

E-Mobility versus E-Fuel Mobility



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He studied and graduated at the University of Vienna. After two years postdoctoral study at the University of Stuttgart he joined the Institute at the University of California at Santa Barbara (UCSB) led by Alan HEEGER, Nobel laureate 2000 for Chemistry. Sariciftci contributed to the fields of physics and chemistry of semiconducting and metallic polymers and solar energy conversion. Inventing conjugated polymer and fullerene based "bulk heterojunction" solar cells Sariciftci published over 600 publications and with over 90000 citations he has the ranking #14 in 2011 by Thompson Reuter of the world in material science.



This paper is dedicated to the centennial anniversary of the creation of Turkish Republic by Mustafa Kemal Atatürk.

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For future mobility two important strategies are crystallizing: One possibility is to transform the entire fleet into electrical propulsion and supply the electrical energy from the electrical grid and on-board batteries (e-mobility). The other is to transform today's carbohydrate fuels from fossil fuels to e-fuels created from renewable energies. Both strategies need renewable primary energy sources to be sustainable. That brings the absolute necessity and priority of worldwide installation of renewable energy power plants like solar parks and windmills. Both avenues have advantages and disadvantages, and both of these strategies will need considerable research and technology in the field of chemistry and chemical engineering. In

this article we intend to roll out the different possibilities, how we can establish a sustainable mobility for the future of human civilization. We want to bring here the idea of conversion of CO₂ into synthetic fuels (CO₂ recycling) repeatedly into attention as a possible approach for transportable storage of renewable energy. Chemical, electrochemical, photoelectrochemical and bioelectrochemical approaches are discussed vividly as new routes towards the conversion of CO₂ into synthetic fuels and/or useful chemicals in the recent literature. The same chemical research fields are also targeting the electrochemical energy storage systems like batteries and supercapacitors and thus, necessary for e-mobility, too.

1. The need for the transformation of global mobility sector into a renewable and sustainable system

As the discussion on the future of mobility becomes more and more politically polarized, it is very important to go back to the seminal work of Svante Arrhenius. He received Nobel Prize for Chemistry in 1903 and surely is one of the most important chemists in the history. Arrhenius calculated in 1896 (!) the change in average global atmospheric temperatures upon increasing the CO₂ content in the atmosphere¹. He calculates 3 degrees increase of the average global atmospheric temperature upon increasing the CO₂ content by a factor of 1.5. In 1900, the CO₂ content in the atmosphere was around 300 ppm¹. Today it is exceeding 410 ppm². It is safe to conclude, that we are on the best way to the predicted increase in average global atmospheric temperature, which will have severe consequences, globally.

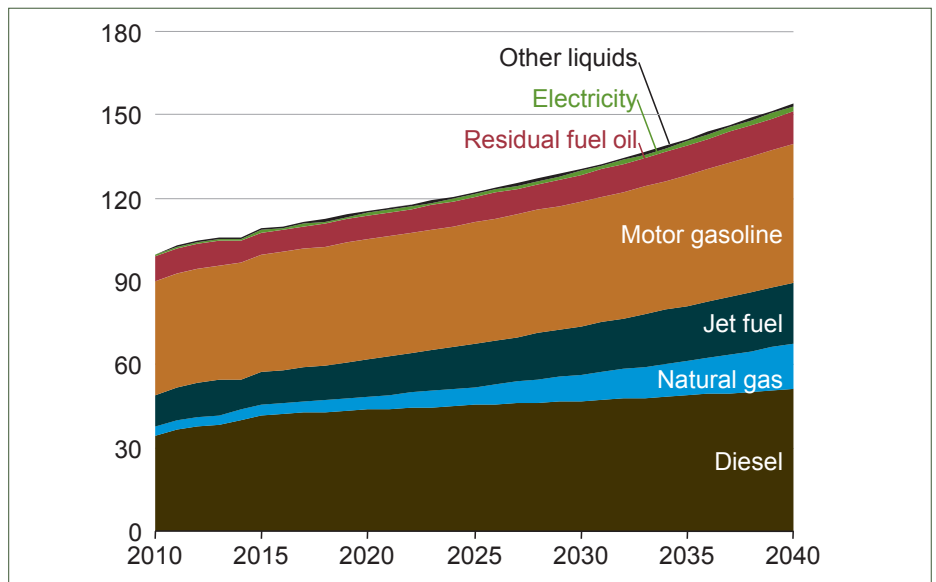


Fig. 2: World transportation sector delivered energy consumption 2010-2040 (quadrillion Btu). Reproduced from International Energy Outlook 2016, p. 127, U.S. Energy Information Administration. Other liquid fuels include natural gas plant liquids, biofuels, gas-to-liquids and coal-to-liquids.

