

Research on the Selectivity of Electoreduction of Carbon Dioxide

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Abstract. Renewable energy conversion of carbon dioxide is a major path to carbon-based fuels and chemicals that hold the promise of powering a sustainable society. Whereas the majority of carbon dioxide reduction (CO₂RR) reactions are conducted in alkaline electrolyte, operating under these conditions often creates spontaneous generation of carbonates, generating unfavorable energy balance and carbon dioxide utilization. In addition to this, possible solutions arise when the conditions are made acidic which reduces these issues, however, selective CO₂RR at high proton concentration has long been a challenge to study. The paper at hand will address the effect of various catalysts on the selectivity of CO₂RR and also examine the effects of pH, proton depletion and the cation. It will then look in to the future and, speculate on the open questions left in this emerging area and what can be done about what can be done to emerge with the practical feasibility of CO₂RR under acid.

Keywords: The selectivity of CO₂RR, Electrolyte pH, Proton Depletion, Cations

1. Introduction

Because the available energy density of the renewable sources, solar, wind, and hydropower, is low and erratic, conversion of renewable electricity into energy-intensive fuels and chemicals is especially important to sustain modern civilization [1]. In this regard, there have been innumerable researches on the electrocatalytic reduction of CO₂ to carbon-based products (CO, CH₃OH and C₂H₄) which may serve as potential green option to deriving the same chemicals by extracting fossil fuels [2].

The solubility of CO₂ in aqueous electrolytes is however very low and this fact complicates attaining the current density necessary to be economically viable [3]. Even though gas diffusion electrodes are promising, the practicality of these sensors is vastly hampered by the nature of their common operation mode: the carbonate problem [4]. Projected reaction step is the initial reaction step of forming *CO₂⁻ on most heterogeneous catalysts, which is not proton-coupled and thus its overpotential is lower under alkaline electrolyte [5]. But, under alkaline conditions, the reaction of CO₂ with OH⁻ to form carbonate species is also spontaneous.

Carbonate issue can be avoided by a bipolar membrane having acid electrolyte on the anode side. The low concentration levels of OH⁻ species will reduce the production of carbonates in acidic conditions [6]. Although at the cathode the pH will soar because of the protons being consumed by

the reaction, any generated carbonates will be brought back to CO_2 because of diffusion into an acidic medium of the main electrolyte [6]. Nevertheless, in the regions of the high local pH precipitation of carbonates can still be the issue and cannot be overlooked. Thus, in the majority of past research works the research field had a tendency to work in alkaline or neutral electrolytes. Nevertheless a couple of recent studies has been a major source of information, which has helped in enhancing the selectivity of CO_2RR in acid mediums.

2. Categories of CO_2RR

Given that CO_2RR is a multi-electron/proton transfer process, as many as 16 products have been identified in CO_2RR reactions on copper catalysts, consisting of a wide range of alkanes, alkenes, aldehydes, ketones, alcohols and carboxylic acids. Strong to severe interaction between the catalyst and substrate ought not to appear to attain high catalytic activity [7]. Conversely, enhancements to the selectivity of CO_2RR to higher value products is harder due to the scaling of binding energies of the various intermediate products by the pair-wise relatedness of their surface chemical natures [8]. Hydrogenation of CO to CHO free energy change is the greatest of 0.75 eV and can therefore be regarded as the rate-determining step (RDS). The surface can preferentially increase the strength of binding CHO with respect to CO to decrease the change in energy. This ambition is however hard to meet due to scaling relationship [9]. Several proposals have been put forward to disrupt the proportionality, including by manipulating the electronic aspect of the catalyst.

2.1. Single-Atom Catalysts (SACs)

Theoretical computations demonstrate that most metal atoms possess electrocatalytic CO_2RR activity of the products. Nonetheless, the electrocatalytic activity remains to be augmented, e.g., the CO selectivity and the catalytic stability. Metal atoms on the carbon-based materials are primarily linked to the substrate with the assistance of heteroatoms to result in stable SACs [10]. The electrocatalytic CO_2 reduction catalytic activity could be enhanced by switching the nature of central metal atom and its coordination environment.

