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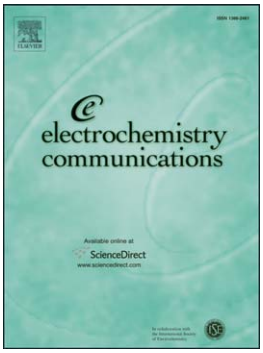

The Cathodic Reduction of Carbon Dioxide – What Can It Realistically Achieve? A Mini Review

Derek Pletcher

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The Cathodic Reduction of Carbon Dioxide – What Can It Realistically Achieve? A Mini Review

Derek Pletcher*

Chemistry, University of Southampton, Southampton SO17 1BJ, UK

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.

Keywords

Carbon dioxide, cathodic reduction, applications, impossible goals.

***dp1@soton.ac.uk**

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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. But, is it viable?

Figure 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 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.

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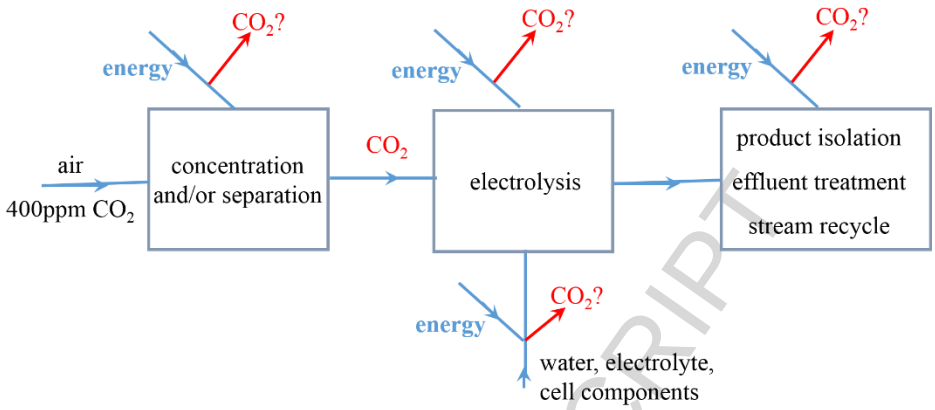

Figure 1 *Scheme for plant to remove CO_2 from the atmosphere using the electrolytic reduction of CO_2 as a key step.*

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 x 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 x 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

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constant level, ie. 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 x 10^{15} Wh/year. This is substantially above the total annual world electricity generation, presently 23 x 10^{15} Wh/year! Whatever is formed in the reduction of CO_2 on this scale is unlikely to have a market or be benign to the environment.

The economics of a process such as that in figure 1 are apparently improved if

(a) the CO_2 is available in a more concentrated stream, eg. flue gas

(b) the product from CO_2 reduction is wanted, eg. formic acid [13-18]. But 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

Figure 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: (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

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formed than removed by the overall cycle. But, of course, the nett 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?

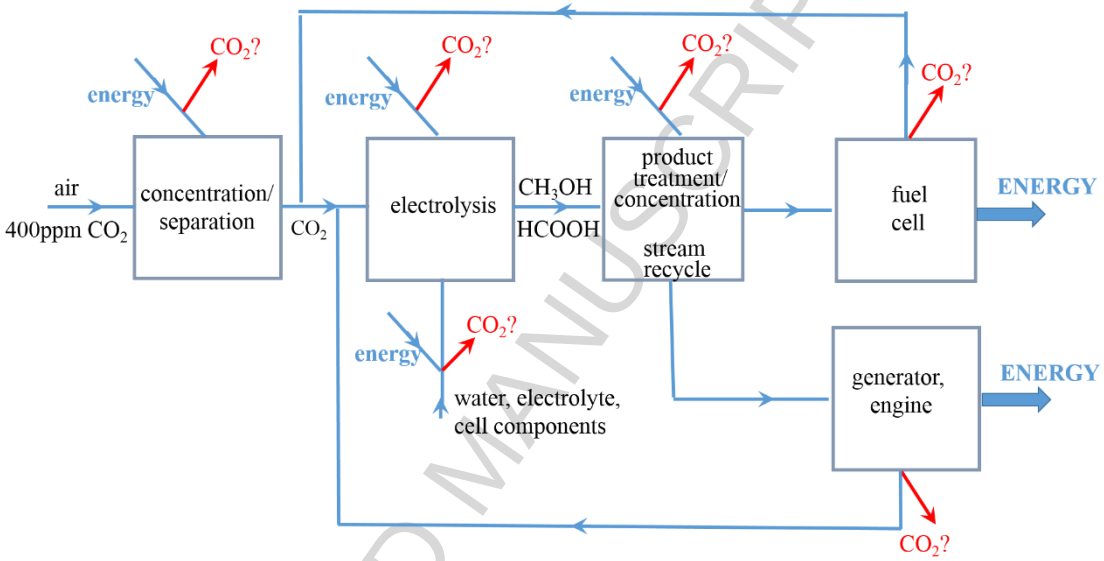

Figure 2 *Scheme for the application of electrolytic CO_2 reduction as part of a sequence for large scale energy storage.*

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, implementation on a large scale seems highly unlikely. The size of the fuel market is just too large; the number/size of plants and the increase in electricity generation capability would be immense, see section 2. On the other hand, electrosynthesis of methanol or formic acid as a fuel for small power sources for eg. electronic devices seems a more feasible goal even if they will not solve the problem of CO_2 emissions.

