Review Article

CO₂ Electroreduction in Organic Aprotic Solvents: A Mini Review

Orest Kuntyi, Galyna Zozulya, and Mariana Shepida

Department of Chemistry and Technology of Inorganic Substances, Lviv Polytechnic National University, Bandery Str. 12, Lviv 79013, Ukraine

Correspondence should be addressed to Mariana Shepida; maryana_shepida@ukr.net

Received 11 April 2022; Accepted 2 July 2022; Published 31 July 2022

Copyright © 2022 Orest Kuntyi et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

An annual increase of CO₂ concentrations in the atmosphere causes global environmental problems, addressed by systematic research to develop effective technologies for capturing and utilizing carbon dioxide. Electrochemical catalytic reduction is one of the effective directions of CO₂ conversion into valuable chemicals and fuels. The electrochemical conversion of CO₂ at catalytically active electrodes in aqueous solutions is the most studied. However, the problems of low selectivity for target products and hydrogen evolution are unresolved. Literature sources on CO₂ reduction at catalytically active cathodes in nonaqueous mediums, particularly in organic aprotic solvents, are analyzed in this article. Two directions of cathodic reduction of CO₂ are considered—nonaqueous organic aprotic solvents and organic aprotic solvents containing water. The current interpretation of the cathodic conversion mechanism of carbon (IV) oxide into CO and organic products and the main factors influencing the rate of CO₂ reduction, Faradaic efficiency of conversion products, and the ratio of direct cathodic reduction of CO₂ are given. The influence of the nature of organic aprotic solvent is analyzed, including the topography of the catalytically active cathode, values of cathode potential, and temperature. Emphasis is placed on the role of water impurities in reducing CO₂ electroreduction overpotentials and the formation of new CO₂ conversion products, including formate and H₂.

1. Introduction

Since 1958, when systematic direct measurements of CO₂ in the atmosphere began, there has been a steady annual increase in its concentration. In 1958, its content was ~315 ppm and in 2021, ~415 ppm [1]. The tendency to further increase CO₂ concentration in the atmosphere causes such negative planetary consequences as the greenhouse effect and increasing acidity of ocean and sea waters. To alleviate such global problems, research has been intensively conducted in the last decade to develop effective technologies for capturing and disposing of atmospheric CO₂. The most efficient direction is converting this gas into valuable chemicals and fuels. The best known and most studied are the following four methods (Figure 1): thermocatalytic [2, 3], photocatalytic [4–6], enzymatic [7, 8], and electrochemical catalytic reduction [9–14].

Electrochemical reduction of CO₂ is marked by vast possibilities in terms of the range of conversion products, including CO, CH₄, C₂H₄, CH₃OH, CH₃COOH, HCOOH, and (COOH)₂. This fact and the increased use of renewable energy sources give grounds to consider the up-and-coming electrochemical methods, particularly in “green” technologies of valuable substances (Figure 2).

Electrochemical conversion of CO₂ at catalytically active electrodes in aqueous solutions has been studied the most [9–14]. Moreover, the transformation mechanism has been studied in detail at copper and copper-containing cathodes [11–14, 16, 17]. Despite the efficiency of such and other metal-containing electrodes, unresolved problems are low selectivity for target products and hydrogen evolution in aqueous solutions. The first is due to the simultaneous course of many electrochemical and chemical reactions due to the relative values of the standard potentials for the formation of essential compounds by the reduction of CO₂ in acidic (1)–(5) and neutral (6)–(10) solutions [18]. In the range \(E = 0\)–\(-1\) V, there is also a parallel cathode reaction of hydrogen evolution (11) and (12).
Electrochemical CO\textsubscript{2} conversion at catalytically active cathodes is investigated in aqueous and nonaqueous solutions. They significantly differ in the limiting electrode potentials and the values of the cathode current densities, the course of electrochemical processes and reduction products, and the selectivity of the latter (Figure 3). Nonaqueous include ionic liquids, methanol solutions, organic aprotic solvents, and salt melts.

Electrochemical reduction of CO\textsubscript{2} in nonaqueous media or solutions with low water content makes it possible to eliminate or reduce these negative factors of aqueous solutions. In addition, CO\textsubscript{2} has a high solubility in organic solutions. Among them, the most studied are ionic liquids [19–26], methanol solutions [27–29], and organic aprotic solvents [30–40]. In recent years, there has also been engagement in the CO\textsubscript{2} electrochemical reduction process in molten salts [41–46]. The following valuable nanomaterials can be obtained in such an environment: carbon nanofibers [43], carbon nanotubes (CNTs), carbon spheres (CPS), and honeycomb carbon [44]. In addition, the simplicity of the design of the diaphragm-free electrolyzer (Figure 4), high conversion speed (\(i_{\text{cathode}} = 100 \text{ mA cm}^{-2}\)), and high Faradaic efficiency (80–90\%) of products [42] make this method promising. However, high-cost ionic liquids and decomposition at a very negative potential of CO\textsubscript{2} [37] limit their practical application. Although CO\textsubscript{2} conversion in salt melts is unique in carbon nanomaterials synthesis, high temperature (\(\geq 500^\circ C\)) is an energy-holding factor.

The relatively low cost of organic aprotic solvents, wide “electrochemical windows,” and high solubility make them a promising medium in the electrochemical conversion of CO\textsubscript{2}.

2. Features of Electrochemical Recovery of CO\textsubscript{2} in Organic Aprotic Solvents

Specifics of CO\textsubscript{2} conversion at catalytically active electrodes in organic aprotic solvents are primarily due to (1) deficiency or absence of protons in nonaqueous solution and (2) high solubility of carbon (IV) oxide. These factors cause new electrochemical and chemical processes, changes in the spectrum of CO\textsubscript{2} conversion products, and even the formation of new compounds and significant acceleration of cathode processes.

2.1. Cathodic Reduction of CO\textsubscript{2} in Nonaqueous Organic Aprotic Solvents. In aqueous solutions at \(E_{\text{cathode}} = -1.1 \ldots -1.3\) V, intensive hydrogen evolution begins in reaction (12), which limits the values of cathode potentials during
Figure 3: Main electrochemical directions of CO₂ conversion in nonaqueous medium.

Figure 4: Schematic diagram of borate-assisted CO₂ electrochemical reduction process in a U-shaped reactor from [42] under the terms of the Creative Commons CC BY license.

