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Article

A Bibliometric Analysis of Research on Membrane Coated Electrodes in the 2001-2019 Period: Potential Application to CO_2 Capture and Utilization

Clara Casado-Coterillo, Aitor Marcos-Madrazo, Aurora Garea, Ángel Irabien

[1] Department of Chemical and Biomolecular Engineering, Universidad de Cantabria, Av. Los Castros s/n, 39005 Santander, Spain
* Correspondence: casadoc@unican.es; Tel.: +34-942-206777 (C.C.C.)

Abstract: The chemistry and electrochemistry basic fields have been active since the last two decades of the past century studying how surface modification of electrodes by coating with conductive films enhances their activity and performance. In the light of the development of alternative sustainable ways of energy storage and carbon dioxide conversion by electrochemical processes, these research studies have jumped in the 21st century to more applied fields such as chemical engineering, energy and environmental science and engineering. The huge amount of literature on experimental works dealing with the development of CO_2 electroreduction processes addresses electrocatalyst development. Membranes can help understanding and controlling the mass transport limitations of current electrodes and reactors designs. The present bibliometric review addresses the papers published in the 21st century regarding membrane coated electrodes and electrocatalysts to enhance electrochemical reactor performance and viability with a special focus on the urgent issue of carbon dioxide capture and utilization.

Keywords; CO_2; conversion; bibliometrics; electrode design; CO_2RR; membrane; flow cell

1. Introduction

The sharp rise of the concentration of carbon dioxide in the atmosphere due to fossil fuels consumption is already acknowledged as the main cause of environmental and health problems threatening humans' living environment irreversibly. The mitigation of the greenhouse gas emissions to the atmosphere is a key target for researchers worldwide. Reducing carbon dioxide emissions while addressing energy shortages requires the conversion of CO_2 into commercial products. Electrochemical reduction of CO_2 is a desirable alternative if the intermittency of renewable electricity production and its storage in energy bonds of chemical fuels that could be commercial if the efficiency of current CO_2-to-fuel technologies were improved. These improvements have been generally addressed by focusing in the optimization of electrocatalysts and electrodes, [1] reactor types and flow cell systems,[2] often differing in the type of ion exchange membrane whose role is limited to separator between cell compartments and ion transfer.[3] Other variables studied are the type of electrolyte and phase, [4,5] as well as strategies on flow channel and anode design left for future steps.[6] Recently, statistical analysis of the large amount of dispersed experimental works has been applied to develop decision trees that help determining the significance of the main variables influencing electrochemical reactor viability in CO_2 conversion, such as faradaic efficiency, production rate and product selectivity.[7]

The status of CO_2 conversion in the past ten years has been recently analyzed using the bibliometric method; the influence of countries and institutions, journal article statistics and other aspects are statistically analyzed, and the research status of carbon dioxide catalytic conversion was briefly introduced.[8]

As mentioned in those previous reviews works, much research effort has been made on the quest of new electrocatalysts optimization. Electrocatalysis is an interfacial phenomenon, the relative ratio

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of CO_2 and $H_2(H^+)$ is dictated by the intrinsic selectivity of surface active sites and the local concentration of reaction compounds involved in the different rate-controlling stages, therefore the need for understanding the mechanisms involved for designing more effective reactors and electrodes.[3]. A range of transition metals exhibits electrical activity for CO_2RR. [9]. Copper is highly preferred as allows tuning the balance of reaction intermediate binding energy for stabilization species leading to hydrocarbons, and the inhibition of further reaction steps and release[10]. Drawing accurate structure–activity relationships has been complicated, not only due to the ill-defined and intricate morphological and mesoscopic structure of electrocatalysts, but also by huge concentration gradients existing between the electrode surface and the bulk solution. [11] The CO_2RR selectivity is strongly influenced by the activation barrier and binding energy of intermediate species to control the catalyst interface and elucidate the role of active sites on the reaction kinetics [12]. The micro and meso structure of the electrode determines the diffusional gradients under steady state conditions, which are the most commonly investigated in a CO_2/HCO_3^- electrolyte because of the slow equilibration kinetics. Heterogeneously structured catalysts have been used to change the electronic properties of the active sites and tune the adsorption energies of the intermediate reactant species to promote product selectivity and /or reduce the energy barriers for CO_2RR [13]. The mass transport limitation on continuous flow electrochemical cells attempted by applying high pressure, gas diffusion electrodes (GDEs) and metal catalyst-coated ion –exchange membrane electrodes can be addressed by according a more active role to the membrane.[14]

Membrane coated electrocatalysts (MCEC) have also been considered as an alternative approach to improve the stability of electrocatalysts in emerging applications where selectivity of the electrochemical device is sought by applying transport-mediated reaction selectivity and protective layers that tune up the mass and ion transport to the metal electrocatalyst [15]. However, this type of electrodes require additional understanding on the reaction and transport mechanism to develop an adequate polyelectrolyte electrochemical membrane reactor for CO_2 capture and utilization.[16]

The membrane coated electrode configurations under investigation are schematized in Figure 1. **Figure 1(a)** is the configuration "Catalyst coated membrane electrode" as with M^+@CCM over Nafion for CO_2 electro reduction to formic acid [5], and **Figure 1(b**) is slightly different in that a sustainable polymer blend based over-layer has been coated on the catalytic layer over the porous substrate to generate a membrane coated electrode.[17]

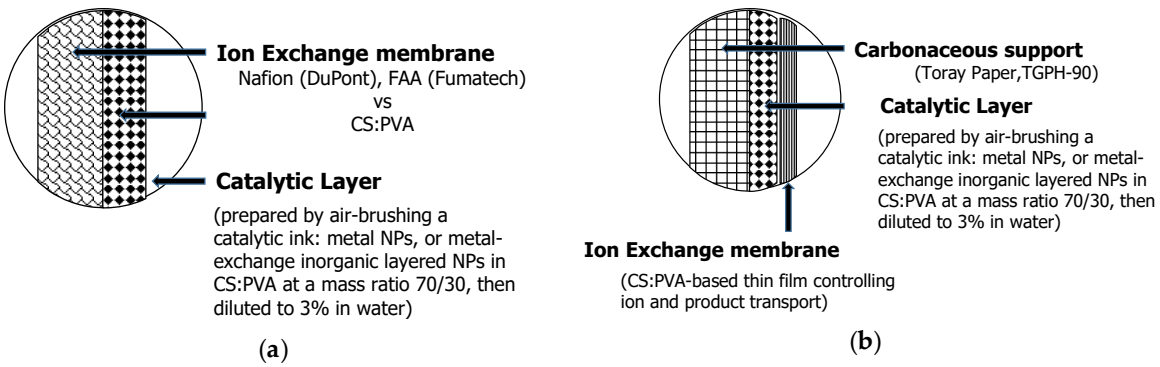

Figure 1. Schematic representation of (**a**) CCM (Catalyst coated membrane) [5], and (**b**) MCEC (Membrane-coated electrodes) [17].

A bibliometric analysis is a tool needed to evaluate comprehensively the generally large number of reports published in a specific research field, thus facilitating researchers an up-to- information and knowledge on the state-of-the-art of the trends and interests in their fields.[18] This technique is based on statistical, quantitative analyses, and indexes to assess the contribution of authors, institutions and countries, as well as subject areas on a specific research output.

2. Results

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The aim of this work is the bibliometric analysis of the literature indexed in Scopus database [19] from 2001 to 2019 related to membrane coated electrodes. The systematic evaluation of the records found is used to quantitatively determine the characteristics of the research and provide an overview of the trends in this topic, regarding most emerging applications, which has not been the object of similar studies before, as far as we know. Therefore, this paper will be useful to focus the global panorama of the research in MCECs and identify the challenges and recommendations for their future development to practical applications.

This section summarizes the bibliometric analysis resulted from the online search within Scopus database carried out in May 2020 by selecting "membrane coated electrode", "membrane coated electrocatalyst" or "surface modified electrode" as keywords in the "Article, Title, Abstract, Keywords" field of the search engine to obtain the complete bibliography with all the records related to the research on MCECs published in the period from 2001 to 2019.

2.1. Bibliometric analysis of research on membrane coated electrodes (2001-2019)

2.1.1. Publication Year, Document Type and Language of Documents

The distribution of annual publications and the evolution of the number of accumulated documents were depicted in **Figure 2**. The total number of articles found for the keywords in Figure 2, was 143, of which 19 corresponded to CO_2 reduction.

Therefore, MCECs has represented a small area within the electrocatalysis research on electrochemical processes in the allocated period, although the monotonously increasing trend allows expecting a significant growth with all the research efforts pursuing increased stability and selectivity concerns of electrocatalysts, as well as environmental applications in the light of the mitigation of carbon emissions and efficient use of resources.