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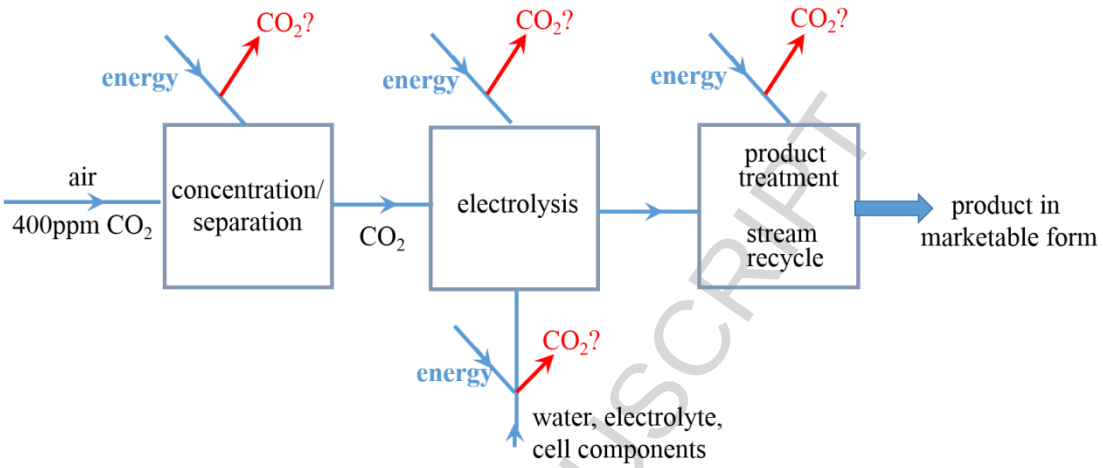

Figure 3 *Scheme for the conversion of CO_2 in the atmosphere to a marketable organic product.*

4. The Synthesis of Organic Compounds

Figure 3 shows a scheme for converting CO_2 to an organic product. Few organic compounds are produced/marketed on a scale of above 25000 tonnes/year. Indeed, many have total markets < 100 tonnes/year. Hence, the driving force for using CO_2 as a feedstock cannot be the impact on the CO_2 level in the atmosphere. On the other hand, there is a very good reason for using CO_2 in synthesis – much synthesis requires an increase in the number of carbon atoms in a molecule and CO_2 is the cheapest 'reactive' form of carbon available. On such a small scale, the overall CO_2 balance is not an issue and the importance of energy consumption will depend on the cost of electricity, plant performance and the value of the product. The economics would certainly favour sites where a concentrated CO_2 stream already exists.

The most straightforward product to form is formate/formic acid since it can be formed in aqueous solution with a current efficiency above 80 %. The major challenges is carrying out the electrolysis with a high enough current density that the cost of cells is acceptable (see section 7) and the energy consumption for larger scale processes. Several papers have described studies of the scale up of the conversion of CO_2 to formate/formic acid using both three-dimensional electrodes and gas diffusion electrodes [13-18]. In aqueous solutions, a variety of other products can be formed depending on the electrode material, its surface preparation and the electrolyte

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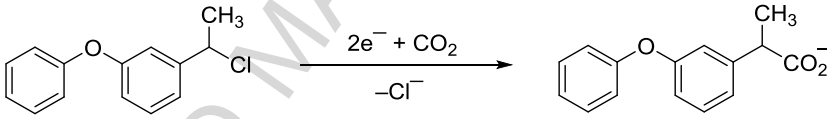
conditions, see section 6 [1-5]. For example, it is possible to find conditions where carbon monoxide are formed in good yields but the current densities are generally very low< < 10 mA cm^{-2}. Carbon monoxide can be seen as a useful starting material for synthesis with the Fischer-Tropsch reaction as the next step.

