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Review

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The latest state-of-the-art on artificial photosynthesis

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Abstract : Conversion of carbon dioxide into value added chemical fuels (methanol and ethanol) using renewable energy (sunlight or electricity derived from sunlight) is of great importance from the point of view of addressing the CO_2 associated global warming, energy crisis (depletion of fossil fuels) and energy storing problems to a great extent. This is process is popularly known as artificial photosynthesis. The importance of electrochemical reduction of CO_2 and the underlying reaction mechanisms, and the latest developments in electrochemical CO_2 reduction process, and the CO_2 speciation are presented and summarized in this article. Further, this manuscript discusses how the electrochemical reduction process is superior over stoichiometric, thermochemical, photoelectrochemical and photocatalytic processes as far as artificial photosynthesis is concerned.

Keywords : Carbon dioxide; Speciation; Electrochemical cells; Artificial photosynthesis; Global warming; Energy crisis.

THE PRIOR ART

Recently, the conversion of carbon dioxide into value added chemicals using exclusively solar energy, which is popularly known as artificial photosynthesis, has received a great deal of attention from the scientific community as it deals with the CO_2 associated global warming problem[1-3] energy crisis (i.e., depletion of fossil fuels)[4-6], and storing energy (electricity or sunlight) in a most desirable form of liquid fuels with sufficiently high energy density[7]. Recently, the Intergovernmental Panel on Climate Change (IPCC) has concluded that the fossil fuel burning and deforestation are responsible for increased CO_2 concentrations in atmosphere. The atmospheric anthropogenic CO_2 concentrations have risen by ~30% from pre-industrial (prior to 1750) levels of 280 ppm to 400 ppm today. The present CO_2 levels in atmosphere are higher than at any time during the last 650000 years for which the reliable data was extracted from ice cores[1-3,8,9]. The CO_2 associated greenhouse effect was first noted by Joseph Fourier in 1824 and was further substantiated quantitatively later on by Svante Arrhenius in 1896. The greenhouse gases warm the planet's atmosphere and surface by absorption and reemission of the infrared radiation of solar light. The civilization and industrialization have not only brought technology, modern life, and convenience to the human beings but also pollution and emissions from factories, vehicles, and chemical plants. Several national governments have signed and ratified the Kyoto Protocol of the United Nations Framework Convention on Climate Change aiming at reducing CO_2 gas emissions[1-3]. Recently, the International Energy Agency (IEA)-World Energy Outlook (WEO) revealed that, based on policies being practiced at the moment, by 2030 CO_2 emissions will attain 63% from today's level, which is almost 90% higher than those of 1990[10]. Hence, to avoid further increase over the next few decades, improved actions than those of currently practiced should be taken, which include the development and employment of technologies to cut down CO_2 emissions[10]. One of such options is to capture the CO_2 generated at major outlets (mainly at thermal power plants), where each tonne of coal is burned to release about 4 tonnes of CO_2, and prevent it from entering into atmosphere by suitably capturing it and then storing in safe places. Further, this captured CO_2 can also be converted into several value added and fuel chemicals[4]. At present, the readily available technology to tackle with CO_2 associated global warming problem is CO_2 sequestration process[10]. This process also called as carbon capture and storage (CCS). On the other hand, the carbon capture and utilization (CCU) process has been considered to be an economically valuable option in comparison to CCS process. Besides economic benefits, the socio-political benefits also come in terms of a positive image for companies adopting policies of utilizing CO_2 formed from fossil fuels[3,7,11].

The use of CO_2 as a building block for the synthesis of chemicals can in fact contribute to a sustainable chemical industry, and as a consequent reduce CO_2 emissions into the atmosphere[11]. Further, CO_2 can also be used as a fluid in several applications. At present, all over the world, there are increased research efforts to develop effective methods that utilize CO_2 as a feed stock[3,7,11]. Many industrial methods have been developed to have an encouraging influence on atmospheric CO_2 so that the captured CO_2 is need not have to be buried or vent into an open atmosphere. Bulk chemicals at present being produced from CO_2 are urea, salicylic acid, and polycarbonate-based plastics[4,11]. CO_2 is also a solvent, for example, supercritical CO_2 (the state existing at 31°C and 72.8 bars pressure) tender several advantages in terms of stereo-chemical control, product purification, and environmental issues for synthesizing certain fine chemicals and pharmaceutical compounds. Other opportunities for using CO_2 include enhanced oil and gas recovery, enhanced agricultural production, and ponds of genetically modified algae so that biodiesel can be produced from power-plant CO_2[11]. All these methods can reduce CO_2 emissions by at least 3.7 gigatons per year (approximately 10% of total present annual CO_2 emissions), which, in fact, can reduce the use of fossil fuels. Further reductions in CO_2 emissions could be possible if these technologies are expanded far widely. Since, total anthropogenic CO_2 emission is ~25 gigatons per year, the CCS process is definitely a major readily available solution to mitigate CO_2 related global warming problem at the moment[10].

