulse electro-reduction [104,108,109], anodic

Table 3
Productivity of CO₂ reduction on *sp* and *d* metals.

Metal	Product		
	Aqueous electrolyte		Nonaqueous electrolyte
<i>sp</i> metals (<i>d</i> ¹⁰ electronic configuration)	<i>sp</i> metals (Hg, In, Sn, Pb, Cd)	Formic acid	Oxalate (Tl, Pb, Hg)
	<i>sp</i> metals (Zn, Ag, Au)	CO	CO
	<i>sp</i> metals (Cu)	C ₂ H ₄ , CH ₄ , HCOOH, CO, and alcohols	CO
<i>d</i> metals (partly filled <i>d</i> orbitals)	<i>d</i> metals (e.g., Pt and Pd)	Adsorbed CO	CO (including Ni)
	<i>d</i> metals (e.g., Ru)	Low yield of Hydrocarbons, alcohols, formaldehyde	
	<i>d</i> metals (Fe, Cr, Mo, Ti, Nb)	Weak performance	Oxalate and CO

polarization [110] and periodic anodic stripping [111] were used to regenerate the electrode, but their effects were limited. The third challenge is to understand the formation mechanism of hydrocarbons [86]; fortunately DFT calculations have been carried out to shed light in understanding the reaction mechanisms on Cu [112–114].

The formation of CO can occur on Ag and Au electrodes with a Faradaic efficiency as high as 90%, slightly greater than that on a Zn electrode in an aqueous solution [75,115,116]. In a non-aqueous electrolyte of 0.1 mol/L TEAP/H₂O, Zn was found to produce formic acid at a higher Faradaic efficiency than CO and H₂ [117]. The formation of hydrocarbons occurs on a Ag electrode by the pulse reduction [118]. The product distribution strongly depends on the anodic (V_a) and the cathodic (V_c) bias. CO and HCOO[−] were preferentially formed at a less negative potential of $V_a > -0.4$ V vs. Ag/AgCl, while CH₄, C₂H₄, and C₂H₅OH were major products at $V_a < -0.4$ V vs. Ag/AgCl. The origin of the selectivity was likely related to the special affinity of hydrogen and/or proton to electrodes. At more negative V_a such as $V_a < -0.4$ V vs. Ag/AgCl, protons are so abundant on the electrode surface that the carbon molecules adsorbed by hydrogen are preferentially formed on a Ag electrode. As a result, the hydrocarbonization reaction between H_{ad} and CO₂^{•−} becomes possible, yielding CH₄, C₂H₄, and C₂H₅OH. On the contrary, at a less negative V_a (> -0.4 V vs. Ag/AgCl), the desorption of H_{ad} occurs, and the adsorbed protons are not abundant enough to promote hydrocarbonization reactions. In this case, both CO and HCOO[−] are preferentially produced. Recently, a N-based organometallic silver catalyst including silver pyrazole (AgPz), silver phthalocyanine (AgPc), and silver 3,5-diamino-1,2,4-triazole (AgDAT) was found to exhibit a comparable performance of CO₂ reduction with Ag [119]. The advantage of the organometallic catalysts lies in their low mass fraction of silver.

The In, Sn, Hg and Pb electrodes all have a high overpotential for H₂ evolution and negligible CO adsorption. In an aqueous electrolyte, formic acid or formate is selectively produced with a Faradaic efficiency between 70% and 100% on In, Sn, Hg and Pb electrodes [120–125]. Sn is extremely interesting because of its abundance, a low cost, and a high selectivity towards the formation of formic acid/formate in aqueous electrolytes, compared to the other three metals [76,115,122,126–130]. The production of formic acid/formate is promising because it is an economically viable way to store energy. Formic acid, with a free energy of combustion of −233 kJ/mol, is a promising fuel for the generation of electricity in fuel cells [131–136]. In addition, producing formic acid is economical as it has a higher retail value compared to its required formation energy than the conventional fuels, such as methanol or methane. The market price of formic acid is about \$1200 per metric ton, yet the invested energy in the creation of formic acid is only around 3000 kWh/ton, which leaves a favorable energy-price gap. The usual CO₂ reduction pathway for the formation of formic acid/formate, as shown in Fig. 8 [76], involves an initial adsorption step followed by a one-electron reduction to form the intermediate CO₂^{•−} species. The weakly adsorbed CO₂^{•−} goes through a protonation reaction, then there is a second electron-transfer to yield formate. The production

Fig. 8. A possible route of electrochemical reduction of CO₂ into formate with the by-product CO on Sn electrode [76].

of formate is accompanied by a parallel disproportionation of the stable CO₂^{•−} radical anion which is adsorbed to produce CO [72,124,137].

So far, a variety of Faradaic efficiencies of formate on Sn electrodes have been reported in literature, which are summarized in Table 4. The difference in the Faradaic efficiency results from the variations in the electrode property, electrolysis conditions, the nature of electrolyte, and the reactor design. In terms of the electrode property, for example, Sn electrodes are natively covered by an oxide film which was recently found to intertwine with CO₂ reduction and influence the activity [138].

3.2.3. Electrochemical reduction of CO₂ on d group metals

This group has a low activity towards CO₂ reduction while H₂ evolution dominates. For example, on Ni electrodes, only CO, HCOOH, CH₄, and C₂H₄ with a Faradaic efficiency < 1% were detected [121]. On Pd electrodes, CO and HCOOH are the main products, with a maximum Faradaic efficiency < 30% for both products [75,121]. Under a high pressure, e.g. 30 atm, the Faradaic efficiency of CO and HCOOH became comparable to that of H₂ [116]. Interestingly, small yield of methanol was reported on Ru electrode [139,140]. The reduction of CO₂ on an alloy Ru-Pd (1:1) mainly produced HCOOH with a maximum Faradaic efficiency of 90% [141]. CO₂ is reduced to CO (CO_{ad}) on Pt catalysts [142,143]. The CO₂ reduction on a series of Pt single crystal electrodes was systematically studied. The activity for CO₂ reduction depends remarkably on the symmetry of the surface. Following activity series are obtained for the stepped surfaces: Pt(111) < Pt(100) < Pt(S)-[n(111) × (100)] < Pt(S)-[n(100) × (111)] < Pt(S)-[n(111) × (111)] < Pt(110). The initial rate of the CO₂ reduction becomes higher with an increase of the step atom density [144]. Moreover, the kinked step surfaces, which contain protruding atoms along the step lines, have a higher activity for CO₂ reduction than the stepped surfaces [144].

3.3. Effects of pressure, temperature and supporting electrolyte

A low CO₂ solubility in an aqueous electrolyte results in a poor mass transport, thus becomes the limitation to obtain high selectivity at high current density. The low solubility is often overcome by operating a cell at a high pressures, low temperature or in an alternate organic medium. For example, the solubility of CO₂ in water increases with decreasing temperature, e.g. 0.058 mol/L at −4 °C compared with 0.033 mol/L at 25 °C under the ambient pressure. At 60 atm and 25 °C, the solubility of CO₂ in water is over 1 mol/L. The solubility can be increased by changing the solvent. For instance, in methanol, the solubility of CO₂ is over 1 mol/L at 25 °C and 8 atm, a considerably

Table 4Summary of CO₂ reduction on Sn electrodes with various electrolysis conditions in literatures.

