An Analysis of Research on Membrane-Coated Electrodes in the 2001–2019 Period: Potential Application to CO$_2$ Capture and Utilization

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Abstract: The chemistry and electrochemistry basic fields have been active for the last two decades of the past century studying how the modification of the electrodes' surface by coating with conductive thin films enhances their electrocatalytic activity and sensitivity. In light of the development of alternative sustainable ways of energy storage and carbon dioxide conversion by electrochemical reduction, these research studies are starting to jump into 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 and reactor configurations. Membranes can help with understanding and controlling the mass transport limitations of current electrodes as well as leading to novel reactor designs. The present work makes use of a bibliometric analysis directed to the papers published in the 21st century on membrane-coated electrodes and electrocatalysts to enhance the electrochemical reactor performance and their potential in the urgent issue of carbon dioxide capture and utilization.

Keywords: CO$_2$; conversion; bibliometrics; electrode design; CO$_2$R; membrane; flow cell

1. Introduction

The sharp rise of the concentration of carbon dioxide in the atmosphere due to fossil fuels consumption is acknowledged as the main cause of environmental and health problems threatening humans' living environment irreversibly. Reducing carbon dioxide emissions while addressing energy shortages requires the conversion of CO$_2$ into commercial products. The electrochemical reduction of CO$_2$ would be a low-temperature alternative if the intermittency of renewable electricity production and its storage in energy bonds of chemical fuels were commercial [1]. These improvements have been generally addressed by focusing on the optimization of electrocatalysts, electrodes, reactor types, and flow cell systems, which often differ in the type of ion exchange membrane whose role is limited to the separator between cell compartments and ion transfer, type of electrolyte, and phase as well as strategies on flow channel and compartments design [2–6].

Electrocatalysis is an interfacial phenomenon, the relative ratio of CO$_2$ and H$_2$(H$^+$) being dictated by the intrinsic selectivity of surface-active sites and the local concentration of reaction compounds involved in the different rate-controlling stages;—there is a need for understanding the mechanisms involved for designing selective and stable reactors and electrodes [2]. A range of transition metals exhibits electrocatalytic activity for CO$_2$R [7,8]. However, the CO$_2$R activity and selectivity is strongly influenced by the activation barrier and binding energy of intermediate species and the metal catalyst [9]. Playing with heterogeneous surface and pore structures as well with functional groups such as OH has

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_2R [10]. Copper allows tuning the balance of reaction intermediate binding energy for stabilization of species leading to hydrocarbons and alcohols, at the expense of selectivity [11], leading to different classes of Cu-based structures, from nanocrystals, nanostructures, nanowires, oxides, mixed oxides, thin-film, polycrystalline, bimetallic, etc. [12]. Recently, statistical analysis of the large amount of dispersed experimental works has been applied to develop decision trees that help to determine the significance of the main variables influencing electrochemical reactor viability in CO_2 conversion, such as Faradaic efficiency (FE), production rate, and the selectivity to a particular product [13], which in complex heterogeneous electrodes may differ from FE [14].

Therefore the interest of CO_2R researchers of developing systems that can tune up the transport of CO_2 and ions to the catalyst active sites [15]. The mass transport limitation on continuous flow electrochemical cells attempted so far 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 than just as separation barrier [16,17].

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 [18]. However, this type of electrode requires additional understanding on the reaction and transport mechanism to develop an adequate polyelectrolyte electrochemical membrane reactor for CO_2 capture and utilization [19,20]. 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 [18]. The role of these OH groups is highly important in the role of alkaline-resistant anion exchange membranes (AAEM) in electrochemical membrane reactors [21,22], with favorable CO_2 conversion by enabling anion transport and work in less corrosive media [23–25]. The OH^- ions near the copper surface lower the CO_2 reduction and CO–CO coupling activating barrier, resulting in the formation of more complex structures such as ethylene [21], although this can be altered by local changes of local pH in the uncoated electrode surface [26].