On the other hand, today, the majority of the world's primary energy requirement is met from fossil fuels. Power plants use fossil fuels (coal, oil or natural gas) to produce electrical energy. As per today's consumption rate, the available coal reserves will last for another 130 years, natural gas for 60 years, and oil for 42 years[3,7]. As shown in Figure 1, Hubbert's curve shows that in next 40 years the recoverable oil becomes significantly low and suggests finding an alternative energy economy in the next 20-year timeframe on an urgent basis[12]. It is important to realize the reliable alternative energy resources, before the oil resources are completely exhausted. Oil and natural gas are the starting materials for several important chemicals that are today used in every day-to-day life of the society. Hence, we cannot afford to use such important limited oil, natural gas and coal resources only to meet just energy needs instead of several other important chemical needs of the future human generations. Further, these resources are not only to use for just few decades of the future but for the continued industrial applications of next several centuries. In addition to these, the current fossil fuel consumption rate, their particular geographic distribution, and the political control over them pose problems for the nations which are fully dependant on fossil fuels. The rapidly growing population and industrialization are also further demanding the increased energy requirement day-after-day[3,7].

Out of today's total energy consumption, about 43% is provided by oil and derived liquid fuels which include gasoline, diesel, jet fuels, gasoil, etc.[3,7]. Only about 17% energy requirement is met by the electricity. It is hard to depend only on electricity as the actual energy density of electricity storing batteries is too low for many energy-intensive applications as their capacity for storing energy per kilogram of weight or for the unit volume is only about 1% in comparison to gasoline's energy density (Figure 2)[3,7]. Even if there

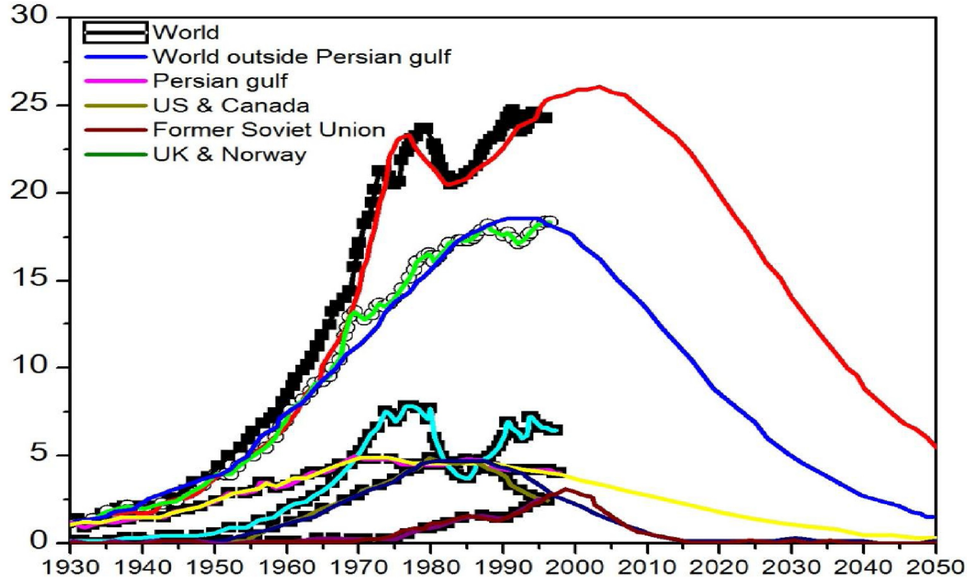


Figure 1 : This graph shows the classic Hubbert curve, indicating that world oil resources are on track to critically deplete within 40 years. While this figure is hotly debated, what is clear is that oil has a host of useful industrial applications and to irreversibly burn oil jeopardizes the future. The vertical scale is in arbitrary relative units, but to get an idea of scale, world production averaged at about 80 million barrels per day in 2008 (adapted from[12]).