Electrochemical reduction of CO₂. In the absence of water and due to the high electrochemical stability of molecules of organic aprotic solvents, electrolysis can be carried out at \( E_{\text{cathode}} = -2.5 \ldots -3.0 \text{ V} \). However, there are reactions to form only two products of CO₂ conversion—oxalate anion and CO [27, 47]. Oxalate anion is formed by reaction (13) due to the formation of solvated radicals \( \cdot \text{CO}_2^{(-)} \) [48], followed by their connection with each other (14). Reaction (15) may occur in parallel with the formation of CO.

\[
\text{CO}_2 + e^- \rightarrow \cdot \text{CO}_2^{(-)} \quad (13)
\]

\[
\cdot \text{CO}_2^{(-)} + \cdot \text{CO}_2^{(-)} \rightarrow (\text{COO})_2^{2-} \quad (14)
\]

\[
2\text{CO}_2 + 2e^- \rightarrow \text{CO} + \text{CO}_3^{2-} \quad (15)
\]

The proportion of reactions (13)–(15), their rate, i.e., the value of \( i_{\text{cathode}} \), Faradaic efficiency of conversion products, and, accordingly, the ratio of products of direct cathodic reduction of CO₂, i.e., oxalate and CO, depend on many factors. Among them, the main ones are as follows: the nature of the organic aprotic solvent; nature and topography of the catalytically active cathode; the value of the cathode potential; temperature.

2.1.1. Influence of the Nature of the Organic Aprotic Solvent. AN, DMF, DMSO, and PC (Table 1) media are most often used for cathodic CO₂ reduction, which, in addition to high electrochemical resistance, are characterized by high values of Donor Number and CO₂ solubility [27]. DN (kJ·mol⁻¹): AN—59.0; DMF—111.4; DMSO—124.8; PC—63.2. CO₂ Solubility (mmol·L⁻¹) is an order of magnitude greater than the value of this value in water: AN—314 ± 6; DMF—194 ± 14; DMSO—131 ± 7; PC—134 ± 9; H₂O—34.5 ± 4.46.

Molecules of the aprotic solvent, due to the indivisible electron pair, act as a Lewis base, causing the donor-acceptor interaction with the carbon atom of the low-polar molecule CO₂ L: → CO₂ and the cathode surface L: → cathode surface.

(1) Influence of Donor Number. The donor-acceptor interaction L: → CO₂ causes inhibition of electron transfer, which affects the ratio of oxalate and CO as products of cathodic reduction of CO₂; namely, with a decreasing electron-donor capability, increased oxalate formation is observed [27]. Therefore, AN, which has the lowest DN value, is often used as a medium for oxalate obtaining with a high value of Faradaic efficiency—\( \sim80\% \) [33], \( \sim62\% \) [51], \( \sim74\% \) [52], and \( \sim97\% \) [53]. However, this dependence [oxalate]: [CO] on DN of aprotic solvent should be considered as a trend because the course of electrochemical reactions (13) and (15) and, accordingly, the value of FE are influenced by the values of cathode potential, cathode nature, and temperature. The electron-donor capability of the aprotic solvent also determines the adsorption of organic molecules on the cathode surface [55–57]. Reactions (13) and (15) take place on the latter, the course of which depends on the adsorption-desorption of CO₂ and CO molecules, CO₂ radicals, and CO₃²⁻ anions. Therefore, due to the predominant content of molecules of an aprotic solvent, the value of their DN should affect the ratio [oxalate]: [CO].

(2) Influence of CO₂ Solubility. Solubility of CO₂ is one of the factors of mass transport, concentration cathodic polarization, and, accordingly, the reaction rates (13) and (15). It is the highest CO₂ solubility in AN that mainly determines the highest values of cathode currents among organic aprotic solvents, for example, at Ga cathode, \( E = -3.0 \text{ V} \) in AN \( i_{\text{cathode}} = 2.3 \text{ mA·cm}^{-2} \) (CO₂ solubility \( \sim314 \text{ mmol·L}^{-1} \)), in DMF—0.7 (\( \sim111.4 \)), and DMSO—1.4 (\( \sim194 \)) [50]. A similar pattern is observed at other catalytically active cathodes. Thus, \( E = -3.0 \text{ V} \) on a boron-doped diamond working electrode in AN, DMF, and PC \( i_{\text{cathode}} = 5.5, \sim2.3, \text{ and } \sim1.2 \text{ mA·cm}^{-2} \), respectively [58]; on Au cathode—\( \sim24, \sim15, \text{ and } \sim7 \) [59].

2.1.2. Nature and Topography of Catalytically Active Cathode. Electrochemical reduction of CO₂ involves the adsorption of carbon (IV) oxide, solvent molecules, ions, intermediates, and end products on the cathode surface. The nature of the latter significantly affects the equilibrium processes of adsorption—desorption due to inappropriate adsorption energies of key reaction intermediates [60]. The result is the dependence of the rate of certain electrochemical reactions and, accordingly, the product selectivities and Faradaic efficiencies of the CO₂ conversion process on the
Table 1: Examples of nonaqueous aprotic solvents used in CO₂ electrochemical reduction by catalytic active cathodes.

| Electrode | Electrolyte | E, V | $i_{\text{cathode}}$ mA cm$^{-2}$ | CO₂ conversion products | Faradaic efficiency, % | References |
|-----------|-------------|------|-----------------|--------------------------|------------------------|------------|
| Cu on basal Pt(hkl) single crystal faces | TBAPF₆ in AN or PC | −1.8 | 0.88 0.88 in AN 0.28 in PC | CO | – | [31] |
| Au foil | TBAP in PC | −2.8 | 16.0 | CO | 84.9 | [32] |
| Cathode: lead gas diffusion electrode | TEAB in AN | −2.5 | 80.0 | Zinc oxalate | 80.0 | [33] |
| Anode: sacrificial zinc | TBAP in AN | −2.2 ... −4.0 | 20.0 ... 80.0 | | | |
| Cathode: Au foil | Catholyte: 0.1 M TBAP in PC Anolyte: 0.1 M H₂SO₄ | −3.0 | 2.8 | CO | 91.8 | [49] |
| Anode: graphite rod Electrolysis cell with proton exchange membrane | | | | | | |
| Bulk gallium | TBACL, TBABr, TBAI and TBAP in DMSO, DMF, NMP, PC and AN | −2.2 | 0.7 in NMP 0.7 in DMF 1.4 in DMSO 1.8 in PC 2.3 in AN 2.7 ... 19.6 | CO | 26.0 in NMP 21.0 in DMF 14.0 in DMSO 32.0 in PC 83.0 in AN | | [50] |
| Cathode: stainless steel | TBAP in AN | −2.5 | 2.0 ... 15.0 | Zinc oxalate | 62.4 | [51] |
| Anode: sacrificial zinc | TBAP in AN | −3.5 | 4.0 ... 12.0 | Zinc oxalate | 73.9 | [52] |
| Cathode: lead | TBAP in AN | −2.2 | 4.0 ... 12.0 | Zinc oxalate | 96.8 | [53] |
| Anode: sacrificial zinc | TBAPF₆ in AN | −2.4 | 25.0 | CO oxalic acid | 30.0 | [54] |
| | | | | | | |
catalytic activity of the cathode surface. Therefore, systematic studies of cathode production → surface structure → catalytic activity → product selectivities and Faradaic efficiencies are a priority in the direction of electrochemical conversion of carbon (IV) oxide.