The membrane-coated electrode configurations under investigation are schematized in Figure 1. Figure 1a is the configuration "Catalyst coated membrane electrode" as with M$^+$@CCM over Nafion for CO_2 electroreduction to formic acid [27], and Figure 1b 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 [28].
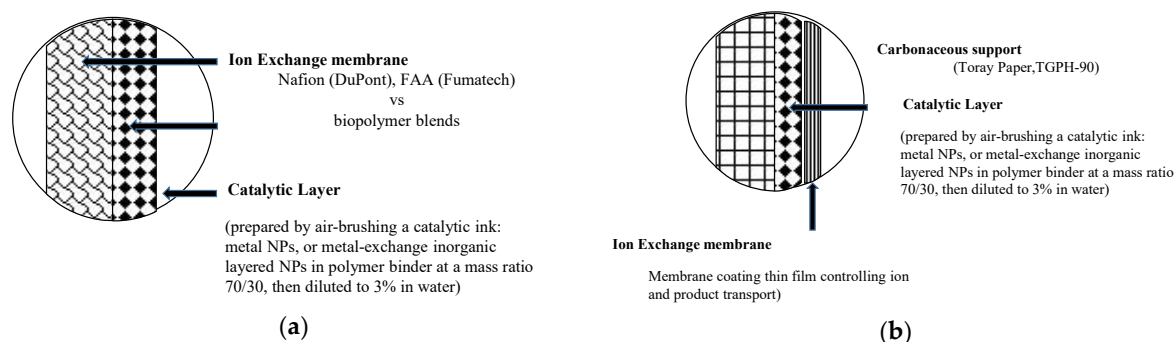

Figure 1. Schematic representation of (**a**) CCM (catalyst-coated membrane) and (**b**) MCEs (membrane-coated electrodes).

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 with up-to-date information and knowledge on the state-of-the-art of the trends and interests in their fields [29]. This technique is

based on statistical analyses, quantitative analyses, and indexes to assess the contribution of authors, institutions, and countries, as well as subject areas on a specific research output. 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 [30]. This work complements that analysis by focusing on membrane-coated electrodes and the role of the membrane.

2. Results and Discussion

The aim of this work is the analysis of the research performed in the last two decades on surface-modified and thin-film-coated electrodes in electrochemistry in the light of how they can address the challenges of CO_2 electroreduction processes in the present. The tool used is a bibliometric analysis of the literature indexed in the Scopus database [31] 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 the 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. The keywords were introduced between inverted commas, because a first search conducted for the same period of time without them led to more than 2500 documents in widely distributed topics, which are not primarily linked with the intended topic of this work.

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 are 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.
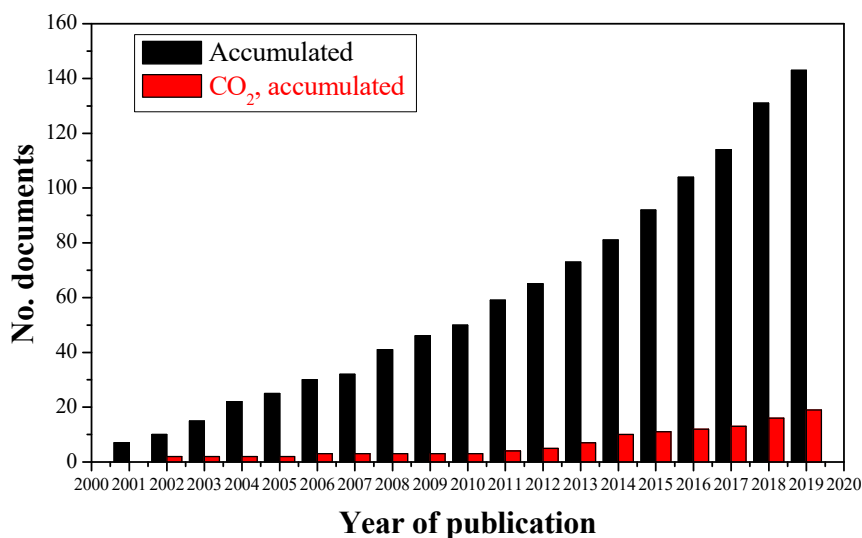

Figure 2. Accumulated publication output for the "membrane-coated electrode" or "membrane-coated electrocatalyst" or "surface-modified electrode" (black) and the "CO_2" applied (red).

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.

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

2.1.2. Distribution of Output in Subject Categories and Journals

The distribution of research subjects can be observed in Table S1 in the Supporting Information, 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.

