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ATMOSPHERIC CO2 REDUCTION AND BIO-ELECTROCHEMICAL CONVERSION OF CO2 TO VALUE-ADDED CHEMICALS

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Abstract

Rapidly increasing CO_2concentration within the atmosphere may be a pressing global challenge, which encompasses a direct implication on temperature change. The utilization of fossil fuels, as an instantaneous or indirect source of energy and in industrial processes, holds answerable for 65% of the overall CO_2 emission. Therefore, it's necessary to develop a deployable carbon neutral technology, capable of recycling CO_2 to valuable fuels and chemicals so as to forestall environmental deterioration and increase reliance on renewable fuels.

CO_2 could be a stable molecule, and thus, the hydrogenation and chain elongation reaction routes to convert it to biochemicals are invariably energy-intensive processes. As an example, conversation of methanol from CO_2 occurs at 200 – 300°C and 50 – 100 bar pressure on the Cu/ZnO-based catalysts (Nieminen et al., 2019). The energy demand for this reaction is estimated to be 49.8–90 kJ/mol. The light-induced and electrochemical CO_2^2 reduction routes have also been demonstrated recently. Unfortunately, these methods don't seem to be suitable to be considered as a practical technology which will capture and utilize CO_2. Against this, researchers have discovered the microbial electrosynthesis (MES) technology—a potential deployable technology—that can recycle CO_2 to desired biochemical and fuels at temperature and pressure using electroactive bacteria (EAB) as biocatalyst. An MES consists of an anode and a cathode situated in separate anodic and cathodic chamber, respectively, or in an exceedingly single chamber sharing the electrolyte. Just in case of a dual chamber MES, a cation exchange membrane (CEM) is mostly accustomed conduct protons from anode to cathode. At the anode, electrons, and protons (H^+) are generated, which are derived to the cathode via an external imposed electrical potential (Noori and Min, 2019). The electrons transferred to the EABs (e.g., Moorella thermoacetica, Sporomusa ovata) assist in converting CO_2 to the biochemicals via the Wood-Ljungdahl pathway (WLP) (Ragsdale and Pierce, 2008). The WLP uses mainly two enzymes: CO dehydrogenase and acetyl-CoA synthase; the previous enzyme helps in reducing CO_2 and therefore the latter enzyme catalyzes formation of the reactive acetyl-CoA, which acts as a building block for the formation of useful products. The poised cathode potential (vs. standard hydrogen electrode, SHE) is a vital think about MES, and at higher potentials than the cathodic potential a spread of product becomes theoretically feasible. For instance, the MES poised with a cathodic potential of −0.8 V (vs. SHE) could produce a mix of C_4 and C_6 carboxylic acids (isobutyric, n-butyric, and n-caproic acids) and therefore the corresponding alcohols (isobutanol, n-butanol, and n-hexanol). However, selectivity of MES depends on the metabolic pathways expressed by the microorganism acting because the biocatalyst. Additionally, the desired amounts of electrical potential may be easily drawn from renewable energy sources, e.g., wind, solar, geothermal, etc. Thus, MES can act as an energy device to accumulate the voltage produced from various renewable energy sources to energy.

Atmospheric CO_2 may be a cheap and abundant source of carbon for synthetic applications. However, the soundness of CO_2 makes its conversion to other carbon compounds difficult and has prompted the extensive development of CO_2 reduction catalysts. Bioelectrocatalysts are generally more selective, highly efficient, can operate under mild conditions, and use electricity because the sole reductant. Improving the communication between an electrode and a bioelectrocatalyst remains a big area of development. Through the samples of CO_2 reduction catalyzed by electroactive enzymes and whole cells, recent advancements during this area are compared and contrasted.
The stability of CO2 makes its conversion to other carbon compounds (e.g. formate, hydrocarbons or carbon monoxide) difficult and has prompted the extensive development of CO2 reduction catalysts.