The influence of the nature of the cathode surface, namely, its electrocatalytic action on the rate of carbon dioxide reduction, selectivity of product selectivities, and Faradaic efficiencies, is most studied for aqueous solutions [9, 11, 14, 16, 27, 61], which allowed to form scientific principles of CO₂ conversion. The peculiarity of the environment of anhydrous organic aprotic solvents determines the course of fundamentally different electrode processes and, accordingly, reduction products. Thus, electron-donor molecules of organic solvent (L) are adsorbed on the electrode surface in parallel with CO₂ molecules (Figure 5). However, due to the high electrochemical stability of organic molecules, their destruction does not occur even at \( E = -3.0 \) V, while in aqueous solutions, there are reactions (11) and (12). This significantly affects product selectivities and Faradaic efficiencies. Adsorption of \( R_4N^+ \) cations is also possible on the cathode surface, as conductive additives, such as \( R_4NCIO_4, R_4NPF_6 \), and \( R_4NCI \) (Table 1), are present in aprotic solvents, which are also characterized by high electrochemical resistance [58]. Thus, the adsorption of organic solvent molecules and tetraalkylammonium cations causes only cathodic polarization. Accordingly, the nature of the cathode surface affects the adsorption energies \( L, R_4N^+ \), and CO₂ (Figure 5), as well as intermediate (CO₂) and final (CO) products.

Depending on the nature of the cathode surface in organic aprotic solvents, the reduction of CO₂ with the formation of oxalate or CO is possible. Thus, according to scheme (Figure 5(a)) on copper [31], gold [32, 49], and gallium electrodes [50], CO is formed, according to scheme (Figure 5(b)) on stainless steel [51, 52] and lead [33, 53] electrodes—oxalate with high values of Faradaic efficiency (Table 1). On the electrode based on MoO₂ [31], the parallel reduction is possible according to schemes (a) and (b) with the formation of two products. However, the amount of literature is still little to discuss the system dependencies of CO₂ conversion products on the nature of the cathode surface.

The use of a lead gas diffusion electrode [33] makes it possible to achieve values of cathode current densities much higher than on those using a lead plate [53] due to the large specific surface area. However, the product of CO₂ conversion is not affected by the topography of the cathode. Even higher efficiency is observed using Cu nanoparticles embedded in N-doped carbon (Cu@NC) arrays (Figure 6).

In nonaqueous media, the effect of nanostructured cathodes on the rate of CO₂ reduction and selectivity of the obtained products is little studied. However, positive results of the use of nanometals in aqueous solutions [63, 64] can also be expected in the environment of organic aprotic solvents. The highest efficiency is manifested in the size of metal nanoparticles of several nanometers and especially nanoclusters [65, 66], the synthesis of which is characterized by simplicity in the technological aspect [67].

2.1.3. Cathodic Potential Values and Temperature. The formation of the \( \cdot CO_2^{(-)} \) radical by the cathodic reaction (13) takes place in the environment of organic aprotic solvents at low values of electrode potentials. Thus, in DMF, \( E^{0}_{CO_2/-} \)
\[ \text{CO}_2 = -2.21 \text{ V} \] according to [68] and \[-1.97 \text{ V} \] according to [58]. Since, in such a nonaqueous medium, \(-CO_2\) is the starting electrochemical stage of \( \text{CO}_2 \) reduction (Figure 5), the quantitative formation of conversion products begins at approximately \(-2.0 \text{ V} \) \([32, 33, 58–60, 69]\) on electrodes of different nature. A typical \(E_{\text{cathode}}\) dependence is shown in Figure 6. The value of \(E_{\text{cathode}}\) is limited by the electrochemical stability of organic aprotic solvents, and in AN, DMF, and PC solutions, it takes values not lower than \(-3.5 \text{ to } -4.0 \text{ V} \).

The environment of some organic aprotic solvents makes it possible to carry out the electrochemical reduction of \( \text{CO}_2 \) in a wide temperature range due to the low values of their melting point and high boiling point. Thus, for AN, DMF, and PC, these values are \(-46 \text{ and } 82^\circ \text{C} \), \(-61 \text{ and } 155^\circ \text{C} \), and \(-49 \text{ and } 242^\circ \text{C} \), respectively. The authors [48] showed that on the inert (Mercury) cathode in the DMF medium, there is an increase in CO yield and, accordingly, a decrease in oxalate yield with decreasing temperature. Thus, at a \( \text{CO}_2 \) concentration of \(152 \text{ mmol} \cdot \text{dm}^{-3} \), the distribution of products is as follows: oxalate, 67%; \( \text{CO} \), 25% and oxalate, 11%; \( \text{CO} \), 89% at temperatures of 25 and \(-20^\circ \text{C} \), respectively.

**Table 2: Examples of \( \text{CO}_2 \) electrochemical reduction by catalytic active cathodes in aprotic solvents with the addition of water.**

