We want to bring the idea of conversion of CO$_2$ into synthetic fuels (CO$_2$ recycling) into attention, as a possible approach for transportable storage of renewable energy. Recycling of CO$_2$ by homogeneous and/or heterogeneous catalytic approaches have been investigated with increasing emphasis within the scientific community. In the last decades, especially using organic and bioorganic systems towards CO$_2$ reduction has attracted great interest. Chemical, electrochemical, photoelectrochemical and bioelectrochemical approaches are discussed vividly as new routes towards the conversion of CO$_2$ into synthetic fuels and/or useful chemicals in the recent literature. Here we want to especially emphasize the new developments in bio-electrocatalysis with some recent examples.

We need renewable and CO$_2$ neutral fuels

In his seminal work Svante Arrhenius calculated in 1896 (1) the increase in global temperature by several degrees upon increasing the CO$_2$ content in the atmosphere. The discussion apparently has started way back then, when coal was the major energy source and air pollutant fueling the early days of industrial revolution. Arrhenius calculates up to 3 degrees increase in global atmospheric temperature upon increasing the CO$_2$ content by a factor of 1.5. Furthermore, increase of global temperature up to 6 degrees is predicted by Arrhenius upon increasing the CO$_2$ content by a factor of 2. The increase of CO$_2$ by a factor of 3 will take us back to Tertiary times when “…arctic temperatures have exceeded the present temperature about 8-9 degrees.”

At those days of Arrhenius, the CO$_2$ content in the atmosphere was around 300 ppm (1). By the time we write this article the CO$_2$ in the atmosphere is exceeding 410 ppm even in this Corona year of 2020. That means we already surpassed a factor of 1.5 and are on the best way to doubling the CO$_2$ content as compared to Arrhenius times. The predicted increase in temperature will have massive consequences for the human life on this planet.

On the other hand, humanity needs for its continued existence not only essentials like food, clean water, shelter and clothing but also large amounts of energy. Ever since our ancestors, the cavemen, cultivated fire, we have been using natural carbon-based energy resources such as wood, coal, oil, gas to create the energy we need. The industrial revolution and the rapid development during the last 300 years burned carbon-based fossil fuels significantly. This overusing enabled the very modern human societies we today are proud of. More than 95% of the energy used in transportation comes from oil. This sector is growing significantly. In a globalized world economy transport of goods is an essential sector.

The existent fossil oil reserves are localized mostly in politically unstable geographies of the world. Their sustainable utilization may be a political challenge. The rapidly growing economies (China, India and others in the Asia-Pacific Rim) are increasing their oil consumption parallel to their economic development. Increasing demand on one side and decreasing or unstable supply of fossil oil with
possible disruptions on the other side, will destabilize the world socially, politically and economically. Which problem will hit earlier is unclear, the effects of global warming or the collapse of world economy due to adverse political effects of depending on fossil oil and gas. Most probably we will experience both disturbing effects simultaneously.

Thus, we need renewable, sustainable and globally available fuels to keep our industrial development without increasing the atmospheric CO₂ content. Is this possible? Yes!

**CO₂ as a new source of carbon feedstock**

The carbon source of fossil fuels is nothing else than atmospheric CO₂, which was converted by natural photosynthesis of green plants and algae over millions of years. In the natural photosynthesis, CO₂ and H₂O are chemically converted to higher hydrocarbons by solar energy input. This makes the discussion highly interesting, since all fossil fuels are thus, a form of recorded and stored solar energy which was shining onto our planet millions of years ago.

After realizing this, scientists can ask the important question: Can we imitate the natural photosynthesis in an artificial chemical process and get our desperately needed fuels by conversion of CO₂ into useful chemicals? The answer is yes and under the different key words such as “solar fuels, power to gas, artificial photosynthesis, photon to fuels, electricity to gas” etc essentially this process of CO₂ conversion to artificial fuels is covered. If realized, the entire energy sector can be converted to these artificial fuels created by solar CO₂ conversion, eventually outperforming the fossil fuel area. As quoted by the former Saudi oil minister, Sheik Ahmed Zaki Yamani, warning his OPEC colleagues: “The Stone Age didn’t end because we ran out of stones.” A new and better technology always prevails.