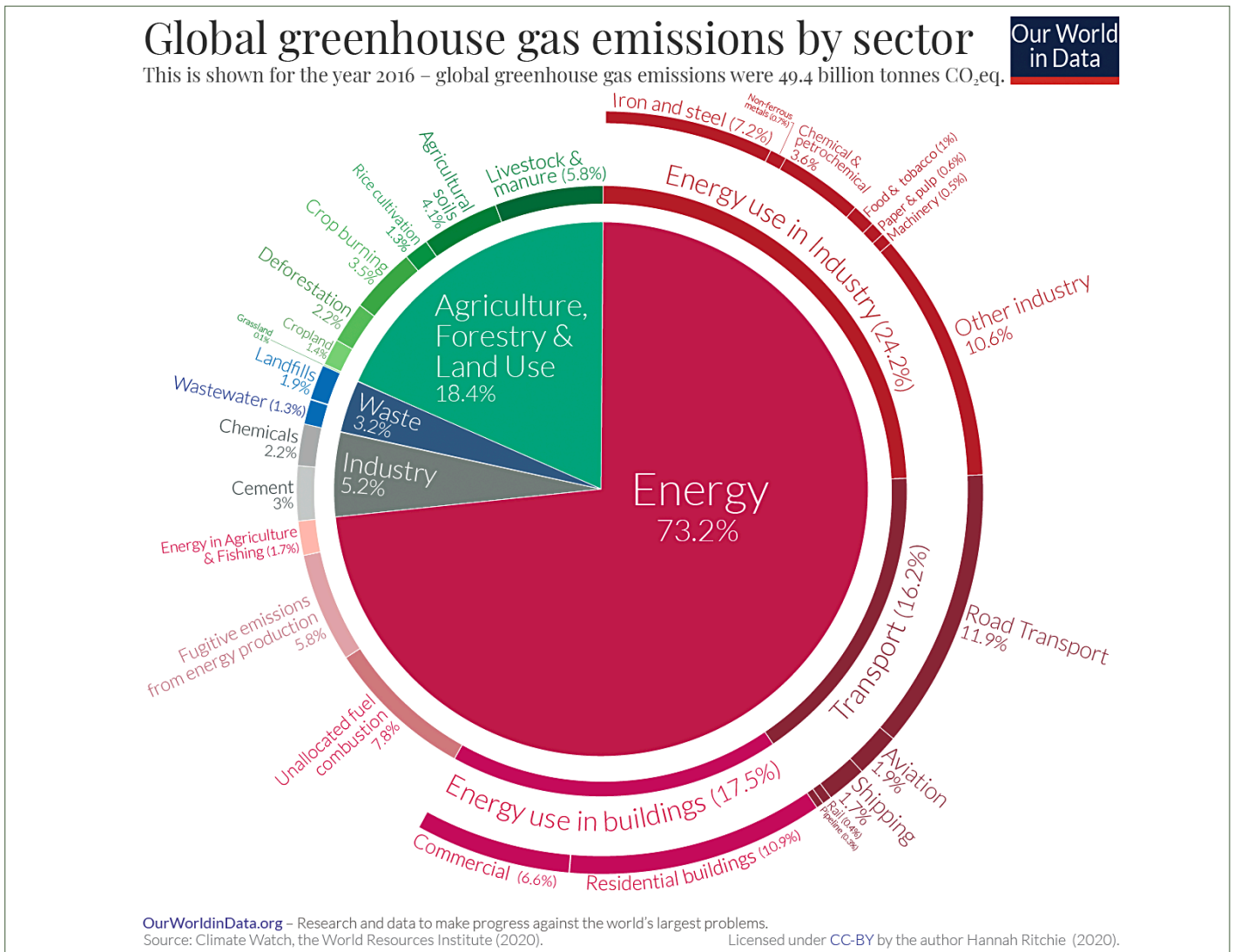
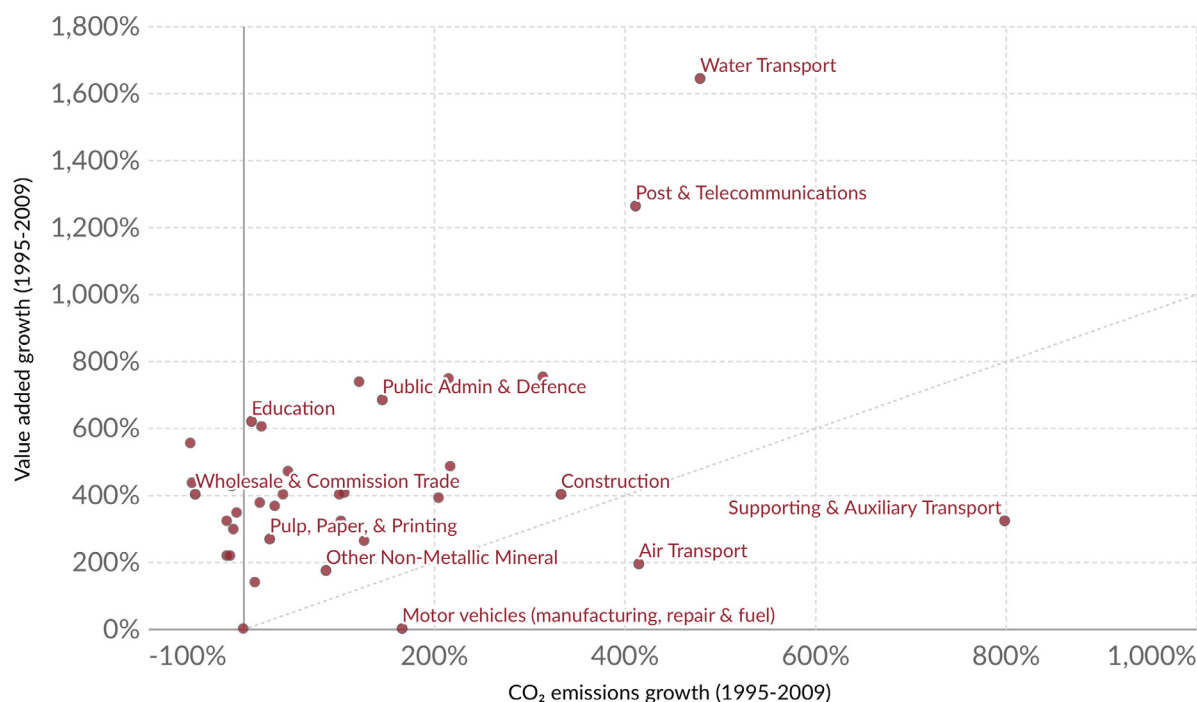