| Electrode | Electrolyte | \(E, \text{V}\) | \(i_{\text{cathode}}\) \(\text{mA-cm}^{-2}\) | \(\text{CO}_2\) conversion products (Faradaic efficiency, %) | References |
|-----------|-------------|----------------|----------------------------------|-------------------------------------------------|------------|
| Cathode: (Cu, Pt, Au, and Pb discs) | “Wet” AN solutions of: 0.1 M TEABF₄ (46 ppm H₂O) 0.1 M TEATfO (184 ppm H₂O) 0.1 M NaTfO (528 ppm H₂O) | \(-2.4\) | 0.5 | CO | [34] |
| Anode: Pt coil | | | | | |
| Cathode: WO₃ nanoparticulate thin films on FTO glass | 0.1 M TBAP in dry AN with <10 ppm H₂O in humid AN | \(-1.2\) (CV) | 0.3 (CV) | CO (42%) | [35] |
| Anode: Pt wire | | | | | |
| Electrolysis cell with proton exchange membrane | | | | | |
| Cathode: Nanoporous TiO₂ | 0.1 M TBAP in dry AN AN + 0.5 M H₂O | \(-1.8\) | 0.8 (CV) | CO (48%), oxalate (12%) CH₃OH (60%), CO (17%) | [36] |
| Anode: Pt wire | | | | | |
| Electrolysis cell with proton exchange membrane | | | | | |
| Cathode: Ag₉[PMo₁₂O₄₀]⁹⁻ on GC | 0.1 M TBAP in DMF + 0.5 vol% H₂O | \(-2.5\) (CV) | 20.0 (CV) | CO (90%) | [37] |
| Anode: Pt wire | | | | | |
| Cathode: Zn foil | Catholyte: 0.1 M TBAP in PC + 6.8 vol% H₂O Anolyte: 0.1 M H₂SO₄ | \(-2.3\) | 6.72 | CO (83%), H₂ (15%) | [38] |
| Anode: a graphite rod | | | | | |
| Electrolysis cell with proton exchange membrane | | | | | |
| Cathode: MoO₂ microparticles on Pb supporting substrate | TBAPF₆ in AN + 0.1 1.4 M H₂O | \(-2.32\) | 2.10 | CO formate | [54] |
| Anode: Pt wire | | | | | |
| Electrolysis cell with proton exchange membrane | | | | | |
| Cathode: Ag₂S, deposited on Ag electrode (two-compartment electrolysis cell) | TBAP in PC + ≤ 6.8 wt% H₂O | \(-2.35\) | 9.85 | CO (92%) | [71] |
| Pt plate | 0.1 M TEAP in AN + 4 mM H₂O | \(-3.2\) (CV) | 5 (const) | Oxalate (71%), formate (11%), CO (8%), H₂ (2%) | [72] |
| Au microelectrode | TBAPF₆ in AN + 0.003 1.0 M H₂O | \(-1.8\) | 0.5 | CO | [73] |

---

**Figure 7:** Influence of water concentration on polarization curves MoO₃/Pb in CO₂-saturated MeCN at \(-20^\circ \text{C} \). Electrolyte: 0.1 M TBAPF₆; scan rate: 50 mV·s⁻¹ from [54] under the terms of the Creative Commons CC BY license.
2.2. Cathodic Reduction of CO₂ in Organic Aprotic Solvents Containing Water. CO₂ electroreduction occurs at high cathode overpotentials in anhydrous organic aprotic solvents in the absence of any proton source, as indicated in Section 2.1.3. High energy consumption does not contribute to technological attractiveness. The addition of water significantly reduces the overpotentials of CO₂ electroreduction but creates conditions for forming new products of CO₂ conversion, including formate and H₂ (Table 2). This is due to the possibility of reactions (2), (11), (12), (16)–(18).

\[
\text{CO}_2^{(-)} + \text{H}_2\text{O} + e \rightarrow \text{HCOO}^- + \text{OH}^- \quad (16)
\]

\[
\text{CO}_2^{(-)}(\text{ads}) + \text{H}_2\text{O} \rightarrow \text{HCO}_2(\text{ads}) + \text{OH}^- \quad (17)
\]

\[
\text{HCO}_2(\text{ads}) + e \rightarrow \text{CO} + \text{OH}^- \quad (18)
\]

With the water increase in the solution composition, cathode currents increase significantly [34, 36, 38, 59, 60, 73]. Thus, for \(E = -2.5\, \text{V}\) in anhydrous acetonitrile solution, \(i_{\text{cathode}} = 0.4\, \text{mA} \cdot \text{cm}^{-2}\), while for the water content of 0.01, 0.25, and 2 mol L\(^{-1}\), it is 0.75, 0.95, and 1.3 mol L\(^{-1}\), respectively [34]. This is also identical to the decrease in cathode potentials by \(i_{\text{cathode}} = \text{const}\) (Figure 7). Low water concentration in the solution composition practically does not reduce the high solubility of CO₂ provided by organic aprotic solvents. The low content of H₂O also does not significantly affect the course of parallel cathodic reactions (11) and (12) with the electrochemical release of H₂. This is due to these organic solvents high electron-donor properties, which promote the formation of stable associates (L⋯H–O–H) or (L⋯–H), weakening the electrochemical activity of water molecules. The water in the solution composition will be limited to 6.8 vol% because, at higher concentrations, the electroconductive organic component of the nonaqueous solution begins to precipitate [59]. In addition, high water concentrations increase the proportion of reactions (11) and (12).

The water content in the aprotic solvent as a source of protons is an important factor influencing the course of reactions (11, 12, 16, 17) and, accordingly, the distribution of the products of cathodic reduction of CO₂ (Figure 8(a)). Moreover, it is natural to increase the share of H₂ with increasing concentrations of H₂O in the solution. Therefore, it is limited to 1-2%. An important factor influencing the distribution of CO₂ conversion products is the value of the cathode potential (Figure 8(b)).

For the controlled synthesis of H₂, it is necessary to ensure a relatively stable concentration of the proton-containing component during long-term electrolysis. One way to solve this problem is to use an electrolyzer separated into two compartments (Figure 9). Proton exchange membranes are preferably used as separators [38, 49, 59, 70, 71]. The cathode part of the cell is filled with the working electrolyte,
the anode—with an aqueous solution of H$_2$SO$_4$. Due to the anodic reaction (19), H$^+$ protons are generated, which penetrate the catholyte through the membrane and participate in the cathodic reactions of formation of CO$_2$ conversion products. Such electrolyzers make it possible to ensure catholyte circulation and implement a continuous process. The authors [49, 59] proposed a basic technological scheme, showing the practical possibility of industrial synthesis of valuable products by CO$_2$ conversion shortly.

$$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^- \quad (19)$$

The mechanism of the effect of water in aprotic solvent—H$_2$O solutions on CO$_2$ reduction products is limited to cathodic reactions involving proton-donor components, in particular (16)–(18). However, as shown in [37], the water factor also depends on the nature of the catalytically active cathode. For $E = -3.0$ V in 0.1 M TBAP nonaqueous PC solution using Ag, Zn, and Au cathode $i_{\text{cathode}} = \sim 4$, $\sim 8$, and
The capture and conversion of CO₂ are one of the areas aiming to solve a complex environmental problem. The most studied methods of converting this gas into valuable chemicals and fuels are thermocatalytic, enzymatic, photocatalytic, and electrochemical catalytic reduction. The latter best meets the criteria of “green” technologies and cost-effectiveness and is characterized by various conversion products: CO, CH₄, C₂H₄, CH₃OH, CH₃COOH, HCOOH, (COOH)₂, etc. One of the ways to solve the problems caused by aqueous solutions is the electrochemical conversion of CO₂ in a nonaqueous medium, mainly organic aprotic solvents. High electrochemical stability of the latter and high solubility of carbon (IV) oxide allows conducting electrochemical processes at cathode potentials −2.5…−3.5 V, providing a high conversion rate and selectivity. Two directions of cathodic reduction of CO₂ are studied—nonaqueous organic aprotic solvents and organic aprotic solvents containing water.