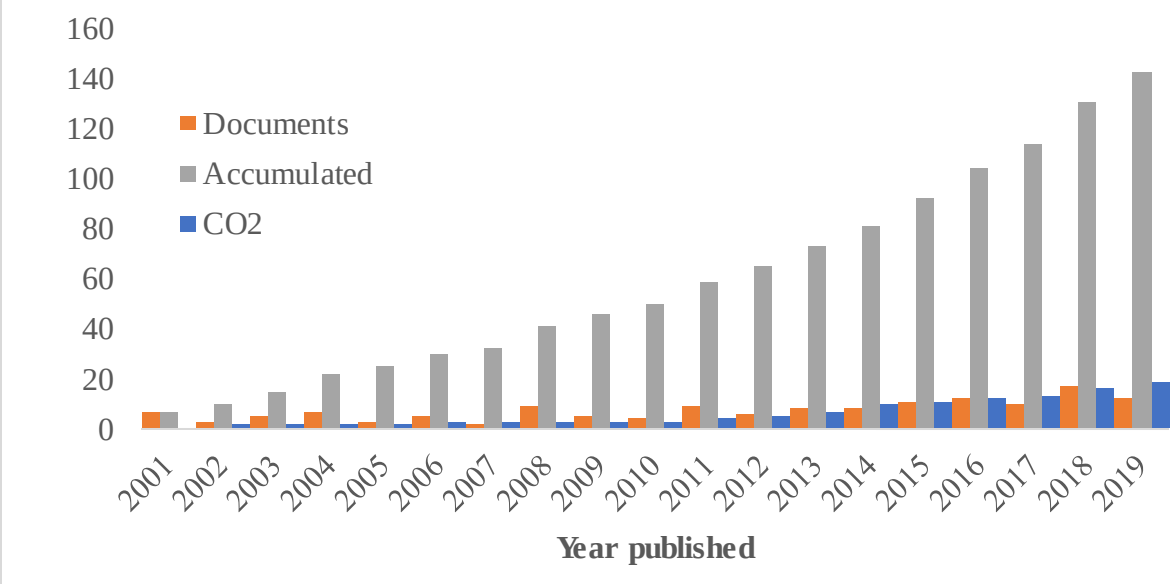

Figure 2. Accumulated publication output for the "membrane coated electrode" or "membrane coated electrocatalyst" or "surface-modified electrode" (grey) and the "CO_2" applied (blue).

After the above screening, English was the language of 99.3% of those publications, of which 119 (83%) were research articles, 14 conference papers (10%) and 9 reviews (6%). When the keyword "CO_2" or "carbon dioxide" was added, the amount of publications ranked to 53, with an increasing progression in the last 5 years. For convenience, the analysis proceeded with the papers applied to CO_2 applications.

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2.2. Distribution of output in subject categories and journals

The distribution of research subjects can be observed in **Table 1**, where the 10 most popular subject categories are shown in order. The categories are non-exclusive and a publication may be related to more than one research area due to interdisciplinary research. There is a significant dispersion of the publications in different subject area categories, which accounts for the multidisciplinary quality of the topic. This is probably the reason why the ranking indicated that Chemistry, Chemical Engineering, Materials Science, Engineering and Energy are the dominant subject areas in the respective fields.

Table 1. The top 5 most popular subject categories.

Ranking	Subject categories	Documents	Percentage (%)
1	Chemistry	110	35.7
2	Chemical Engineering	49	15.9
3	Materials Science	41	13.3
4	Engineering	32	10.4
5	Energy	23	7.6
6	Physics & Astronomy	19	6.3
7	Biochemistry, Genetics & Molecular Biology	13	4.3
8	Environmental Science	7	2.6
9	Medicine	4	1.3
10	Computer Science	3	1.0

The distribution of publications in journals is shown in **Table 2**. The corresponding values (year 2019) of impact factors (IF) of the Web of Science database and the SCImago Journal Rank (SJR) index of Scopus of the journals were included. The journal that published most documents was *Electrochimica Acta* (19%), thus in line with the interdisciplinarity of the research and application of these electrodes. It is significant the presence of journals on surface and interface science and technology, such as ACS Interface Applied Materials, ACS Catalysis and ChemElectroChem.

Table 2. The top most productive journals.

Ranking	Journal	IF (WoS)	SJR (Scopus)	Documents	Percentage (%)
1	*Electrochimica Acta*	6.215	1.467	15	19
2	*Journal of Electroanalytical Chemistry*	3.807	0.758	9	12
3	*Journal of Power Sources*	8.248	1.946	9	12
4	*Electroanalysis*	2.544	0.651	5	6
5	*ACS Catalysis*	12.340	4.633	4	5
5	*Journal of Solid State Sciences*	2.510	0.559	4	5
6	*Trac. Trends in Analytical Chemistry*	9.801	2.153	4	5
7	*ChemElectroChem*	4.154	1.149	3	4
8	*Journal of Applied Electrochemistry*	2.384	0.602	3	4
9	*Journal of the Electrochemical Society*	3.721	1.153	3	4
10	*ACS Applied Materials & Interfaces*	8.758	2.568	2	2.7

2.3. Publication distribution of countries and institutions

The analysis of the author's countries was based on papers in which the address and affiliation of at least one author was provided. The total number of references used in the analysis was 142,

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since the affiliation field for one of the conference papers was blank. One paper was produced by a single author. This author was the correspondent of two more collective papers. **Table 3** shows the top countries ranked by the number of total publications. Other information in the table is the ranking and percentage of contributions according to single country or internationally collaborating papers. Only countries with more than 2 documents in the studied search are collected in **Table 3**. The most productive countries are United States of America (16%), Japan (11%), China (11%), India (8%) and Australia (7%), constituting the majority of the international co-authorships in the sample under study, whereas Japanese contributions are retained in the same country. Other countries also collected in Table 3 with contributions in MCEC and CO_2, are Chile, Spain, Turkey and the United Kingdom, mostly by authors from the same or different affiliations within the same country. These results also confirm the dispersion and multidisciplinary character of the area under study, and the relevance of the main research centers and the main coal –dependent countries in the present century.

Table 3. The top 7 most productive countries. Number of documents and percentage (%) between brackets.

Country	TP	SPR	ICPR	FAPR	CAPR
United States	27 (19%)	16 (11%)	11 (8%)	21 (15%)	22 (15%)
China	18 (13%)	10 (7%)	8 (6%)	14(10%)	11 (8%)
Japan	18 (13%)	16 (11%)	2 (1%)	16 (11%)	18 (13%)
India	13 (9%)	8 (6%)	5 (4%)	11 (8%)	9 (6%)
Australia	11 (8%)	9 (6%)	2 (4%)	9 (6%)	10 (7%)
South Korea	9 (6%)	7 (5%)	2 (1%)	8 (6%)	8 (6%)
Italy	8 (5%)	6 (75%)	2 (25%)	6 (75%)	7 (88%)
Canada	7 (5 %)	4 (4%)	2 (1%)	6 (4%)	6 (4%)
United Kingdom	7 (5%)	6 (4%)	5 (4%)	5 (4%)	4 (3%)
Spain	4 (3%)	2 (1%)	2 (1%)	4 (3%)	3 (75%)
Chile	3 (2%)	2 (1%)	1 (1%)	3 (2%)	3 (2%)
Turkey	2 (2%)	3 (2%)	0	3 (2%)	3 (2%)

[1] TP. Total publications; SPR: Single country publication rank; ICPR: International collaboration publication rank; FAPR: First author publication rank; CAPR: corresponding author publication rank

The top institutions producing more than 1 paper on under the search terms used in this study, are ranked in **Table 4**. These values confirm the distribution between the most productive countries in **Table 3** (United States of America, Japan and China), although the top ranked productive institution is an Australian University. It is again remarkable the wide dispersion of institutions publishing on these subjects, which is related with the low amount of international collaboration discussed above. Although the University of North Caroline at Chapel Hill (U.S.A.) produced some of the first (as far as we know) papers regarding polymer coated electrodes for electroreduction of CO_2 as early as 1989, reason why they are not included in this bibliometric analysis [20,21].

Table 4. The top 5 rank of the most productive institutions.

Ranking	Institutions	Documents	Percentage (%)
1	Murdoch University	7	14.9
2	University of Western Australia	6	12.8
3	University of Tokyo	4	8.5
	Korea Institute of Science and Technology	4	8.5
	Nanjing University	4	8.5
4	University of Kurdistan	3	6.7

	Forschungszentrum Jülich FZJ	3	6.7
	Universita di STudi di Firenze	3	6.7
	Tokyo Institute of Technology	3	6.7
	Columbia University of the City of New York	3	6.7
	York University	3	6.7
5	Universidad de Granada	2	4.3
	Pontificia Universidad de Chile	2	4.3

2.4. Most cited papers and author keywords

The most frequently cited articles of the bibliometric review, restricted to CO_2 reduction, are collected in **Table 5** below. The most cited work was published in the *Journal of Power Sources* in 2013 and has been cited 120 times, which represents the growing impact of the research on classical electrochemical applications devoted last century to enhance the selectivity of analytical sectors and protection of surfaces from corrosion to the improvement of CO_2 electroreduction in 21st century.