Two main approaches are being suggested to cope with CO₂ which are Carbon Capture and Sequestration (CCS) and Carbon Capture and Utilization (CCU). CCS describes the capture of CO₂ at its human-made origin (factories, power plants etc.) and its sequestration in underground (oil wells, under ocean and underground bedrocks etc.) without utilizing CO₂ as such. It is not clear if this storage over long times is sustainable, thus CCS can eventually be combined with CCU as a concentrated source of stored CO₂. Differently, CCU approach covers a broad number of processes which can be applied to address the issue where CO₂ is not only captured but also used as a feedstock for various chemicals like formic acid, carbon monoxide, methanol and methane. Michele Aresta from Bari and others have shown many different ways to utilize CO₂ as chemical feedstock.

Technically, the heterogeneous catalysts using metallic systems are in use since over hundred years in the industry. Fischer-Tropsch type catalysts are used to convert CO₂/CO mixtures into hydrocarbons since back in early 1900s in Kaiser Wilhelm Institute for Coal Research (today May Planck Institute for Coal Research in Mülheim Germany). In most of the available power-to-gas systems today, the energy is provided in the form of solar and wind hydrogen, which then reacts with CO₂ resulting in methane (CH₄). This process has been first described by Paul Sabatier and awarded with Nobel Prize for Chemistry in 1912.

The widely used forms of renewable energy conversion (solar, wind and hydropower) deliver electricity as output. Therefore, we will concentrate on electrocatalysis, photo-electro-catalysis as well as bio-electrocatalysis in the passages below. Pure photocatalysis is also an active area of research but as of today less efficient. Photovoltaic conversion of solar energy with efficiencies around 20% and the highly efficient electrolysis systems which go above 60% efficiency for hydrogen, makes the electrocatalysis systems at the end above 12-15% efficient from solar to chemical energy. This is clearly more feasible as compared to pure photochemical conversion. Furthermore, the fact that wind energy is also directly usable by the electrocatalysis systems, makes such systems even more attractive for large scale implementation.

Many scientists suggest the direct use of hydrogen gas as the future chemical fuel and energy vector. Jeremy Rifkin in his influential book “Beyond Oil and Gas: The Methanol Economy”, Olah (Nobelpize 1994)
states: “... the challenges that lie in the way to the hydrogen economy are enormous. Fundamental problems will have to be solved if hydrogen gas is ever to become a practical, everyday fuel that can be filled into tanks of our motor cars or delivered to our homes as easily and safely as gasoline...”

Therefore, we advocate to focus on CO₂ conversion into hydrocarbons as a feasible energy vector. By creating hydrogen gas and immediately converting it to hydrocarbons using CO₂ (Sabatier process) we will be better off, since the infrastructure for hydrocarbon fuels is readily available worldwide in form of pipelines, tankers, trucks as well as distribution networks.

On the other hand, equally important, this method of using CO₂, recycling to make artificial fuels using renewable energies is immediately and direct method of large scale storage. We have well established natural gas pipeline networks in many countries. Such a pipeline network has tremendous capacity of energy storage.

**Electrocatalysis of CO₂ conversion to hydrocarbons**

Below we give some illustrative and recent examples to make photoelectro- and electrocatalytic conversion of CO₂ into synthetic fuels. It is shear impossible to give a comprehensive review of scientific literature here. We refer interested readers to the listed books and the references therein. The three main sections describe the homogenous (where the catalyst and CO₂ are in same phase), the heterogeneous catalysis (where the catalyst material is in solid phase while CO₂ is dissolved in the electrolyte solution) and the bio-electrocatalysis.

Throughout the text, applied potentials and/or the potential ranges are reported versus reference electrodes like normal hydrogen electrode (NHE), saturated calomel electrode (SCE), silver-silver chloride electrode (Ag/AgCl) or the potential ranges are reported versus dissolved in the electrolyte solution) and the references therein.

The three main sections describe the homogenous (where the catalyst and CO₂ are in same phase), the heterogeneous catalysis (where the catalyst material is in solid phase while CO₂ is dissolved in the electrolyte solution) and the bio-electrocatalysis.