Fig. 1: The humanity needs transport of goods and persons globally for the continuing development of the economic and social life. Transport is an essential part of human civilization like food, shelter, clothing and consumes large amounts of energy. Most of the energy used in transportation sector today comes from fossil carbohydrates.

Value added growth vs. CO₂ emissions growth in China

Gross domestic product (GDP) growth of individual sectors (adjusted for inflation) versus growth in carbon dioxide (CO₂) emissions over the period 1995-2009. Sectors in the top left quadrant have decoupled their emissions from economic growth - whilst their emissions fell, their economic value grew. Direct emissions of households are not included.



Data source: (WIOD) World Input-Output Dataset

OurWorldInData.org/co2-and-greenhouse-gas-emissions | CC BY

Fig. 3: As an example, we display here the growth of the transport sector and associated CO₂ emissions in China

Furthermore, increase of average global temperature up to 6 degrees is predicted by Arrhenius upon increasing the CO₂ content by a factor of 2. The increase of CO₂ by a factor of 3 will take us back to Tertiary times when "...arctic temperatures have exceeded the present temperature about 8-9 degrees".

The dilemma consists of the fact that our civilization is based on and driven by carbon based energy resources. Ever since the cavemen cultivated fire, we continuously have been burning natural resources such as wood, coal, oil and gas to create the energy we need³. It is indeed remarkable, how little progress we made in the energy sector as compared to the medicine and mechanical engineering as well as information technology. We are still burning hydrocarbon fuels today.

In many discussions the argument appears, that the world economy is growing therefore the energy consumption is also increasing. But especially the transport sector is not linearly growing but the CO₂

emissions increase more than the value added growth of the sector.

In addition, the global transport sector is in grave risk, since the existent fossil fuel reserves are localized mostly in politically unstable regions of the world. This will be a massive political challenge for the rapidly growing economies in China, India and others in the Asia-Pacific Rim.

We need a renewable, sustainable, CO₂ neutral and globally available energy for our transportation system to keep our industrial development without increasing the atmospheric CO₂ content. Is this possible? Yes!

2. The two strategies: E-Mobility versus E-Fuel Mobility

Definitions:

Firstly, both e-mobility and e-fuel mobility need renewable and CO₂ neutral primary energy supply such as solar and wind energy. The prime directive should be creating and distributing renewable energy all around the world to meet the "Terawatt

challenge" as stated by Rick Smalley (Nobel Prize for Chemistry in 1996)⁴. This challenge urges us to install the renewable energy conversion systems preferably in locations, where efficiency will be maximum, and the transportation of that energy is possible. That means the solar power plants shall be built at the sites with maximum solar irradiation and wind mills should be erected in places with maximum efficiency and continuity of wind power generation. Furthermore, this Terawatt challenge will only be possible to be solved, if we convert the primary renewable energy created in such locations into a storable and transportable form. Details below.

There is quite a confusion with this important point in the energy sector. Let's clarify the important condition for CO₂ neutrality:

It may bring some improvement towards the energy efficiency driving an electrical car by fossil fuelled electrification. But global CO₂ emissions will be surely increasing after all. If Titanic would have electrical motors for propulsion it will still remain a coal powered ship. Therefore, e-mobility with fossil fuel

electrification is a cul-de-sac. Driving an electrical car does not make it automatically CO₂ neutral. We always have to ask the important question: "Where does the electricity come from? Which primary energy mix is used in local electrical grid?"

The same applies to the production of "grey hydrogen" as fuel. One can create hydrogen gas by stripping hydrogen atoms from a fossil carbohydrates, also producing CO₂ in molar proportions. Therefore, such synthetic hydrogen is not CO₂ neutral. Grey hydrogen systems, which are in discussion and implementation in many places under the name of "The Hydrogen Economy", lead to the same cul-de-sac. A hydrogen based energy vector does not lead automatically to CO₂ neutral energy/transport systems. We always must ask the important question: "Where does the hydrogen gas come from? What kind of primary energy is used to create such fuels?"

All electrification and all e-fuel production must be fully driven by the primary input of renewable energies to call them "green gas", "green e-fuel" or "CO₂ neutral".