The mechanism of CO₂ reduction in nonaqueous aprotic solvents involves the formation of only two products—CO and oxalate. The values of the cathode current density, Faradaic efficiency of conversion products, and, accordingly, the ratio of direct CO₂ reduction products depend on the following main factors: the nature of the organic aprotic solvent; nature and topography of the catalytically active cathode; values of cathode potential and temperature. The most effective among aprotic solvents is acetonitrile, which has the highest solubility of CO₂ and provides the highest rate of oxalate and CO with Faradaic efficiency up to 90%. The nature of the cathode significantly affects the mechanism of CO₂ reduction, which causes the formation of oxalate or CO: it produces mainly CO on copper, gold, and gallium electrodes; it produces oxalate with high Faradaic efficiency on stainless steel and lead electrodes. A highly developed and nanostructured cathode surface contributes to higher values of cathode current density but has virtually no effect on product selectivity. As the values of the cathode potentials increase, starting from −1.8…−2.0 V, the cathode currents increase, which makes this parameter one of the main ones to ensure a high rate of CO₂ conversion.

In the environment of organic aprotic solvents with low water content, the cathode overpotentials of CO₂ electroreduction are significantly reduced, which makes it possible to carry out the process at high cathode currents. At the same time, the presence of water causes the formation of additional products—formate and H₂. The water content in the aprotic solvent is a factor influencing the course of cathodic reactions and, accordingly, the distribution of CO₂ reduction products. To date, the interdependence between the nature of the organic solvent, water content, the nature of the cathode, and the value of the cathode potential is little studied, which constrains the practical application of CO₂ electroreduction in aprotic solvent-H₂O.

3. Conclusions

The capture and conversion of CO₂ are one of the areas aiming to solve a complex environmental problem. The most studied methods of converting this gas into valuable chemicals and fuels are thermocatalytic, enzymatic, photocatalytic, and electrochemical catalytic reduction. The latter best meets the criteria of “green” technologies and cost-effectiveness and is characterized by various conversion products: CO, CH₄, C₂H₄, CH₃OH, CH₃COOH, HCOOH, (COOH)₂, etc. However, several unresolved problems of electrochemical reduction of CO₂ in aqueous solutions, primarily low speed, low selectivity for target products, and Faradaic efficiency, constrain its widespread industrial application.

One of the ways to solve the problems caused by aqueous solutions is the electrochemical conversion of CO₂ in a nonaqueous medium, mainly organic aprotic solvents. High electrochemical stability of the latter and high solubility of carbon (IV) oxide allows conducting electrochemical processes at cathode potentials −2.5…−3.5 V, providing a high conversion rate and selectivity. Two directions of cathodic reduction of CO₂ are studied—nonaqueous organic aprotic solvents and organic aprotic solvents containing water.

The mechanism of CO₂ reduction in nonaqueous aprotic solvents involves the formation of only two products—CO and oxalate. The values of the cathode current density, Faradaic efficiency of conversion products, and, accordingly, the ratio of direct CO₂ reduction products depend on the following main factors: the nature of the organic aprotic solvent; nature and topography of the catalytically active cathode; values of cathode potential and temperature. The most effective among aprotic solvents is acetonitrile, which has the highest solubility of CO₂ and provides the highest rate of oxalate and CO with Faradaic efficiency up to 90%. The nature of the cathode significantly affects the mechanism of CO₂ reduction, which causes the formation of oxalate or CO: it produces mainly CO on copper, gold, and gallium electrodes; it produces oxalate with high Faradaic efficiency on stainless steel and lead electrodes. A highly developed and nanostructured cathode surface contributes to higher values of cathode current density but has virtually no effect on product selectivity. As the values of the cathode potentials increase, starting from −1.8…−2.0 V, the cathode currents increase, which makes this parameter one of the main ones to ensure a high rate of CO₂ conversion.

In the environment of organic aprotic solvents with low water content, the cathode overpotentials of CO₂ electroreduction are significantly reduced, which makes it possible to carry out the process at high cathode currents. At the same time, the presence of water causes the formation of additional products—formate and H₂. The water content in the aprotic solvent is a factor influencing the course of cathodic reactions and, accordingly, the distribution of CO₂ reduction products. To date, the interdependence between the nature of the organic solvent, water content, the nature of the cathode, and the value of the cathode potential is little studied, which constrains the practical application of CO₂ electroreduction in aprotic solvent-H₂O.

### Abbreviations

| Abbreviation | Description |
|--------------|-------------|
| AN           | Acetonitrile |
| DMF          | N, N-Dimethylformamide |
| DMSO         | Dimethylsulfoxide |
| PC           | Propilencarbonate |
| NMP          | N-Methyl-2-pyrroldione |
| IL           | Ionic liquid |
| L            | Electron-donor molecules of organic aprotic solvent |
| FE           | Faradaic efficiency |
| E₀           | Standard electrode potential |
| E            | Electrode potential |
| Ecathode     | Cathode electrode potential |
| icathode     | Cathode current density |
| MNCs         | Metal nanoclusters |
| MNP         | Metal nanoparticles |
| NWS          | Nanowires |
| DN           | Donor number |
| FTO          | Fluorine doped tin oxide |
| TBAP         | Tetraethylammonium perchlorate |
| TEAB         | Tetraethylammonium tetrafluoroborate |
| TBACL        | Tetraethylammonium chloride |
| TBABr        | Tetraethylammonium bromide |
| TBAI         | Tetraethylammonium iodide |
| TBAPF₆       | Tetraethylammonium hexafluorophosphate |
| TEABF₄       | Tetraethylammonium tetrafluoroborate |
| TEATO        | Tetraethylammonium trifluoromethanesulfonate |

### Data Availability

All related data used to support the findings of the study are mentioned within the article with references.
Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this article.

Acknowledgments

This work was carried out with the partial financial support of the National Research Foundation of Ukraine; Project registration no.: 2020.02/0309 ("Design of polyfunctional nanomaterials: preparation, characterization, and preliminary results"). The project was started in 2020 and is expected to be completed in 2022.

The authors declare that there are no conflicts of interest regarding the publication of this article.