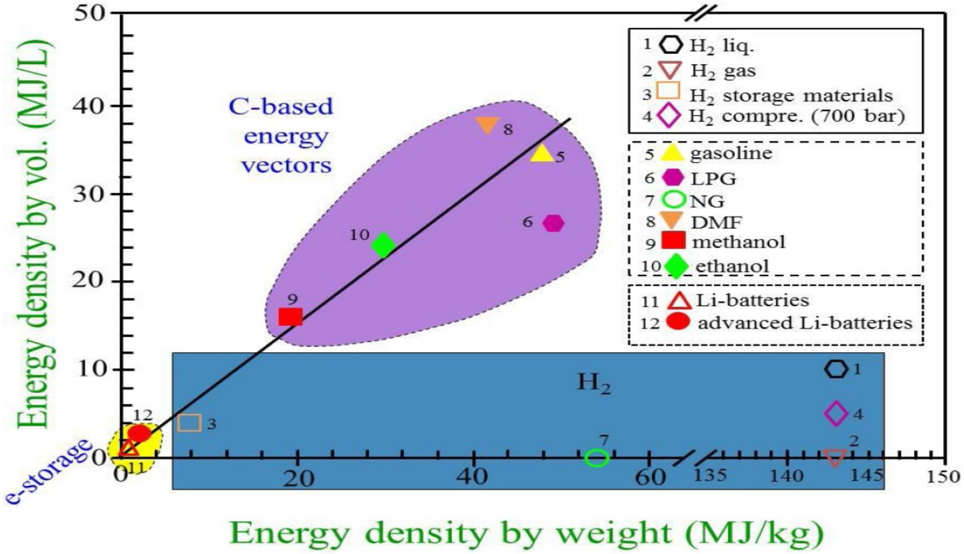


Figure 2 : Energy density per weight vs. per volume in a series of liquid and gaseous fuels (from fossil sources, or renewable such as ethanol and DMF), H_2 (liquid, gas, compressed at 700 bar, and stored in advanced nano-material) and electrical energy (Li ion batteries, conventional and advanced). NG: natural gas; DMF: dimethyl furan; LPG: liquefied petroleum gas (adapted from[7]).

is a breakthrough in the research of energy storage in batteries, these batteries cannot meet the requirement of many of the existing applications. Further, batteries also have certain limitations with respect to their cost, lifetime, time of recharge, etc.. It has been estimated that even if all the vehicles run with electricity in the future, the demand for electricity would increase by only <1% extra[3,7]. Besides this, at the moment, batteries cannot be used to run certain heavy vehicles such as, planes, buses, trucks, etc., as they need an on-board energy feeding with high energy density and easy to fill fuels (liquids)[3,7]. Liquid fuels possess about 100 times higher energy density (~50 MJ kg^{-1}) in comparison to many of the available energy storage methods (Figure 2). Hence, carbon-neutral, sustainable and easy to scale-up fuel storage methods are required to be developed as alternatives to the fossil fuels.

ENERGY DENSITY COMPARISON OF VARIOUS FUEL CHEMICALS

The important resources of renewable energy are biomass, solar, wind, tides and hydro-based systems. Except, biomass all others produce electricity. The production of liquid fuels from biomass has been identified to be quite laborious, and probably much research is still needed to find out a more economic and easier way[3,7]. The both nuclear and biomass (non-fossil energy alternatives) cannot supply the today's total energy demand that is met from fossil fuels. Furthermore, other than liquid fuels, even if any fuel is produced from renewable energy resources like sunlight, that will disturb the present energy supply infrastructure leading to substantial consequences to the global economy. In the recent past, it was thought that H_2 could replace the fossil fuels, but it could not do so. At this moment, the main source of the most of commercial H_2 is still fossil fuels (mainly natural gas) and for generating a unit of heat from H_2, more CO_2 is generated than directly burning those fossil fuels. At present, H_2 produced following electrolysis methods is expansive and it cannot be compared with the cost of H_2 produced from fossil fuels. As on today, the self-sufficiency in energy is each and every country's primary objective. In fact, most of the following strategies for achieving this goal are either environmentally unacceptable and are not feasible except those depend on fossil fuel based resources such as natural gas[3,7]. As the conventional nuclear power plants need uranium, which is limited and has always associated with the problems of radiation leakage due to natural calamities, etc., the solar energy is considered to be the only potent non-fossil fuel renewable energy resource. It is estimated that in a two weeks' time, the surface of the earth receives the energy that is equal to the total energy that is present in the entire world's fossil fuel resources (10^{16} kW)[13]. The mean solar irradiance at normal incidence outside the atmosphere is 1360 W/m^2 and the total annual incidence of solar energy in India alone is about 10^7 kW and for the southern region, the daily average is about 0.4 kW/m^2. In every hour, the earth receives solar energy that is equal to the entire world people's energy requirement in a year. Further, solar energy is clean, non-polluting, inexhaustible and carbon-free, hence no question of climatic problems such as global warming[13].