Table 5. The top most cited articles mentioned coated electrodes or electroctalysts.

Ranking	Article	Times cited
1	Electrochemical reduction of CO_2 over Sn-Nafion® coated electrode for a fuel cell-like device Author(s): Prakash, G.K.S., Viva, F.A., Olah, A. Source: Journal of Power Sources Published: 2013	120
2	Electrochemical reduction of carbon dioxide at low overpotential on a polyaniline /Cu_2O nanocomposite based electrode Author(s): Grace, A.N., Choi, S.Y., Vinoba, M., Bhagiyalakshmi, M., Chu, D.H., Yoon, Y., Nam, S.C., Jeong, S.K. Source: Applied Energy Published: 2014	61
3	Electrochemical reduction of carbon dioxide on polypyrrole coated copper electrocatalyst under ambient and high pressure in methanol Authors: Aydin, R., Dogan, H.T., Koleli, F. Source: Applied Catalysis B: Environmental Published: 2013	44
5	Electro and photoelectrochemical reduction of carbon dioxide on multimetallic porphyrins/polyoxotungstate modified electrodes Author(s): García M., Aguirre M.J., Canzi G., Kubiak C.P., Ohlbaum M., Isaacs M. Source: Electrochimica Acta Published: 2014	42
6	Poly-Amide Modified Copper Foam Electrodes for Enhanced Electrochemical Reduction of Carbon Dioxide Authors: Ahn, S., Kiyukin, K., Wakeham, R.J., Rudd, J.A., Lewis, A.R., Alexander, S., Carla, F., Alexandrov, V., Andreoli, E. Source: ACS Catalysis Published: 2018	31
7	Study of the electrochemical reduction of CO_2 on a polypyrrole electrode modified by rhenium and copper -rhenium microalloy in methanol media	28

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	Authors: Schrebler, R., Cury, P., Muñoz, E., Gómez, H., Córdova, R. Source: Journal of Electroanalytical Chemistry Published: 2002	
	Facet- and structure-dependent catalytic activity of cuprous oxide/polypyrrole particles towards the efficient reduction of carbon dioxide to methanol	15
8	Author(s): Periasamy A.P., Ravindranath R., Senthil Kumar S.M., Wu W.-P., Jian T.-R., Chang H.-T. Source: Nanoscale Published: 2018	
	Sustainable Membrane-coated electrodes for CO_2 electroreduction to methanol in alkaline media	2
9	Author(s): Marcos-Madrazo, A., Casado-Coterillo, C., Irabien, A. Source: ChemElectroChem Published: 2019	

Figure 3 represents the mostly encountered author keywords in the analyzed works of this bibliometric analysis. Mostly are related to composite materials coated or surfaced modified electrodes or electrocatalysts, as well as solid polymer electrolyte. As mentioned above, the first works on surface modified or coated electrodes by conductive materials are devoted to sensors in diverse applications, but most recently this feedback is being utilized in the design of CO_2 reduction electrolyzers o added value products. The variability of the keyword's accounts for the variability of the materials and applications under study, and less than 2 times cited keywords, mostly dealing with the insight in understanding the transport and reaction mechanisms and equations modelling, are not included in **Figure 3**, but mentioned here given their relevance to the development of the process.

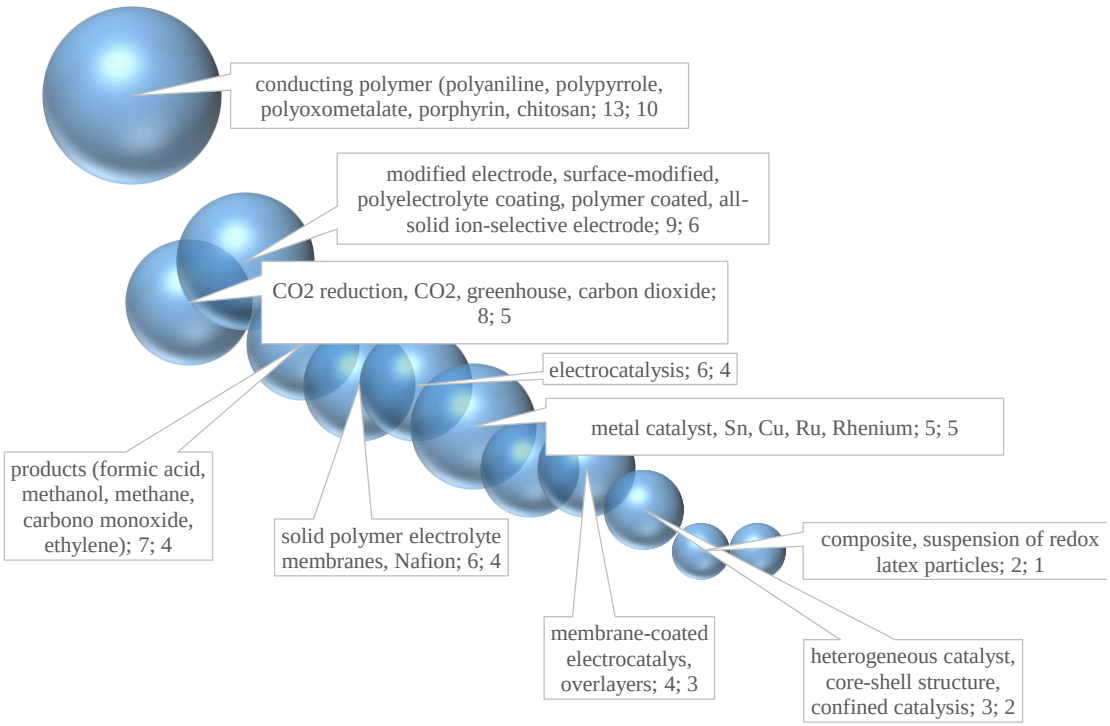

Figure 3. Most common author keywords.

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3. Some keynotes for discussion

The evolution of MCEC and MCE in electrochemical engineering and catalytic literature has evolved from GDE preparation by coating metal catalysts dispersed in Nafion ionomer [22] to enhancing the selectivity of the electrocatalysts by coating the electrode with a conductive polymer, usually polypyrrole-based when the reaction media is methanol [23,24] and most recently aqueous media [25]. For CO_2 electrochemical selective reduction conversion in alkaline media, the understanding of the role of the membrane coating in the diffusion and reaction must be understood for the optimal design of optimal reactors, as will be discussed briefly in this article.

3.1. Role of membranes for CO_2 electroreduction.

In order to avoid the challenges of using liquid electrolytes, as the low CO_2 solubility and recovery of liquid products as formate [4,26], solid polymer electrolyte membranes were introduced into the design of electrochemical flow continuous reactors. The role of the membrane is only that of the solid polyelectrolyte barrier that separates the anode and cathode of the cell and mediates the flow of ions from one-half reaction to another while simultaneously attenuating product cross over.[2,27–29] Anion exchange membranes (AEMs) work by facilitating the flow of anions (e.g. OH^-) from the cathode to the anode [30]. In CO_2 electrolyzers in alkaline conditions, OH^- ions rapidly react in the presence of CO_2 to form HCO_3^- and CO_3^{2-} but the lower mobility of the latter ions compared to OH- may inhibit ion transport and reduce CO_2 reduction efficiency [31]. However, the OH^- ions generated in the cathode that are not neutralized by the H^+ in the anode may increase the pH value in the catholyte at steady state, resulting in larger efficiencies when comparing undivided and divided cell reactors.

The low solubility of CO_2 in aqueous solutions is a relevant concern regarding its transport to the catalyst [32], especially in high pH media when CO_2 rapidly reacts to form carbonates [33]. Gas Diffusion Electrodes are the most studied approach to solve this issue, as the CO_2 is able to diffuse through the porous layer and reach the catalyst prior to any interaction with the electrolyte [34]. **Figure 4** shows a typical cell configuration in which a GDE is employed.

