Recent Advances in Bioelectrochemical conversion of CO_2 to chemicals: Electrosynthesis via bacteria and enzymes

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Abstract

Background

With the share of renewable electricity increasing in the energy sector, moments of overproduction will occur more often as well as points in time for which not enough production is available to fulfill the needs. The estimation is that in a scenario of 100% renewable energy, about 20% of the yearly production will need to be stored in one way or another to keep the system in balance. Since the Antwerp-Rotterdam-Rhine-Ruhr (ARRR) cluster is the European region where the highest CO_2-emissions are measured (highest production, but also highest population density and energy supply), this region is well positioned to focus on CO_2 and 'peak shaving' of renewable energy. Since this region is also one of the biggest chemical clusters, the conversion of CO_2 into new molecules makes sense guaranteeing that the final balance on energy use and CO_2-emissions are lower than in the classical production. Different initiatives are ongoing in The Netherlands to focus on 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 building blocks for the chemical sector. Making technological choices is very difficult, since the selected technology depends on the quality of the CO_2 feedstock. Each of the impurities in the CO_2 emission will have its impact on the process. Thus ongoing activities are focusing on listing the different CO_2-emissions and its quality/composition. The different technologies have to be benchmarked for their robustness and flexibility towards feedstock and energy peaks.

Microbial Electrosynthesis

Research over the years has proven that generation of electric current is possible from the metabolism of organic substrates in microbial fuel cells (MFCs), with bacteria acting as electrocatalyst. By converting the chemical 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 other hand, microbial electrolysis cells (MECs) have been used for the production of hydrogen at the cathode by providing a small amount of external electric energy. However, in recent years, a new concept of microbial electrosynthesis has been applied wherein there are same kind of setups—generally known as microbial electrochemical systems (MXCs) or bioelectrochemical systems (BES). These systems are being used for the production of chemicals using bacteria as electrocatalyst [1]. Already the bioelectrochemical reduction of carbon dioxide to acetate has been achieved [2], as well as the reduction of CO_2 to methane and multi-carbon compounds [3]. Global efforts are underway to utilize several other types of bacteria using a wide variety of substrates for production of an array of compounds. The key

advantage foreseen here is the use of excess electricity that is often generated renewably such as from solar cells and wind mills, all of which cannot be utilized immediately. This excess electricity can be fed into a BES system to produce chemical compounds. I will share our results with specific bacteria towards bioelectrochemical conversion of CO_2 to organic compounds. Acetogens like *Sporomusa* and *Clostridium* sps. were experimented for their bioelectrochemical CO_2 reduction capacity at -0.6 V vs Ag/AgCl cathode potential [4]. Adjustment of reduction potential and optimization of cell conditions were carried out in a fed batch reactor with an activated carbon cathode. Starting from a production of 670 mg/L in 2014 to current 12 g/L with mixed culture as biocatalyst was the most remarkable achievement.

Enzymatic Electrosynthesis

Similar to the microbial systems, enzymes can also be used for numerous chemical transformations to be catalyzed by redox-active enzymes including both the reduction and oxidation of substrates. In one of our projects, ElectroEnzeQuest, CO_2 is used as substrate for the production of methanol which will have a significant positive impact on environment as well as energy crisis [5]. Electrosynthesis of formic 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 product was observed after 45 minutes of enzyme addition and then reversibility commenced, depicting a lower and stable formic acid concentration throughout the subsequent time of operation. In this presentation, the preliminary step towards methanol synthesis i.e. formic acid production from CO_2, using formate dehydrogenase at cathode will be presented.

Finally, I will present a techno-economic evaluation of the technology to produce chemicals from CO_2 with selected chemicals (formic acid, acetic acid, oxalic acid) as examples [6].

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