The distribution of publications in journals is collected in Table S2, which can be found in the Supporting Information. 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 the most documents was *Electrochimica Acta* (19%), which is in line with the interdisciplinarity of the research and application of these electrodes. The papers published in the most productive journals resulting from the bibliometric search deal with the surface modification of carbon-based electrodes aimed at improving chemical sensing properties in biomedical or environmental applications. There is a significant presence of journals regarding surface and interface science and technology, such as ACS Interface Applied Materials, ACS Catalysis, and ChemElectroChem, which are already focusing on the effect of the coated thin film on the electrocatalytic behavior of the electrode [28,32,33].

2.1.3. 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, since the affiliation field of 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 1 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 two documents in the studied search are collected in Table 1. The most productive countries are the 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 1 with contributions in MCEC and CO_2 are Chile, Spain, Turkey, and the United Kingdom, which are 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, as recently reviewed for the electrochemical CO_2 conversion in general [5].

Table 1. The top 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%)

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 productive institutions producing more than one paper under the search terms used in this study are ranked in Table S3 (Supporting Information). These values differ from the distribution between the most productive countries in Table 1 (United States of America, Japan, and China), because the most productive institution is an Australian university, publishing reports regarding the potentiometric titration of surface-modified electrodes for batteries and sensors. This highlights the wide dispersion of institutions publishing on these subjects, which is related to 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 the electroreduction of CO_2 as early as 1989, they are not included in this analysis [34,35].

2.1.4. Most Cited Papers and Author Keywords

The most frequently cited articles of the bibliometric review, now already restricted to CO_2 reduction, are collected in Table 2 below. The most cited work was published in the *Journal of Power Sources* in 2013 and has been cited 120 times [36], and seven belong to journals in the applied catalysis and electrochemical or environmental engineering, dating from 2013 onwards. This fact represents the growing impact of the research on classical electrochemical studies by coating a polymer or composite thin film on the electrodes to the improvement of CO_2 electroreduction processes. They go from activating the CO_2 reduction of metal catalysts by reducing the activation barrier by conductive polymers [37–39] in organic media to aqueous electrolytes [40,41], most directly scalable to large applications [42,43], although aqueous media may complicate the understanding of the reaction mechanisms occurring in the already difficult Cu-based electrocatalytic conversion system [44,45].

Table 2. The top most cited articles mentioned coated electrodes or electrocatalysts.

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 Authors: Schrebler, R., Cury, P., Muñoz, E., Gómez, H., Córdova, R. Source: Journal of Electroanalytical Chemistry Published: 2002	28
8	Facet- and structure-dependent catalytic activity of cuprous oxide/polypyrrole particles towards the efficient reduction of carbon dioxide to methanol Author(s): Periasamy A.P., Ravindranath R., Senthil Kumar S.M., Wu W.-P., Jian T.-R., Chang H.-T. Source: Nanoscale Published: 2018	15
9	Sustainable membrane-coated electrodes for CO_2 electroreduction to methanol in alkaline media Author(s): Marcos-Madrazo, A., Casado-Coterillo, C., Irabien, A. Source: ChemElectroChem Published: 2019	2

Figure 3 represents the most often encountered author keywords in the analyzed works of this bibliometric analysis. Most are related to composite materials—coated or surfaced-modified electrodes or electrocatalysts, as well as solid polymer electrolytes. 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 for added value products. The variability of the keywords accounts for the variability of the applications under study, although the materials are generally repeated, as conducting polymers (polyaniline, polypyrrole, porphyrin, chitosan . . .) [28,39,40] and metal oxide (mostly, SiO_x) matrices to metal catalyst nanoparticles [32,33,46] and Nafion as the principal solid polymer electrolyte membrane [36,47]. In fact, conductive poly(4-vinyl pyridine) (PVP) polymer and hydrophilic chitosan