References

[1] Recent Monthly CO2 Average Mauna Loa Earth System Research Laboratory, 2018, https://www.esrl.noaa.gov/gmd/ccgg/trends.

[2] A. I. Tsiotias, N. D. Charisiou, I. V. Yentekakis, and M. A. Goulia, “The role of alkali and alkaline earth metals in the CO2 methanation reaction and the combined capture and methanation of CO2,” Energy and Fuels, vol. 30, no. 11, pp. 8815–8831, 2016.

[3] O. V. Ischenko, A. G. Dyachenko, I. Saldan et al., “Methanation of CO2 on bulk Co-Fe catalysts,” International Journal of Hydrogen Energy, vol. 46, no. 76, pp. 37860–37871, 2021.

[4] A. Francis, S. S. Priya, S. H. Kumar, K. Sudhakar, and M. Tahir, “A review on recent developments in solar-photoreactors for carbon dioxide conversion to fuels,” Applied Energy, vol. 204, pp. 963–970, 2018.

[5] H. Pan and M. D. Heagy, “Photons to formate: a review on photocatalytic reduction of CO2 to formic acid,” Nano- materials, vol. 10, no. 12, 2020.

[6] C. B. Hiragond, N. S. Powar, and S. I. In, “Recent developments in lead and lead-free halide perovskite nanostructures towards photocatalytic CO2 reduction,” Nanomaterials, vol. 10, no. 12, 2020.

[7] J. Shi, Y. Jiang, Z. Ji et al., “Enzymatic conversion of carbon dioxide,” Chemical Society Reviews, vol. 44, no. 17, pp. 5981–6000, 2015.

[8] S. Kondaveeti, I. M. Abu-Reesh, G. Mohanakrishna, M. Bulut, and D. Pant, “Advanced routes of biological and bio-electrocatalytic carbon dioxide (CO2) mitigation toward carbon neutrality,” Frontiers in Energy Research, vol. 8, 2020.

[9] R. A. Tufa, D. Chanda, M. Ma et al., “Towards highly efficient electrochemical CO2 reduction: cell designs, membranes and electrocatalysts,” Applied Energy, vol. 277, Article ID 115557, 2020.

[10] S. Jin, Z. Hao, K. Zhang, Z. Yan, and J. Chen, “Advances and challenges for the electrochemical reduction of CO2 to CO: from fundamentals to industrialization,” Angewandte Chemie, vol. 133, 2021.

[11] S. Dongare, N. Singh, H. Bhunia, P. K. Bajpai, and A. K. Das, “Electrochemical reduction of carbon dioxide to ethanol: a review,” ChemistrySelect, vol. 6, no. 42, pp. 11603–11629, 2021.

[12] S. Nitopi, E. Bertheussen, S. B. Scott et al., “Progress and perspectives of electrochemical CO2 reduction on copper in aqueous electrolyte,” Chemical Reviews, vol. 119, no. 12, pp. 7610–7672, 2019.

[13] W. Quan, Y. Lin, Y. Luo, and Y. Huang, “Electrochemical CO2 reduction on Cu: synthesis-controlled structure preference and selectivity,” Advanced Science, vol. 8, 2021.

[14] Y. Zhong, S. Wang, M. Li et al., “Rational design of copper-based electrocatalysts and electrochemical systems for CO2 reduction: from active sites engineering to mass transfer dynamics,” Materials Today Physics, vol. 18, Article ID 100354, 2021.

[15] S. A. S. Mohammed, W. Z.-N. Yahya, M. A. Bustam, and M. G. Kibria, “Elucidation of the roles of ionic liquid in CO2 electrochemical reduction to value-added chemicals and fuels,” Molecules, vol. 26, no. 22, 2021.

[16] U. J. Etim, R. Semi, and Z. Zhong, “CO2 valorization reactions over Cu-based catalysts: characterization and the nature of active sites,” American Journal of Chemical Engineering, vol. 9, no. 3, pp. 53–78, 2021.

[17] S. Saìdar Hossain, S. U. Rahman, and S. Ahmed, “Electrochemical reduction of carbon dioxide over CNT-supported nanoscale copper electrocatalysts,” Journal of Nanomaterials, vol. 2014, Article ID 374318, 10 pages, 2014.

[18] R. Francke, B. Schille, and M. Roemelt, “Homogeneously catalyzed electroreduction of carbon dioxide—methods, mechanisms, and catalysts,” Chemical Reviews, vol. 118, no. 9, pp. 4631–4701, 2018.

[19] S. K. Shukla, S. G. Khokarale, T. Q. Bui, and J. P. T. Mikkola, “Ionic liquids: potential materials for carbon dioxide capture and utilization,” Frontiers in Materials, vol. 6, no. 42, 2019.

[20] K. K. Maniam and S. Paul, “Ionic liquids and deep eutectic solvents for CO2 conversion Technologies→A review,” Materials, vol. 14, no. 16, 2021.

[21] M. M. S. Pupo and R. Kortlever, “Electrolyte effects on the electrochemical reduction of CO2,” ChemPhysChem, vol. 20, pp. 1–11, 2019.

[22] S. Zhang, J. Sun, X. Zhang, J. Xin, Q. Miao, and J. Wang, “Ionic liquid-based green processes for energy production,” Chemical Society Reviews, vol. 43, no. 22, pp. 7838–7869, 2014.

[23] Q. Lu, J. Rosen, and F. Jiao, “Nanostructured metallic electrocatalysts for carbon dioxide reduction,” ChemCatChem, vol. 7, no. 1, pp. 38–47, 2015.

[24] M. Alvarez-Guerra, J. Albo, E. Alvarez-Guerra, and A. Irabien, “Ionic liquids in the electrochemical valorisation of CO2,” Energy & Environmental Science, vol. 8, no. 9, pp. 2574–2599, 2015.

[25] J. Feng, S. Zeng, J. Feng, H. Dong, and X. Zhang, “CO2 electroreduction in ionic liquids: a review,” Chinese Journal of Chemistry, vol. 36, no. 10, pp. 961–970, 2018.

[26] D. V. Vasilyev and P. J. Dyson, “The role of organic promoters in the electroreduction of carbon dioxide,” ACS Catalysis, vol. 11, no. 3, pp. 1392–1405, 2021.

[27] M. König, J. Vaes, E. Klemm, and D. Pant, “Solvents and supporting electrolytes in the electrocatalytic reduction of CO2,” iScience, vol. 19, pp. 135–160, 2019.

[28] M. Murugananthan, S. Kaneco, H. Katsumata, T. Suzuki, and M. Kuma, “Electro-catalytic reduction of CO2 in methanol medium,” Green Carbon Dioxide Advances in CO2 Utilization, vol. 7, pp. 191–214, 2014.