Materials	Reduction condition	Electrolyte	Faradaic efficiency (%)			Ref.
			HCOO ⁻	CO	H ₂	
Sn	H-type cell, -1.40 V vs. SCE, room temperature (RT)	0.5 mol/L KHCO ₃	65.5–79.5	2.4–4.1	13.4–40.8	[115]
Sn GDE	-1.8 V vs. SCE, 20 °C	0.35 mol/L Na ₂ SO ₄ (pH = 2)	57	7	12	[125]
Sn	H-type cell, -2.0 V vs. Ag/AgCl, RT	0.1 mol/L TEAP/H ₂ O	67.5	9.1	29.9	[117]
Sn (99.999%)	-1.86 V vs. Ag/AgCl, 25 °C	0.1 mol/L KHCO ₃	63	7.3	26	[205]
Sn	H-type cell, -2.2 V vs. SCE, 0 °C	0.05 mol/L KHCO ₃	0.285	1.4	67.50	[121]
Sn	H-type cell, -1.63 V vs. Ag/AgCl, 18.5 °C	0.1 mol/L KHCO ₃	88.4	7.1	4.6	[75]
Sn	High pressure cell, -1.8 V vs. Ag/AgCl, RT	0.5 mol/L KHCO ₃	99.2	—	—	[123]
Sn (99.9%)	163 mA cm ⁻² , 25 °C, 30 atm	0.1 mol/L KHCO ₃	92.3	8	1.3	[116]
Sn (>99.5%)	E = -1.5 V vs. SCE, ambient pressure and temperature	0.01 mol/L benzalkonium chloride in methanol	0	28	4.40	[206]
Sn granules	a fixed-bed reactor, -2.0 V vs. SCE, RT	0.1 mol/L K ₂ CO ₃	14.25	—	—	[122]
	a fixed-bed reactor, -2.0 V vs. SCE, RT	0.5 mol/L KHCO ₃	47	—	—	
Sn GDE	Microfluid, reactor, -3.0 V	0.5 mol/L KCl (pH = 4)	~90	—	—	[155]
Sn foil	H-type cell, -1.32 V vs. Ag/AgCl, RT	0.5 mol/L NaHCO ₃	~30	—	—	[130]

lower pressure than that required to maintain an equivalent concentration in an aqueous system. The dominance of H₂ evolution can be shifted to CO₂ reduction on d group electrodes by increasing the pressure [116,121]. The formation of hydrocarbons on Cu electrode decreased upon increasing pressure [116,145], while lowering the temperature improved the hydrocarbons formation [93,121,146–148]. The effects of temperature and pressure on the stability of the electrode performance are unknown. What we do know is that the operation temperature and pressure do play a role on the performance degradation of the electrodes for the oxygen reduction reaction in fuel cells [149–154].

The nature of the supporting electrolyte, including the chemistry of anions and cations and their respective concentrations, affects the selectivity and current density towards CO₂ reduction. A greater Faradaic efficiency towards formate production was observed in 0.1 mol/L KHCO₃ than in 0.5 mol/L K₂CO₃ with a Sn electrode [122]. The Faradaic efficiency of formate increased with decreasing electrolyte concentration, reaching to a maximum ~ 88.4% in 0.1 mol/L KHCO₃ [75] versus ~70% in 0.5 mol/L KHCO₃ [115]. Electrolytes with a lower pH could promote the formation of formic acid on Sn electrodes [155]. Different cationic types in the aqueous electrolyte influence the product distribution. On Cu electrodes, both Li⁺ and Na⁺ favors the formation of CH₄, while K⁺, Rb⁺ and Cs⁺ prefer the production of C₂H₄. The Faradaic efficiency for the formation of C₂H₄ increased with the cation radius in the order of Cs⁺ > K⁺ > Na⁺ > Li⁺ [156–158]. A similar trend was observed on Ag electrode for CO₂ reduction to CO [159].

Non-aqueous solvent system has been utilized in order to obtain a higher concentration of CO₂. Among the various non-aqueous solvents, methanol is an extensively investigated alternate [160–162]. Methanol, a protic solvent, is expected to serve as a hydrogen atom source for the formations of H₂ and/or hydrocarbons. Methanol and CO₂ are completely miscible with each other. The concentration of CO₂ reaches 0.17 mol/L at 1 atm, ~ 8 mol/L at 40 atm, and ~ 17 mol/L at 60 atm in a CO₂-methanol mixture at 25 °C [160]. Moreover, methanol

is a stable electrolyte which does not participate in the reduction reaction [121,163]. In the CO₂-methanol system, the Faradaic efficiency of the target products is higher than that in an aqueous solution [164,165]. In a cold and high pressure CO₂-methanol system, the CO₂ reduction was enhanced even more [166].

3.4. State-of-art of the reactor design for the electrochemical reduction of CO₂

The reactors for the direct gas-phase CO₂ reduction were developed in order to overcome the low solubility of CO₂ in an aqueous electrolyte. The earlier work focused on the application of a composite electrode comprised of a metal-solid polymer electrolyte (SPE) with metal catalysts coating on one side of SPE. A typical SPE cell configuration is CO_{2(g)}/metal-catalyst/SPE/aqueous electrolyte/Pt as shown in Fig. 9(a) [167,168]. With an SPE, the product of CO₂ reduction was separated from the anode reaction. In addition, the protons can easily transfer through SPE from the anode to cathode. When the metal was Cu and SPE was a proton conducting membrane (Nafion), hydrocarbons such as CH₄ and C₂H₄ were formed, but the Faradaic efficiency was < 10% [167–169]. When the Nafion was replaced with an anion solid polymer electrolyte membrane, the main product was HCOOH with a Faradaic efficiency of ~ 10% [169]. The SPE composite electrodes consisting of Au and Ag also showed activity towards the gas-phase CO₂ reduction and the Faradaic efficiency of CO was lower compared to the liquid phase CO₂ reduction [121,170,171]. The low selectivity towards CO₂ reduction in an SPE cell may result from the acidity of the Nafion membrane, because the formation of C₂H₄ and CH₄ on the Cu SPE cell decreases as the pH of the electrolyte decreases [172]. However, in the condition of a limited supply of protons, the product may shift to HCOOH as in the case of the use of an anion solid polymer electrolyte membrane.

The gas diffusion electrode (GDE) was incorporated into a cell for the gas-phase CO₂ reduction with a typical configuration, as shown in Fig. 9(b). The reaction at the triple-phase

Fig. 9. Schematic of reactor designs for CO₂ reduction. (a) An SPE cell; (b) A GDE cell; (c) A full electrolysis cell with the same configuration of PEMFC; (d) A full electrolysis cell including an electrolyte buffer layer [168,169].

(gas-liquid-solid, GLS) boundaries not only increased the current density but also promoted the conversion of CO₂ to products [173–175]. The Faradaic efficiency of C₂H₄ increased drastically at a GLS interface of a Cu GDE, compared to a liquid-solid (LS) interface [176,177]. A similar phenomenon of the enhanced CO₂ conversion to CO was observed on a Ag-based GDE [178]. The formation of CH₄ from CO₂ was reported on a Pt GDE at a high pressure [179,180]. Formic acid was formed on a Ru-Pd (1:1) alloy GDE with a Faradaic efficiency as high as 90% [141]. Ethanol was formed at a Faradaic efficiency of 31% at a current density of 180 mA/cm² on a GDE containing La_{1.8}Sr_{0.2}CuO₄ [181].