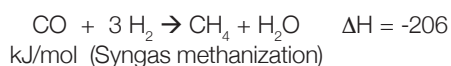
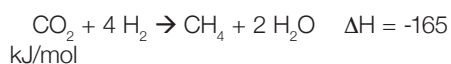
3. What about bio-fuels?

This question is indeed important and shall be addressed here shortly. The biofuels such as bio-diesel from canola oil, bio-gas as well as bio-ethanol from sugar cane etc. are often seen as game changer. However, these "first generation" biofuels are competing with the food sector directly over the available agricultural land. This brings a limit for the large scale use of these biofuels. If the use of land is limited than food sector has the absolute priority. It is not acceptable, that rich countries buy bio-fuels for a CO₂ neutral mobility at high prices and large populations of the poor countries cannot compete with these prices for agricultural products and starve. Ethical and economical limits will thus hinder the growth of such bio-fuel economy.

The "second and third generations" of biofuels are based on bio-technology of agricultural waste, bio-algae even photo-synthetic bacteria and can be cultivated in water. Therefore, such "advanced biofuels" shall be preferred against the "agriculture crop based" bio-fuels. Here we just want to mention our expectation, that this field of advanced bio-technology for fuel production will develop into new horizons by the next generation of biochemistry. In this paper we will not go into details of this beautiful and vast biochemical research field.

4. Paul Sabatier forever

The historical breakthrough reactions, relevant to our discussion here are from Paul Sabatier:



The Paul Sabatier reactions (1897) for catalytic hydrogenation of carbon dioxide and carbon monoxide are named after the French chemist who received Nobel Prize for Chemistry in 1912. Even though historically these reactions are used to transform coal and steam into methane gas, they are also basis for e-fuels. These equations are the basis for all other dehydrogenation techniques like steam reforming of methane to produce "grey hydrogen". Synthetic natural gas production as well as Fischer-Tropsch liquid fuel production from syngas mixtures are also derivatives of these Sabatier equations using water-gas shift reaction and/or dry reforming, they result in many different hydrocarbons. All these processes are only CO₂ neutral, when they are driven with renewable energy sources.

If we have a green hydrogen gas produced for example using solar or wind energy from green electrolysis of water (Hydrogen H₂(g) ΔH= 285.8 kJ/mol) these Sabatier reactions are called today, power-to-gas, e-gas, e-fuels, etc. From basic considerations the standard reaction heat of methane gas CH₄ (ΔH = -890.4 kJ/mol) can never be fully compensating the energetic input to create the 4 moles of hydrogen gas (4x 285.8 = 1143.2 kJ) to reduce CO₂ with the loss of -165 kJ/mol. If we use the syngas reaction with 3x H₂ input of 857.4 kJ it looks energetically better but we have to create CO from CO₂ and this is also energetically costly.

All these considerations are indeed necessary to understand that the e-fuels are demanding a large amount of energy input. Therefore, we have to give credit to the argument, that to create e-fuels need large amounts of primary renewable energy. Why not use the renewable electrical energy from wind and solar directly in electrical cars? It is of course tempting to go in this political direction which takes place in European politics today. However, the picture looks very different, if we calculate the storage of the renewable energies globally. Another basic problem is to build the e-mobility infrastructure worldwide. Such high power electrical charging stations and distribution grids for them is indeed a financial and logistical challenge. We will need a completely new and powerful electrical distribution network worldwide. We have to consider this investment also carefully

5. CO₂ neutral e-fuels as storage medium for renewable energies

These same Sabatier equations above can also be used to produce green methane, and the other "green" CO₂ neutral e-fuels, when we insert green hydrogen into these equations above. Such green hydrogen shall be fabricated from electrolysis of water using renewable energies like solar and wind. In burning those "green" e-fuels we will emit the same amount of CO₂, which was used for the creation of the green e-fuels themselves, i.e. such e-fuels are CO₂ neutral. Such e-fuels can be used directly in standard combustion engines without adding CO₂ to the atmosphere. That implies, we can use the existing transport fleet in its entirety and still be CO₂ neutral, if we use these green hydrogen or CO₂ neutral e-fuels. This can be saving time and investment cost

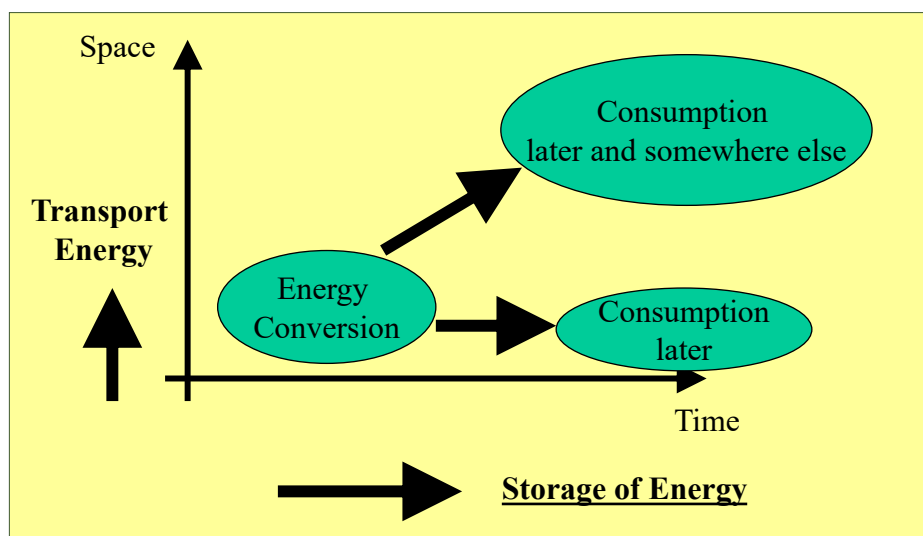


Figure 4. Space-Time diagram explaining the relation between transport and storage of energy. For a sustainable use of renewable energies these problems of storage and transport have to be solved.