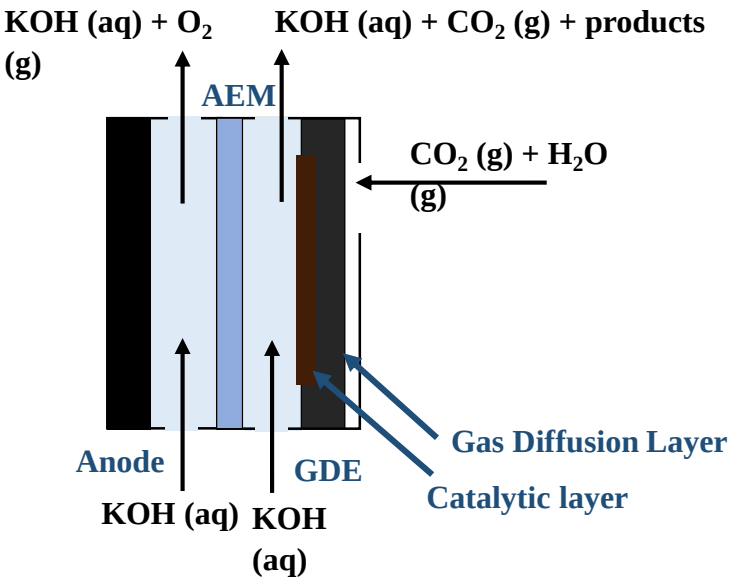

Figure 4. Electrochemical cell reactor configuration using aqueous electrolytes in both compartments.

The advantages of this cell configuration are the mentioned facilitation of CO_2 transport through the gas diffusion layer, and the influence of the pH. The employment of KOH or $KHCO_3$ as electrolyte in the cathode chamber has been widely discussed, and generally concluding that the higher alkaline

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conditions provided by KOH significantly reduced the ohmic losses due to higher electrolyte conductivity (than $KHCO_3$) [34] and promotion of CO_2R reaction kinetics [33]. Thus, this ion transport mechanism is more suitable for CO_2 reduction in AEMs than cationic exchange membrane (CEM) system, *i.e.* Nafion, because the forward reaction of CO_2 to products is encouraged without the delivery of H^+ to the cathode. Through AEMs, the rate of product crossover is proportional to the current density, and even neutral alcohols experience crossover, as is the case for AEM fuel cells. Some of the best performing membranes in CO_2 flow cells known today use AEMs [35,36]. Aeshala et al. [37,38] highlighted the improved CO_2RR efficiency of quaternary ammonium groups in anionic solid polymer electrolytes. Dioxide Materials has developed anion-exchange Sustainion® membranes that contain imidazolium functional groups, which were found to improve the performance and selectivity of CO_2 reduction to CO [35].

The main disadvantage of such alkaline anion exchange membrane reactor configuration is the carbonation of the electrolyte by the unreacted CO_2.[39] This issue affects the pH of the reaction medium, leading to the generation of great gradients between bulk/electroactive sites of the catalyst, which is why mass transport limitations still remain as an important concern in the overall performance of CO_2 electrolyzes [40]. By eliminating the aqueous electrolyte in the cathodic chamber (**Figure 5**) or even in both compartments (**Figure 6**) this issue might be overcome. In these configurations, the Anion Exchange Membrane (AEM) is directly in contact with the cathode or with both electrodes. The connection membrane-electrodes and the multiple alternatives have been discussed in the literature [28].

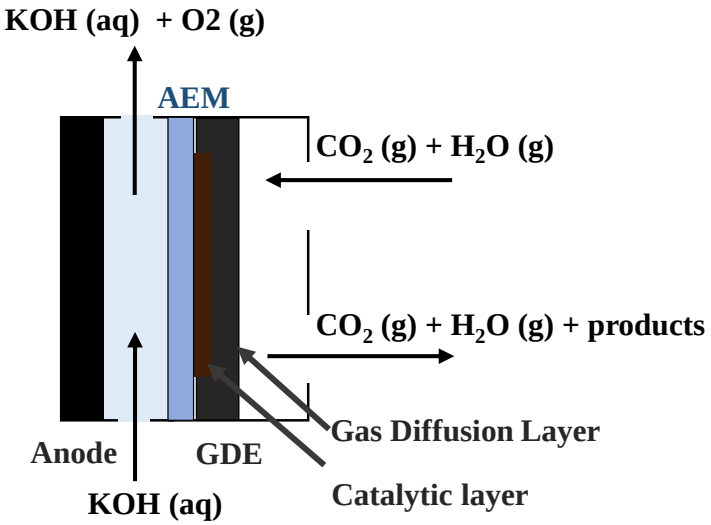

Figure 5. Electrochemical cell reactor configuration using liquid aqueous electrolytes only in the anode chamber.

With these configurations, no interaction should occur between CO_2 and the aqueous electrolyte. The role of the membrane gains more relevance as it should maintain the alkaline conditions throughout the process. When an aqueous anolyte is supplied, as in the schemes shown in **Figure 5**, an ion exchange takes place with the membrane that provides the OH^- concentration in the diffusion layer and facilitates the hydration of the membrane.

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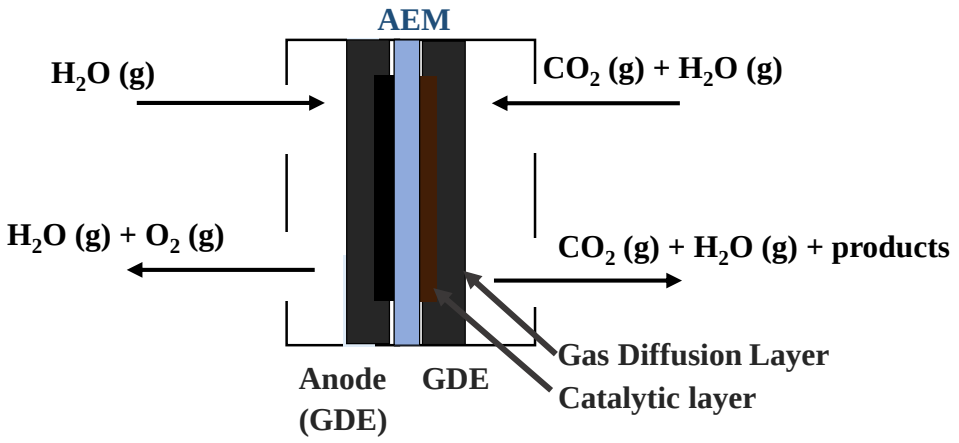

Figure 6. Electrochemical cell reactor configuration without liquid phase electrolytes.

One approach to eliminate the liquid electrolyte are gas-phase electrochemical reactors, using a humidified gaseous CO_2 feed stream increased the performance, demonstrating the importance of adequate hydration within the cell during gas electrolysis [41]. The water film generated on the gas diffusion electrodes (GDE) should be kept thin to reduce mass transfer resistance, water crossover and membrane swelling. Water management is a key issue in ion exchange membrane processes in alkaline conditions as documented by recent reviews and perspective papers [42–44]. Water and CO_2 delivery/management can also be impacted by the macroscale geometry of the chemically-benign electrolyzer components that govern the fluid dynamics of gas /liquid flows within a reactor, 3D printing techniques allow for instance rapid prototyping and optimization of different flow field geometries [2]. These geometries are related directly with the reactor design, from H-type to continuous flow reactors. The design and tuning of hydrophilic conductive mixed matrix membranes containing active catalyst sites may be an attractive strategy toward enhancing the CO_2RR performance in membrane-type reactors needed for large-scale implementation [45]. The suppression of aqueous electrolytes in both chambers is represented in **Figure 5**. Aeshala et al focused on the design of electrolyzers with this configuration, in which the membrane is a solid alkaline polyelectrolyte [46]. This configuration may overcome the problem of the aqueous electrolyte carbonation and other common issues regarding the use of liquids, primarily leaks and corrosion. A disadvantage of new highly conductive Sustainion® membrane based electrolyzers is that the lack of aqueous electrolytes hinders the transport of liquid products, mainly alcohols and formate, which is why they are focused on the generation of gas products, mainly CO [36,47]. Therefore, the role of the membrane becomes crucial and not only limited to separation barrier between the cathode and anode compartments, providing the charge transfer between electrodes while maintaining a constant alkaline media for the reaction.

3.2. *Membrane-coated electrodes in the framework of CO_2 electroreduction*

Regardless the cell configuration selected, a relevance concern appears when employing GDE: material losses and degradation. The coating of the catalyst material with a conductive polymeric layer is promising approach to face its deactivation [23,48]. Moreover, it may provide new pathways for CO_2 and products transport, leading also with mass transport limitations [15]. The membrane layer applied as coating must meet some requirements: high conductivity to minimized ohmic losses and high ion exchange capacity to supply the OH^- and maintain the alkaline media, which are related to its hydrophilicity, and of course it must be selective to CO_2. The stages of the membrane coated electrode, transport and catalytic limitations are schematized in **Figure 7**.

Coating a tunable membrane on the electrode allows controlling the mass transport limitation. This avoids the diffusion barrier created by adsorption and inactivating the electrocatalyst, modulating pH and access to active sites by anticipating that rapid transport to the electrode through

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the selective sufficiently thin and thick membrane and electrolyte pre-concentration in the membrane enhances sensitivity by modulating pH and CO_2 concentration near the active sites.[49,50] Encapsulation of metal particles into conductive polymers has enhanced the activity of Cu_2O electrocatalysts on the reduction of CO_2 even in aqueous media [25,51].