2.2. Bimetallic and multimetallic catalysts

SACs can be extended to include a bimetallic and multimetallic catalyst which offers expanded adsorption surface area to the reaction intermediates. Compared to SACs, the addition of the second and third metal atoms does not only enhance the control of electronic structure further, but also expand new adsorption active sites, get out of the restriction of linear relationship. DACs can be primarily classified by the type of metal, and all of them can be homobimetallic and heterobimetallic.

2.3. Alloy catalysts

One of the alternative substrates of CO_2RR has become alloys since they have the benefits of having a stable mechanism between the constituent elements, conductivity is improved and they have more active sites.

2.4. Metal-Organic Framework catalysts (MOFs)

The good chemical and thermal stability of porous carbon-based materials predisposes them as good CO₂-capture catalysts or carrier [11]. Metal-organic frameworks (MOFs) are a type of porous carbon-based material with precise crystallinity and porous structure, that are made of numerous organic ligands and whose synthesis occurs through a wide range [12]. MOFs have now made outstanding catalytic scaffolds as a result of their enhanced physicochemical stability, structural variety, highly ordered porous framework, consistent pore size and environment, significant specific surface area, and functional organic bonds [13]. As a result of these distinctive physical and chemical properties, MOF derivatives are more stable, conductive, and exercise increased catalytic activity and can be used extensively in the use of CO₂RR.

2.5. Covalent Organic Frameworks (COFs)

Conjugated organic frameworks (COFs) are a family of periodic network solid materials including molecular building blocks composed of functional organic ligands [14]. COFs as possible alternative materials to electrocatalytic CO₂ reduction primarily possess the increased exposed surface area and active sites, modifiable structures, and the possibility of depositing numerous metals (including cobalt, copper and nickel) in their structures, which endows COFs with their active centres as well as adjustable [15].

3. The influence of Electrolyte pH

The Influence of Electrolyte pH Electrocatalytic reactions may be proton-coupled (transfer of H⁺ and electrons are coupled) or uncoupled. Even though the equilibrium potential of proton approximations thermo-genesis (PCET) reactions do not vary on the RHE scale, the same cannot typically be said of uncoupled reactions [16]. This is believed to be one of the reasons the CO₂/CO₂⁻ is easier to take place at high pH ranges. Thus, the effect causes CO₂RR to be more challenging at low pH [17]. Since the adsorption of CO₂ varies with pH value on the reason of different adsorption coverage on selected catalyst surface, the potential shifts further the zero charge point, so the interfacial electric field can also be higher and, in this way, favors the formation of intermediate products with high dipole moments (like *CO) and of opposite polarity to the electric field [18]. This can alter the preferential adsorption of that CO₂RR intermediate at different locations (terraces, edges, corners, and defects) in turn influencing both the efficiency and selectivity of CO₂RR [19]. Greater electric field density will also influence cation adsorption tendencies on the catalyst surface, along with impeding the use of the catalytic site in the hydrogen-evolving reaction (HER) and raising the reorganization energy state of water in the hydrogen adsorption process [20]. Last, pH of the electrolyte influences the protonation of different buffer compounds, thus, facilitating HER or protonated CO₂RR clusters. As an example, bicarbonate in lower pH favors HER reaction on polycrystalline gold, hence decreasing the system CO₂RR selectivity [21].