and accelerate thus the transition from fossil energy driven transport to the CO₂ neutral transport worldwide in a short time.

The Storage-Transport Challenge of Renewable Energies:

The real problem starts with the storage of the large amounts of renewable energies we create to utilize them in the human society. Thus, the sunshine and wind are not continuous and have to be stored for further use in a later time (pure storage) and/or to be consumed at somewhere else (transportable storage). The transportation of the electrical energy in large scale is costly and have to be built worldwide. In contrast, if we create a CO₂ neutral e-fuel from these renewable energies, the entire fleet of tankers, large pipelines, distribution networks and gas-line stations are existent. We do not need to create a new energy vector. We will use the existing fleet and start using renewable and CO₂ neutral fuels immediately.

The widely used forms of renewable energy conversion (solar, wind and hydropower) deliver electricity as output. 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 % efficient from solar to chemical energy. This is clearly more feasible as compared to photosynthetic energy 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.

There is a great momentum for the direct use of hydrogen gas as the future chemical e-fuel and energy vector. Jeremy Rifkin, in his book "The Hydrogen Economy", describes a future where hydrogen gas is the global energy vector. As of today, the storage of hydrogen gas as well as feasible supply of liquid hydrogen are still a problem. In his influential book "Beyond Oil and Gas: The Methanol Economy", George Olah (Nobelprize 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 the conversion of CO₂ into hydrocarbons as a feasible e-fuel. By converting the renewable hydrogen gas immediately to hydrocarbons using CO₂ (see Sabatier process) we will be better off and faster to implement, since the infrastructure

for hydrocarbon fuels is existing and readily available worldwide.

On the other hand, equally important, this method of using CO₂ recycling to make artificial fuel is an excellent method to store the renewable energies in a transportable chemical fuel (Fig. 4). When we are talking on Terawatthours of energy storage capacity, it is nearly impossible to supply this with battery systems. Such a conversion of CO₂ into artificial fuels using renewable energies is immediate and direct method of large scale energy storage. We have well established natural gas pipeline networks in many countries. Such a pipeline network has tremendous capacity of energy storage.

6. The photo/electrocatalytic conversion of CO₂ to hydrocarbons

In this journal we already outlined our research in an illustrated article before⁵. There is ample scientific and patent literature and it will go well beyond the scope of this commentary article to list them all. Interested reader is guided to some milestone books listed below and the references therein.

In general this research field in chemistry is divided into three big lines:

1. Homogeneous catalysis of CO₂ using catalysts also in the same phase. The products are in most of the cases not very selective and therefore there is a challenge to separate the products as well as regain the catalysts from the reaction chamber mixture.
2. Heterogenous catalysis of CO₂ using catalytically functionalized electrodes. In this way the catalysts are immobilized at the electrodes and the products are easily separable from the catalysts.
3. Bio-electro catalysis using enzymes as well as living bacteria immobilized directly on the electrodes. The perfect selectivity of such enzymes and their operation at room temperature are their most important advantages.

Assessing the catalyst performance is of high importance for comparing different catalyst materials. There are several figures of merit given through the papers, namely, Faradaic efficiency, catalytic rate constant *k*, overpotential and turnover number.

Faradaic efficiency (FE) defines the selectivity of a catalyst towards a particular product and can be calculated as: (moles product / moles of electrons passed) × (number of electrons needed for conversion).

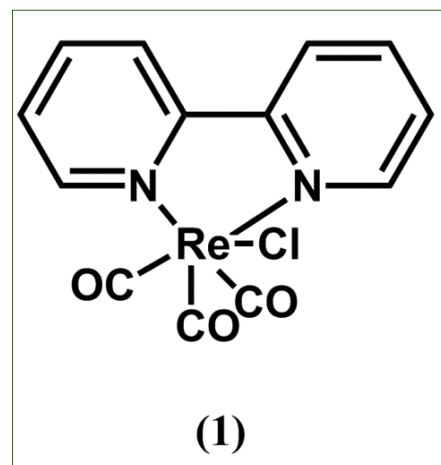


Figure 5. Molecular structure of Re(bpy)(CO)₃Cl (Lehn's catalyst)

Catalytic rate constant (*k*) can be defined as a coefficient related to the rate of a chemical reaction (in this case reduction of CO₂) at a given temperature and the concentration of reactant.

Overpotential = (applied potential – thermodynamic (or formal) potential) for conversion.

Turnover number (TON) = moles of desired products / number of catalytically active sites (or moles of catalyst).

