A Bibliometric Analysis of Research on Membrane Coated Electrodes in the 2001-2019 Period: Potential Application to CO₂ Capture and Utilization

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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 CO₂ 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: CO₂; conversion; bibliometrics; electrode design; CO₂RR; 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 CO₂ into commercial products. Electrochemical reduction of CO₂ 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 CO₂-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 CO₂ conversion, such as faradaic efficiency, production rate and product selectivity.[7] The status of CO₂ 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
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$_2$RR. [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$_2$RR 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$_2$RR [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]

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
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.


2.1.1. 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 CO₂ 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 "CO₂" applied (blue).](https://preprints.org)
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.

<table>
<thead>
<tr>
<th>Ranking</th>
<th>Subject categories</th>
<th>Documents</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Chemistry</td>
<td>110</td>
<td>35.7</td>
</tr>
<tr>
<td>2</td>
<td>Chemical Engineering</td>
<td>49</td>
<td>15.9</td>
</tr>
<tr>
<td>3</td>
<td>Materials Science</td>
<td>41</td>
<td>13.3</td>
</tr>
<tr>
<td>4</td>
<td>Engineering</td>
<td>32</td>
<td>10.4</td>
</tr>
<tr>
<td>5</td>
<td>Energy</td>
<td>23</td>
<td>7.6</td>
</tr>
<tr>
<td>6</td>
<td>Physics &amp; Astronomy</td>
<td>19</td>
<td>6.3</td>
</tr>
<tr>
<td>7</td>
<td>Biochemistry, Genetics</td>
<td>13</td>
<td>4.3</td>
</tr>
<tr>
<td>8</td>
<td>Environmental Science</td>
<td>7</td>
<td>2.6</td>
</tr>
<tr>
<td>9</td>
<td>Medicine</td>
<td>4</td>
<td>1.3</td>
</tr>
<tr>
<td>10</td>
<td>Computer Science</td>
<td>3</td>
<td>1.0</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Ranking</th>
<th>Journal</th>
<th>IF (WoS)</th>
<th>SJR (Scopus)</th>
<th>Documents</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Electrochimica Acta</td>
<td>6.215</td>
<td>1.467</td>
<td>15</td>
<td>19</td>
</tr>
<tr>
<td>2</td>
<td>Journal of Electroanalytical Chemistry</td>
<td>3.807</td>
<td>0.758</td>
<td>9</td>
<td>12</td>
</tr>
<tr>
<td>3</td>
<td>Journal of Power Sources</td>
<td>8.248</td>
<td>1.946</td>
<td>9</td>
<td>12</td>
</tr>
<tr>
<td>4</td>
<td>Electroanalysis</td>
<td>2.544</td>
<td>0.651</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>5</td>
<td>ACS Catalysis</td>
<td>12.340</td>
<td>4.633</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>6</td>
<td>Journal of Solid State Sciences</td>
<td>2.510</td>
<td>0.559</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>8</td>
<td>ChemElectroChem</td>
<td>4.154</td>
<td>1.149</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>9</td>
<td>Journal of Applied Electrochemistry</td>
<td>2.384</td>
<td>0.602</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>10</td>
<td>Journal of the Electrochemical Society</td>
<td>3.721</td>
<td>1.153</td>
<td>3</td>
<td>4</td>
</tr>
</tbody>
</table>

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,
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.

<table>
<thead>
<tr>
<th>Country</th>
<th>TP</th>
<th>SPR</th>
<th>ICPR</th>
<th>FAPR</th>
<th>CAPR</th>
</tr>
</thead>
<tbody>
<tr>
<td>United States</td>
<td>27</td>
<td>16</td>
<td>11</td>
<td>21</td>
<td>22</td>
</tr>
<tr>
<td>China</td>
<td>18</td>
<td>10</td>
<td>8</td>
<td>14</td>
<td>11</td>
</tr>
<tr>
<td>Japan</td>
<td>18</td>
<td>16</td>
<td>2</td>
<td>16</td>
<td>18</td>
</tr>
<tr>
<td>India</td>
<td>13</td>
<td>8</td>
<td>5</td>
<td>11</td>
<td>9</td>
</tr>
<tr>
<td>Australia</td>
<td>11</td>
<td>9</td>
<td>2</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>South Korea</td>
<td>9</td>
<td>7</td>
<td>2</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Italy</td>
<td>8</td>
<td>6</td>
<td>2</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>Canada</td>
<td>7</td>
<td>4</td>
<td>2</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>7</td>
<td>6</td>
<td>5</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>Spain</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>Chile</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Turkey</td>
<td>2</td>
<td>3</td>
<td>0</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

*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.