Key-words: *Electrosynthesis, bioproduction, electro-active bacteria, CO2 reduction, carboxylic acid, ethanol, acid, enzymes.*

Introduction

With the share of renewable electricity increasing within the energy sector, moments of overproduction will occur more often also as points in time that not enough production is out there to meet the wants. The estimation is that in an exceedingly scenario of 100% renewable energy, about 20% of the yearly production will must be stored in a technique or another to stay the system in balance. Since the Antwerp-Rotterdam-Rhine-Ruhr (ARRR) cluster is that the European region where the best CO_2-emissions are measured (highest production, but also highest population density and energy supply), this region is well positioned to concentrate on CO_2 and 'peak shaving' of renewable energy. Since this region is additionally one among the largest chemical clusters, the conversion of CO_2 into new molecules is smart guaranteeing that the ultimate balance on energy uses and CO_2-emissions are less than within the classical production. Different initiatives are ongoing within the Netherlands to specialise in underground storage (CCS). Nordrhein-Westfalen is putting its money on power to gas. The harbor of Antwerp, University of Antwerp and VITO have started an initiative to explore technologies for converting CO_2, preferentially coupled to 'peak shaving', to assembling blocks for the chemical sector. Making technological choices is incredibly difficult, since the chosen technology depends on the standard of the CO_2 feedstock. Each of the impurities within the CO_2 emission will have its impact on the method. Thus ongoing activities are that specialize in listing the various CO_2-emissions and its quality/composition. The various technologies should be benchmarked for his or her robustness and adaptability towards feedstock and energy peaks.

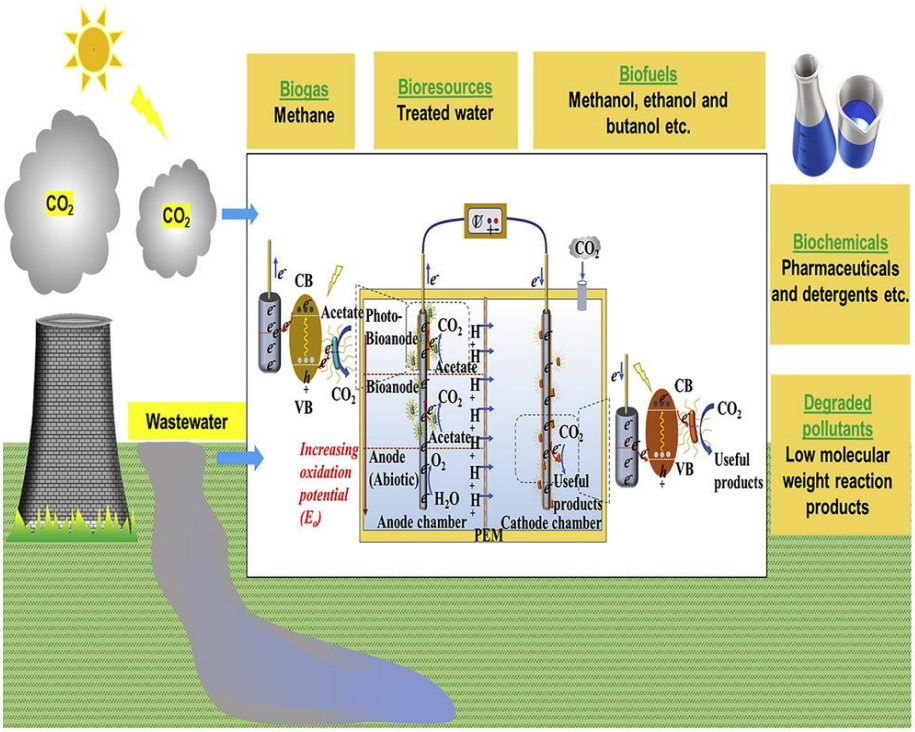
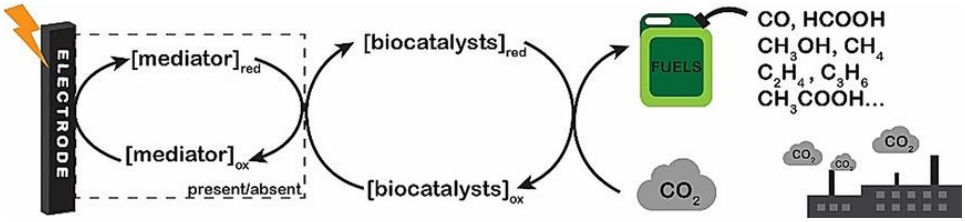


Figure: Overall advantages of PMES to attain environmental sustainability and develop a carbon neutral circular economy

The stability of CO_2 makes its conversion to other carbon compounds (e.g. formate, hydrocarbons or carbon monoxide) difficult and has prompted the extensive development of CO_2 reduction catalysts. This literary criticism compares and contrasts recent developments in bioelectrocatalysis for CO_2 reduction.