Example of organometallic homogeneous catalyst: Jean Marie Lehn catalyst

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 (Nobel Prize 1987) group. As homogeneous catalyst for electrochemical reduction of carbon dioxide to carbon monoxide Re(bpy)(CO)₃Cl (Fig. 5) 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 evoked many other studies thereafter⁶.

Examples of heterogeneous catalysts for CO₂ reduction

Metal electrodes and/or metal nanoparticles decorated electrodes make the major field of research in the heterogenous catalysis of CO₂ and H₂.

Copper has always been the choice of metal for higher hydrocarbons like methanol, methane, propanol, formic acid etc. Readers are highly advised to read the detailed work of Hori on the electrochemical reduction of CO₂ using various kinds of metals⁷.

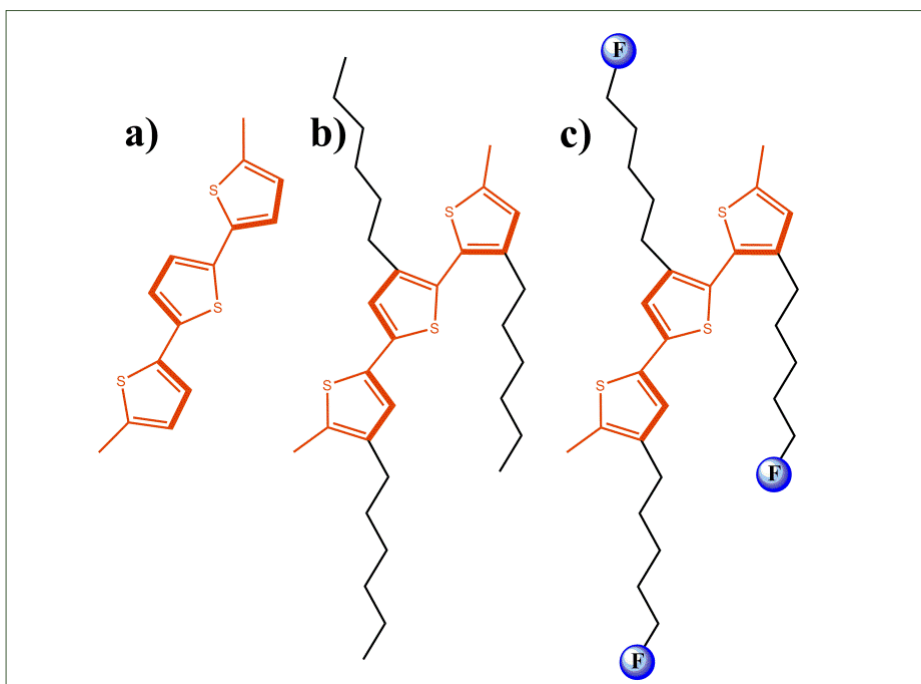


Figure 6. Three generations of conjugated conducting polymers; a) Polymers with good conductivity but low processability, b) Polymers with alkyl chains allowing solubility hence processability, c) Polymers with improved and/or new physical/chemical and catalytic properties. Reproduced with permission from reference 12.

On the organometallic catalysis, the study from Lieber and Lewis was one of the earliest which addressed a heterogeneous approach⁹. Using pyrolytic graphite as electrode modified with Cobalt Phthalocyanine, they reached faradaic efficiencies up to 60% for CO and 35% for H₂. A magnificent turnover number of 370000 was reached in this study.

Hupp and co-workers came up with the idea of incorporating Fe-tetraphenyl porphyrin (Fe-TPP), into a metal-organic-framework (MOF)⁹. The choice of MOF facilitated the access of solvent, reactant and electrolyte deep into the electroactive sites via their open nanomorphology.

One of the early studies from Halmann used p-type gallium phosphide (GaP) as the photoelectrode for driving the reduction of CO₂¹⁰. GaP was immersed in electrolyte solution together with a graphite rod as the counter electrode where saturated calomel electrode served as reference electrode. The 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)²⁺ and its catalytic activity towards reduction of HCO₃⁻ to HCO₂⁻ in presence of H₂¹¹. A faradaic efficiency of 80% was achieved.

Third Generation of Conducting Polymers (Figure 6) are synthesized where a solution processable and catalytical side chain functionalized conjugated polythiophene structure is achieved¹².

Apaydin *et al.* investigated polythiophene structures with pendant Lehn catalyst for the photoelectrochemical reduction of CO₂¹².

Examples of immobilized enzyme-functionalized electrodes

Natural enzymes work at ambient conditions with a remarkable selectivity toward educts and products. To utilize them in bio-electro-catalysis requires the immobilization of the enzymes on the electrodes as well as their feeding with electrons, either directly or via electron shuttle molecules¹³.

Schlager *et al.* demonstrated the immobilization of alcohol dehydrogenase on highly porous carbon felt electrodes using alginate-silicate hybrid gel as the immobilization matrix¹³.

7. Summary and outlook

In this general review, we attempted to make the discussion for the pro and contra for the two mobility solutions of the future: E-mobility versus e-fuel mobility.