In year 2004, the world's energy requirement was about 18 TW and it is expected to reach 28 TW in the year 2030. One of the energy agencies predicted that if the solar irradiance of 1% of the Earth's surface is converted into storable energy with 10% efficiency, it would provide a resource base of 105 TW that is equal to the several times of the estimated world energy requirement in the year 2050[7]. Whereas, the amount of energy that could be extracted in the same year 2050 from wind, tides, biomass, and geothermal would be only 2–4 TW, 2–3 TW, 5–7 TW, and 3–6 TW, respectively. Furthermore, energy needs to be supplied continuously day and night without any interruption. Even though, solar light energy is enough; it is not available in the nights and on cloudy days. Hence, to supply solar energy continuously to the society, a proper method is required to store it in a suitable form[7]. However, the most of the solar energy storage methods developed so far are associated with low energy densities. The energy density by mass of compressed air (300 atm.), batteries, flywheels, super-capacitors, H_2O pumped 100 meters uphill are estimated to be ~0.5 MJ kg^{-1}, ~0.1–0.5 MJ kg^{-1}, ~0.5 MJ kg^{-1}, ~0.01 MJ kg^{-1}, and ~0.001 MJ kg^{-1}, respectively[7]. Although several technologies including photovoltaic cells, Peltier (or Seebeck) modules, Fresnel lenses, concentrated solar radiation, solar thermal energy, etc., have already been developed for converting sunlight into electricity, there is a discontinuity between solar irradiation and power consumption during the year and in terms of geographical distribution[7]. The same is true even for wind and tide based energy resources. Therefore, it is required to realize a suitable method to store and transport the solar energy in the suitable chemical form. Using technologies available today, solar energy can be stored in the form of hydrogen by splitting water into hydrogen and oxygen using electricity that is produced from solar energy (eq. 1)[7]. Although, methods like bio-routes (that use cyano-bacteria or green algae), high temperature thermochemical routes (that use concentrated solar radiation), photoelectrochemical water splitting or photo-electrolysis routes, etc., produce H_2 at atmospheric pressure, eventually this H_2 needs to be compressed in a pressure cylinder for using it in any of its intended applications.

$$2H_2O + h\nu \text{ (light)} + \text{semiconductor} \rightarrow 2H_2 + O_2 \qquad (1)$$

Recently, several advantages and disadvantages associated with various hydrogen production routes have been reviewed in the literature[14]. It has been estimated that about 40% of the produced H_2 value is required to spend to compress it into a pressure cylinder before use it in any of its applications[14]. Among various methods developed so far for producing H_2 gas from water, the photovoltaics based technology has been identified to be the best. Figure 2 illustrates the energy densities of various materials such as, liquid fuels (from fossil or renewable sources), H_2 (gas, liquid, compressed or in storage materials), electrical energy (in conventional or new generation Li-batteries), etc.[7]. In fact, the practical applications require high energy densities per weight and per volume. In the case of light weight H_2 gas, energy density per volume is the main criterion. It can also be clearly seen from Figure 2 that the energy densities of H_2 and electrical storage are far low in compared to those of liquid fuels based on fossil or renewable (biomass) sources. Furthermore, H_2 gas usage requires large costs for a new energy infrastructure as it cannot be directly employed in the present existing energy infrastructure including the automobile vehicles, thus not allowing a smooth transition from fossil fuel based energy vectors to the renewable and/or solar energy based energy vectors. This demands that the production of fuels in the liquid form (even if it is carbon-based) is preferred, because it can be employed directly in place of fossil fuels, which are presently being used to meet the energy requirements of the society beings[7]. Further, liquid fuels can be preserved for the future needs too with suitable additives[3,7].