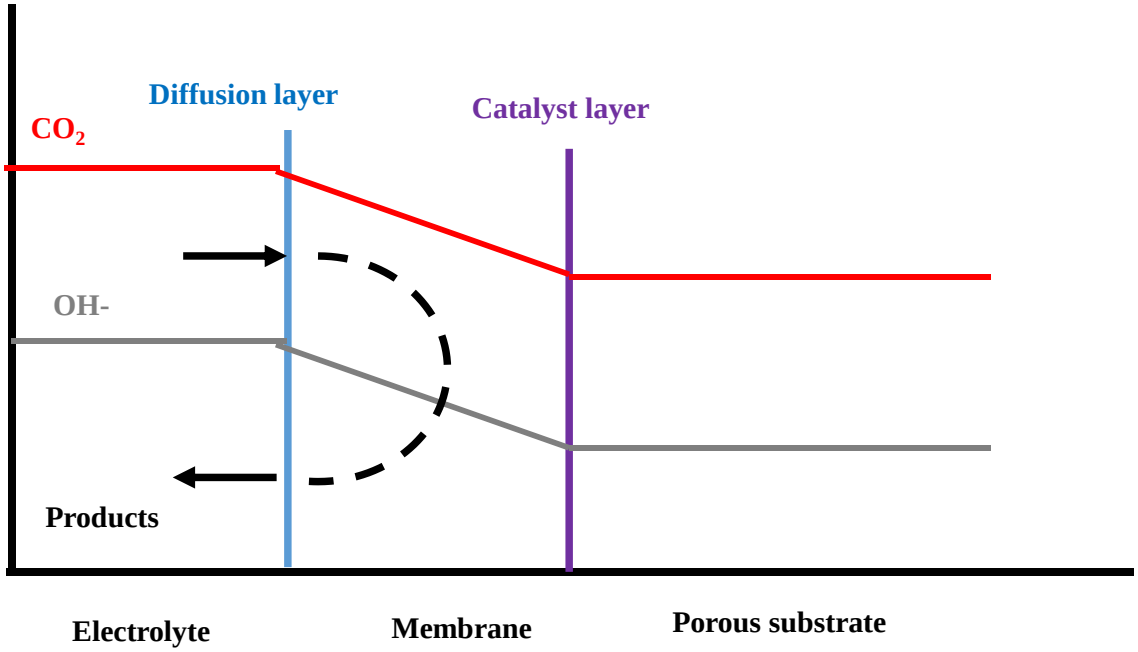

Figure 7. Schematic illustrating gas and ion transport in the MCE configuration, adapted from the conventional GDE configuration proposed by Liu et al. [50].

Likewise, the dispersion of metal particles into a polymeric matrix provides the possibility of activating specific areas of metal catalyst and thus improve catalytic efficiency [51,52]. In CO_2 electroreduction, the catholyte is not only the medium that provides dissolved CO_2 as cathode reactant, but it also transfers electrons and ions. However, the use of electrolytes causes solubility problems so it has to be removed in order to recover liquid products as formate or methanol [4,26]. Since the water film in the GDE must be as thin as possible to reduce mass transfer resistance, water crossover and membrane swelling, Lin et al. coated Nafion membranes by a silica-sol-gel derived over-layer to improve tune up the hydrophilicity and crossover of these membranes in fuel cells. [53] The encapsulation of metal nanoparticles in an over-layer containing OH functional groups to interact with the metal catalyst and CO_2-derived reagents has been reviewed recently [15]. The role of these OH- groups is highly important in the role of alkaline resistant anion exchange membranes in electrochemical membrane reactors [54,55].

On the other hand, the embedding of the catalyst in different types of polymers has been reported to have a significant influence on the catalytic selectivity and stability of electrodes, depending on the nature of the functional groups of the polymer.[56] Coating the electrode by a conductive polymer also improved the efficiency of electrochemical reduction efficiency in CO_2, O_2 or H_2 reduction in organic and aqueous media [20,57]. Aydin observed that the coating of Cu derived nanoparticles in polypyrrole over a Nafion 117 membrane controlled HER, compared to blank Cu as electrocatalyst, with FE of 25 % and 20% towards CH_4 and formate, respectively, thus shifting the product selectivity and catalyst activity [23]. Grace et al. observed improvement in the Faradaic efficiency of CO_2 to acetic acid and formic acid by coating Cu_2O nanoparticle electrode with a polyaniline film [58]. Electrochemical impedance spectroscopy studies revealed that the CO_2 reduction to formic acid on polymer-coated electrodes caused a fast charge transfer at the interface, up to a maximum polymer layer thickness, while the transport practices unaffected by film thickness [59]

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This highlights the role of the membrane layer as a means of overcoming the trade-off between performance and stability, by focusing on the influence of the mass transfer through the nano-thick membrane coated layer on top of an electroactive surface to keep electrocatalytic performance. The embedding of metal ions into inorganic structures avoids the dissolution of metal nanoparticles and enhances the synergy of active sites for catalysis and transport [15,60] and facilitates the membrane film fabrication as a mixed matrix membrane containing metal ions [61]. This new electrode configuration invoke novel research regarding the study of how reaction and transport mechanisms influence the geometry of reactor configurations, in order to optimize the cathodic and anodic efficiencies, avoiding catalyst loss or deactivation, gas-phase flooding, and control product delivery [62].

In this regard, **Figure 8** proposes a cell configuration employing a Membrane Coated Electrode, in which the catalyst is protected by the polymer-based membrane overlayer of tunable composition.[17] In this reactor design, CO_2 diffuses through the selective membrane and reaches the catalyst. No aqueous solution is directly in contact with the catalyst material, thus the alkaline environment is also provided by the membrane. The products then are transported through the porous layer provided by the support and are driven out of the cell by the electrolyte. An AEM is used to separate catholyte and anolyte compartments, in a configuration similar to that presented in **Figure 4**. The membrane coated over catalyst layer just provided protection to enlarge the electrode durability compared to the GDE morphology. Furthermore, the gas, ion and electron transport is decoupled, and obtained significant results for ethylene production, as studied in [63].

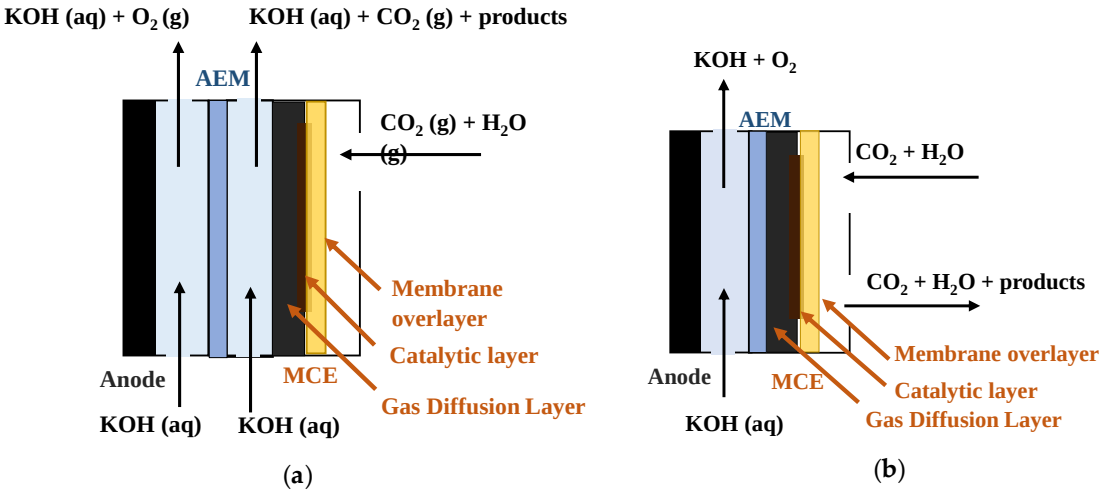

Figure 8. Electrochemical cell reactor configuration using an MCE where the membrane overlayer is facing the CO_2 inlet flow (**a**) and no aqueous electrolyte in the cathode chamber (**b**)

Similar to the previous cell designs reported with the GDE, it is possible to remove the aqueous electrolyte in the cathodic compartment, as represented in **Figure 9(b).** The problem with this configuration is that the catalyst particles are embedded within the membrane overlayer of the MCE and another AEM is employed as separator between the electrodes, creating 3-compartment reactor similar to those inspired by chlor–alkali and hydrogen purification large-scale polyelectrolyte membrane reactor reported in literature [36]. The products can diffuse through any of the membranes, which may complicate their recovery procedure out of the cell and the validation of the transport and reaction mechanisms in CO_2R.[16]