**Examples of Organometallic Complexes**

Without doubt organometallic complexes are the most popular class of materials in the field of CO₂ reduction. Among them, Rhenium containing complexes reported by Jean Marie Lehn group (Nobel Prize 1987) in 1984. As homogeneous catalyst for electrochemical reduction of carbon dioxide to carbon monoxide Re(bpy)(CO)₃Cl (Fig. 4) can produce 32mL of CO when held at a potential of -1250mV vs. NHE for 14h without any degradation giving a remarkable faradaic efficiency of 98% and a TON of 300. This study was a door opener in the field of carbon dioxide reduction and evoked many other studies thereafter.

In 2012, Portenkirchner and co-workers investigated the effect of extended π-conjugation on the catalytic activity of Lehn catalyst. Electrochemical characteristics of (6) were investigated with cyclic voltammetry technique and are displayed in Figure 6. It yielded a more positive reduction wave around -750mV vs. NHE which is 330mV more positive compared to the...
first reduction peak of Lehn’s catalyst. This might be explained by the increased π-conjugation.

**Examples of Heterogeneous Catalysts for CO$_2$ reduction**

Homogeneous catalysis approaches for CO$_2$ reduction have been widely used throughout the history of the field. However, as seen in the previous chapter electrochemical addressing of the catalyst material which is swimming far away from the electrochemical double layer might be an issue. Also recovery of the catalyst or separating the product from the homogeneous mixture with it, is a technological problem. Different mechanisms can lead to degradation, inhibition and eventual decrease in overall efficiency. Bearing these drawbacks in mind, researchers focused on the direct addressing of catalysts using the idea of heterogeneous catalysis.

Copper has always been the choice of metal when several products and higher hydrocarbons like methanol, methane, propanol, formic acid etc. were desired. Readers are highly advised to read the detailed work of Hori on the electrochemical reduction of CO$_2$ using various kinds of metals.$^8$

On the organometallic catalysis, the study from Lieber and Lewis was one of the earliest which addressed a heterogeneous approach.$^9$ Pyrolytic graphite or carbon cloth were used as electrodes and they were modified with Cobalt Phthalocyanine, via drop casting or adsorption from solutions in THF. They reached faradaic efficiencies up to 60% for CO and 35% for H$_2$. A magnificent turnover number of 370000 was reached in this study.

Hupp and co-workers came up with the idea of incorporating a known catalyst, namely Fe-tetraphenyl porphyrin (Fe-TPP), into a metal-organic-framework (MOF)$^{10}$. Authors note that the choice of MOF facilitated the access of solvent, reactant and electrolyte solution further into the electroactive sites via their open nanomorphology. Furthermore, the metalloporphyrinic linkers within the MOFs served as both electrocatalysts and as redox-hopping-based moieties for the delivery of reducing equivalents to catalytic sites. Authors reached faradaic efficiencies up to ~60% for CO production.

One of the early studies from Halmann used p-type gallium phosphide (GaP) as the photoelectrode for driving the reduction of CO$_2$. GaP was immersed in electrolyte solution together with a graphite rod as the counter electrode where saturated calomel electrode served as reference electrode. The choice of counter electrode was of strategic decision since it was reported that carbon does not oxidize formic acid and other carbohydrates back to carbon dioxide.

Figure 7. Three generations of conjugated conducting polymers; a) Polymers with good conductivity but low processability, b) Polymers with alkyl chains allowing solubility hence processability, c) Polymers with improved and/or new physical/chemical and catalytic properties. Reproduced with permission from reference.$^{13}$

Figure 8. Cyclic voltammogram depicting the potentiodynamic polymerization of [3HRe(bpy)(CO)$_3$Cl-Th]. Inset: Photo of a very thick film of the polymer in shiny gold color. Reproduced with permission from reference.$^{13}$
GaP electrode was illuminated using a Hg arc lamp and was biased with -1000mV vs. SCE, revealing formic acid, formaldehyde and methanol after 18 hours of irradiation.

Wrighton group reported the immobilization of Pd in a bipyridine based polymer (PQ) and its catalytic activity towards reduction of HCO$_3^-$ to HCO$_2^-$ in presence of H$_2$. Authors first polymerized the bipyridine monomer on W wires and then impregnated the polymer matrix with Pd which was achieved by consecutive dipping of the electrode first into K$_2$PdCl$_4$ and then into 0.1M KCl solution and final electrochemical treatment to yield metallic Pd. After potentiostatic electrolysis in carbonate containing de-oxygenated solutions with $^{13}$C enriched carbonate solutions they confirmed the production of formate using NMR techniques. A faradaic efficiency of 80% was achieved.