The development of full electrochemical cells aims at taking advantage of the SPE electrode and GDE. The first attempt was to utilize the configuration of proton exchange membrane fuel cells (PEMFCs), as shown in Fig. 9(c), to directly convert gas phase CO₂ to other species in gas phases [182]. Various hydrocarbons, including CH₄, C₂H₄ and C₂H₆, were observed on a Cu electrode deposited on the Nafion® 117 membrane. The overall Faradaic efficiency, however was ~1% due to the acidity of the Nafion® membrane, which promoted the competitive hydrogen evolution reaction over the CO₂ reduction reaction [172,183]. Similar results were observed on the Ag electrode, on which the hydrogen evolution reaction dominated [183]. However, when an anion exchange membrane was used, CO was detected, though the Faradaic efficiency was low. Modifications in the physical structure of PEMFCs were adopted to improve the selectivity of the electrodes towards CO₂ reduction [155,183–190].

One design was to modify the cathode, for instance, a 3D cathode consisting of a Sn-Cu mesh screen, which allowed a co-current flow of CO₂ and catholyte through the cathode, thus providing an aqueous environment for CO₂ reduction [184]. As a consequence, the Faradaic efficiency toward formate formation was substantially improved to ~86% at a cell potential of 3 V. The high operation voltage resulted from a large ohmic loss and a cathodic overpotential [9]. In addition, the low solubility of CO₂ in the aqueous electrolyte [10] significantly affected cell performance at higher current densities because of mass transfer constraints. An alternative design concept was to insert a layer of an aqueous electrolyte between the cathode GDE and SPE (Fig. 9(d)). Thus, the acidity of Nafion® was mediated by the aqueous electrolyte while Nafion® could still function as a proton transfer medium and gas separator. Based on this concept, a glass fiber saturated with 0.5 mol/L KHCO₃ was inserted between the Nafion® membrane and a Ag GDE to prevent excessive buildup of protons near the cathode, which resulted in a significant increase of selectivity towards CO₂ reduction to CO [183].

The glass fibers, however could become dry during the electrolysis due to the evaporation of water, resulting in the degradation of cell performance. One approach to circumvent the drying problem was to operate the cell with a flowing electrolyte stream in place of the saturated glass fiber [155,187]. With a continuous flowing electrolyte, the formate production on a Sn GDE was achieved at a Faradaic efficiency of ~70% by using 0.5 mol/L KCl as the electrolyte at pH = 7, while the efficiency increased to ~90% at pH = 4. The cell, however, was operated

at high voltages to obtain formate [155]. A high pressure cell of flowing electrolyte was design to enhance the selectivity towards CO formation on a Ag GDE. CO generated at 15 atm was 5 times that observed at ambient pressure with a Faradaic efficiency as high as 92% observed at 350 mA/cm² at which the cell potential was higher than 3 V [191]. Recently, an ionic liquid was used as the catholyte with Ag GDE to convert CO₂ to CO, which showed substantial improvement over both Faradaic efficiency (~100%) and the overpotential (less negative than -0.2 V) towards CO formation [14]. The ionic liquid, EMIMBF₄, was considered to react with CO₂ to form a complex such as CO₂-EMIM at potentials more negative than -0.1 V with respect to a standard hydrogen electrode (SHE). This complex substantially lowered the barrier for formation of the intermediate CO₂ and suppressed H₂ evolution [192].

4. Remaining technical challenges and opportunities regarding the electrochemical reduction of CO₂

4.1. Simultaneously high efficiency and high stability of an electrocatalyst

Cu, Ag and Sn are the most extensively scrutinized electrocatalysts, which can convert CO₂ to CO, CH₄, C₂H₄, alcohols and carboic acid in aqueous electrolytes [93,111,193,194]. A long-lasting challenge in the electrosynthesis of fuels from CO₂ is to achieve a durable electrochemical performance, an equally important characteristic of an electrode as the activity and selectivity, but it has not yet been clearly addressed in the open literature. Hypotheses for the origin of the deactivation of CO₂ reduction electrode included the formation of intermediates like oxide, hydroxide [91,111] and carbon species [93,193], as well as the accumulation of a soluble CO₂ reduction product in the electrolyte causing a remarkable decrease in the selectivity [195]. Hori et al. [106] examined the deactivation of Cu electrode and postulated that the degradation of the cell performance was originated from the deposition of iron and zinc contaminants in the electrolyte on the active surface of the catalyst. The impurity alone, however, cannot explain the degradation since the ultrapure electrolyte coupled with pre-electrolysis was used, in which the degradation was still observed. The performance degradation mechanism for metallic electrocatalysts has remained obscure and necessitates further investigations.

4.2. The competition between CO₂ reduction and hydrogen evolution

The selectivity of the electrocatalysts for the conversion of CO₂ has been subject to intensive investigations, aiming at the electrosynthesis of C1 or C2 fuels on metallic electrodes. A generic electroreduction of CO₂ is a proton-coupled electron transfer reaction [196], CO₂ + H⁺ + e⁻ → fuels, which competes with the hydrogen evolution reaction, 2H⁺ + 2e⁻ → H₂. The evolution of hydrogen via electrolysis is known to generally occur at a low overpotential [197]. Hence, an effective electrocatalyst for CO₂ conversion must be sluggish towards hydrogen evolu-

tion while exhibiting a low overpotential for CO₂ reduction in order to suppress hydrogen evolution and promote carbon dioxide reduction reaction. However, the experimental evidence is needed to address questions such as: (1) how and why hydrogen evolution reaction is suppressed, (2) what are the sites, are these sites for CO₂ reduction, and (3) what is the chemical nature of hydrogen during these reactions?

4.3. CO₂ chemistry in the electrolyte and at the electrode surface

CO₂ reduction with the presence of an electrolyte is often considered to be originated from gaseous CO₂ molecules, which has not been clarified. An understanding of CO₂ chemistry in the electrolytes can help us improve the design of solvent systems for CO₂ capture using chemical or physical absorption. During the electrochemical reduction of CO₂, the carbon atom goes through nucleophilic attack at the electrode surface. Provided we understand the interactions between the actual CO₂-based intermediates and solvents, it will be possible to tune the selectivity of a desirable product. However, there are no such reports available in literature yet regarding how CO₂ chemistry in a solvent influences electrocatalysis. Experimental evidence detailing the interactions of intermediates formed during CO₂ electrocatalysis with solvents is needed, particularly at the electrode surface.

4.4. The development of nonmetallic catalysts

The current literature is overwhelmed with metallic electrocatalysts, in which Cu and Sn are the most well-known ones. Cu was found to be active towards the formation of hydrogen carbon and alcohols [84,93,111,196]. Sn exhibits a superior selectivity towards the formation of formate with a Faradaic efficiency up to 98% [130]. A rapid performance degradation was observed in both Sn- and Cu-based electrode after approximately 30 min from the start of CO₂ electrolysis [183,184,198,199]. Recent work by Wu et al. [200–202] on N-doped carbon nanostructures showed that these materials were highly efficient, selective and more importantly, stable catalysts to achieve CO₂ conversion to CO. The catalytic activity of N-doped carbon nanotubes (NCNTs) was further benchmarked against other metallic catalysts reported in literature. Compared to noble metals (Ag and Au), these NCNTs exhibited a lower overpotential to achieve similar selectivity towards CO formation. The nonmetallic catalysts appear to be an area worth of exploring, including carbides, oxides, carbon and so on.