Microbial Electrosynthesis

Research over the years has proven that generation of electrical current is feasible from the metabolism of organic substrates in microbial fuel cells (MFCs), with bacteria acting as electrocatalyst. By converting the energy stored in organic substrates to electricity, MFCs can substantially reduce the operational cost of wastewater treatment plants, or when fully

operational even achieve energy self- sufficiency. On the opposite hand, microbial electrolysis cells (MECs) are used for the assembly of hydrogen at the cathode by providing atiny low amount of external electric energy. However, in recent years, a brand new concept of microbial electrosynthesis has been applied wherein there are same types of setups—generally referred to as microbial electrochemical systems (MXCs) or bio-electrochemical systems (BES). These systems are getting used for the assembly of chemicals using bacteria as electrocatalyst. Already the bio-electrochemical reduction of greenhouse gas to acetate has been achieved, still because the reduction of CO_2 to methane and multi-carbon compounds. Global efforts are underway to utilize several other styles of bacteria employing a wide range of substrates for production of an array of compounds. The key advantage foreseen here is that the use of excess electricity that's often generated renewably like from solar cells and wind mills, all of which can't be utilized immediately. This excess electricity will be fed into a BES system to provide chemical compounds.

Acetogens like Sporomusa and Clostridium sps. were experimented for his or her bio-electrochemical CO_2 reduction capacity at -0.6 V vs Ag/AgCl cathode potential. Adjustment of reduction potential and optimization of cell conditions were distributed in an exceedingly fed batch reactor with a C cathode. Ranging from a production of 670 mg/L in 2014 to current 12 g/L with mixed culture as biocatalyst was the foremost remarkable achievement.

Enzymatic Electrosynthesis

Similar to the microbial systems, enzymes can even be used for varied chemical transformations to be catalyzed by redox-active enzymes including both the reduction and oxidation of substrates. ElectroEnzeQuest, CO_2 is employed as substrate for the assembly of methanol which can have a major positive impact on environment also as energy crisis. Electrosynthesis of acid was higher at an operational voltage of -1 V vs. Ag/AgCl (9.37 mg L -1 CO_2) compared to operation at -0.8 V (4.73 mg L-1 CO_2) which was strongly supported by the reduction catalytic current.

Voltammograms also depicted a reversible redox peak throughout operation at -1 V, indicating NAD+ recycling for proton transfer from the source to CO_2. Saturation of the merchandise was observed after 45 minutes of enzyme addition so reversibility commenced, depicting a lower and stable acid concentration throughout the next time of operation.

Chemicals from carbonic acid gas

In carbon fixation, plants convert greenhouse gas into sugars, from which many biosynthetic pathways originate. The catalyst to blame for this conversion, RuBisCO, is that the most typical protein on earth. Some anaerobic organisms employ enzymes to convert CO_2 to monoxide, from which fatty acids are often made.

In industry, some products are made of CO_2, including urea, 2-hydroxybenzoic acid, methanol, and certain inorganic and organic carbonates. Within the laboratory, greenhouse emission is usually wont to prepare carboxylic acids in a very process called carboxylation. No electrochemical CO_2 electrolyzer that operates at temperature has been commercialized. Elevated temperature solid oxide electrolyzer cells (SOECs) for CO_2 reduction to CO are commercially available. As an example, Haldor Topsoe offers SOECs for CO_2 reduction with a reported 6-8 kWh per Nm^3 CO produced and purity up to 99.999% CO.

Hydrosilanes reduce dioxide (to methane): Unfortunately such reactions are stoichiometric and exclusively of educational interest.