Another interesting approach is thus represented in **Figure 9(a**). Here, the membrane over layer functions as the selective barrier between electrodes, which allows simplifying the structure of the reactor by removing the electrolyte and the AEM. It should be remarked that the previously mentioned barrier properties of the membrane layer in **Figure 9** should be selectively tuned in order to avoid the crossover of products to the anode. This gives scope not only to the research and

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innovation on electrode and zero –gap reactor design [64], but also on mixed matrix membranes with controllable ion exchange properties. [17]

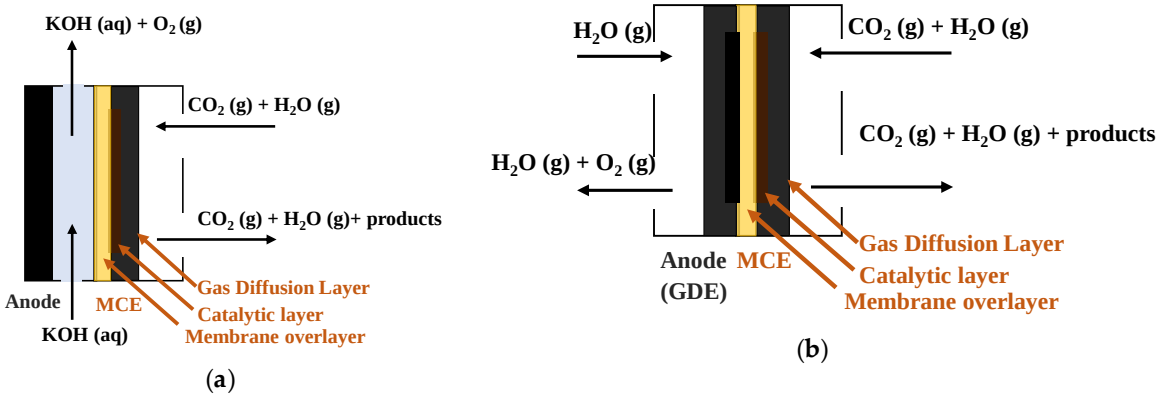

Figure 9. Electrochemical cell reactor configuration using a MCE with the membrane over layer as selective barrier between electrodes (**a**), and as solid polyelectrolyte barrier (**b**).

The development of advanced membrane materials with transport and catalytic properties may allow the implementation of the MCE in a reactor cell configuration where the membrane functions as solid catalytic polyelectrolyte, as represented in **Figure 9(b).** In this case, the anodic GDE is placed directly next to the membrane of the MCE. This cell design would eliminate all the aforementioned disadvantages of working with liquid electrolytes, but the role of the membrane is extremely important for the reactor behavior, thus the fabrication of an MCE for this structure is a challenging task that could be facilitated by the introduction of advanced polymers and materials into the design of novel electrode configuration [65] and the understanding of the mechanisms involved in their performance [64].

The placement and location of the membrane in the reactor configuration should help adapting the recently appeared works on modeling regarding anion-exchange membranes [16,66] to develop of new membrane designs enabling the improvement of CO_2R reactors by taking into account a more active role of the membrane in membrane-type reactors needed for large-scale implementation [45].

4. Conclusions

In the past decade, research on the development of heterogeneous catalysts and electrode architectures to improve the performance of electrochemical devices and processes has been boosted for many applications, and since one of the challenges is the loss due to mass transport, the use of membranes to enhance electrode performance has also been explored for many applications, from sensors to the protection of surfaces. The potential of this knowledge to enhance the conversion of carbon dioxide into high value-added products has increased in the last years exponentially as well, due to the urgent need to control greenhouse emissions and energy resources. In this light, China and United States of America have collaborated in the research of such architectures and their application I environmental challenges; whereas other countries such as Japan, Taiwan, Chile, and so on have also reported largely cited papers in the CO_2 conversion field, with collaborations within the frontiers of their countries. Most publications report experimental studies at laboratory scale, but in the last two years an interest has arisen to gain understanding on the role of membrane over-layer coated on the electrode and several modelling works have seen the light, shifting the subject area and sources devoted to this topic from analytical chemistry towards chemical engineering.

By screening and analyzing the keywords, we found that modified electrodes surface by coating is a most widely studied method to increase the sensitivity of the electrochemical devices, therefore its relevance to increase the efficiency of CO_2 electroreduction. Still many of the works agree that the choice of catalyst is the key element to improve the selectivity of the product and multi-electron transport abilities. However, the new electrode architectures require the understanding of the

electrochemistry and mass transport in alkaline media at an engineering level in order to design the right reactor for the CO_2 conversion and energy storage the planet needs.

Author Contributions: For research articles with several authors, a short paragraph specifying their individual contributions must be provided. The following statements should be used "Conceptualization and writing – original draft preparation, C.C.C. and A.M.M.; methodology, C.C.C.; formal analysis, investigation and resources, A.G. and A.I.G.; all.; visualization, C.C.C.; supervision and project administration, A.G. and A.I..; All authors have read and agreed to the published version of the manuscript

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References

[1] M. Gattrell, N. Gupta, A. Co, A review of the aqueous electrochemical reduction of CO2 to hydrocarbons at copper, J. Electroanal. Chem. 594 (2006) 1–19. https://doi.org/10.1016/j.jelechem.2006.05.013.

[2] D.M. Weekes, D.A. Salvatore, A. Reyes, A. Huang, C.P. Berlinguette, Electrolytic CO2 Reduction in a Flow Cell, Acc. Chem. Res. 51 (2018) 910–918. https://doi.org/10.1021/acs.accounts.8b00010.

[3] W. Yang, K. Dastafkan, C. Jia, C. Zhao, Design of Electrocatalysts and Electrochemical Cells for Carbon Dioxide Reduction Reactions, Adv. Mater. Technol. 3 (2018) 1–20. https://doi.org/10.1002/admt.201700377.

[4] W. Lee, Y.E. Kim, M.H. Youn, S.K. Jeong, K.T. Park, Catholyte-Free Electrocatalytic CO2 Reduction into Formate, Angew. Chemie Int. Ed. 10.1002/an (2018) 10–15. https://doi.org/10.1002/anie.201803501.

[5] G. Díaz-Sainz, M. Alvarez-Guerra, J. Solla-Gullón, L. García-Cruz, V. Montiel, A. Irabien, Catalyst coated membrane electrodes for the gas phase CO 2 electroreduction to formate, Catal. Today. (2018). https://doi.org/10.1016/j.cattod.2018.11.073.

[6] R. Lin, J. Guo, X. Li, P. Patel, A. Seifitokaldani, Electrochemical reactors for CO2 conversion, Catalysts. 10 (2020) 27–30. https://doi.org/10.3390/catal10050473.

[7] M.E. Günay, L. Türker, N.A. Tapan, Decision tree analysis for efficient CO2utilization in electrochemical systems, J. CO2 Util. 28 (2018) 83–95. https://doi.org/10.1016/j.jcou.2018.09.011.

[8] Y. Xing, Z. Ma, W. Su, Q. Wang, X. Wang, H. Zhang, Analysis of Research Status of CO 2 Conversion, Catalysts. 10 (2020) 1–18. https://doi.org/doi: 10.3390/catal10040370.

[9] Y. Hori, Electrochemical CO 2 Reduction on Metal Electrodes, in: C.G. Vayenas, R.E. White (Eds.), Mod. Asp. Electrochem., Springer, New York, 2008: pp. 89–189.

[10] S. Nitopi, E. Bertheussen, S.B. Scott, X. Liu, A.K. Engstfeld, S. Horch, B. Seger, I.E.L. Stephens, K. Chan, C. Hahn, J.K. Nørskov, T.F. Jaramillo, I. Chorkendorff, Progress and Perspectives of Electrochemical

CO2 Reduction on Copper in Aqueous Electrolyte, Chem. Rev. 119 (2019) 7610–7672. https://doi.org/10.1021/acs.chemrev.8b00705.

[11] K. Yang, R. Kas, W.A. Smith, In Situ Infrared Spectroscopy Reveals Persistent Alkalinity near Electrode Surfaces during CO2 Electroreduction, J. Am. Chem. Soc. 141 (2019). https://doi.org/10.1021/jacs.9b07000.

[12] G.O. Larrazábal, A.J. Martín, S. Mitchell, R. Hauert, J. Pérez-Ramírez, Enhanced Reduction of CO2 to CO over Cu-In Electrocatalysts: Catalyst Evolution Is the Key, ACS Catal. 6 (2016) 6265–6274. https://doi.org/10.1021/acscatal.6b02067.

[13] S. Das, J. Pérez-Ramírez, J. Gong, N. Dewangan, K. Hidajat, B.C. Gates, S. Kawi, Core-shell structured catalysts for thermocatalytic, photocatalytic, and electrocatalytic conversion of CO2, Chem. Soc. Rev. 49 (2020) 2937–3004. https://doi.org/10.1039/c9cs00713j.