4.5. Development of high-efficiency electrodes consisting of active electrocatalysts

The high current density (> 1000 mA/cm²) and high energy efficiency are the key to develop a commercial electroreduction approach to make “value added” products from CO₂. Hence, it is of critical importance to overcome the sluggish kinetics of CO₂ reduction and low solubility of CO₂ in an electrolyte. GDEs have

already applied in a direct gas-phase CO₂ reduction to avoid the low CO₂ solubility in the aqueous electrolyte. The further improvement relies on the optimization of catalyst structure in GDEs via tuning the component volume percentage and using advanced processing methods in order to increase the triple-phase boundary length. The cathode microstructure of proton exchange membrane fuel cells (PEMFCs) plays a critical role in gas diffusion, charge exchange and transfer, and subsequently oxygen reduction reaction (ORR) as well as the overall fuel cell performance [203,204]. Similar to ORR, the addition of Nafion in the catalyst layer improved the electrocatalytic activity towards CO₂ reduction by increasing the triple-phase boundary among reactant gases, electrolyte and catalyst particles. More research is needed to translate the basic understanding of electrocatalytic reactions to better design efficient electrodes by investigating the role of cathode microstructure on the activity, selectivity and durability of an electrode.

4.6. Technical and economic analysis

The ultimate goal of CO₂ utilization is to generate “value added” products. There is still lack of bench-scale full electrochemical cell for CO₂ reduction coupling solar energy. The full electrochemical cell based on a PEMFC configuration which can take the advantage of the existing technology in fuel cells, for example, the flow field optimization, the membrane electrode assembly preparation, and even the assembly of fuel cell stacks. A feasible electrolysis cell not only favors CO₂ reduction over H₂ evolution, but also operates energy-efficiently. Though some flowing electrolyte cells have demonstrated a high selectivity towards target products, but the operation requires high overpotential. A new design of full electrochemical cell enabling future “solar driven” is needed to achieve a low energy consuming operation.

5. Summary

In summary, mastery of the electrochemical conversion of CO₂ and H₂O to fuels using renewable electricity can shed light on (1) understanding the nature of artificial photosynthesis and (2) offering an approach to mitigate the negative impact of anthropogenic CO₂ emissions on the planet. Remarkable achievements have been made in the electrochemical reduction of CO₂ in the past two decades, including the design of metallic and nonmetallic catalysts, the role of aqueous or non-aqueous, the role of surface oxide scale, and the theoretical modeling. Despite of these, much more research and development are needed to elucidate the aforementioned challenges and eventually develop an electrochemical system that is capable of converting CO₂ economically.

References

- [1] P. Friedlingstein, R. M. Andrew, J. Rogelj, G. P. Peters, J. G. Canadell, R. Knutti, G. Luderer, M. R. Raupach, M. Schaeffer, D. P. van Vuuren, C. Le Quere, *Nat. Geosci.*, **2014**, 7, 709–715.
- [2] B. Metz, O.R. Davidson, P.R. Bosch, R. Dave, L.A. Meyer eds., *Climate Change 2007: Mitigation of Climate Change*, Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, **2007**.
- [3] S. Bachu, *Progr. Energy Combust. Sci.*, **2008**, 34, 254–273.
- [4] C. Song, *Catal. Today*, **2006**, 115, 2–32.
- [5] B. Hu, C. Guild, S. L. Suib, *J. CO₂ Utilization*, **2013**, 1, 18–27.
- [6] G. Centi, E. A. Quadrelli, S. Perathoner, *Energy Environ. Sci.*, **2013**, 6, 1711–1731.
- [7] H. Li, P. H. Opgenorth, D. G. Wernick, S. Rogers, T. Y. Wu, W. Higashide, P. Malati, Y. X. Huo, K. M. Cho, J. C. Liao, *Science*, **2012**, 335, 1596.
- [8] M. Q. Yang, Y. J. Xu, *Nanoscale Horizons*, **2016**, 1, 185–200.
- [9] L. Yuan, Y. J. Xu, *Appl. Surf. Sci.*, **2015**, 342, 154–167.

Graphical Abstract

Chin. J. Catal., 2016, 37: 999–1015 doi: 10.1016/S1872-2067(16)62455-5

Catalytic conversion of CO₂ to value added fuels: Current status, challenges, and future directions

Jingjie Wu, Xiao-Dong Zhou*
University of South Carolina, USA

An overview summarizes recent advances in catalytic conversion of CO₂ to value-added fuels and presents the challenges and future directions in this field.