[29] B. Cardenas, V. Climent, and J. M. Feliu, “Effect of surface structure of platinum single crystal electrodes on the electrochemical reduction of CO2 in methanol-water mixtures,” Journal of Electroanalytical Chemistry, vol. 793, pp. 157–163, 2017.

[30] Y. Matsubara, D. C. Grills, and Y. Kuwahara, “Thermodynamic aspects of electrocatalytic CO2 reduction in acetonitrile and with an ionic liquid as solvent or electrolyte,” ACS Catalysis, vol. 5, no. 11, pp. 6440–6452, 2015.
electroreduction on Cu-modified platinum single crystal electrodes in aprotic media," *Electrocatalysis*, vol. 6, no. 1, pp. 42–50, 2015.

[32] J. Shi, T.-Y. Chen, F. Shi et al., "Non-membrane electrolysis cell for CO₂ reduction to CO in propylene carbonate/tetra-butylammonium perchlorate," *Journal of the Electrochemical Society*, vol. 165, no. 3, 2018.

[33] M. König, S.-H. Lin, J. Vaes, D. Pant, and E. Klemm, "Integration of aprotic CO₂ reduction to oxalate at a Pb catalyst into a GDE flow cell configuration," *Faraday Discussions*, vol. 230, pp. 360–374, 2021.

[34] M. C. Figueriredo, I. Ledezma-Yanez, and M. T. M. Koper, "In situ spectroscopic study of CO₂ electroreduction at copper electrodes in acetonitrile," *ACS Catalysis*, vol. 6, no. 4, pp. 2382–2392, 2016.

[35] N. E. Mendieta-Reyes, A. K. Diaz-Garcia, and R. Gómez, "Simultaneous electrocatalytic CO₂ reduction and enhanced electrochromic effect at WO₃ nanostructured electrodes in acetonitrile," *ACS Catalysis*, vol. 8, no. 3, pp. 1903–1912, 2018.

[36] N. E. Mendieta-Reyes, W. Chequepán, A. Rodes, and R. Gómez, "Spectroelectrochemical study of CO₂ reduction on TiO₂ electrodes in acetonitrile," *ACS Catalysis*, vol. 10, no. 1, pp. 103–113, 2020.

[37] S.-X. Guo, F. Li, L. Chen, D. R. MacFarlane, and J. Zhang, "Polyoxometalate-promoted electrocatalytic CO₂ reduction at nanostructured silver in dimethylformamide," *ACS Applied Materials & Interfaces*, vol. 10, no. 15, pp. 12690–12697, 2018.

[38] F.-x. Shen, J. Shi, T.-Y. Chen et al., "Electrochemical reduction of CO₂ to CO over Zn in propylene carbonate/tetra-butylammonium perchlorate," *Journal of Power Sources*, vol. 378, pp. 555–561, 2018.

[39] R. J. Gomes, C. Birch, M. M. Cencer et al., "Probing electrolyte influence on co2 reduction in aprotic solvents," *ChemRxiv*, 2021.

[40] M. M. Cencer, C. Li, G. Agarwal, R. J. Gomes Neto, C. V. Amanchukwu, and R. S. Assary, "Interactions of CO₂ anion radicals with electrolyte environments from first-principles simulations," *ACS Omega*, vol. 7, no. 21, pp. 18131–18138, 2022.

[41] S. Frangini and A. Masi, "Molten carbonates for advanced and sustainable energy applications: Part II. Review of recent literature," *International Journal of Hydrogen Energy*, vol. 41, 2016.

[42] L. Hu, B. Deng, Z. Yang, and D. Wang, "Buffering electrolyte alkalinity for highly selective and energy-efficient transformation of CO₂ to CO," *Electrochemistry Communications*, vol. 121, 2020.

[43] L. Hu, B. Deng, K. Du, R. Jiang, Y. Dou, and D. Wang, "Tunable selectivity and high efficiency of CO₂ electroreduction via borate-enhanced," *Molten Salt Electrolysis*, vol. 23, no. 10, Article ID 101607, 2020.

[44] P. Wang, M. Wang, and J. Lu, "Electrochemical conversion of CO₂ into value-added carbon with desirable structures via molten carbonates electrolysis," *RSC Advances*, vol. 11, no. 46, pp. 28535–28541, 2021.

[45] D. Chery, V. Albin, V. Lair, and M. Cassir, "Thermodynamic and experimental approach of electrochemical reduction of CO₂ in molten carbonates," *International Journal of Hydrogen Energy*, vol. 39, no. 23, pp. 12330–12339, 2014.

[46] A. Melendez-Caballero, A. Brouzgou, C. Crapart, V. Albin, V. Lair, and M. Cassir, "Chronopotentiometric approach of CO₂ reduction in molten carbonates," *Journal of the Electrochemical Society*, vol. 164, 2017.

[47] U. Kaiser and E. Heitz, "Zum Mechanismus der elektrochemischen Dimerisierung von CO₂ zu Oxalsäure," *Reports of the Bunsen Society for Physical Chemistry*, vol. 77, pp. 818–823, 1973.

[48] D. C. Grills and S. V. Lyman, "Radiolytic formation of the carbon dioxide radical anion in acetonitrile revealed by transient IR spectroscopy," *Physical Chemistry Chemical Physics*, vol. 20, no. 15, pp. 10011–10017, 2018.

[49] J. Shi, Q.-Y. Li, F. Shi et al., "Design of a two-compartment electrolysis cell for the reduction of CO₂ to CO in tetra-butylammonium perchlorate/propylene carbonate for renewable electrical energy storage," *Journal of the Electrochemical Society*, vol. 163, no. 7, pp. G82–G87, 2016.

[50] T. Chen, J. Hu, K. Wang, K. Wang, G. Gan, and J. Shi, "Specifically adsorbed anions enhance CO₂ electrochemical reduction to CO over a gallium catalyst in organic electrolytes," *Energy and Fuels*, vol. 35, no. 21, pp. 17784–17790, 2021.

[51] W. X. Lv, R. Zhang, P. R. Gao, C. X. Gong, and L. X. Lei, "Electrochemical reduction of carbon dioxide on stainless steel electrode in acetonitrile," *Advanced Materials Research*, pp. 1322–1325, 2013.

[52] S. Subramanian, K. R. Athira, M. Anbu Kulandainathan, S. Senthil Kumar, and R. C. Barik, "New insights into the electrochemical conversion of CO₂ to oxalate at stainless steel 304L cathode," *Journal of CO₂ Utilization*, vol. 36, pp. 105–115, 2020.