The challenges for converting CO_2 into value added chemicals including methanol are great, but the potential rewards are also enormous. The conversion of CO_2 into methanol using energy that has not come from fossil fuels has been suggested to be one of the best ways to store the energy and solve both global warming and energy crisis problems to a considerable extent[7]. Furthermore, methanol could be employed smoothly into the existing energy distribution infrastructure today without making any major changes to it. The additional advantages in producing methanol from CO_2 include i) high energy density by volume and by weight; ii) no need high pressure to store methanol at room temperature like H_2, iii) safe to handle, and shows limited risks in its distribution (non-technical) use; iv) no need to modify the internal combustion engines of the vehicles to use methanol; and v) no impact on the environment during production and usage, and methanol could be a primary feedstock for many of the organic compounds, and is a vital intermediate for several bulk chemicals used in humans life such as silicone, paint, and plastics[5,11]. Furthermore, methanol is a green fuel and has almost half of the energy density in comparison to mostly used fuel gasoline.

At present, the most of the commercial methanol is produced from synthetic gas (also called as syngas ($CO+H_2$)) on a quite large scale in industrial plants in a several millions tons per year capacity. Besides this, the processes like, selective oxidation of methane, catalytic gas phase oxidation of methane, liquid phase oxidation of methane, mono-halogenation of methane, microbial and photochemical conversion of methane, etc., are also being employed to produce methanol[5,11]. Nevertheless, production of methanol from CO_2 using solar energy to drive the reaction is highly attractive as it saves the natural fossil fuel resources. Nature converts CO_2 into bioenergy via natural photosynthesis using exclusively solar energy. In this process, somewhat less than 1% of the solar energy is converted into bioenergy in the form of plant materials, which when accumulated and transformed over geologic ages yielded fossil fuels[15]. Thus, artificial photosynthesis has a tremendous potential and it is a scientific challenge, and upon successful development of it, the market would be gigantic. Owing to CO_2's extremely stable chemical nature, converting it back to a useful value added chemical, which is an endothermic reaction, on the same scale and with the same rate currently that is being produced is out of today's scientific and technological ability. However, a close study of the existing information on this subject hints that the successful development of artificial photosynthesis (i.e., conversion of CO_2 into value added chemicals used only renewable energy) is no longer an unrealistic dream[11,16-18]. Furthermore, this process could be developed quite efficiently in comparison to the natural photosynthesis. For example, there are certain endothermic reactions which are being practiced in thermochemical routes to produce syngas, H_2, and methanol over certain metal oxide catalysts. A considerably great amount of efforts have already made to convert CO_2 into several industri-

TABLE 1 : A list of review articles published on CO_2 utilization and its other aspects.

first author	article title	year	ref.
I. Taniguchi	Electrochemical and photoelectrochemical reduction of carbon dioxide	1989	[31]
K.W. Frese	Electrochemical and electrocatalytic reactions of carbon dioxide	1993	[32]
Y. Hori	CO_2 reduction catalyzed by metal electrodes	2003	[33]
G.A. Olah	Chemical recycling of carbon dioxide to methanol and dimethyl ether: from greenhouse gas to renewable, environmentally carbon neutral fuels and synthetic hydrocarbons	2009	[34]
G. Centi	CO_2-based energy vectors for the storage of solar energy	2011	[7]
T. Sakakura	Transformation of carbon dioxide	2007	[35]
H. Arakawa	Catalysis research of relevance to carbon management: progress, challenges, and opportunities	2001	[5]
C. Song	Global challenges and strategies for control, conversion and utilization of CO_2 for sustainable development involving energy, catalysis, adsorption and chemical processing	2006	[36]
M. Gattrell	A review of the aqueous electrochemical reduction of CO_2 to hydrocarbons at copper	2006	[37]
Z. Jiang	Turning carbon dioxide into fuel	2010	[38]
T. Seki	Catalytic oxidations in dense carbon dioxide	2009	[39]
W. Li	Electrocatalytic reduction of CO_2 to small organic molecule fuels on metal catalysts	2010	[40]
Y. Oh	Organic molecules as mediators and catalysts for photocatalytic and electrocatalytic CO_2 reduction	2013	[41]
D.C. Webster	Cyclic carbonate functional polymers and their applications	2003	[42]
D.J. Darensbourg	Chemistry of carbon dioxide relevant to its utilization: a personal perspective	2010	[43]
M. Jitaru	Electrochemical reduction of carbon dioxide on flat metallic cathodes	1997	[44]
J.-P. Collin	Electrochemical reduction of carbon dioxide mediated by molecular catalysts	1989	[45]
B. A. Rosen	Low temperature electrocatalytic reduction of CO_2 utilizing room temperature ionic liquids	2010	[25]
S. C. Roy	Toward solar fuels: photocatalytic conversion of carbon dioxide to hydrocarbons	2010	[46]
M.T.H. Le	Electrochemical reduction of CO_2 to methanol	2011	[47]
D. Chaturvedi	Versatile use of carbon dioxide in the synthesis of carbamates	2006	[48]
I. Ganesh	Conversion of carbon dioxide to methanol using solar energy-a brief review	2011	[9]
W. Wang	Recent advances in catalytic hydrogenation of carbon dioxide	2011	[49]
I. Omae	Aspects of carbon dioxide utilization	2006	[50]
M. North	Synthesis of cyclic carbonates from epoxides and CO_2	2010	[51]
I. Ganesh	Conversion of carbon dioxide into several potential chemical commodities following different pathways – a review	2013	[11]

