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Mini review

The cathodic reduction of carbon dioxide—What can it realistically achieve? A mini review

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ABSTRACT

There is a very large literature and continued interest in the electrochemical reduction of carbon dioxide. The reasons for the continued study of this reaction are reviewed. Suggestions that the electrolytic reduction of carbon dioxide can be used to reduce the level of this greenhouse gas in the atmosphere are shown to be wishful thinking. Also, using this reaction as part of a cycle for large-scale energy storage is not a promising technology. More realistic goals are using CO_2 as a cheap source of carbon in electrosynthesis and the development of sensors for CO_2. The reduction of CO_2 is also important from a fundamental viewpoint. Many different products have been confirmed depending on the electrolysis conditions (particularly electrode material and electrolyte medium), and understanding this variation would be a major boost to our understanding of electrode reactions in general. The reduction of CO_2 is also an ideal model reaction for developing approaches to increasing the current density for large-scale electrolysis with gaseous reactants.

Contents

1. Introduction

There is a very extensive literature on the electrochemical reduction of carbon dioxide [1–5], and the topic still attracts much interest. The reasons stated for this interest are diverse and not all seem valid. This short review comments on the reasons for studying the cathodic reduction of carbon dioxide.

2. Carbon dioxide capture from the atmosphere

The level of carbon dioxide in the earth's atmosphere is increasing at an alarming rate [6,7]. Each year, it increases by ~ 2 ppm, recently reaching a level of 400 pppm for the first time. At first sight, the application of electrochemical technology to the control of the CO_2 level seems a very laudable goal. However, is it viable?

Fig. 1 shows a possible scheme for employing electrolysis to remove CO_2 from the atmosphere. It notes that the electrolysis cells would only be part of the plant. In addition, there would need to be units (a) to extract pure CO_2 (or at least a concentrated CO_2 stream) from the atmosphere as feed to the electrolysis cells and (b) to isolate the product in marketable form (if a market on an appropriate scale exists; see below) or convert all the cell products it into a safe form prior to discharge into the environment. Two likely products, carbon monoxide and formic acid, are highly toxic and, on the scale that they would be formed, would require very stringent trapping before any discharges in a safe form. Hydrogen evolution is a probable competing reaction at

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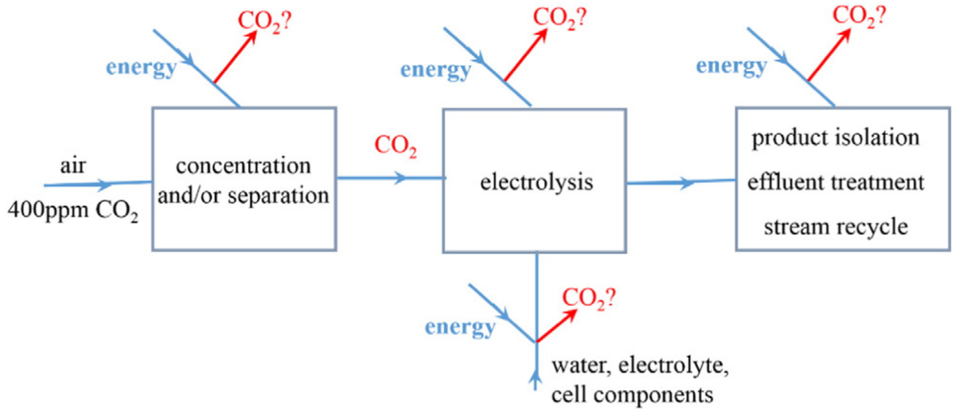

Fig. 1. Scheme for plant to remove CO_2 from the atmosphere using the electrolytic reduction of CO_2 as a key step.

many cathode materials and this also needs to be burnt or converted to a marketable form. All units for CO_2 concentration and output processing require an energy input and the production of this energy will lead to the emission of CO_2.

The complete process must be considered when calculating the energy and CO_2 balances. Clearly, a successful process must have both an acceptable energy consumption and the overall procedure must lead to a reduction of CO_2 level taking into account that formed by energy generation for all units in the overall plant.