biopolymer were coated over Cu electrodes before the time range of this study in electrochemistry studies for electroreduction reaction [48] and enhancing Cu sensitivity in humidity sensors [49] and used again for the development of coated electrodes [28,50]. In addition, the keywords cited less than two times mostly deal with the insight in understanding the transport and reaction mechanisms and equations modeling, and they are not included in Figure 3, but they are mentioned here given their relevance to the development of the process.
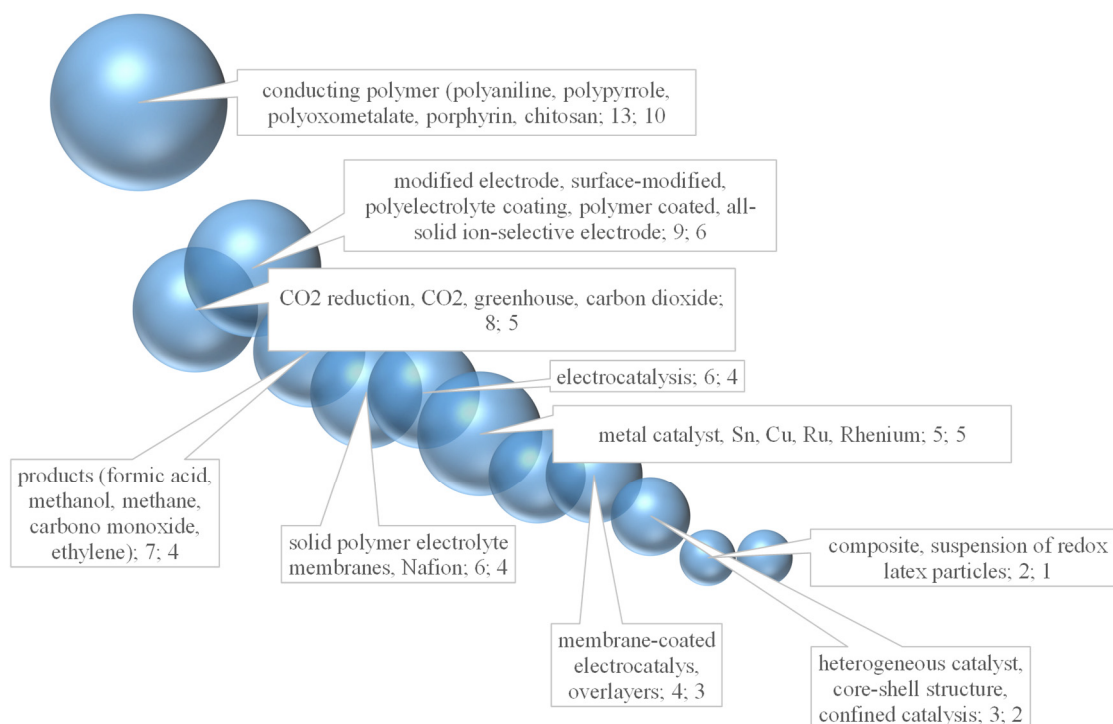
Figure 3. Most common author keywords.

2.2. Some Keynotes for Discussion

The evolution of MCEC and membrane-coated electrode (MCE) in electrochemical engineering and catalytic literature has evolved from gas diffusion electrodes (GDE) preparation by coating metal catalysts dispersed in Nafion ionomer [36] to enhancing the selectivity of the electrocatalysts by coating the electrode with a conductive polymer, which is usually polypyrrole-based when the reaction media is methanol [37,38] and most recently aqueous media [40], as mentioned above in the bibliometric analysis. For CO_2 electrochemical selective reduction conversion in alkaline media, the understanding of the role of the membrane coating in the diffusion and interaction metal–matrix must be improved for the optimal design of electrodes and reactors, as will be discussed briefly in this article.

2.2.1. Role of Membranes for CO_2 Electroreduction

The traditional role of the membrane in zero-gap CO_2 electrolyzers has been just that of the solid polyelectrolyte barrier that separates the anode and cathode and controls the flow of ions from one-half reaction to another while simultaneously attenuating the product crossover. They are usually cation-exchange membranes, as Nafion®, allowing CO_2 and H^+ transport at acidic or neutral pH [3,4,51,52]. In alkaline conditions, 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. On the other hand, anion exchange membranes (AEMs) work by facilitating the flow of OH^- anions from the cathode to the anode [53]. The low solubility of CO_2 in aqueous solutions is a relevant concern regarding its transport to the catalyst [54], especially in high pH media when CO_2 rapidly reacts to form HCO_3^- and CO_3^{2-}, whose