While strictly not involving the direct reduction of CO_2, a successful, general cathodic reaction is the trapping of carbanion intermediates with CO_2 in aprotic media to insert a carboxylic acid function. The carbanions can result from the reduction of aromatic hydrocarbons, aryl or alkyl halides, aryl ketones and activated alkenes in aprotic media [27]. This chemistry was used by SNPE in France to produce a range of non-steroidal, anti-inflammatory drugs with an arylpropionic acid structure [28,29]. The company used magnesium anode dissolution to design a clean synthesis for the drug, fenoprofen, on a pilot scale (batches of 60 kg).

cathode 

anode $Mg - 2e^- \longrightarrow Mg^{2+}$

The plant used the 'pencil sharpener' cell developed specifically for the dissolving Mg anode and a narrow interelectrode gap. The electrolyte was dimethylformamide containing tetrabutylammonium bromide and an elevated pressure, 5 bar, was used to increase the solubility of the CO_2 and hence the current density (to 100 mA cm^{-2}).

In aprotic solvents, the direct reduction of CO_2 leads to the very reactive intermediate, $CO_2^{\cdot -}$ although at rather negative potentials. In the absence of a trap it is common for dimerisation to occur and oxalate to be formed in good yield. When a difficult to reduce alkene or alkyne, eg. ethene or butadiene, is present in solution, the radical formed adds to the unsaturated molecule to give rather complex mixtures of carboxylate products. For example, with ethane [30], a mixture of monocarboxylates and dicarboxylates with 2 – 8 carbon atom chains while with butadiene [31] a mixture of C_5, C_6 and C_{10} unsaturated carboxylic acids were reported.

5. Sensors for CO_2 in Atmospheres

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There is a substantial market for sensors for CO_2 in atmospheres - for pollution monitoring, in breath within clinical medicine and in various industrial environments such as fermentation. Voltammetry of solutions in both aqueous and aprotic media containing CO_2 commonly leads to well-formed reduction waves that appear to offer opportunities for analysis. The problem is that the atmospheres almost always contain an excess of oxygen and O_2 is more readily reduced than CO_2 so for a sensor it is essential to eliminate the interference of O_2 to the CO_2 response.

A number of sensors have employed the aprotic solvent, dimethylsulfoxide (DMSO) in a sensor with an electrode covered by a gas permeable membrane (usually thin PTFE). They differ in the way the interference from O_2 is overcome. In an early example with a rather complex design [32], the O_2 was removed using a gold covered membrane as an electrode in aqueous solution before the CO_2 passed through a second membrane to a silver electrode in DMSO. The sensor gave a slow but linear response but only for atmospheres with a high level of CO_2 (5 – 100 %); greater sensitivity and faster response are necessary. This was achieved using a double potential step procedure [33]. In DMSO, oxygen is reduced in a reversible $1e^-$ step to the stable superoxide ion. But in the presence of CO_2 the superoxide reacts rapidly

$$2O_2^- + 2CO_2 \longrightarrow C_2O_6^{2-} + O_2$$

and the loss of superoxide, estimated via double potential step chronoamperometry, can be related to the concentration of CO_2 in the atmosphere in contact with the solution. The sensor gave a variable response in air over the range 0.2 – 5 % v/v CO_2 and the response was fast enough to monitor human breath on a breath-by-breath basis. A later sensor [34] overcame the O_2 interference using a different double potential step sequence at a membrane covered gold microdisc (diameter 5 μm) in DMSO. A long first step was employed to decrease the O_2 response to the steady state and the second determined the CO_2 level early in the transient response. The sensor, again membrane covered, gave a linear response over the range 2 – 10 % v/v CO_2. Hahn [35] has reviewed the application of electrochemical sensors in the hospital environment.

A quite different approach [36] to overcoming O_2 interference was based on the fact that aqueous solutions become acid in contact with an atmosphere containing CO_2

$$CO_2 + H_2O \longrightarrow HCO_3^- + H^+$$

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The resulting pH was monitored in an aqueous chloride medium containing a Cu(II) complex via the equilibrium

$$CuL_2^{2+} + H^+ + 2Cl^- \longrightarrow HL^+ + CuCl_2^-$$

where L is an appropriate ligand (L = $NH_2CH_2CH_2CH_2NH_2$ was the preferred ligand) and monitoring voltammetrically the concentration of the chloride complex formed; the chloride complex is reduced in a $1e^-$ step at a potential less negative than that for the reduction of the diamine complex. The sensor gave a linear response over the CO_2 range 0.1 – 2 % v/v in air with a response time of a few minutes. Sensors based on this chemistry have been marketed for monitoring CO_2 in industrial environments.

While these sensors have been successful, there remain opportunities for new, improved devices.