Using energy from renewable sources will only be helpful when no energy is produced from coal, oil or gas. Otherwise, the correct use for energy from renewable sources is to capture markets from power stations fuelled by coal or oil and hence retire such CO_2 generating equipment from service. This leads to a direct decrease in CO_2 emissions and avoids the inefficiencies inherent in both energy generation and electrolytic processes for CO_2 reduction.

Even more importantly, the scale of the problem must be considered. In 2013, the total world emission of CO_2 was 36×10^9 tonnes [6,7]; the relative importance of major sources can be seen from the UK data in Table 1. The chlor-alkali industry is a very large electrolytic technology. A typical plant may produce 10^5 tonnes/year of chlorine with total world production being 60×10^6 tonnes/year. The comparison of plant sizes between an existing, large electrolytic industry and that required to control CO_2 shows the enormity of the challenge. Moreover, a chlor-alkali cell operates with a current density of some 400 mA cm^{-2} (cf. CO_2 reduction commonly at < 10 mA cm^{-2}). The size/number of plants needed to control CO_2 emissions is therefore certainly very large, difficult to envisage and scary. Another way to understand the scale of the problem is to estimate the power required to maintain the CO_2 in the atmosphere at a constant level, i.e., remove all the CO_2 emitted in a year; assuming $n = 2$ and making very optimistic assumptions about performance (a cell voltage of 3 V and a current efficiency of 100%), the power consumption is 140×10^{15} Wh/year. This is substantially above the total annual world electricity generation, presently 23×10^{15} Wh/year [12]. Whatever is formed in the reduction of CO_2 on this scale is unlikely to have a market or be benign to the environment.

Table 1
Major sources of CO_2 emissions in the UK during 2013. Data from UK Government reports.

Source	CO_2 emitted/tons	Reference
Cars	72×10^6	[8]
Aircraft flights from UK	40×10^6	[9]
Electricity generation	169×10^6	[10,11]

The economics of a process such as that in Fig. 1 is apparently improved if

(a) the CO_2 is available in a more concentrated stream, e.g., flue gas
(b) the product from CO_2 reduction is wanted, e.g., formic acid [13–18]. However, the market for the product must be large enough to impact the CO_2 level in the atmosphere and this is highly unlikely.

Hence, it must be concluded that the concept of electrochemical technology being used to remove CO_2 from the atmosphere is just wishful thinking. The same arguments are likely to apply to other technologies involving chemistry. The only viable way forward is to reduce the emission of CO_2 into the atmosphere and here electrochemical technology can be a major contributor to this future world. Opportunities exist for renewable energy generation, energy storage within a renewable energy economy, an increased role for hydrogen, power systems for electric vehicles, etc.

3. Carbon dioxide reduction for fuels and energy storage

Fig. 2 shows a scheme where the objective of the cathodic reduction of CO_2 is the production of a fuel either as a replacement for existing carbonaceous fuels or to be fed to a fuel cell as part of an energy storage technology [1,19–22]. Possible fuels cited include methanol [23,24], formic acid [25] and hydrocarbons [26].

The key questions with such applications are as follows: (a) What is the energy efficiency of a complete cycle? Because of the inefficiencies inherent in both CO_2 reduction and the fuel cell (overpotentials, IR drop, etc.) or generator/engine, the energy output will always be substantially lower than the energy input. (b) What is the CO_2 balance? Again, because of the inefficiencies in the cycle, it is inevitable that more CO_2 is formed than removed by the overall cycle. But, of course, the net emission will be significantly less than if the fuel was coal or oil. (c) What are the environmental and economic consequences byproducts formed in the CO_2 reduction step?

A realistic consideration of such technology would require large improvement in the performance of the electrochemical steps, particularly the identification of cheap electrocatalysts for both CO_2 reduction that give a low overpotential and high charge efficiency as well as the fuel cell anode (also cathode) that operate with high current density at low overpotentials and high selectivity. These advances have, as yet, proved difficult to make. At the present time, hydrogen would hold many advantages over a fuel produced from carbon dioxide.

But even with the successful development of such electrocatalysts, the implementation on a large scale seems highly unlikely. The size of