- [10] Z. H. Duan, R. Sun, C. Zhu, I. M. Chou, *Marine Chem.*, **2006**, 98, 131–139.
- [11] M. K. Nikoo, N. A. S. Amin, *Fuel Processing Technol.*, **2011**, 92, 678–691.
- [12] D. T. Whipple, P. J. A. Kenis, *J. Phys. Chem. Lett.*, **2010**, 1, 3451–3458.
- [13] Y. B. Vassiliev, V. S. Bagotsky, N. V. Osetrova, O. A. Khazova, N. A. Mayorova, *J. Electroanal. Chem. Interfacial Electrochem.*, **1985**, 189, 271–294.
- [14] B. A. Rosen, A. Salehi-Khojin, M. R. Thorson, W. Zhu, D. T. Whipple, P. J. A. Kenis, R. I. Masel, *Science*, **2011**, 334, 643–644.
- [15] B. Metz, O. Davidson, H. de Coninck, M. Loos, L. Meyer, *IPCC Special Report on Carbon Dioxide Capture and Storage*, Cambridge University Press, London, **2005**, 195–276.
- [16] R. S. Haszeldine, *Science*, **2009**, 325, 1647–1652.
- [17] L. Shi, G. H. Yang, K. Tao, Y. Yoneyama, Y. S. Tan, N. Tsubaki, *Acc. Chem. Res.*, **2013**, 46, 1838–1847.
- [18] C. Crisafulli, S. Scirè, R. Maggiore, S. Minicò, S. Galvagno, *Catal. Lett.*, **1999**, 59, 21–26.
- [19] J. Yoshihara, C. T. Campbell, *J. Catal.*, **1996**, 161, 776–782.
- [20] J. Yoshihara, S. C. Parker, A. Schafer, C. T. Campbell, *Catal. Lett.*, **1995**, 31, 313–324.
- [21] C. Song, *Chem. Innovation*, **2001**, 31, 21–26.
- [22] B. Kumar, M. Llorente, J. Froehlich, T. Dang, A. Sathrum, C. P. Kubiak, *Ann. Rev. Phys. Chem.*, **2012**, 63, 541–569.
- [23] A. J. Morris, G. J. Meyer, E. Fujita, *Acc. Chem. Res.*, **2009**, 42, 1983–1994.
- [24] H. Takeda, O. Ishitani, *Coord. Chem. Rev.*, **2010**, 254, 346–354.
- [25] B. Durham, J. V. Caspar, J. K. Nagle, T. J. Meyer, *J. Am. Chem. Soc.*, **1982**, 104, 4803–4810.
- [26] C. A. Craig, L. O. Spreer, J. W. Otvos, M. Calvin, *J. Phys. Chem.*, **1990**, 94, 7957–7960.
- [27] J. Grodkowski, P. Neta, E. Fujita, A. Mahammed, L. Simkhovich, Z. Gross, *J. Phys. Chem. A*, **2002**, 106, 4772–4778.
- [28] J. Grodkowski, T. Dhanasekaran, P. Neta, P. Hambright, B. S. Brunshwig, K. Shinozaki, E. Fujita, *J. Phys. Chem. A*, **2000**, 104, 11332–11339.
- [29] J. Hawecker, J. M. Lehn, R. Ziessel, *J. Chem. Soc. Chem. Commun.*, **1983**, 536–538.
- [30] J. F. Liu, B. Chuyu, *J. Electroanal. Chem.*, **1992**, 324, 191–200.
- [31] B. Aurian-Blajeni, M. Halmann, J. Manassen, *Solar Energy Mater.*, **1983**, 8, 425–440.
- [32] I. Taniguchi, B. Aurian-Blajeni, J. O. M. Bockris, *Electrochim. Acta*, **1984**, 29, 923–932.
- [33] K. Hirota, D. A. Tryk, T. Yamamoto, K. Hashimoto, M. Okawa, A. Fujishima, *J. Phys. Chem. B*, **1998**, 102, 9834–9843.
- [34] S. Kaneco, H. Katsumata, T. Suzuki, K. Ohta, *Chem. Eng. J.*, **2006**, 116, 227–231.
- [35] W. M. Sears, S. R. Morrison, *J. Phys. Chem.*, **1985**, 89, 3295–3298.
- [36] R. Hinogami, T. Mori, S. Yae, Y. Nakato, *Chem. Lett.*, **1994**, 23, 1725–1728.
- [37] R. Hinogami, Y. Nakamura, S. Yae, Y. Nakato, *Appl. Surf. Sci.*, **1997**, 121–122, 301–304.
- [38] P. Usubharatana, D. McMartin, A. Veawab, P. Tontiwachwuthikul, *Ind. Eng. Chem. Res.*, **2006**, 45, 2558–2568.
- [39] T. Shimidzu, T. Iyoda, Y. Koide, *J. Am. Chem. Soc.*, **1985**, 107, 35–41.
- [40] M. Anpo, S. Dohshi, M. Kitano, Y. Hu, M. Takeuchi, M. Matsuoka, *Ann. Rev. Mater. Res.*, **2005**, 35, 1–27.
- [41] M. Kitano, M. Matsuoka, M. Ueshima, M. Anpo, *Appl. Catal. A*, **2007**, 325, 1–14.
- [42] J. P. Petit, P. Chartier, M. Beley, J. P. Deville, *J. Electroanal. Chem. Interfacial Electrochem.*, **1989**, 269, 267–281.
- [43] M. Beley, J. P. Collin, J. P. Sauvage, J. P. Petit, P. Chartier, *J. Electroanal. Chem. Interfacial Electrochem.*, **1986**, 206, 333–339.
- [44] E. E. Barton, D. M. Rampulla, A. B. Bocarsly, *J. Am. Chem. Soc.*, **2008**, 130, 6342–6344.
- [45] T. Arai, S. Sato, K. Uemura, T. Morikawa, T. Kajino, T. Motohiro, *Chem. Commun.*, **2010**, 46, 6944–6946.
- [46] B. Aurian-Blajeni, I. Taniguchi, J. M. Bockris, *J. Electroanal. Chem. Interfacial Electrochem.*, **1983**, 149, 291–293.
- [47] S. Ichikawa, R. Doi, *Catal. Today*, **1996**, 27, 271–277.
- [48] J. Liu, G. Z. Cao, Z. G. Yang, D. H. Wang, D. Dubois, X. D. Zhou, G. L. Graff, L. R. Pederson, J. G. Zhang, *ChemSusChem*, **2008**, 1, 676–697.
- [49] C. Cheung, U. Erb, G. Palumbo, *Mater. Sci. Eng. A*, **1994**, 185, 39–43.
- [50] Z. L. Zhan, L. Zhao, *J. Power Sources*, **2010**, 195, 7250–7254.
- [51] S. D. Ebbesen, M. Mogensen, *J. Power Sources*, **2009**, 193, 349–358.
- [52] S. H. Jensen, P. H. Larsen, M. Mogensen, *Int. J. Hydrogen Energy*, **2007**, 32, 3253–3257.
- [53] T. J. Huang, C. L. Chou, *Electrochem. Commun.*, **2009**, 11, 1464–1467.
- [54] T. Kim, S. Moon, S. I. Hong, *Appl. Catal. A*, **2002**, 224, 111–120.
- [55] F. Bidrawn, G. Kim, G. Corre, J. T. S. Irvine, J. M. Vohs, R. J. Gorte, *Electrochem. Solid-State Lett.*, **2008**, 11, B167–B170.
- [56] J. M. Saveant, *Chem. Rev.*, **2008**, 108, 2348–2378.
- [57] F. Abba, G. De Santis, L. Fabbri, M. Licchelli, A. M. Manotti Lanfredi, P. Pallavicini, A. Poggi, F. Ugozzoli, *Inorg. Chem.*, **1994**, 33, 1366–1375.
- [58] J. M. Smieja, C. P. Kubiak, *Inorg. Chem.*, **2010**, 49, 9283–9289.
- [59] M. Rakowski, D. L. Dubois, *Acc. Chem. Res.*, **2009**, 42, 1974–1982.
- [60] R. Angamuthu, P. Byers, M. Lutz, A. L. Spek, E. Bouwman, *Science*, **2010**, 327, 313–315.
- [61] C. Finn, S. Schnittger, L. J. Yellowlees, J. B. Love, *Chem. Commun.*, **2012**, 48, 1392–1399.
- [62] E. Fujita, C. Creutz, N. Sutin, D. J. Szalda, *J. Am. Chem. Soc.*, **1991**, 113, 343–353.
- [63] J. W. Raebiger, J. W. Turner, B. C. Noll, C. J. Curtis, A. Miedaner, B. Cox, D. L. DuBois, *Organometallics*, **2006**, 25, 3345–3351.
- [64] A. Miedaner, B. C. Noll, D. L. DuBois, *Organometallics*, **1997**, 16, 5779–5791.
- [65] D. Ooyama, T. Tomon, K. Tsuge, K. Tanaka, *J. Organometal. Chem.*, **2001**, 619, 299–304.
- [66] R. J. Haines, R. E. Wittrig, C. P. Kubiak, *Inorg. Chem.*, **1994**, 33, 4723–4728.
- [67] M. Beley, J. P. Collin, R. Ruppert, J. P. Sauvage, *J. Am. Chem. Soc.*, **1986**, 108, 7461–7467.
- [68] M. Shionoya, E. Kimura, Y. Iitaka, *J. Am. Chem. Soc.*, **1990**, 112, 9237–9245.
- [69] I. S. Weitz, J. L. Sample, R. Ries, E. M. Spain, J. R. Heath, *J. Phys. Chem. B*, **2000**, 104, 4288–4291.
- [70] E. Barton Cole, P. S. Lakkaraju, D. M. Rampulla, A. J. Morris, E. Abelev, A. B. Bocarsly, *J. Am. Chem. Soc.*, **2010**, 132, 11539–11551.
- [71] G. Seshadri, C. Lin, A. B. Bocarsly, *J. Electroanal. Chem.*, **1994**, 372, 145–150.
- [72] M. Jitaru, D. A. Lowy, M. Toma, B. C. Toma, L. Oniciu, *J. Appl. Electrochem.*, **1997**, 27, 875–889.
- [73] A. Bandi, J. Schwarz, C. U. Maier, *J. Electrochem. Soc.*, **1993**, 140, 1006–1008.
- [74] S. Ikeda, T. Takagi, K. Ito, *Bull. Chem. Soc. Jpn.*, **1987**, 60, 2517–2522.
- [75] Y. Hori, H. Wakebe, T. Tsukamoto, O. Koga, *Electrochim. Acta*, **1994**, 39, 1833–1839.
- [76] R. P. S. Chaplin, A. A. Wragg, *J. Appl. Electrochem.*, **2003**, 33, 1107–1123.