mobility is lower than that of OH^- and thus may inhibit ion transport and reduce CO_2 reduction efficiency [21]. As commented earlier in the introduction, gas diffusion electrodes are the most studied approach to solve this issue, allowing CO_2 to diffuse faster through the porous layer and reach the catalyst's active sites before reacting with the electrolyte [23]. Figure 4 shows a typical cell configuration in which a GDE is employed.
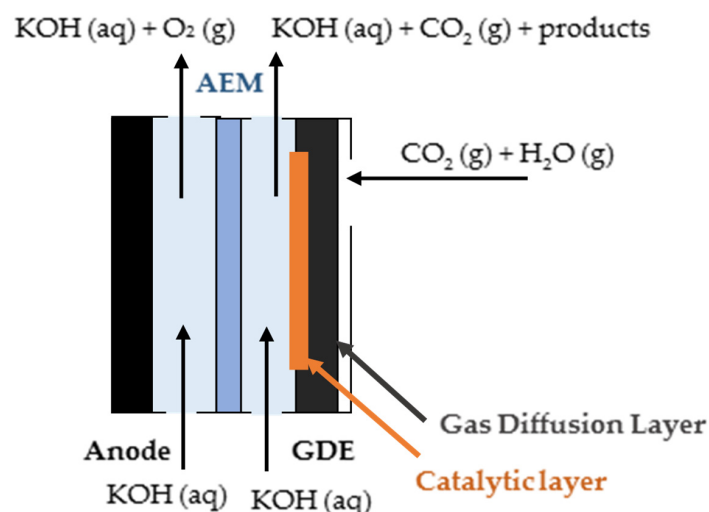

Figure 4. Electrochemical cell reactor configuration using aqueous electrolytes in both compartments.

The advantages of this cell configuration are the mentioned facilitation of CO_2 transport through the gas diffusion layer and the influence of pH. The employment of KOH or $KHCO_3$ as electrolyte in the cathode chamber has been widely discussed, generally concluding that the higher alkaline conditions provided by KOH significantly reduced the ohmic losses due to higher electrolyte conductivity (than $KHCO_3$) [23] and the promotion of CO_2R reaction kinetics [21]. Thus, the anion transport mechanism is more suitable for CO_2 reduction in AEM than cation exchange membrane (CEM) systems, 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 [24,25]. Aeshala et al. [55,56] highlighted the improved CO_2RR efficiency of quaternary ammonium groups in anionic solid polymer electrolytes. Dioxide Materials have 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 [24].

The main disadvantage of such an alkaline AEM reactor configuration is the carbonation of the electrolyte by the unreacted CO_2 [57]. This 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 electrolyzers [26]. One approach to eliminate the liquid electrolyte is using gas-phase electrochemical reactors, as using a humidified gaseous CO_2 feed stream increased the performance, demonstrating the importance of adequate hydration within the cell during gas electrolysis [58]. 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 [59–61]. 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; for instance, 3D printing techniques allow rapid prototyping and the optimization of different flow field geometries, directly with the reactor design, from H-type to continuous flow reactors [52].

By eliminating the liquid aqueous electrolyte in the cathodic chamber (Figure 5a) or even in both compartments (Figure 5b), this issue might be overcome. When an aqueous anolyte is supplied, as in Figure 5a, an ion exchange takes place with the membrane that provides the OH^- concentration in the diffusion layer and facilitates the hydration of the membrane.
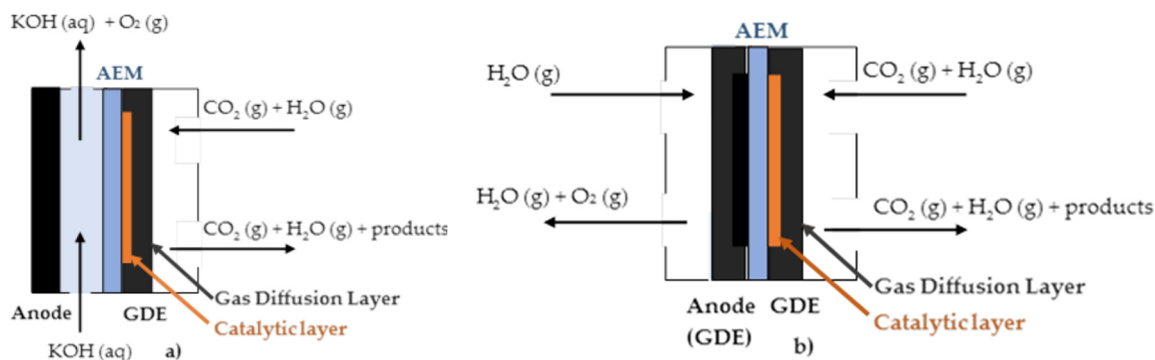

Figure 5. Electrochemical cell reactor configuration (**a**) using liquid aqueous electrolytes only in the anode chamber and (a) without liquid phase electrolytes (**b**).

