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A review on the electrochemical reduction of CO_2 in fuel cells, metal electrodes and molecular catalysts

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ABSTRACT

In this review article, we report the development and utilisation of fuel cells, metal electrodes in aqueous electrolyte and molecular catalysts in the electrochemical reduction of CO_2. Fuel cells are able to function in both electrolyser and fuel cell mode and could potentially reduce CO_2 and produce energy at the same time. However, it requires considerably high temperatures for efficient operation. Direct reduction using metal electrodes and molecular catalysts are possible at room temperatures but require an additional applied potential and generally have low current densities. Density functional theory (DFT) studies have been used and have begun to unveil possible mechanisms involved which could lead to improvements and development of more efficient catalysts.

1. Introduction

Since the industrial revolution, atmospheric carbon dioxide (CO_2) level of about 278 ppm has continuously increased due to extensive use of fossil fuels [1]. Recent report showed that atmospheric CO_2 level has reached the 400 ppm mark [2] and it is expected to continue to rise. The climate modelling study performed by Solomon et al. has shown that the effects of climate change due to the increase in greenhouse gases would have lasting effects of up to 1000 years even when there is zero emission of greenhouse gases [3–5]. Currently, the release of CO_2 into the environment is uncontrolled from various industrial and anthropogenic processes. The open loop nature of these processes which releases CO_2 into the environment is not only unsustainable; but is also contrary to the natural carbon cycle which is a closed loop process. Although the study by Solomon et al. [3,4] do not take into account forced or artificial sequestration of greenhouse gases especially CO_2, it is still important that the release of CO_2 into the environment has to cease as soon as possible to minimise the adverse impact of climate change. Instead of sequestrating atmospheric CO_2 only, the captured CO_2 should also be turned into fuels which not only closes the open loop processes that we have but also reduces our dependency on fossil fuels. Various other potential uses for CO_2 in the industry has also been highlighted where the utilisation of CO_2 may reach an upper limit of 700 Mt/yr [6]. Being able to efficiently turn CO_2 into fuels would have the largest benefit and impact in the effort to reduce CO_2 emissions. This is because 80% of our energy is derived from fossil fuels [7].

Energy from carbon neutral sources such as renewables and/or nuclear can be used to synthesise these fuels by storing the energy in a chemical form. Besides, it would be possible to utilise existing infrastructures to transport and store the fuels [8,9]. Energy from renewables and nuclear is generally in the form of electricity, hence electrochemistry potentially plays an important role in the production of fuels from CO_2. The Fischer–Tropsch (FT) process is also an important process in the endeavour to turn CO_2 into fuels. The FT process utilises carbon monoxide (CO) and hydrogen (H_2) or synthesis gas (syngas) and produces hydrocarbons in the presence of iron or cobalt catalyst (Eq. (1)) [10]. A side and competing reaction is the water–gas shift (WGS) reaction where CO_2 is produced instead (Eq. (2)).

$$CO + 2.15H_2 \rightarrow \text{hydrocarbons} + H_2O \quad (1)$$

$$CO + H_2O \leftrightharpoons CO_2 + H_2 \quad (2)$$

Various studies in the electrochemical reduction of CO_2 have reported the formation of CO [11–13]. Studies on high temperature electrochemical reduction of CO_2 produces only CO and H_2 as

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main products, have good current densities and does not require an applied potential [12,13]. The selectivity and production of CO in the aqueous electrochemical reduction of CO_2 at room temperature is dependent on the electrode material [11]. The main drawback of this process is that it requires an additional applied potential and relatively low current density. However, it is possible to obtain other products such as hydrocarbons, formate and alcohols from this process which is not possible in the high temperature electrochemical reduction process [14–18].

It is much more favourable thermodynamically to form stable molecules via proton-coupled multi-electron steps rather than single electron steps. However, the formation kinetics is not favourable as confirmed by other studies where higher applied potentials are required [14–18]. Briefly, Eqs. (3)–(8) are used to estimate the standard reduction potential (with respect to the standard hydrogen electrode (SHE)) from formation energies in aqueous media at pH 7, atmospheric pressure and 25 °C [19].

$$CO_2 + e^- \leftrightharpoons CO_2{}^- \quad (-1.90\,V) \tag{3}$$

$$CO_2 + H_2O + 2e^- \leftrightharpoons CO + 2OH^- \quad (-0.52\,V) \tag{4}$$

$$CO_2 + 6H_2O + 8e^- \leftrightharpoons CH_4 + 8OH^- \quad (-0.25\,V) \tag{5}$$

$$2CO_2 + 8H_2O + 12e^- \leftrightharpoons C_2H_4 + 12OH^- \quad (-0.34\,V) \tag{6}$$

$$2CO_2 + 9H_2O + 12e^- \leftrightharpoons C_2H_5OH + 12OH^- \quad (-0.33\,V) \tag{7}$$

$$3CO_2 + 13H_2O + 18e^- \leftrightharpoons C_3H_7OH + 18OH^- \quad (-0.32\,V) \tag{8}$$

Other than metal electrodes, metal complexes have also been studied for electrochemical reduction of CO_2. The three types of metal complexes for electrochemical reduction are metal complexes with (a) macrocyclic ligands, (b) bipyridine ligands and (c) phosphine complexes [20]. The combination of metal complexes with a gas diffusion electrode was found to have an extremely high current efficiency for the formation of CO [21].