- [77] D. F. Gao, H. Zhou, J. Wang, S. Miao, F. Yang, G. X. Wang, J. G. Wang, X. H. Bao, *J. Am. Chem. Soc.*, **2015**, 137, 4288–4291.
- [78] F. Fischer, O. Prziza, *Berichte Der Deutschen Chemischen Gesellschaft*, **1914**, 47, 256–260.
- [79] R. Ehrenfeld, *Berichte Der Deutschen Chemischen Gesellschaft*, **1905**, 38, 4138–4143.
- [80] M. Gattrell, N. Gupta, A. Co, *J. Electroanal. Chem.*, 2006, 594, 1–19.
- [81] H. Noda, S. Ikeda, Y. Oda, K. Ito, *Chem. Lett.*, **1989**, 289–292.
- [82] Y. Hori, A. Murata, R. Takahashi, *J. Chem. Soc., Faraday Trans.*, **1989**, 85, 2309–2326.
- [83] J. L. Qiao, M. Y. Fan, Y. S. Fu, Z. Y. Bai, C. Y. Ma, Y. Y. Liu, X. D. Zhou, *Electrochim. Acta*, **2015**, 153, 559–565.
- [84] M. Y. Fan, Z. Y. Bai, Q. Zhang, C. Y. Ma, X. D. Zhou, J. L. Qiao, *RSC Adv.*, **2014**, 4, 44583–44591.
- [85] W. Tang, A. A. Peterson, A. S. Varela, Z.P. Jovanov, L. Bech, W.J. Durand, S. Dahl, J.K. Nørskov, I. Chorkendorff, *Phys. Chem. Chem. Phys.*, **2012**, 14, 76–81.
- [86] K. P. Kuhl, E. R. Cave, D. N. Abram, T. F. Jaramillo, *Energy Environ. Sci.*, **2012**, 5, 7050–7059.
- [87] Y. Hori, I. Takahashi, O. Koga, N. Hoshi, *J. Phys. Chem. B*, **2001**, 106, 15–17.
- [88] R. L. Cook, R. C. MacDuff, A. F. Sammells, *J. Electrochem. Soc.*, **1988**, 135, 1320–1326.
- [89] Y. Terunuma, A. Saitoh, Y. Momose, *J. Electroanal. Chem.*, **1997**, 434, 69–75.
- [90] S. Ishimaru, R. Shiratsuchi, G. Nogami, *J. Electrochem. Soc.*, 2000, 147, 1864–1867.
- [91] G. Kyriacou, A. Anagnostopoulos, *J. Electroanal. Chem.*, **1992**, 322, 233–246.
- [92] Y. H. Chen, C. W. Li, M. W. Kanan, *J. Am. Chem. Soc.*, **2012**, 134, 19969–19972.
- [93] D. W. DeWulf, T. Jin, A.J. Bard, *J. Electrochem. Soc.*, **1989**, 136, 1686–1691.
- [94] S. Gao, Y. Lin, X. C. Jiao, Y. F. Sun, Q. Q. Luo, W. H. Zhang, D. Q. Li, J. L. Yang, Y. Xie, *Nature*, **2016**, 529, 68–71.
- [95] J. K. W. Frese, *J. Electrochem. Soc.*, **1991**, 138, 3338–3344.
- [96] M. Le, M. Ren, Z. Zhang, P. T. Sprunger, R. L. Kurtz, J. C. Flake, *J. Electrochem. Soc.*, **2011**, 158, E45–E49.
- [97] M. Watanabe, M. Shibata, A. Kato, M. Azuma, T. Sakata, *J. Electrochem. Soc.*, **1991**, 138, 3382–3389.
- [98] M. Watanabe, M. Shibata, A. Katoh, M. Azuma, T. Sakata, *Denki Kagaku*, **1991**, 59, 508–516.
- [99] M. Watanabe, M. Shibata, A. Katoh, T. Sakata, M. Azuma, *J. Electroanal. Chem.*, **1991**, 305, 319–328.
- [100] A. Katoh, H. Uchida, M. Shibata, M. Watanabe, *J. Electrochem. Soc.*, **1994**, 141, 2054–2058.
- [101] Y. Hori, H. Wakebe, T. Tsukamoto, O. Koga, *Surf. Sci.*, **1995**, 335, 258–263.
- [102] I. Takahashi, O. Koga, N. Hoshi, Y. Hori, *J. Electroanal. Chem.*, **2002**, 533, 135–143.
- [103] Y. Hori, I. Takahashi, O. Koga, N. Hoshi, *J. Mol. Catal. A*, **2003**, 199, 39–47.
- [104] R. Shiratsuchi, Y. Aikoh, G. Nogami, *J. Electrochem. Soc.*, **1993**, 140, 3479–3482.
- [105] B. D. Smith, D.E. Irish, P. Kedzierzawski, J. Augustynski, *J. Electrochem. Soc.*, **1997**, 144, 4288–4296.
- [106] Y. Hori, H. Konishi, T. Futamura, A. Murata, O. Koga, H. Sakurai, K. Oguma, *Electrochim. Acta*, **2005**, 50, 5354–5369.
- [107] P. Friebe, P. Bogdanoff, N. Alonso-Vante, H. Tributsch, *J. Catal.*, **1997**, 168, 374–385.
- [108] G. Nogami, H. Itagaki, R. Shiratsuchi, *J. Electrochem. Soc.*, **1994**, 141, 1138–1142.
- [109] J. Yano, S. Yamasaki, *J. Appl. Electrochem.*, **2008**, 38, 1721–1726.
- [110] J. Yano, T. Morita, K. Shimano, Y. Nagami, S. Yamasaki, *J. Solid-State Electrochem.*, **2007**, 11, 554–557.
- [111] B. Jermann, J. Augustynski, *Electrochim. Acta*, **1994**, 39, 1891–1896.
- [112] A. A. Peterson, F. Abild-Pedersen, F. Studt, J. Rossmeisl, J. K. Nørskov, *Energy Environ. Sci.*, **2010**, 3, 1311–1315.
- [113] A. A. Peterson, J. K. Nørskov, *J. Phys. Chem. Lett.*, **2012**, 3, 251–258.
- [114] W. J. Durand, A. A. Peterson, F. Studt, F. Abild-Pedersen, J. K. Nørskov, *Surf. Sci.*, **2011**, 605, 1354–1359.
- [115] Y. Hori, K. Kikuchi, S. Suzuki, *Chem. Lett.*, **1985**, 1695–1698.
- [116] K. Hara, A. Kudo, T. Sakata, *J. Electroanal. Chem.*, **1995**, 391, 141–147.
- [117] S. Ikeda, T. Takagi, K. Ito, *Bull. Chem. Soc. Jpn.*, **1987**, 60, 2517–2522.
- [118] R. Shiratsuchi, G. Nagami, *J. Electrochem. Soc.*, **1996**, 143, 582–586.
- [119] C. E. Tornow, M. R. Thorson, S. Ma, A. A. Gewirth, P. J. A. Kenis, *J. Am. Chem. Soc.*, **2012**, 134, 19520–19523.
- [120] B. Innocent, D. Liaigre, D. Pasquier, F. Ropital, J. M. Leger, K. B. Kokoh, *J. Appl. Electrochem.*, **2009**, 39, 227–232.
- [121] M. Azuma, K. Hashimoto, M. Hiramoto, M. Watanabe, T. Sakata, *J. Electrochem. Soc.*, **1990**, 137, 1772–1778.
- [122] F. Koleli, T. Atilan, N. Palamut, A. M. Gizir, R. Aydin, C. H. Hamann, *J. Appl. Electrochem.*, **2003**, 33, 447–450.
- [123] T. Mizuno, K. Ohta, A. Sasaki, T. Akai, M. Hirano, A. Kawabe, *Energy Sources*, **1995**, 17, 503–508.
- [124] S. Kaneco, R. Iwao, K. Iiba, K. Ohta, T. Mizuno, *Energy*, **1998**, 23, 1107–1112.
- [125] M. N. Mahmood, D. Masheder, C.J. Harty, *J. Appl. Electrochem.*, **1987**, 17, 1159–1170.
- [126] J. J. Wu, P. P. Sharma, B. H. Harris, X. D. Zhou, *J. Power Sources*, **2014**, 258, 189–194.
- [127] J. J. Wu, F. G. Risalvato, S. G. Ma, X. D. Zhou, *J. Mater. Chem. A*, **2014**, 2, 1647–1651.
- [128] J. J. Wu, F. G. Risalvato, P. P. Sharma, P. J. Pellechia, F. S. Ke, X. D. Zhou, *J. Electrochem. Soc.*, **2013**, 160, F953–F957.
- [129] J. J. Wu, B. Harris, P. P. Sharma, X. D. Zhou, *ECS Trans.*, **2013**, 58, 71–80.
- [130] J. J. Wu, F. G. Risalvato, F. S. Ke, P. J. Pellechia, X. D. Zhou, *J. Electrochem. Soc.*, **2012**, 159, F353–F359.
- [131] C. Rice, S. Ha, R. I. Masel, P. Waszczuk, A. Wieckowski, T. Barnard, *J. Power Sources*, **2002**, 111, 83–89.
- [132] Y. M. Zhu, S. Y. Ha, R. I. Masel, *J. Power Sources*, **2004**, 130, 8–14.
- [133] C. V. Rao, C. R. Cabrera, Y. Ishikawa, *J. Phys. Chem. C*, **2011**, 115, 21963–21970.
- [134] N. V. Rees, R. G. Compton, *J. Solid State Electrochem.*, **2011**, 15, 2095–2100.
- [135] T. T. Cheng, E. L. Gyenge, *J. Electrochem. Soc.*, **2008**, 155, B819–B828.
- [136] K. L. Chu, M. A. Shannon, R. I. Masel, *J. Electrochem. Soc.*, **2006**, 153, A1562–A1567.
- [137] R. P. S. Chaplin, A. A. Wragg, *J. Appl. Electrochem.*, **2003**, 33, 1107–1123.
- [138] Y. H. Chen, M. W. Kanan, *J. Am. Chem. Soc.*, **2012**, 134, 1986–1989.
- [139] J. P. Popić, M. L. Avramov-Ivić, N. B. Vuković, *J. Electroanal. Chem.*, **1997**, 421, 105–110.
- [140] K. W. Frese, S. Leach, *J. Electrochem. Soc.*, **1985**, 132, 259–260.
- [141] N. Furuya, T. Yamazaki, M. Shibata, *J. Electroanal. Chem.*, **1997**, 431, 39–41.