Third Generation of Conducting Polymers (Figure 7) are synthesized where a solution processable and catalytical side chain functionalized conjugated polythiophene structure is achieved.$^{13}$

Apaydin et al. investigated polythiophene structures with pendant Lehn catalyst for the photoelectrochemical reduction of CO$_2$. This is one of the few studies where the use of an organic semiconducting polymer and its light absorbing properties are used to drive photoelectrochemical reduction of with low overpotentials (250mV) (Fig. 9).

**Immobilized Enzyme-Functionalized Electrodes**

The most selective catalysts are natural enzymes. They work at ambient conditions with a remarkable selectivity toward educts and products. To utilize them in bio-electrocatalysis requires the immobilization of the enzymes on the electrodes as well as their feeding with electrons, either directly or via electron shuttle molecules.¶

Schlager et al. demonstrated the immobilization of alcohol dehydrogenase on highly porous carbon felt (CF) electrodes using alginate-silicate hybrid gel as the immobilization matrix.$^{12}$ Step-by-step preparation of matrix as well as the enzyme-entrapped electrode is given in (Fig. 10).

Alcohol dehydrogenase was used in a control experiment with immobilized enzyme in the same matrix (alginate-silicate) driven only with NADH as the electron and proton donor to check the activity of the enzymes over time. They reached a 96% conversion when NADH was the electron/proton donor$^{15}$. Formation of methanol using the same matrix but using only electro-chemical energy input without NADH resulted in a Faradaic efficiency of 10% at a constant potential of -1200mV vs. Ag/AgCl (Fig. 11 and 12).

Very recently Hathaichanok Seelajeroen et al. demonstrated the immobilization of three different enzymes on a functionalized graphene. In these nano-bio-catalysts we used graphene as electrical platform to hook three different enzymes thereon and perform the biocatalysis from CO$_2$ over formate over formaldehyde all the way to methanol (see Fig. 13).

This study showed the successful immobilization and electrochemical addressing of enzymes to achieve bio-electrocatalytic reduction of CO$_2$. NADH can be replaced in the reaction cascade with direct electron injection to enzymes. Biocatalytic systems such as enzymes and bacteria are working at mild conditions like room temperature, atmospheric pressure and are superior to all other catalysts in their selectivity.

**Summary and Outlook**

In this general review, we attempted to make the case for the idea of CO$_2$ conversion to artificial fuels using renewable energies. Using metallic, organometallic, organic and bioorganic catalysts one can initiate electrocatalytic, photoelectrocatalytic and bioelectrocatalytic reactions to achieve this goal.

CO$_2$ reduction using heterogeneous catalytic approach has advantages: The immobilization of catalyst...
material on the working electrode can allow the direct electrical addressing of catal-
yst bypassing the diffusion step as in homogenous cata-
lysts swimming in the solu-
tion. Another advantage of
course is the easy recovery of
catalyst material as opposed to
homogenous catalysis in a mixed
medium of the educts, products
and catalysts together. Economics
of electrocatalytic CO\(_2\) reduction
is still under discussion whether it will be
feasible or not in near future. Hybrid sys-
tems where the catalyst is of bio origin and
the electron source is ideally a photo-elec-
tro active compound can pave the way for
energy efficient and selective conversion of
CO\(_2\). Biocatalytic systems work at room tem-
perature, atmospheric pressure and have
superior selectivity. This can play a decisive
role in the economical calculations of large
scale CO\(_2\) reduction processes.

This avenue of making a cyclic use of car-
bon will be creating a carbon neutral fuel,
which is important to transform our energy
sector. Our future energy vector shall have
this sustainable, cyclic use of materials and
processes in accordance with the sustaina-
ble development goals (SDG) of the United
Nations. As Arrhenius stated it, our future
planetary life may depend on it.

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Figure 12. Reduction mechanisms for CO\(_2\) catalyzed by dehydrogenases. Three-step reduction of CO\(_2\) to methanol
using NADH as sacrificial coenzyme (A) and via a direct electron transfer to the enzyme without any coenzyme (B).
Reproduced with permission from reference 6.

Figure 13: Schematic description of electrically addressing three different enzymes immobilized on a functionalized
graphene sheet as described in reference 6.