ally important chemicals following a great variety of methods in which different forms of energy was utilized to perform the endothermic CO_2 reduction reactions into the value added chemicals[5,11]. These efforts can be seen from a large body of literature summarized in several review articles as listed in TABLE 1, which focuses on CO_2 conversion into value added chemicals.

CURRENT MAJOR CO_2 INDUSTRIAL APPLICATIONS

Although, at present, the utilization of CO_2 volume is very meagre in the industrial applications, it is important to realize that several such small volumes can make a real considerable impact on the total CO_2 related global warming mitigation strategy[11]. CO_2 can be a feedstock to produce several useful chemicals. This in fact saves the money being spent for transporting CO_2 from thermal power plants and other industry to store it in ocean and other safe places as a part of CO_2 sequestration process[7]. Furthermore, there are also several other considerable advantages if CO_2 is used as a chemical feedstock in some of the existing chemical processes wherever possible. For example, i) CO_2 is an inexpensive and non-toxic gas, hence, it could be a substitute to replace several toxic chemicals such as phosgene of isocyanates, ii) CO_2 is a renewable feedstock unlike oil or coal, iii) production of chemicals from CO_2 can lead to a all new industrial productivity, and iv) new routes to existing chemical intermediates and products could be economical than current methods[11]. Thus, the research on CO_2 conversion and utilization could be a proactive approach to the sustainable industrial and energy development[11]. Hence, transformation of CO_2 into more useful organic substances has been a promising long term objective.

Usually, most of the CO_2 producing plants are considerably far from the sites used for CO_2 sequestration or CCS process[7]. In certain areas like Europe, transportation of CO_2 in pipelines to storage sites is difficult and it will increase the cost of CCS process by at least 15-20%, which is considered to be unacceptable. The Department of Energy (DOE), USA estimated that transportation of CO_2 in tankers on road is not acceptable if distance is more than 100 km[7]. In such cases, carbon dioxide capturing and utilization (CCU) is the more beneficial option to CCS. In the total CCS process, about 35-40% is the transportation and storage costs. It is estimated that it would be between 35 and 50 €/ton for early commercial phase (after year 2020) and between 60 and 90 €/ton during demonstration phase, when transportation of CO_2 is made by pipelines for distances not over 200-300 km. If the transportation of CO_2 is by road (for example in certain European countries), this cost would further increase. In such cases, CCU is much more beneficial to CCS option. The cost of methanol in Europe is about 225-240 €/ton. This cost would further increase by about 15% (about 20-30 €/ton) if methanol is produced from a mixture of CO_2 and H_2 instead of from syngas following the existing industrial thermochemical routes. For CCS process, an average cost is >20-30 €/ton. These cost values suggest that conversion of the waste CO_2 gas into methanol from a mixture of CO_2 and H_2 is beneficial to CCS process as the value of formed methanol would be become a bonus in the former case. If renewable energy (such as, solar light, wind, hydro, etc.,) is utilized for this reaction, the benefits would further increase. These benefits imply that CCU could be a considerably better option than the CCS process being practiced at present[7].