[14] C. Costentin, M. Robert, J.M. Savéant, Current Issues in Molecular Catalysis Illustrated by Iron Porphyrins as Catalysts of the CO2-to-CO Electrochemical Conversion, Acc. Chem. Res. 48 (2015) 2996–3006. https://doi.org/10.1021/acs.accounts.5b00262.

[15] D. V. Esposito, Membrane-Coated Electrocatalysts - An Alternative Approach to Achieving Stable and Tunable Electrocatalysis, ACS Catal. 8 (2018) 457–465. https://doi.org/10.1021/acscatal.7b03374.

[16] L.C. Brée, M. Wessling, A. Mitsos, Modular modeling of electrochemical reactors: Comparison of CO2-electolyzers, Comput. Chem. Eng. 139 (2020) 10.1016/j.compchemeng.2020.106890. https://doi.org/10.1016/j.compchemeng.2020.106890.

[17] A. Marcos-Madrazo, C. Casado-Coterillo, Á. Irabien, Sustainable Membrane-Coated Electrodes for CO2 Electroreduction to Methanol in Alkaline Media, ChemElectroChem. 6 (2019) 5273–5282. https://doi.org/10.1002/celc.201901535.

[18] R. Abejón, H. Pérez-Acebo, A. Garea, A bibliometric analysis of research on supported ionic liquid membranes during the 1995-2015 period: Study of the main applications and trending topics, Membranes (Basel). 7 (2017) 1–28. https://doi.org/10.3390/membranes7040063.

[19] Elsevier, Scopus, SCOPUS. (2019). https://www.scopus.com/search/form.uri?display=basic (accessed May 31, 2020).

[20] T.R. O'Toole, T.J. Meyer, B. Patrick Sullivan, Electrocatalytic Reduction of CO 2 by Thin Polymeric Films Containing Metallic Rhodium, Chem. Mater. 1 (1989) 574–576. https://doi.org/10.1021/cm00006a004.

[21] T.R. O'Toole, B.P. Sullivan, M.R.M. Bruce, L.D. Margerum, R.W. Murray, T.J. Meyer, Electrocatalytic reduction of CO2 by a complex of rhenium in thin polymeric films, J. Electroanal. Chem. 259 (1989) 217–239. https://doi.org/10.1016/0022-0728(89)80049-X.

[22] G.K.S. Prakash, F.A. Viva, G.A. Olah, Electrochemical reduction of CO 2 over Sn-Nafion ® coated electrode for a fuel-cell-like device, J. Power Sources. 223 (2013) 68–73. https://doi.org/10.1016/j.jpowsour.2012.09.036.

[23] R. Aydin, H.Ö. Doğan, F. Köleli, Electrochemical reduction of carbon dioxide on polypyrrole coated copper electro-catalyst under ambient and high pressure in methanol, Appl. Catal. B Environ. 140–141 (2013) 478–482. https://doi.org/10.1016/j.apcatb.2013.04.021.

[24] R. Schrebler, P. Cury, F. Herrera, H. Gómez, R. Córdova, Study of the electrochemical reduction of CO2 on electrodeposited rhenium electrodes in methanol media, J. Electroanal. Chem. 516 (2002) 23–30. https://doi.org/10.1016/s0022-0728(01)00638-6.

[25] A.P. Periasamy, R. Ravindranath, S.M. Senthil Kumar, W.P. Wu, T.R. Jian, H.T. Chang, Facet- and structure-dependent catalytic activity of cuprous oxide/polypyrrole particles towards the efficient reduction of carbon dioxide to methanol, Nanoscale. 10 (2018) 11869–11880. https://doi.org/10.1039/c8nr02117a.

[26] A. Del Castillo, M. Alvarez-Guerra, J. Solla-Gullón, A. Sáez, V. Montiel, A. Irabien, Sn nanoparticles on gas diffusion electrodes: Synthesis, characterization and use for continuous CO2electroreduction to formate, J. CO2 Util. 18 (2017) 222–228. https://doi.org/10.1016/j.jcou.2017.01.021.

[27] Q. Lu, F. Jiao, Electrochemical CO2 reduction: Electrocatalyst, reaction mechanism, and process engineering, Nano Energy. 29 (2016) 439–456. https://doi.org/10.1016/j.nanoen.2016.04.009.

[28] I. Merino-Garcia, E. Alvarez-Guerra, J. Albo, A. Irabien, Electrochemical membrane reactors for the utilisation of carbon dioxide, Chem. Eng. J. 305 (2016) 104–120. https://doi.org/10.1016/j.cej.2016.05.032.

[29] B. Endrődi, G. Bencsik, F. Darvas, R. Jones, K. Rajeshwar, C. Janáky, Continuous-flow electroreduction of carbon dioxide, Prog. Energy Combust. Sci. 62 (2017) 133–154. https://doi.org/10.1016/j.pecs.2017.05.005.

[30] J.R. Varcoe, P. Atanassov, D.R. Dekel, A.M. Herring, M.A. Hickner, P.A. Kohl, A.R. Kucernak, W.E. Mustain, K. Nijmeijer, K. Scott, T. Xu, L. Zhuang, Anion-exchange membranes in electrochemical energy systems, Energy Environ. Sci. 7 (2014) 3135–3191. https://doi.org/10.1039/c4ee01303d.

[31] C. Dinh, T. Burdyny, G. Kibria, A. Seifitokaldani, C.M. Gabardo, F.P.G. de Arquer, A. Kiani, J.P. Edwards, P. De Luna, O.S. Bushuyev, C. Zou, R. Quintero-Bermudez, Y. Pang, D. Sinton, E.H. Sargent, CO2 electroreduction to ethylene via hydroxide -mediated copper catalysis at an abrupt interface, Science (80-.). 360 (2018) 1–5. https://doi.org/10.1126/science.aas9100.

[32] W. Lee, Y.E. Kim, M.H. Youn, S.K. Jeong, K.T. Park, Catholyte-Free Electrocatalytic CO 2 Reduction to Formate, Angew. Chemie - Int. Ed. 57 (2018) 6883–6887. https://doi.org/10.1002/anie.201803501.

[33] C.T. Dinh, T. Burdyny, G. Kibria, A. Seifitokaldani, C.M. Gabardo, F. Pelayo García De Arquer, A. Kiani, J.P. Edwards, P. De Luna, O.S. Bushuyev, C. Zou, R. Quintero-Bermudez, Y. Pang, D. Sinton, E.H. Sargent, F.P.G. de Arquer, A. Kiani, J.P. Edwards, P. De Luna, O.S. Bushuyev, C. Zou, R. Quintero-Bermudez, Y. Pang, D. Sinton, E.H. Sargent, Sustained high-selectivity CO 2 electroreduction to ethylene via hydroxide-mediated catalysis at an abrupt reaction interface, Science (80-.). 360 (2018) 783–787. https://doi.org/10.1126/science.aas9100.

[34] S. Ma, M. Sadakiyo, R. Luo, M. Heima, M. Yamauchi, P.J.A. Kenis, One-step electrosynthesis of ethylene and ethanol from CO2 in an alkaline electrolyzer, J. Power Sources. 301 (2016) 219–228. https://doi.org/10.1016/j.jpowsour.2015.09.124.

[35] R.B. Kutz, Q. Chen, H. Yang, S.D. Sajjad, Z. Liu, I.R. Masel, Sustainion Imidazolium-Functionalized Polymers for Carbon Dioxide Electrolysis, Energy Technol. 5 (2017) 929–936. https://doi.org/10.1002/ente.201600636.

[36] H. Yang, J.J. Kaczur, S.D. Sajjad, R.I. Masel, Electrochemical conversion of CO2 to formic acid utilizing Sustainion™ membranes, J. CO2 Util. 20 (2017) 208–217. https://doi.org/10.1016/j.jcou.2017.04.011.

[37] L.M. Aeshala, R.G. Uppaluri, A. Verma, Effect of cationic and anionic solid polymer electrolyte on direct electrochemical reduction of gaseous CO2 to fuel, J. CO2 Util. 3–4 (2013) 49–55. https://doi.org/10.1016/j.jcou.2013.09.004.

[38] L.M. Aeshala, S.U. Rahman, A. Verma, Effect of solid polymer electrolyte on electrochemical reduction of CO 2, Sep. Purif. Technol. 94 (2012) 131–137. https://doi.org/10.1016/j.seppur.2011.12.030.

[39] N. Ziv, W.E. Mustain, D.R. Dekel, The Effect of Ambient Carbon Dioxide on Anion-Exchange Membrane Fuel Cells, ChemSusChem. 11 (2018) 1136–1150. https://doi.org/10.1002/cssc.201702330.

[40] K. Yang, R. Kas, W.A. Smith, In Situ Infrared Spectroscopy Reveals Persistent Alkalinity near Electrode Surfaces during CO 2 Electroreduction, J. Am. Chem. Soc. 141 (2019) 15891–15900. https://doi.org/10.1021/jacs.9b07000.