In these configurations, the AEM is directly in contact with the cathode or with both electrodes.

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 constant throughout the process at both sides of the membrane, as well as the water uptake and ion exchange properties [57,59], opening up the potential of novel membrane materials in the development of zero-gap electrolyzers.

The suppression of aqueous electrolytes in both chambers separated by a solid alkaline polyelectrolyte membrane similar to that used by Aeshala et al. is represented in Figure 5b. Aeshala et al. used a similar configuration to avoid problems of liquid electrolytes as those mentioned earlier, and also leaks and corrosion [62]. However, it has been observed that the lack of aqueous electrolytes hinders the transport of liquid products, mainly alcohols and formate, through the Sustainion® AEM, which is why they are focused on the generation of gas products, mainly CO [25,63]. Therefore, the role of the membrane becomes crucial and not only limited to the separation barrier between the cathode and anode compartments, providing the charge transfer between electrodes while maintaining a constant alkaline media for the reaction, giving scope to the development of novel electrode architectures such as those presented in this paper.

2.2.2. Membrane-Coated Electrodes in the Framework of CO_2 Electroreduction

Regardless of the cell configuration selected, a relevance concern appears when employing GDE: material losses and degradation. Coating a thin film of conductive material over the electrode allows controlling catalyst deactivation and provides new pathways for CO_2 and products transport, altering the diffusion barrier and modulating pH and access to active sites of the catalyst buried in a solid oxide matrix. [46]. The membrane layer applied as coating must meet some requirements: high conductivity to minimize 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 alkaline anion-exchange membrane-coated electrode's transport and catalytic limitations are schematized in Figure 6.
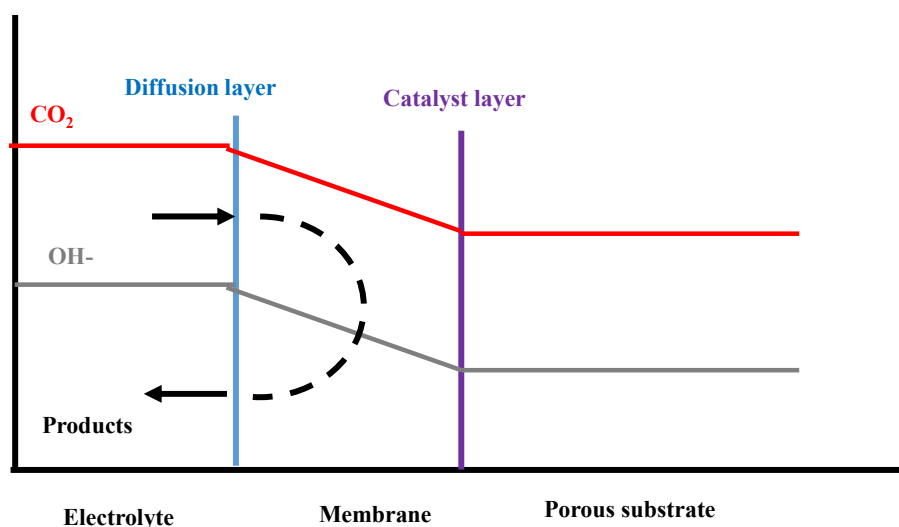
Figure 6. Schematic illustrating gas and ion transport in the membrane-coated electrode (MCE) configuration, adapted from the conventional gas diffusion electrodes (GDE) configuration proposed by Liu et al. [15].

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 is practically unaffected by film thickness [64]. In order to reduce the thickness of the water film in the GDE and reduce the 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 [47]. Coating Pt electrodes by chitosan biopolymer reduced the decline of deactivation voltage in fuel cells [65]. As mentioned earlier, coating the electrode by a conductive polymer also improved the efficiency of electrochemical reduction efficiency in CO_2, O_2, or H_2 reduction to methane in organic media [34,66]. Aydin et al. observed that the coating of Cu-derived nanoparticles in polypyrrole over a Nafion 117 membrane-controlled hydrogen evolution reaction (HER), compared to blank Cu as electrocatalyst, with an FE of 25% and 20% toward CH_4 and formate, respectively, thus shifting the product selectivity and catalyst activity [37]. Grace et al. observed an improvement in the Faradaic efficiency of CO_2 to acetic acid and formic acid by coating a Cu_2O nanoparticle electrode with a polyaniline film [39]. The encapsulation of metal particles into conductive polymers has enhanced the activity of Cu_2O electrocatalysts on the reduction of CO_2 in aqueous media, leading to alcohol production [40,67].