E-mobility is directly using the renewable electrical energy and has therefore the advantage of avoiding conversion losses. The big disadvantage is the non-existing infrastructure for the charging stations for large scale deployment of electrical energy therein. Where it is possible to have existing infrastructure (like in developed countries'

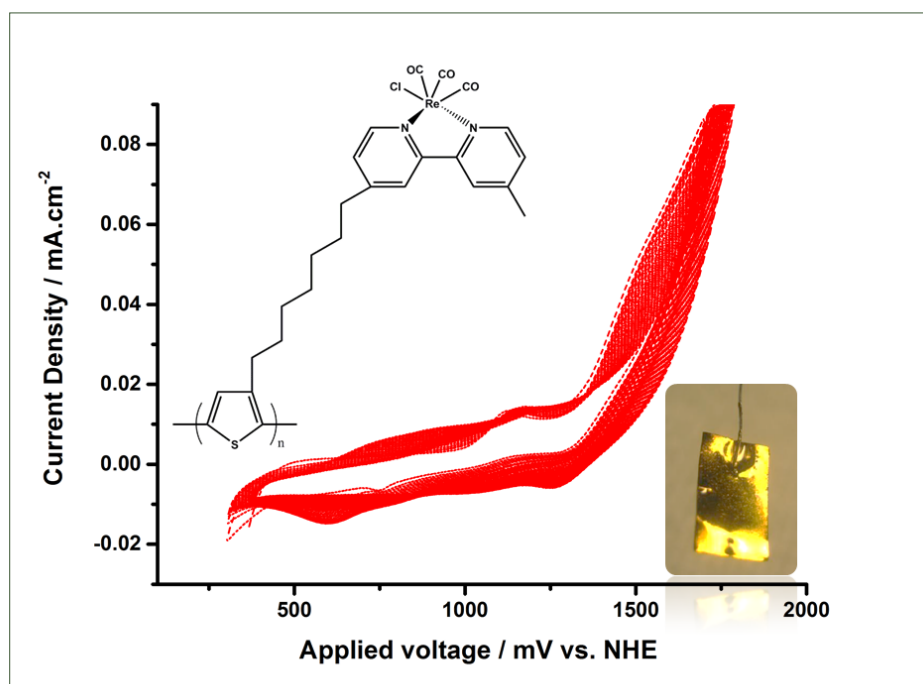


Figure 7. Cyclic voltammogram depicting the potentiodynamic polymerization of [3HRe(bpy)(CO)₃Cl-Th]. Inset: Photo of a very thick film of the polymer in shiny gold color. Reproduced with permission from reference 12.