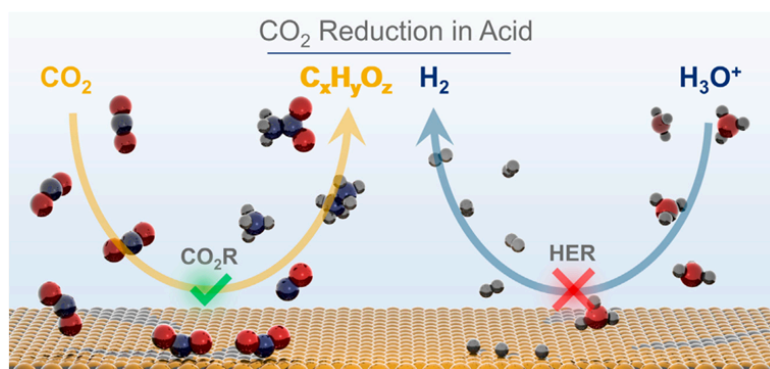


Figure 1. Schematic diagram of CO₂ reduction under acidic conditions [22]

4. Proton depletion and the role of cations

An acidic environment (pH 2.5 in perchloric acid) with polycrystalline copper was used to perform the CO₂RR experiment, and RDE (rotating disk electrode) was used to disentangle the proton (HER), water (HER) and CO₂RR reaction pathways [23]. At lower overpotentials (compared to RHE, -0.2 to -1.2 V) proton reduction was prevalent but at higher (>1.2 V), reduced water started. When CO₂ or CO was added to the electrolyte, the current of water reduction [24] was minimized. This observation, in conjunction with the spectral lines of CO adsorbed on the copper surface, showed that CO inhibited the reaction sites along the pathway of water reduction as a measure of promoting CO₂RR selectivity under these reaction conditions. It was also observed in weakly acidic electrolytes (0.25-1.0 mM HCO₄) that CO₂RR on gold (Au) electrodes would impede the HER [25]. Results indicated that with a high enough partial pressure of CO₂, the gold electrode was able to produce near 100% selectivity to CO due to all of the available protons being consumed in the CO₂-CO reduction. cations are useful catalysts especially in the selective CO₂RR in strongly acidic media. In one study, trifluoromethanesulfonic acid (0.1 mol/L) was used as the source of acid and the addition of potassium trifluoromethanesulfonate, a solvent to add K⁺ to the solution without significantly affecting the other parameters, was explored [26].

In the case of an addition of 0.4 mol/L K⁺ to the electrolyte, tin oxide and gold catalysts delivered Faraday efficiencies of more than 90% to the formation of HCOOH and CO with partial current densities greater than 150 mA/cm₂, and copper catalyst produced a mixture of HCOOH and CO and a combination of secondary C₂ products. The extent of each of the cations to promote selectivity of CO₂RR showed a Cs⁺ > K⁺ > Na⁺ > Li⁺ trend. The density of hydrated cations determines the amount of ions that can be trapped in the double layer and consequently the larger the density of Cs⁺ the greater the electric field created, and this aspect explains the CO₂RR selectivity trend with cation properties.

CO-selective CO₂RR was also applied in an Au catalyst. At pH 2 to 4 in 1 mol/L Cs₂SO₄, the gold catalyst was found to be more selective at higher current densities and was maximized at ca. 100 mA/cm² [27]. However, with the use of Li₂SO₄, HER was the reaction of interest. Cations did not seem to influence HER activity, though cation hydration strength was thought-to be critical to CO₂RR. Weakly hydrated ionized Cs⁺ was postulated to bind more readily to the second intermediate in the reaction mechanism, *CO₂⁻ and strongly hydrated Li⁺ cations were unable to do exactly the same.

Ag and Cu catalysts decomposed water only to form pure H₂ in the absence of metal cations. The selectivity of the Ag catalyst when K⁺ to the electrolyte was added to attain 3 mol/L was 50/50 with

CO and HCOOH, whereas the selectivity of the Cu catalyst led to 27/27 CH₄. Fine tuning of the selectivity of multi-carbon products was done by incorporating a cation supported layer (CAL) on the copper catalyst.