<table>
<thead>
<tr>
<th>Ranking</th>
<th>Institutions</th>
<th>Documents</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Murdoch University</td>
<td>7</td>
<td>14.9</td>
</tr>
<tr>
<td>2</td>
<td>University of Western Australia</td>
<td>6</td>
<td>12.8</td>
</tr>
<tr>
<td>3</td>
<td>University of Tokyo</td>
<td>4</td>
<td>8.5</td>
</tr>
<tr>
<td></td>
<td>Korea Institute of Science and Technology</td>
<td>4</td>
<td>8.5</td>
</tr>
<tr>
<td>4</td>
<td>Nanjing University</td>
<td>4</td>
<td>8.5</td>
</tr>
<tr>
<td>5</td>
<td>University of Kurdistan</td>
<td>3</td>
<td>6.7</td>
</tr>
</tbody>
</table>
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 electrocatalysts.

<table>
<thead>
<tr>
<th>Ranking</th>
<th>Article</th>
<th>Times cited</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Electrochemical reduction of CO$_2$ over Sn-Nafion® coated electrode for a fuel cell-like device</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>Author(s): Prakash, G.K.S., Viva, F.A., Olah, A.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Source: <em>Journal of Power Sources</em> Published: 2013</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Electrochemical reduction of carbon dioxide at low overpotential on a polyaniline/Cu$_2$O nanocomposite based electrode</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td>Author(s): Grace, A.N., Choi, S.Y., Vinoba, M., Bhagiyalakshmi, M., Chu, D.H., Yoon, Y., Nam, S.C., Jeong, S.K.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Source: <em>Applied Energy</em> Published: 2014</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Electrochemical reduction of carbon dioxide on polypyrrole coated copper electrocatalyst under ambient and high pressure in methanol</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>Authors: Aydin, R., Dogan, H.T., Koleli, F.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Source: <em>Applied Catalysis B: Environmental</em> Published: 2013</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Electro and photoelectrochemical reduction of carbon dioxide on multimetallic porphyrins/polyoxotungstate modified electrodes</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>Author(s): García M., Aguirre M.J., Canzi G., Kubiak C.P., Ohlbaum M., Isaacs M.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Source: <em>Electrochimica Acta</em> Published: 2014</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Poly-Amide Modified Copper Foam Electrodes for Enhanced Electrochemical Reduction of Carbon Dioxide</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>Source: <em>ACS Catalysis</em> Published: 2018</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Study of the electrochemical reduction of CO$_2$ on a polypyrrole electrode modified by rhenium and copper-rhenium microalloy in methanol media</td>
<td>28</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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

Source: Nanoscale
Published: 2018
Sustainable Membrane-coated electrodes for CO₂ electroreduction to methanol in alkaline media

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 CO₂ reduction electrolysers as 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.
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 polymeric-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 poly electrolyte 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
conditions provided by KOH significantly reduced the ohmic losses due to higher electrolyte conductivity (than KHCO₃) [34] and promotion of CO₂:R reaction kinetics [33]. Thus, this ion transport mechanism is more suitable for CO₂ reduction in AEMs than cationic exchange membrane (CEM) system, i.e. Nafton, because the forward reaction of CO₂ 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 CO₂ flow cells known today use AEMs [35,36]. Aeshala et al. [37,38] highlighted the improved CO₂RR 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 CO₂ reduction to CO [35].

The main disadvantage of such alkaline anion exchange membrane reactor configuration is the carbonation of the electrolyte by the unreacted CO₂ [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 CO₂ electrolyzers [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 CO₂ 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.
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$_2$RR 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$_2$ [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...
the selective sufficiently thin and thick membrane and electrolyte pre-concentration in the membrane enhances sensitivity by modulating pH and CO\textsubscript{2} concentration near the active sites.[49,50] Encapsulation of metal particles into conductive polymers has enhanced the activity of Cu\textsubscript{2}O electrocatalysts on the reduction of CO\textsubscript{2} even in aqueous media [25,51].

![Diagram of MCE configuration](image)

**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\textsubscript{2} electroreduction, the catholyte is not only the medium that provides dissolved CO\textsubscript{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\textsubscript{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\textsubscript{2}, O\textsubscript{2} or H\textsubscript{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\textsubscript{4} and formate, respectively, thus shifting the product selectivity and catalyst activity [23]. Grace et al. observed improvement in the Faradaic efficiency of CO\textsubscript{2} to acetic acid and formic acid by coating CuO nanoparticle electrode with a polyaniline film [58]. Electrochemical impedance spectroscopy studies revealed that the CO\textsubscript{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].
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\textsubscript{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\textsubscript{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\textsubscript{2}:R.[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
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 overlayer as a selective barrier between electrodes (a), and as a 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 new membrane designs enabling the improvement of CO2R 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 to environmental challenges; whereas other countries such as Japan, Taiwan, Chile, and so on have also reported largely cited papers in the CO2 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 modeling 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 CO2 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 CO₂ 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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