In this article we review the works on the electrochemical reduction of CO_2 using solid oxide fuel cells, metal electrodes in aqueous solution and metal complexes and advances in understanding the mechanisms involved.

2. Solid oxide fuel cells

Solid oxide fuel cells (SOFCs) have been studied extensively for the generation of power. The authors would like the readers to refer to the review by Choudhury et al. for the recent progress made in the study of SOFCs [22]. Briefly, SOFCs have the capability to generate power of up to 300 kW and up to several MW when combined with a steam or gas turbine. Efficiencies that could be achieved ranged from 50% to 80% depending on the design of the process. The types of fuels used are natural gas, methane or pure hydrogen with exhaust products consisting of mainly water, CO, CO_2, H_2 and heat. Methanol can also be used as fuel for SOFCs [23]. It is also possible to reduce CO_2 to CO by reforming with methane (Eq. (9)) over rhodium, iridium or nickel [24]. This reforming process (dry reforming) is not only able to produce syngas with favourable H/CO ratios but may potentially reduce the amount of CO_2 in the environment [23].

$$CO_2 + CH_4 \rightarrow 2CO + 2H_2 \tag{9}$$

Reports of using CO_2 as a fuel in SOFCs have begun to increase in the recent years [12,15,25–32]. Nickel [13,25,27,28], platinum [29–32], copper [12] and palladium [26] had been reported to be the active components. Despite having different active components, the main component of the electrolytes used is essentially the same which is non-porous yttria-stabilized zirconia (YSZ). The YSZ electrolyte functions as an oxygen ion conductor at very high temperatures (800–900 °C) [29]. This oxygen ion transfer phenomenon occurs due to the vacancies present in the crystal lattice of the electrolyte.

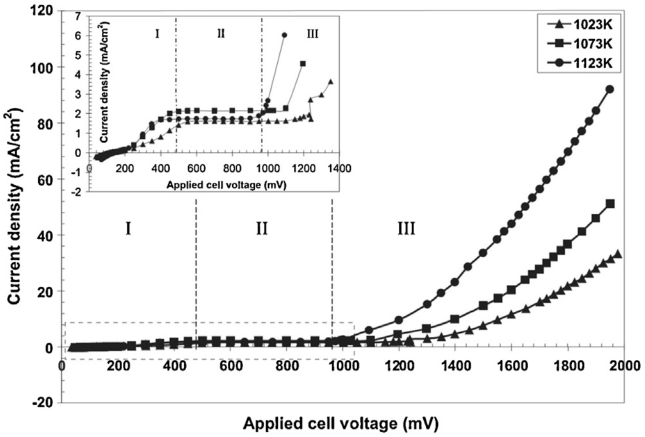

Fig. 1. CO_2 electrolysis current density vs applied cell potential for Pt based SOFC. Roman numerals indicate low (I), constant (II) and high (III) current density regions. Reproduced from Ref. [31] by permission from Elsevier.

2.1. Platinum

Initially, the main goal of using SOFCs to reduce CO_2 was to produce oxygen from the CO_2 rich atmosphere of Mars in future missions; not energy [29,30]. The electrolyte was sandwiched between porous platinum electrodes and a potential of less than −2.0 V was applied to the cell. The current flow of this process was found to be completely due to the flow of oxygen ions and not due to electron transport [29]. Oxygen-containing species (OCS) present during electrolysis increased the resistance of the oxygen ion flow. Two main types of OCS that were identified are weakly adsorbed oxygen ($O\cdots(Pt)_n$) and stable oxides ($O(Pt)_n$) [30]. The OCS partially blocks available sites for oxygen transfer at the electrode/electrolyte interface thus causing an increase in resistance of oxygen ion flow. Further studies were conducted to determine the rate determining steps and to improve the performance and efficiency of the cell [31,32]. The rate determining step in the low and constant current density region was found to be the gas diffusion whereas in the high current density region it was the kinetics of CO_2 electrolysis (Fig. 1) [31]. Significant improvements were made using Pt-YSZ cermet electrodes which reduced the anode overpotentials, ohmic resistance and an increased electrochemical reaction at the interfaces [32].

2.2. Nickel

Due to the rarity and high prices of platinum which may affect commercialization, other researchers have turned their focus to use nickel as the active agent in the reduction of CO_2. Similar to platinum, initial study using nickel was to isolate oxygen therefore a potential is applied to perform the reduction process [25]. Methane formation was reported as the mixture of CO_2 and H_2 was used as fuel instead of pure CO_2 as in studies using platinum. Nickel supported on zeolite together with YSZ and silver electrodes was used. The zeolite present adsorbed CO_2 and facilitated the methanation process over the nickel particles through a one-step reaction (Eq. (10)). It was postulated that (a) oxygen is first converted to water by the Ni/zeolite catalyst and then transferred through the YSZ electrolyte after the water is ionised, (b) CO_2 dissociation on the cathode