- [142] S. P. Chen, S. Q. Xia, S. G. Sun, *Spectrosc. Spectr. Anal.*, **2000**, 20, 610–611.
- [143] S. G. Sun, Z. Y. Zhou, *Phys. Chem. Chem. Phys.*, **2001**, 3, 3277–3283.
- [144] N. Hoshi, T. Suzuki, Y. Hori, *J. Electroanal. Chem.*, **1996**, 416, 61–65.
- [145] K. Hara, A. Tsuneto, A. Kudo, T. Sakata, *J. Electrochem. Soc.*, **1994**, 141, 2097–2103.
- [146] S. Kaneco, N. Hiei, Y. Xing, H. Katsumata, H. Ohnishi, T. Suzuki, K. Ohta, *Electrochim. Acta*, **2002**, 48, 51–55.
- [147] S. Kaneco, H. Katsumata, T. Suzuki, K. Ohta, *ACS Symp. Series*, **2003**, 852, 169–182.
- [148] T. Mizuno, A. Naitoh, K. Ohta, *J. Electroanal. Chem.*, **1995**, 391, 199–201.
- [149] Y. Y. Shao, G. P. Yin, Z. B. Wang, Y. Z. Gao, *J. Power Sources*, **2007**, 167, 235–242.
- [150] Y. Y. Shao, G. P. Yin, Y. Z. Gao, *J. Power Sources*, **2007**, 171, 558–566.
- [151] Z. G. Lu, X. D. Zhou, J. Templeton, J. W. Stevenson, *J. Electrochem. Soc.*, **2010**, 157, B964–B969.
- [152] J. J. Wu, F. J. Xia, M. Pan, X. D. Zhou, *J. Electrochem. Soc.*, **2012**, 159, B654–B660.
- [153] X. D. Zhou, L. R. Pederson, J. W. Templeton, J. W. Stevenson, *J. Electrochem. Soc.*, **2010**, 157, B220–B227.
- [154] X. D. Zhou, J. W. Templeton, J. W. Stevenson, *ECS Trans.*, **2011**, 35, 1985–1994.
- [155] D. T. Whipple, E. C. Finke, P. J. A. Kenis, *Electrochem. Solid-State Lett.*, **2010**, 13, D109–D111.
- [156] S. Kaneco, K. Iiba, H. Katsumata, T. Suzuki, K. Ohta, *J. Solid State Electrochem.*, **2007**, 11, 490–495.
- [157] A. Murata, Y. Hori, *Bull. Chem. Soc. Japan*, **1991**, 64, 123–127.
- [158] G. Z. Kyriacou, A. K. Anagnostopoulos, *J. Appl. Electrochem.*, **1993**, 23, 483–486.
- [159] M. R. Thorson, K. I. Siil, P. J. A. Kenis, *J. Electrochem. Soc.*, **2013**, 160, F69–F74.
- [160] E. Brunner, W. Hültschmidt, G. Schlichthärle, *J. Chem. Thermodyn.*, **1987**, 19, 273–291.
- [161] S. Kaneco, K. Iiba, N. Hiei, K. Ohta, T. Mizuno, T. Suzuki, *Electrochim. Acta*, **1999**, 44, 4701–4706.
- [162] S. Kaneco, H. Katsumata, T. Suzuki, K. Ohta, *Electrochim. Acta*, **2006**, 51, 3316–3321.
- [163] A. Naitoh, K. Ohta, T. Mizuno, H. Yoshida, M. Sakai, H. Noda, *Electrochim. Acta*, **1993**, 38, 2177–2179.
- [164] T. Saeki, K. Hashimoto, A. Fujishima, N. Kimura, K. Omata, *J. Phys. Chem.*, **1995**, 99, 8440–8446.
- [165] S. Kaneco, K. Iiba, M. Yabuuchi, N. Nishio, H. Ohnishi, H. Katsumata, T. Suzuki, K. Ohta, *Ind. Eng. Chem. Res.*, **2002**, 41, 5165–5170.
- [166] S. Kaneco, K. Iiba, H. Katsumata, T. Suzuki, K. Ohta, *Electrochim. Acta*, **2006**, 51, 4880–4885.
- [167] R. L. Cook, R. C. Macduff, A. F. Sammells, *J. Electrochem. Soc.*, **1990**, 137, 187–189.
- [168] R. L. Cook, R. C. Macduff, A. F. Sammells, *J. Electrochem. Soc.*, **1988**, 135, 1470–1471.
- [169] S. Komatsu, M. Tanaka, A. Okumura, A. Kungi, *Electrochim. Acta*, **1995**, 40, 745–753.
- [170] M. Maeda, Y. Kitaguchi, S. Ikeda, K. Ito, *J. Electroanal. Chem.*, **1987**, 238, 247–258.
- [171] Y. Hori, H. Ito, K. Okano, K. Nagasu, S. Sato, *Electrochim. Acta*, **2003**, 48, 2651–2657.
- [172] D. W. Dewulf, A. J. Bard, *Catal. Lett.*, **1988**, 1, 73–79.
- [173] N. Furuya, K. Matsui, S. Motoo, *Denki Kagaku*, **1988**, 56, 980–984.
- [174] R. L. Cook, R. C. Macduff, A. F. Sammells, *J. Electrochem. Soc.*, **1990**, 137, 607–608.
- [175] M. Schwartz, M. E. Vercauteren, A. F. Sammells, *J. Electrochem. Soc.*, **1994**, 141, 3119–3127.
- [176] H. Yano, F. Shirai, M. Nakayama, K. Ogura, *J. Electroanal. Chem.*, **2002**, 519, 93–100.
- [177] H. Yano, T. Tanaka, M. Nakayama, K. Ogura, *J. Electroanal. Chem.*, **2004**, 565, 287–293.
- [178] H. Yano, F. Shirai, M. Nakayama, K. Ogura, *J. Electroanal. Chem.*, **2002**, 533, 113–118.
- [179] K. Hara, T. Sakata, *J. Electrochem. Soc.*, **1997**, 144, 539–545.
- [180] K. Hara, A. Kudo, T. Sakata, M. Watanabe, *J. Electrochem. Soc.*, **1995**, 142, L57–L59.
- [181] M. Schwartz, R. L. Cook, V. M. Kehoe, R. C. Macduff, J. Patel, A. F. Sammells, *J. Electrochem. Soc.*, **1993**, 140, 614–618.
- [182] T. Yamamoto, D. A. Tryk, A. Fujishima, H. Ohata, *Electrochim. Acta*, **2002**, 47, 3327–3334.
- [183] C. Delacourt, P. L. Ridgway, J. B. Kerr, J. Newman, *J. Electrochem. Soc.*, **2008**, 155, B42–B49.
- [184] H. Li, C. Oloman, *J. Appl. Electrochem.*, **2005**, 35, 955–965.
- [185] H. Li, C. Oloman, *J. Appl. Electrochem.*, **2006**, 36, 1105–1115.
- [186] H. Li, C. Oloman, *J. Appl. Electrochem.*, **2007**, 37, 1107–1117.
- [187] E. J. Dufek, T. E. Lister, M. E. McIlwain, *J. Electrochem. Soc.*, **2011**, 158, B1384–B1390.
- [188] E. J. Dufek, T. E. Lister, M. E. McIlwain, *Electrochem. Solid-State Lett.*, **2012**, 15, B48–B50.
- [189] C. Delacourt, J. Newman, *J. Electrochem. Soc.*, **2010**, 157, B1911–B1926.
- [190] A. S. Agarwal, Y. M. Zhai, D. Hill, N. Sridhar, *ChemSusChem*, **2011**, 4, 1301–1310.
- [191] E. J. Dufek, T. E. Lister, S. G. Stone, M. E. McIlwain, *J. Electrochem. Soc.*, **2012**, 159, F514–F517.
- [192] B. A. Rosen, J. L. Haan, P. Mukherjee, B. Braunschweig, W. Zhu, A. Salehi-Khojin, D. D. Dlott, R. I. Masel, *J. Phys. Chem. C*, **2012**, 116, 15307–15312.
- [193] S. Wasmus, E. Cattaneo, W. Vielstich, *Electrochim. Acta*, **1990**, 35, 771–775.
- [194] S. Zhang, P. Kang, T. J. Meyer, *J. Am. Chem. Soc.*, **2014**, 136, 1734–1737.
- [195] P. Friebe, P. Bogdanoff, N. Alonso-Vante, H. Tributsch, *J. Catal.*, **1997**, 168, 374–385.
- [196] Z. F. Chen, P. Kang, M. T. Zhang, B. R. Stoner, T. J. Meyer, *Energy Environ. Sci.*, **2013**, 6, 813–817.
- [197] D. Voiry, H. Yamaguchi, J. Li, R. Silva, D. C. B. Alves, T. Fujita, M. Chen, T. Asefa, V. B. Shenoy, G. Eda, M. Chhowalla, *Nat. Mater.*, **2013**, 12, 850–855.
- [198] P. Kedzierski, J. Augustynski, *J. Electrochem. Soc.*, **1994**, 141, L58–L60.
- [199] F. Koleli, T. Atilan, N. Palamut, A. M. Gizir, R. Aydin, C. H. Hamann, *J. Appl. Electrochem.*, **2003**, 33, 447–450.
- [200] J. J. Wu, M. J. Liu, P. P. Sharma, R. M. Yadav, L. L. Ma, Y. C. Yang, X. L. Zou, X. D. Zhou, R. Vajtai, B. I. Yakobson, J. Lou, P. M. Ajayan, *Nano Lett.*, **2016**, 16, 466–470.
- [201] J. J. Wu, R. M. Yadav, M. J. Liu, P. P. Sharma, C. S. Tiwary, L. L. Ma, X. L. Zou, X. D. Zhou, B. I. Yakobson, J. Lou, P. M. Ajayan, *ACS Nano*, **2015**, 9, 5364–5371.
- [202] P. P. Sharma, J. J. Wu, R. M. Yadav, M. J. Liu, C. J. Wright, C. S. Tiwary, B. I. Yakobson, J. Lou, P. M. Ajayan, X. D. Zhou, *Angew. Chem. Int. Ed.*, **2015**, 54, 13701–13705.
- [203] E. Antolini, L. Giorgi, A. Pozio, E. Passalacqua, *J. Power Sources*, **1999**, 77, 136–142.