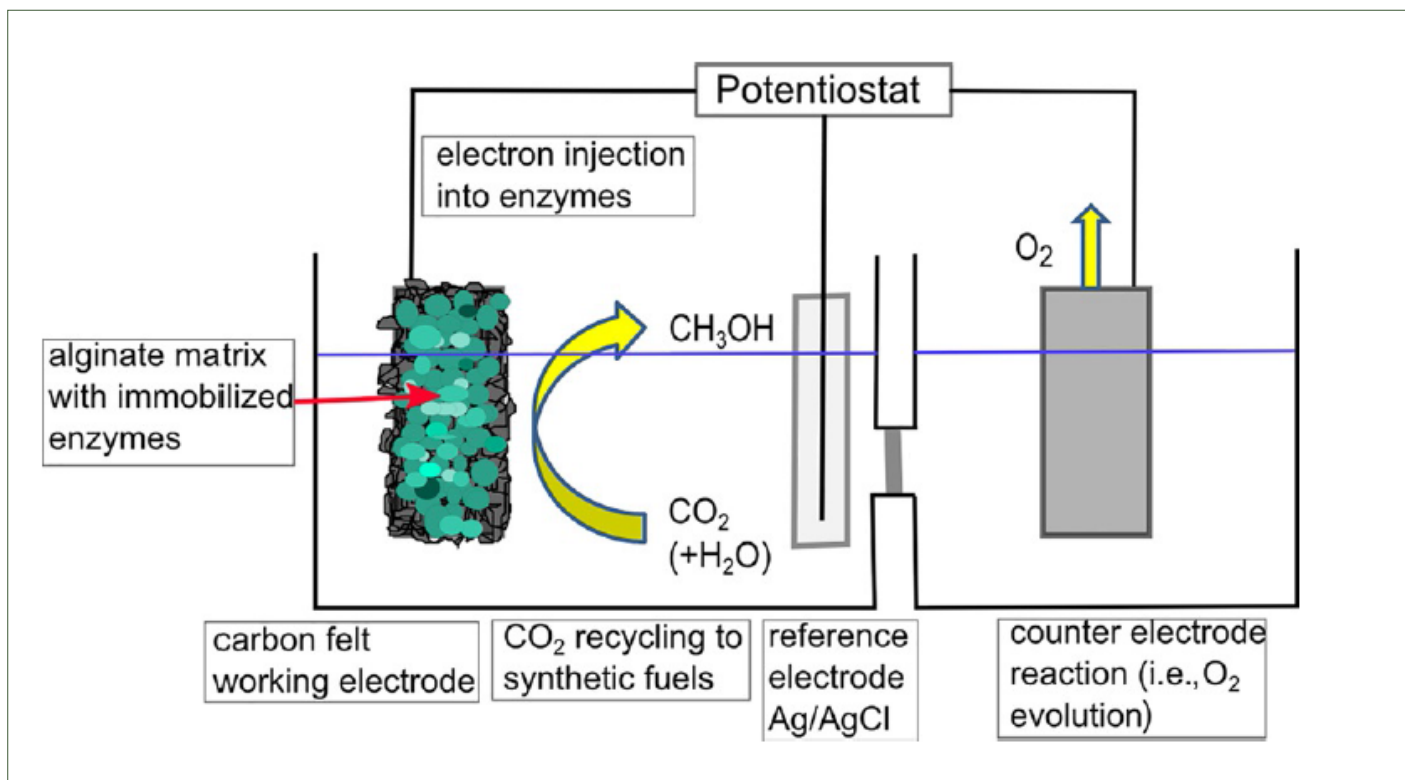


Figure 8. Representation of the electrochemical CO₂ reduction using enzymes. Electrons are injected directly into the enzymes, which are immobilized in an alginate–silicate hybrid gel (green) on a carbon-felt working electrode. CO₂ is reduced at the working electrode. Oxidation reactions take place at the counter electrode. *Reproduced with permission from reference 13.*

single homes or small towns) renewable energy can be used directly at very short vicinity and for individual energy autarky. E-mobility makes a lot of sense in such application environments. However, even then, the unsolved problem of renewable energy storage is waiting to be solved.

E-fuel mobility solves two big problems at the same time:

1. The availability of existent infrastructure of fuel distribution, pipelines, tankers, gasoline stations as well as the transportation fleet saves the investment for a new worldwide grid. This saving on investment shortens the timescale of deployment.

2. The storage of the supply driven renewable energies in chemical energy makes them transportable and deployable with our demand oriented energy system. Maybe this is the most critical argument in favor of the e-fuel mobility.

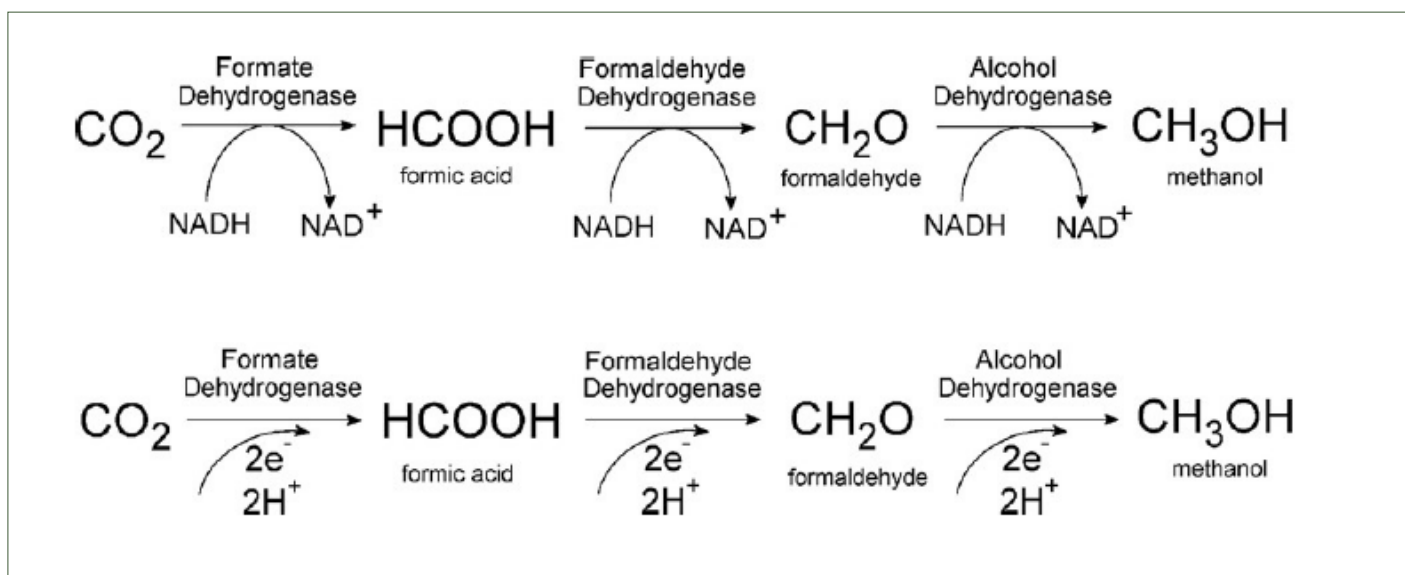


Figure 9. Reduction mechanisms for CO₂ catalyzed by dehydrogenases. Three-step reduction of CO₂ to methanol using NADH as sacrificial coenzyme (A) and via a direct electron transfer to the enzyme without any coenzyme (B). *Reproduced with permission from reference 13.*

A cyclic use of carbon will be creating a carbon neutral fuel making our future energy vector sustainable in accordance with the sustainable development goals (SDG) of the United Nations.

This is a civilization step if we can convert the energy system from linear use of carbon to a cyclic use very similar to the photosynthesis-metabolism cycle of carbon in nature. Therefore, many specialists call this discipline of the e-fuel catalysis as “artificial photosynthesis”.

Acknowledgement:

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