5. Future prospects

5.1. Existing technical bottlenecks and challenges

Even though the CO₂RR technology has advanced extensively, a lot remains to be done in testing the technology to a practical application. On the one hand, the catalysts are rather active, but their preparation prices are normally elevated, and their lifetime is short. Most of high-performance catalysts have a complicated preparation procedure. As an example of a new generation of high-performance single-atom catalysts, MOF-based catalysts exhibit high activity in acidic conditions but rapidly lose activity once subjected to a high level of constant use (20 hours) [28]. Besides, the catalytic activity of copper-based catalysts at high current densities has a tendency to change their structure or oxidation state and, hence, rapidly reduce the level of C₂⁺ selectivity [28, 29]. Second, the system energy efficiency is not high. The energy efficiency of the system in electrolysis is lower than 40% because of various losses, including ohmic resistance and reaction overpotential; the full-cell energy efficiency can not wait 40 years [30]; even the high-performance C₂⁺ synthesis systems (CuZn alloy) only can reach 31 +/- 2%. In addition, high selectivity in the acidic systems may necessitate a significant overpotential (like Zr-MOF-In), driving up energy consumption [31]. Third, there is a problem with product separation and carbon efficiency. Calcium-aboration: In alkaline electrolyte systems, as much as 70 percent of carbon may also be lost to the reaction CO₂ + OH⁻ - H CO₃⁻. Though it is possible to avoid this process in acidic systems, a high K⁺ concentration (> 3M in the electrolyte) required to promote selectivity is costly and the separation of products is not easy [32, 33]. Also, in flow electrolyzers, the rate of conversion of CO₂ when using single pass is below 30%, and there is an added complication of recycling and compressing gasses that remain unreacted and leads to more operational expenses [30].

5.2. Future development directions

In order to eliminate these challenges, there is a requirement to conduct future work in various directions.

5.2.1. Catalyst design

Referring to the lumbers between the OINs and Vietnamese, these lumbers are generally quite similar to those between the IHOs and Vietnamese, with the main difference being that short echelons seem to directly affect the OINs and Vietnamese in a much more significant way, when compared to the IHOs and Vietnamese. Catalyst design On the basis of machine learning and high-throughput computation, develop quantitative structure-activity relationships between catalyst descriptors (d-band center, adsorption energy) and selectivity; when screening a large number of molecular modifiers, researchers at the Xiamen University group found that octanedithiol can increase the selectivity of ethanol remarkably, and this is a promising strategy [28]; the strategy should be further applied to multi-component alloys, defect engineering, and other systems to help the design of high-stability catalysts.

5.2.2. Electrolyzer and membrane technology innovation

The separation of the air may be characterized by two factors, namely the cooling and the cooling. Innovation in electrolyzer and membrane technology Form pure formic acid solutions by developing solid-state electrolytes and bipolar membranes, which can prevent carbonate formation and product contamination; preparation of pure formic acid solution using Zr-MOF-In solid-state electrolyte samples shows that it is quite possible [31]; to achieve current densities of the degree of industrialization ($>1 \text{ A cm}^{-2}$), the mass transfer channel should be optimized through the biomimetic design of three-phase boundaries (e.g., gas diffusion electrodes). Interdisciplinary integration: Integrate electrochemical engineering and artificial intelligence to learn intelligent control of reactors; apply in situ / operando characterization methods (synchrotron XAS, operando FTIR) to remain knowledgeable of the genesis of active sites during real working conditions, and to direct the development of durable catalysts; develop multi-scale simulation modes at the atom scale to the system scale to design and optimize the atom distribution and performance of catalysts, and devise methods to optimize the process and overall management of energy conversion processes with minimum energy use as the objective of CO.

6. Conclusion

In order to achieve carbon neutrality, the development of CO₂RR necessitates cooperative innovation on many levels, e.g., the design of catalysts that are efficient at an industrial scale, knowledge of CO₂ conversion mechanisms, system Integration. It should be improved to high-activity and high-selectivity single-atom catalysts instead of low-efficiency copper-based catalysts; the control of microenvironment on a local side to the overall optimization of electrodes the carbon conversion of the overall reaction process can be gradually improved, but until large-scale application, the problems of the catalyst life, system energy consumption and separation of the products remain to be solved. In the future, we are to optimize the catalyst structure and system energy management specifically to the atomic level and system level by means of methods like artificial intelligence.

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