Likewise, the dispersion of metal particles into a polymeric matrix provides the possibility of activating specific areas of metal catalyst and thus improving the catalytic efficiency and selectivity of electrodes, depending on the nature of the functional groups of the polymer [68]. Recently, even complex Cu-containing nanostructures such as HKUST-1 have been embedded in the polypyrrole to enhance the electrocatalytic activity of electrodes by altering ion adsorption and diffusion barriers [69].

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 thin 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 [46] and facilitates the membrane film fabrication as a mixed matrix membrane containing metal ions [70]. This membrane-coated electrode (MCE) configuration invokes 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 controlling product delivery [71].

In this regard, Figure 7 proposes a cell configuration similar to those proposed above in Figure 4, only substituting the GDE by the MCE, where the catalytic particles are protected by the polymer-based membrane overlayer of tunable composition, which is made of Cu exchanged in 2D and 3D zeolite-like inorganic fillers embedded in an anion-exchangeable chitosan (CS):poly(vinyl alcohol) (PVA) polymer matrix [28]. In this scheme, CO_2 is expected to diffuse through the selective membrane and reach the catalyst. Non-aqueous solution is directly in contact with the catalyst material; thus, the alkaline stability and water uptake are also provided by the membrane layer. The products are transported through the porous layer provided by the support and are driven out of the cell by the electrolyte. The membrane coated over the catalyst layer just provided protection to enlarge the electrode durability compared to the GDE morphology. Furthermore, the gas, ion, and electron transport through thin layers of different characters can be decoupled, leading to ethanol or ethylene production, as observed by Pelayo-García de Arquer et al. upon coating Cu-based catalyst with hydrophilic perfluorinated sulfonic acid (PFSA) over hydrophobic porous support [72].
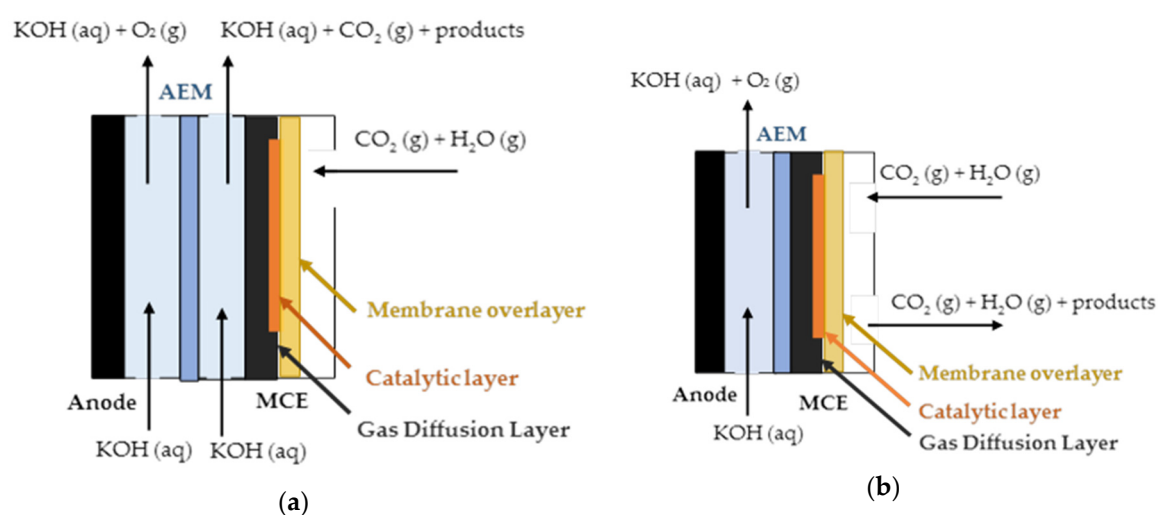

Figure 7. Electrochemical cell reactor configuration using an MCE where the membrane overlayer is facing the CO_2 inlet flow (**a**) and there is no aqueous electrolyte in the cathode chamber (**b**).

As commented above in previous reactor designs in Figures 5 and 6, it would be desirable to remove the aqueous electrolyte from the cathodic compartment, as shown in Figure 7a. 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 a separator between the electrodes, creating a three-compartment reactor similar to those inspired by chlor-alkali and a hydrogen purification large-scale polyelectrolyte membrane reactor reported in the literature [25]. 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 [20].