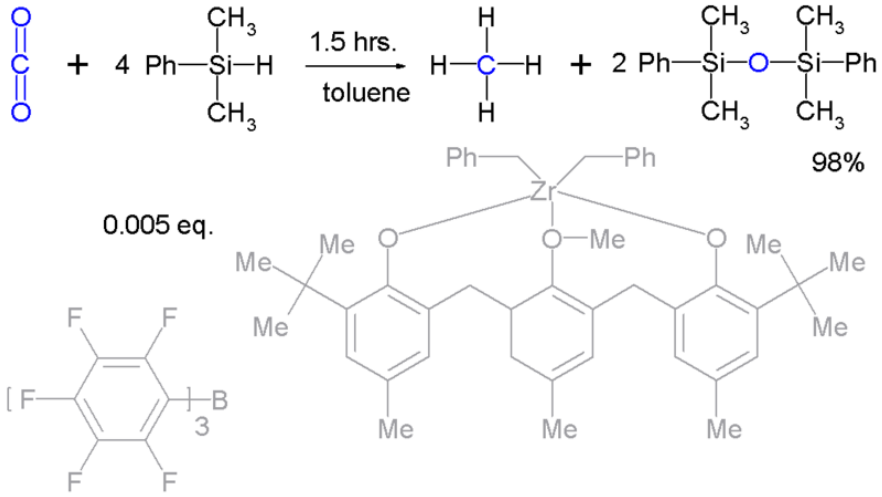


Figure: Carbon dioxide reduction

Electrocatalysis

The electrochemical reduction of carbon dioxide to various products is usually described as:

Reaction	**Reduction Potential E^o (V)**
$CO_2 + 2\ H^+ + 2\ e^- \rightarrow HCOOH$	−0.61
$CO_2 + 2\ H^+ + 2\ e^- \rightarrow CO + H_2O$	−0.53
$CO_2 + 8\ H^+ + 8\ e^- \rightarrow CH_4 + 2\ H_2O$	−0.24
$2\ CO_2 + 12\ H^+ + 12\ e^- \rightarrow C_2H_4 + 4\ H_2O$	−0.349
$2\ CO_2 + 12\ H^+ + 12\ e^- \rightarrow C_2H_5OH + 3\ H_2O$	−0.329

The redox potentials for these reactions are just like that for hydrogen evolution in aqueous electrolytes, thus electrochemical reduction of CO_2 is typically competitive with hydrogen evolution reaction.

Electrochemical methods have gained significant attention: 1) at ambient pressure and room temperature; 2) in reference to renewable energy sources 3) competitive controllability, modularity and scale-up are relatively simple. The electrochemical reduction or electro-catalytic conversion of CO_2 can produce value-added chemicals such methane, ethylene, ethanol, etc., and also the products are mainly captivated with the chosen catalysts and operating potentials (applying reduction voltage).

A variety of homogeneous and heterogeneous catalysts are evaluated. Many such processes are assumed to work via the intermediacy of metal CO_2 complexes.

Many processes suffer from high over-potential, low current efficiency, low selectivity, slow kinetics, and/or poor catalyst stability.

The composition of the electrolyte may be decisive. Gas-diffusion electrodes are beneficial.

Conclusion

The recent concept of microbial electro-synthesis (MES) has evolved as an electricity-driven production technology for chemicals from low-value greenhouse gas (CO_2) using micro-organisms as biocatalysts. MES from CO_2 comprises bio-electrochemical reduction of CO_2 to multi-carbon organic compounds using the reducing equivalents produced at the electrically-polarized cathode. The employment of CO_2 as a feedstock for chemicals is gaining much attention, since CO_2 is abundantly available and its use is independent of the food supply chain. MES supported CO_2 reduction produces acetate as a primary product. In order to elucidate the performance of the bio-electrochemical CO_2 reduction process using different operation modes (batch vs. continuous), an investigation was dispensed employing a MES system with a flow-through bio-cathode furnished with 20 : 80 (v/v) or 80 : 20 (v/v) $CO_2 : N_2$ gas.

The highest acetate production rate of 149 mg L^{-1} d^{-1} was observed with a 3.1 V applied cell-voltage under batch mode. While running in continuous mode, high acetate production was achieved with a maximum rate of 100 mg L^{-1} d^{-1}.

Within the continuous mode, the acetate production wasn't sustained over long-term operation, likely because of insufficient microbial biocatalyst retention within the bio-cathode compartment (i.e. suspended micro-organisms were washed out of the system). Restarting batch mode operations resulted in a very renewed production of acetate. This showed a visible

domination of suspended biocatalysts over the attached (bio-film forming) biocatalysts. long run CO_2 reduction at the bio-cathode resulted within the accumulation of acetate, and more reduced compounds like ethanol and butyrate were also formed. Improvements within the production rate and different biomass retention strategies (e.g. selecting for bio-film forming micro-organisms) should be investigated to enable continuous biochemical production from CO_2 Certainly, other process optimizations are going to be required to determine MES as an innovative sustainable technology for manufacturing bio-chemicals from CO_2 as a next generation feedstock.

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