6. Fundamentals 1 – What Determines the Product?

There is no other electrode reaction where so many different products can be formed and the product spectrum is so sensitive to the electrolysis conditions. Products reported include carbon monoxide, formate, oxalate, methanol, formaldehyde, dimethyl carbonate, ethane, methane and higher alkanes. Most commonly the reduction of CO_2 leads to a mixture of products and hydrogen evolution occurs as a competing reaction [1-5]. Of course the choice of solvent (aqueous, methanol, aprotic, room temperature ionic liquid, supercritical CO_2) has a major impact on the product formed but the literature shows that the product spectrum also depends strongly on the choice of electrode material, the structure of its surface, surface pretreatment, electrode potential , electrolyte, pH, temperature, concentration of CO_2 etc. Some generalisations are possible, for example (a) Hg or Pb cathodes in aprotic media give oxalate (b) Pt or Au cathodes in aqueous media give CO (c) Cu cathodes in aqueous solutions give methanol, formaldehyde or hydrocarbons. On the other hand, we do not have a base of evidence to understand the variations that are seen. Answers to the questions

- What properties of the cathode and medium determine the product?
- How may the product spectrum be controlled and manipulated to give a high yield of a particular product?

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- What factors determine the ratio of H_2 evolution and CO_2 reduction and how may the charge efficiency for CO_2 reduction be optimised?

would benefit our understanding of CO_2 reduction but, more importantly, would have a much broader impact on our fundamental knowledge of electrode reactions in general. Moreover, CO_2 reduction is well suited to such studies as it may be investigated over a wide range of conditions, the different products implying quite different reaction pathways and the properties of CO_2 and products such as CO and $HCOO^-$ that support spectroscopic observation of intermediates.

7. Fundamentals 2 - Increasing the Current Density for CO_2 Reduction

The current density for a reaction determines the electrode area required to meet any goal and the electrode area is a major factor in determining the size and cost of a plant. For most electrolytic applications, the current density must be > 100 mA cm^{-2} and it is commonly advantageous to push towards higher value. Hence, one objective of process development is usually to maximise the current density in the electrolysis cell. There are several approaches to increasing the current density for CO_2 reduction and this allows it to provide lessons to process development, in general. It should be recognised, however, that the approaches to increasing current density, emphasised here, can also lead to a large improvement in the charge efficiency for CO_2 reduction and major changes to the product spectrum.

In aqueous solutions, the current density for CO_2 reduction is limited by the low solubility of CO_2 in water to < 10 mA cm^{-2}. The solubility is significantly higher in methanol and aprotic solvents and even higher in some ionic liquids [37] and this opens the possibility of higher current densities. The solubility can also be enhanced by a substantial factor by using CO_2 clathrates [38]. Another obvious approach is to increase the pressure and this was used in a pilot plant for the preparation of carboxylic acids [28,29]. Other high pressure studies have been reported over the past 20 years including studies in water and methanol [39,40]. High pressure also gives access to supercritical media with CO_2 as one component and the electrochemical reduction of CO_2 reduction has been shown to lead to oxalic acid and CO [41] with reasonable charge efficiency but the current density is low for synthesis. Three dimensional electrodes is another pathway to increasing current density. Granules of tin (dimensions

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~ 0.3 mm) were used as in a cathode bed (thickness 3.2 mm) in a trickle bed cell and operation was possible at 300 mA cm^{-2} (membrane) current density although with a charge efficiency for formate of only 40 %. This rose to > 80 % at a lower current density, 100 mA cm^{-2}. The most successful way to increase the current density for CO_2 reduction has, however, proven to be the application of gas diffusion electrodes (GDEs) [16-18,42-44] with a variety of active metals including Pb, Sn, Ni and Ag. The performance of such electrodes depends strongly of the design and fabrication of the GDE as well as the active metal. The lead based GDE in aqueous bicarbonate electrolyte with a CO_2 feed at atmospheric pressure were reported to operate with a current density of 200 mA cm^{-2} and a charge efficiency for formate of 90 %. [16,17]. Using an high pressure CO_2 feed (18.4 atmospheres) to a silver catalysed GDE [44], the current density was increased to 350 mA cm^{-2} but the product was then CO, charge efficiency up to 92 %.

8. Conclusions

There are good reasons for the study of the cathodic reduction of carbon dioxide. It is a cheap source of carbon for synthesis while the reaction can be used in sensing CO_2 in clinical and industrial environments . It is also a reaction that is well suited to improving our fundamental understanding of electrode reactions as well as the scale up of electrolytic technology. In contrast, it is illogical and ridiculous to suggest that the reduction of CO_2 can be used to remove CO_2 from the atmosphere or as part of technology for large scale energy storage. Electrochemical technology will never be viable for such tasks.

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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

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

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Highlights

The reasons for the continued study of the electrochemical reduction of carbon dioxide are reviewed.

Suggestions that the electrolytic reduction of carbon dioxide can be used to reduce CO_2 levels in the atmosphere are critically addressed.

The use of carbon dioxide reduction as part of a cycle for large scale energy storage is questioned.

Many different products of the reduction of CO_2 have been confirmed and understanding this variation would give insight into the corresponding electrode reactions.

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