- [204] H. R. Jhong, F. R. Brushett, P. J. A. Kenis, *Adv. Energy Mater.*, **2013**, 3, 589–599.
- [205] H. Noda, S. Ikeda, Y. Oda, K. Imai, M. Maeda, K. Ito, *Bull. Chem. Soc. Japan*, **1990**, 63, 2459–2462.
- [206] K. Ohta, M. Kawamoto, T. Mizuno, D. A. Lowy, *J. Appl. Electrochem.*, **1998**, 28, 717–724.

CO₂催化转化为高附加值燃料：现状、挑战及其未来方向

Jingjie Wu, Xiao-Dong Zhou^{*}

南卡罗来纳大学化学工程系, 哥伦比亚, 南卡罗来纳29208, 美国

摘要: CO₂电化学还原, 特别是与间歇性的可再生电能相结合转化为液体燃料提供了一条很有前景的将电能存储为化学能的途径, 它既降低了人们对化石燃料的依赖, 又减轻了因人类活动而排放的CO₂对地球的不利影响。尽管CO₂转化为燃料本身不是一个新概念, 但在过去的30多年里该领域的研究也没有很大的进展。这主要是由于结构型电催化剂的开发、以及可有效收集反应物和分离产物的膜组件的开发存在很大的挑战。本文总结了CO₂催化转化的最新进展, 提出了制备高附加值燃料的挑战和未来的方向。

关键词: 高附加值燃料; 电催化剂; 催化转化; 二氧化碳; 可持续性

收稿日期: 2016-04-25. 接受日期: 2016-05-16. 出版日期: 2016-07-05.

*通讯联系人. 电话: +803-777-7540; 传真: +803-777-0973; 电子信箱: zhou.teaching@gmail.com

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).