[41] G. Wang, J. Pan, S.P. Jiang, H. Yang, Gas phase electrochemical conversion of humidified CO2 to CO and H2 on proton-exchange and alkaline anion-exchange membrane fuel cell reactors, J. CO2 Util. 23 (2018) 152–158. https://doi.org/10.1016/j.jcou.2017.11.010.

[42] Y. Zheng, U. Ash, R.P. Pandey, A.G. Ozioko, J. Ponce-gonza, M. Handl, T. Weissbach, J.R. Varcoe, S. Holdcroft, M.W. Liberatore, R. Hiesgen, D.R. Dekel, Water Uptake Study of Anion Exchange Membranes, Macromolecules. 51 (2018) 3264–3278. https://doi.org/10.1021/acs.macromol.8b00034.

[43] D.R. Dekel, Review of cell performance in anion exchange membrane fuel cells, J. Power Sources. 375 (2018) 158–169. https://doi.org/10.1016/j.jpowsour.2017.07.117.

[44] C.E. Diesendruck, D.R. Dekel, Water – A key parameter in the stability of anion exchange membrane fuel cells, Curr. Opin. Electrochem. 9 (2018) 173–178. https://doi.org/10.1016/j.coelec.2018.03.019.

[45] O.G. Sánchez, Y.Y. Birdja, M. Bulut, J. Vaes, T. Breugelmans, D. Pant, Recent advances in industrial CO2 electroreduction, Curr. Opin. Green Sustain. Chem. https://do (2019). https://doi.org/10.1016/j.cogsc.2019.01.005.

[46] L.M. Aeshala, R. Uppaluri, A. Verma, Electrochemical conversion of CO 2 to fuels: Tuning of the reaction zone using suitable functional groups in a solid polymer electrolyte, Phys. Chem. Chem. Phys. 16 (2014) 17588–17594. https://doi.org/10.1039/c4cp02389g.

[47] Z. Liu, H. Yang, R. Kutz, R.I. Masel, CO2 electrolysis to CO and O2 at high selectivity, stability and efficiency using sustainion membranes, J. Electrochem. Soc. 165 (2018) J3371–J3377. https://doi.org/10.1149/2.0501815jes.

[48] S. Ponnurangam, I. V. Chernyshova, P. Somasundaran, Nitrogen-containing polymers as a platform for CO2 electroreduction, Adv. Colloid Interface Sci. 244 (2017) 184–198. https://doi.org/10.1016/j.cis.2016.09.002.

[49] M.E.S. Beatty, H. Chen, N.Y. Labrador, B.J. Lee, D. V. Esposito, Structure-property relationships describing the buried interface between silicon oxide overlayers and electrocatalytic platinum thin films, J. Mater. Chem. A. 6 (2018) 22287–22300. https://doi.org/10.1039/C8TA06969G.

[50] Y. Liu, K.Y. Leung, S.E. Michaud, T.L. Soucy, C.C.L. McCrory, Controlled Substrate Transport to Electrocatalyst Active Sites for Enhanced Selectivity in the Carbon Dioxide Reduction Reaction, Comments Inorg. Chem. 39 (2019) 242–269. https://doi.org/10.1080/02603594.2019.1628025.

[51] S. Sato, B.J. McNicholas, R.H. Grubbs, Aqueous electrocatalytic CO2 reduction using metal complexes dispersed in polymer ion gels, Chem. Commun. 56 (2020) 4440–4443. https://doi.org/10.1039/d0cc00791a.

[52] I.G. Casella, An electrochemical and XPS study of Ag-Pb binary alloys incorporated in Nafion® coatings, J. Appl. Electrochem. 31 (2001) 481–488. https://doi.org/10.1023/A:1017535203548.

[53] Y. Lin, H. Li, C. Liu, W. Xing, X. Ji, Surface-modified Nafion membranes with mesoporous SiO2 layers via a facile dip-coating approach for direct methanol fuel cells, J. Power Sources. 185 (2008) 904–908. https://doi.org/10.1016/j.jpowsour.2008.08.067.

[54] C.T. Dinh, T. Burdyny, G. Kibria, A. Seifitokaldani, C.M. Gabardo, F. Pelayo García De Arquer, A. Kiani, J.P. Edwards, P. De Luna, O.S. Bushuyev, C. Zou, R. Quintero-Bermudez, Y. Pang, D. Sinton, E.H. Sargent, CO2 electroreduction to ethylene via hydroxide-mediated copper catalysis at an abrupt interface, Science (80-.). 360 (2018) 783–787. https://doi.org/10.1126/science.aas9100.

[55] L. García-Cruz, C. Casado-Coterillo, J. Iniesta, V. Montiel, A. Irabien, Chitosan: Poly (vinyl) alcohol composite alkaline membrane incorporating organic ionomers and layered silicate materials into a PEM electrochemical reactor, J. Memb. Sci. 498 (2016) 395–407. https://doi.org/10.1016/j.memsci.2015.08.040.

[56] W. Phompan, N. Hansupalak, Improvement of proton-exchange membrane fuel cell performance using platinum-loaded carbon black entrapped in crosslinked chitosan, J. Power Sources. 196 (2011) 147–152. https://doi.org/10.1016/j.jpowsour.2010.06.110.

[57] R. Schrebler, P. Cury, C. Sua, E. Mun, R. Co, Study of the electrochemical reduction of CO2 on a polypyrrole electrode modified by rhenium and copper-rhenium microalloy in methanol media, J. Electroanal. Chem. 533 (2002) 167–175. https://doi.org/10.1016/S0022-0728(02)01086-0.

[58] A.N. Grace, S.Y. Choi, M. Vinoba, M. Bhagiyalakshmi, D.H. Chu, Y. Yoon, S.C. Nam, S.K. Jeong, Electrochemical reduction of carbon dioxide at low overpotential on a polyaniline/Cu2O nanocomposite based electrode, Appl. Energy. 120 (2014) 85–94. https://doi.org/10.1016/j.apenergy.2014.01.022.

[59] A. Sacco, Electrochemical impedance spectroscopy as a tool to investigate the electroreduction of carbon dioxide: A short review, J. CO2 Util. 27 (2018) 22–31. https://doi.org/10.1016/j.jcou.2018.06.020.

[60] J.E. Robinson, N.Y. Labrador, H. Chen, B.E. Sartor, D. V. Esposito, Silicon Oxide -Encapsulated Platinum Thin Films as Highly Active Electrocatalysts for Carbon Monoxide and Methanol Oxidation, ACS Catal. 8 (2018) 11423–11434. https://doi.org/10.1021/acscatal.8b03626.

[61] A. Marcos-Madrazo, C. Casado-Coterillo, L. García-Cruz, J. Iniesta, L. Simonelli, V. Sebastián, M. Encabo-Berzosa, M. Arruebo, A. Irabien, Preparation and Identification of Optimal Synthesis Conditions for a Novel Alkaline Anion-Exchange Membrane, Polymers (Basel). 10 (2018) 913. https://doi.org/10.3390/polym10080913.

[62] S.C. Perry, P. Leung, L. Wang, C.P. de León, Developments on carbon dioxide reduction: their promise, achievements and challenges, Curr. Opin. Electrochem. 20 (2020) 88–98. https://doi.org/10.1016/j.coelec.2020.04.014.

[63] F. Pelayo-García de Arquer, C.-T. Dinh, A. Ozden, J. Wicks, C. McCallum, A.R. Kirmani, D.H. Nam, C. Gabardo, A. Seifitokaldani, X. Wang, Y.C. Li, F. Li, J. Edwards, L.J. Richter, S.J. Thorpe, D. Sinton, E.H. Sargent, CO2 electrolysis to multicarbon products at activities greater than 1 A cm−2, Science (80-.). 367 (2020) 661–666. https://doi.org/10.1126/science.aay4217.

[64] J.B. Vennekoetter, R. Sengpiel, M. Wessling, Beyond the catalyst: How electrode and reactor design determine the product spectrum during electrochemical CO2 reduction, Chem. Eng. J. 364 (2019) 89–101. https://doi.org/10.1016/j.cej.2019.01.045.

[65] C.M. Gabardo, R.C. Adams-McGavin, B.C. Fung, E.J. Mahoney, Q. Fang, L. Soleymani, Rapid prototyping of all-solution-processed multi-lengthscale electrodes using polymer-induced thin film wrinkling, Sci. Rep. 7 (2017) 1–9. https://doi.org/10.1038/srep42543.

[66] H. Deng, D. Wang, X. Xie, Y. Zhou, Y. Yin, Q. Du, K. Jiao, Modeling of hydrogen alkaline membrane fuel cell with interfacial effect and water management optimization, Renew. Energy. 91 (2016) 166–177. https://doi.org/10.1016/j.renene.2016.01.054.