This leads to attempting another approach, which is represented in Figure 8b. Here, the membrane over-layer acts as a selective barrier between electrodes, simplifying the structure of the reactor by removing the electrolyte and the AEM. This requires the membrane to maintain hydration, ion exchange, and diffusion properties along the process interval, which has been proved by Park et al. in the development of self-humidifying membrane structures where the hydrophilic membrane is protected by a hydrophobic thin layer [73]. This structure is similar to that recently reported by Pelayo-García de Alquer et al. upon tuning hydrophilic and hydrophobic moieties to enhance Cu-based electrocatalysts to convert CO_2 directly to ethylene with high current efficiency [72].
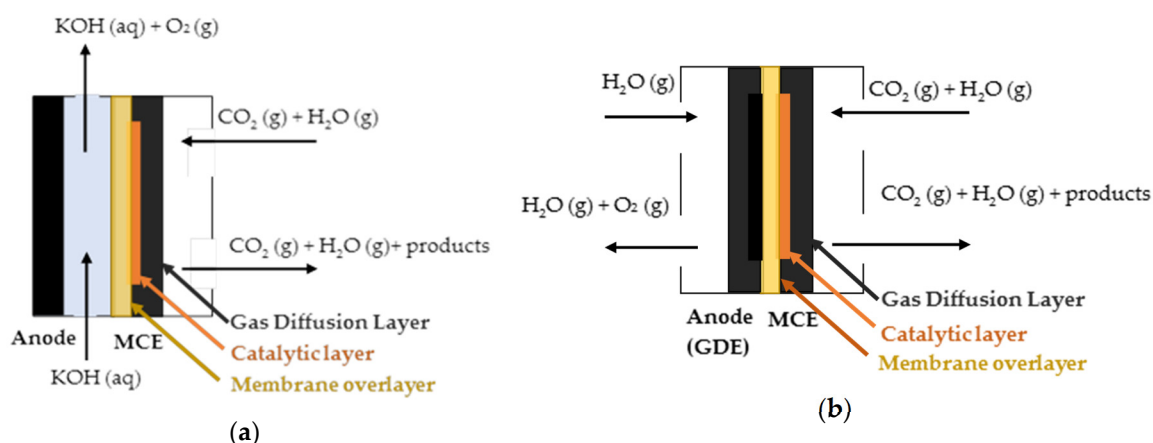
Figure 8. Electrochemical cell reactor configuration using an MCE with the membrane over-layer as a selective barrier between electrodes (**a**) and as a solid polyelectrolyte barrier (**b**).

The fabrication of this kind of structure into a membrane film adequately crosslinked to tune transport and catalytic properties in order to avoid the crossover of products to the anode and allow ions and charge transfer to the cathode, as depicted in Figure 8. This gives scope not only to the research and innovation on electrode and zero-gap reactor design [74], but also on mixed matrix membranes with controllable ion exchange properties [28].

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 a solid catalytic polyelectrolyte, as represented in Figure 8a. 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 [75] and the understanding of the mechanisms involved in their performance [74].

The placement and location of the membrane in the reactor configuration should help adapting the recently appeared works on modeling regarding anion-exchange membranes [20,76] to develop new membrane designs enabling the improvement of CO_2R reactors by considering a more active role of the membrane in membrane-type reactors needed for large-scale implementation [42].

3. 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 thin-film coatings, i.e., membranes, to enhance electrode performance has also been explored for issues as diverse as sensors' sensitivity or the protection of surfaces. The potential of this knowledge to address the challenges of the electrochemical conversion of carbon dioxide into valuable products has increased in the last few years exponentially as well, due to the urgent need to control greenhouse emissions and energy resources. By screening and analyzing the keywords of the bibliometric analysis, we found that the modified electrodes surface by coating is the most widely studied method to increase the sensitivity of the electrochemical devices; therefore, its relevance to increase the efficiency of CO_2 electroreduction. In this light, most publications report experimental studies at the laboratory scale, and 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, in the last couple of years, interest has arisen to gain understanding of the role of the membrane over-layer coated on the electrode, and several modeling works have seen light, shifting the subject area and sources devoted to this topic from analytical chemistry to chemical engineering. In particular, the new electrode architectures require an

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.

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