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Review

Electrochemical membrane reactors for the utilisation of carbon dioxide

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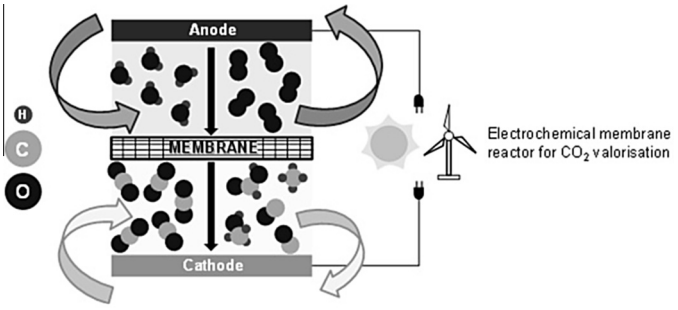
HIGHLIGHTS

- The evolution of electrochemical reactors for CO_2 utilisation is analysed.
- An analysis of different electrochemical reactor configurations is presented.
- The different products observed are analysed in terms of Faradaic efficiency.
- An analysis about the types of membranes and catalysts used is performed.

GRAPHICAL ABSTRACT



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ABSTRACT

Climate change is among the greatest challenges for humankind in the 21st century. Carbon Capture and Utilisation (CCU) allows the production of value-added chemicals from CO_2, reducing at the same time the undesirable effects of global warming.

Among the available methods for CO_2 utilisation, the electrochemical reduction appears as a promising technological solution to store intermittent renewable energy in the form of chemical bonds, leading to valuable chemicals such as formic acid, methanol or methane, which can be put back into the market.

The application of electrochemical membrane reactors (ecMRs) for the valorisation of CO_2 allows the separation of the catholyte and anolyte compartments, leading to an enhanced separation of reaction products and avoiding their re-oxidation. Among these membrane-based reactors, the utilisation of Membrane Electrode Assemblies (MEAs), where the cathode and anode are coupled with a conductive membrane, are gaining importance. Besides, gas diffusion electrodes (GDEs) are able to reduce mass transfer limitations and therefore, enhance efficiencies in the process of CO_2 electroreduction.

Thus, the aim of the present review is to compile the literature on the application of membrane reactors for CO_2 electroreduction, paying special attention to the type of membrane, reactor configuration and catalytic material in electrochemical reactors. Then, a performance comparison in terms of Faradaic efficiency for different products reported to date, is carried out.

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1. Introduction

Climate change is one of the most significant challenges to achieving sustainable development. The emissions of carbon dioxide (CO_2) to the atmosphere need therefore to be drastically reduced in order to alleviate the proven effects of global warming [1,2].

Among the available CO_2 mitigation strategies, Carbon Capture and Utilisation (CCU) to produce useful chemicals from CO_2 [3–5] is particularly interesting, since it may alleviate our rely on fossil fuels for energy and chemical synthesis [6], promoting, at the same time, new technical sinks in the carbon life cycle.

There are different techniques to activate and convert CO_2 at low temperatures. Among them, photoreduction (photocatalysis), electrochemical reduction (electrocatalysis) and reforming of CO_2 are considered the most interesting ones [7]. However, the technology for CO_2 photoreduction is still incipient. Photocatalytic materials seem to be unstable and current efficiencies are still low. Besides, plasma methods are clean and fast, but their energy efficiency is still very low (around 6%). On the other hand, conventional methods (i.e. reforming) involve high cost associated to the needs of high thermal power [7].

In contrast, the electrocatalytic reduction of CO_2 is an attractive solution since it allows obtaining hydrocarbons and oxygenates with a simple procedure at low operation temperatures. In addition, this technique shows promise to reduce greenhouse gas emissions and control the anthropogenic carbon cycle by transforming CO_2 to fuels and chemicals [8]. Due to the environmental and potential economic benefits, different systems have been developed for the electrochemical conversion of CO_2 [9]. The efficiency of this process can be enhanced by selecting a highly active electrocatalytic material, increasing the pressure of CO_2 or applying efficient electrochemical reactor configurations (using gas diffusion electrodes (GDEs)), among others [10].

Besides, the application of membranes in electrochemical reactors for CO_2 reduction is also interesting, since it allows separating the cathodic and anodic reactions that occur simultaneously in a redox system. Thus, studies on CO_2 conversion in divided electrochemical membrane reactors (ecMRs) are commonly found in literature [11]. Membranes may play a very important role, since they allow the use of different catholyte and anolyte volumes, enhancing the separation of products and leading to technical advantages in the reduction process. Besides, Membrane Electrode Assemblies (MEAs), where cathode and anode are coupled with conductive membrane materials, are also an interesting approach. The literature shows the application of different ion exchange membranes for the electrochemical reduction of CO_2 in divided cells, namely cation exchange membranes (CEMs), usually Nafion®, and anion exchange membranes (AEMs) such as Selemion™. In addition, the phases involved in these reactors has also been taken into account. Works based on gas phase at the cathode side are emerging with the aim to improve mass transfer limitations occurring in liquid phase systems due to the low solubility of CO_2 in water [12]. Moreover, the utilisation of gas phase in both, the cathode and anode compartments, has been reported in a few works [13,14], although the efficiencies of those systems are still low and further developments are needed.

There are several reviews on different aspects related to CO_2 electrochemical conversion [6,9,15–17]. However, none of them pays specific interest to the discussion on membrane reactor configurations for CO_2 electroreduction. Thus, the aim of the present review is to discuss the reports on different electrochemical membrane reactor configurations for CO_2 utilisation. A discussion of relevant studies on the topic are presented, emphasising on: membrane materials, electrochemical reactor designs and electrocatalysts for each system.

2. Electrocatalytic reaction analysis

The performance of a CO_2 electrochemical reduction process is in general evaluated in terms of *Faradaic efficiency* (*FE*), *energy efficiency (EE)* and *current density (CD)*. The *FE* represents the percentage of electrons that end up in the desired product:

$$FE\ (\%) = \frac{z \cdot n \cdot F}{Q} \times 100 \tag{1}$$

where z is the number of exchanged electrons, n is the number of moles for a product, F is the Faraday constant (96,485 C mol^{-1}), and Q represents the charge passed in the system (C).

Besides, the *EE* refers to the amount of energy in the products divided by the amount of electrical energy put into the system [8], as defined by Eq. (2):

$$EE = \sum_k \frac{E_k^0 \cdot FE_k}{E_k^0 + \eta}\ (dimensionless) \tag{2}$$

where E_k^0 is the equilibrium cell potential for a specific product k (V), FE_k is the *FE* of product k, and η is the cell overpotential (V) [6].

And finally, the *CD*, which is related to the conversion rate of the electrochemical reaction, usually expressed in mA cm^{-2}.

The goal for an efficient CO_2 electroreduction process is to achieve high *EEs* and reaction rates for CO_2 conversion (i.e., high *CDs*). Therefore, high *FEs* and low overpotentials on the cathode and anode are necessary in order to bring the technology closer to an industrial scale.

Moreover, the reduction products obtained from the electroreduction of CO_2 are diverse, mainly including carbon monoxide (CO), formic acid (HCOOH), formaldehyde (CH_2O), methanol (CH_3OH), methane (CH_4), ethylene (C_2H_4) or ethanol (CH_3CH_2OH), depending on the number of electrons involved as shown from Eqs. (3)–(9). It is also very common to find a mixture of products [6,16,18].

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \tag{3}$$