[53] W. Lv, R. Zhang, P. Gao, C. Gong, and L. Lei, "Electrochemical reduction of carbon dioxide with lead cathode and zinc anode in dry acetonitrile solution," *Journal of Solid State Electrochemistry*, vol. 17, no. 11, pp. 2789–2794, 2013.

[54] Y. Oh, H. Vrubel, S. Guidoux, and X. Hu, "Electrochemical reduction of CO₂ in organic solvents catalyzed by MoO₂," *Chemical Communications*, vol. 50, no. 29, pp. 3878–3881, 2014.

[55] T. Ludwig, A. R. Singh, and J. K. Nørskov, "Nonaqueous solvent adsorption on transition metal surfaces with density functional theory: interaction of N, N-dimethylformamide (DMF), tetrahydrofuran (THF), and dimethyl sulfoxide (DMSO) with Ag, Cu, Pt, Rh, and Re surfaces," *Journal of Physical Chemistry C*, vol. 125, no. 40, 2021.

[56] T. Ludwig, A. R. Singh, and J. K. Nørskov, "Acetonitrile transition metal interfaces from first principles," *Journal of Physical Chemistry Letters*, vol. 11, no. 22, pp. 9802–9811, 2020.

[57] X.-J. Zou, K. N. Ding, Y. F. Zhang, and J. Q. Li, "A DFT study of acetonitrile adsorption and decomposition on the TiO₂ (110) surface," *International Journal of Quantum Chemistry*, vol. 111, no. 5, pp. 915–922, 2011.

[58] T. C. Berto, L. Zhang, R. J. Hamers, and J. F. Berry, "Electrolyte dependence of CO₂ electroreduction: tetraalkylammonium ions are not electrocatalysts," *ACS Catalysis*, vol. 5, no. 2, pp. 703–707, 2015.

[59] J. Shi, F.-x. Shen, F. Shi et al., "Electrochemical reduction of CO₂ into CO in tetraethylammonium perchlorate/propylene carbonate: water effects and mechanism," *Electrochimica Acta*, vol. 240, pp. 114–121, 2017.

[60] S. Mena, E. Ribas, C. Richart et al., "Electrochemical tools to disclose the electrochemical reduction mechanism of CO₂ in aprotic solvents and ionic liquids," *Journal of Electroanalytical Chemistry*, vol. 895, Article ID 115411, 2021.

[61] R. Kortlever, J. Shen, K. J. P. Schouten, F. Calle-Vallejo, and M. T. M. Koper, "Catalysts and reaction pathways for the electrochemical reduction of carbon dioxide," *Journal of Physical Chemistry Letters*, vol. 6, no. 20, pp. 4073–4082, 2015.
[62] X. Zhang, Y. Zhang, F. Li, C. D. Easton, A. M. Bond, and J. Zhang, “Ultra-small Cu nanoparticles embedded in N-doped carbon arrays for electrocatalytic CO2 reduction reaction in dimethylformamide,” *Nano Research*, vol. 11, no. 7, pp. 3678–3690, 2018.

[63] S. S. Bhargava, F. Proietto, D. Azmoodeh et al., “System design rules for intensifying the electrochemical reduction of CO2 to CO on Ag nanoparticles,” *Chemelectrochem*, vol. 7, no. 9, pp. 2001–2011, 2020.

[64] K. Gupta, M. Bersani, and J. A. Darr, “Highly efficient electro-reduction of CO2 to formic acid by nano-copper,” *Journal of Materials Chemistry*, vol. 4, no. 36, pp. 13786–13794, 2016.

[65] J. W. Vickers, D. Alfonso, and D. R. Kauffman, “Electrochemical carbon dioxide reduction at nanostructured gold, copper, and alloy materials,” *Energy Technology*, vol. 5, no. 6, pp. 775–795, 2017.

[66] R. Reske, H. Mistry, F. Behafarid, B. Roldan Cuenya, and P. Strasser, “Particle size effects in the catalytic electroreduction of CO2 on Cu nanoparticles,” *Journal of the American Chemical Society*, vol. 136, no. 19, pp. 6978–6986, 2014.

[67] O. Kuntyi, G. Zozulya, and A. Kytsya, “‘Green’ synthesis of metallic nanoparticles by sonoelectrochemical and sonogalvanic replacement methods,” *Bioinorganic Chemistry and Applications*, vol. 2021, Article ID 9830644, 17 pages, 2021.

[68] E. Lamy, L. Nadjo, and J. Saveant, “Standard potential and kinetic parameters of the electrochemical reduction of carbon dioxide in dimethylformamide,” *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, vol. 78, no. 2, pp. 403–407, 1977.

[69] A. Gennaro, A. A. Isse, J.-M. Savéant, M.-G. Severin, and E. Vianello, “Homogeneous electron transfer catalysis of the electrochemical reduction of carbon dioxide. Do aromatic anion radicals react in an outer-sphere manner?” *Journal of the American Chemical Society*, vol. 118, no. 30, pp. 7190–7196, 1996.

[70] A. Aljabour, H. Coskun, D. H. Apaydin et al., “Nanofibrous cobalt oxide for electrocatalysis of CO2 reduction to carbon monoxide and formate in an acetonitrile-water electrolyte solution,” *Applied Catalysis B: Environmental*, vol. 229, pp. 163–170, 2018.

[71] F.-X. Shen, J. Shi, F. Shi et al., “Fabrication of Ag2S electrode for CO2 reduction in organic media,” *Ionics*, vol. 25, no. 4, 2019.

[72] Y. Tomita, S. Teruya, O. Koga, and Y. Hori, “Electrochemical reduction of carbon dioxide at a platinum electrode in acetonitrile-water mixtures,” *Journal of the Electrochemical Society*, vol. 147, no. 11, pp. 4164–4167, 2000.

[73] A. V. Rudnev, U. E. Zhumaev, A. Kuzume et al., “The promoting effect of water on the electroreduction of CO2 in acetonitrile,” *Electrochimica Acta*, vol. 189, pp. 38–44, 2016.

[74] B. A. Rohr, A. R. Singh, J. A. Gauthier, M. J. Statt, and J. K. Nørskov, “Micro-kinetic model of electrochemical carbon dioxide reduction over platinum in non-aqueous solvents,” *Physical Chemistry Chemical Physics*, vol. 22, no. 16, pp. 9040–9045, 2020.

[75] A. Bagger, O. Christensen, V. Ivanistsev, and J. Rossmeisl, “Catalytic CO2/CO reduction: gas, aqueous and aprotic phases,” *ACS Catalysis*, vol. 12, 2022.