If the chemical activation of the inert CO_2 is achieved with only the required thermodynamic energy input without much of extra kinetic energy (i.e., over-potential) requirement, there could be a boost for large scale industrial applications of CO_2 as a chemical feedstock[4]. At present, the major chemicals being produced from CO_2 are urea, salicylic acid, inorganic carbonates, ethylene/propylene carbonates, and polycarbonates[11]. Further, it is also used as an additive to CO in the production of methanol from syngas[3]. The production of sodium carbonate (calcined soda) by the Solvay method also consumes considerable volumes of CO_2. At present, the annual production of sodium carbonate is about 30 million tons in entire industry. In the salicylic acid synthesis also, reasonably high amount of CO_2 is consumed. Furthermore, CO_2 is also employed in the carboxylation of phenol under pressure (Kolbe-Schmitt reaction). The co-oligomerization of unsaturated hydrocarbons and CO_2 results in the formation of various synthetic intermediates including acids, esters, lactones and pyrones[11]. The reaction of alkynes with CO_2 (to form 2-pyrones catalyzed by 3d metal complexes) is one of the few examples of a homogeneous catalytic reaction, which leads to the formation of C”C bond on CO_2 insertion. The variation of alkyne substituents could result into a wide range of 2-pyrones[11]. It is known that the widespread use of CO_2 as a C1 feedstock needs a higher thermodynamic energy input (>1.5 V), hence, these processes will not be economical if fossil fuels are used as a energy aid. This indicates the need of solar energy and judicious usage of catalysts for activating CO_2. Microalgae use solar energy to activate CO_2[15]. In the laboratory, a great variety of catalysts and methods have been employed to activate CO_2 to react with and form several value added chemicals[15].

THERMOCHEMICAL CO_2 REDUCTION

Methanol can be prepared from CO_2 by catalytic hydrogenation (eq. 2) and thus obtained methanol could be transformed into dimethyl ether via dehydration (eq. 3). These two reactions can also be performed together in a single-step. In the catalytic hydrogenation of CO_2 to methanol, the first step is believed to be the reverse water-gas shift (RWGS) reaction (eq. 4). In the conventional process, methanol is formed from syngas (eq. 5) over copper-zinc-oxide-based catalysts under extreme reaction conditions (125-525°C under 2-12 MPa pressure). About 40 Mtons of methanol per year is being produced every year following the latter route[4]. In this process, about 3% CO_2 is supplied together with syngas to enhance the reaction rate. Since, RWGS is a reversible reaction; a same catalyst can be employed to carry out water-gas shift (WGS) and RWGS reactions. The best catalyst noted for these reactions has been a multicomponent $Cu/ZnO/ZrO_2/Al_2O_3/SiO_2$ catalyst[4]. Since, all these reactions are same equilibrium reactions, they occur almost at the same temperature and on the same catalyst.

$$CO_2 + 3H_2 \leftrightharpoons CH_3OH + H_2O \quad (2)$$

$$2CH_3OH \leftrightharpoons CH_3OCH_3 + H_2O \quad (3)$$

$$CO + 3H_2 + H_2O \rightarrow CO_2 + 4H_2 \text{ (water gas shift reaction)} \quad (4)$$

$$(2n + 1)H_2 + nCO \rightarrow CnH_{2n+2} \text{ (e.g., } CH_4, CH_3OH) + nH_2O \quad (5)$$

When methanol was synthesized from CO_2/H_2 mixture (eq. 2) instead of from syngas (eq. 5), the noted productivity was about 3 to 10 times lower. The water formed in this reaction as a side-product was found to inhibit the reaction rate. It has been suggested that if water formed during this reaction is continuously removed by catalytic distillation or by the use of inorganic H_2O permselective membranes, the yield is expected to increase[11]. The possible membranes for this process could be hydrophilic nano-pore zeolite (NaA) film deposited on a ceramic tubular support. This membrane is used at present for pervaporation of water-ethanol solutions. Apart from low yields, in direct methanol synthesis process from CO_2, almost one third of H_2 is consumed in the formation of water as a side-product. Hence, synthesis of methanol from syngas is really profitable. Nevertheless, considerable research efforts are still being made with a main aim of developing highly efficient catalysts for direct methanol synthesis from CO_2 for industrial applications[11]. For this reaction, Cu has been found to be most active so far. In a study, the effect of metal oxide support on 5 wt.% Cu catalyst was investigated and developed several kinds of excellent Cu-ZnO based catalysts that include $Cu-ZnO-Al_2O_3-Cr_2O_3$, $Cu-ZnO-TiO_2$, $Cu-ZnO-Ga_2O_3$ and $Cu-ZnO-ZrO_2-Al_2O_3-Ga_2O_3$[4]. Surprisingly, addition of small amount of CO to the H_2/CO_2 feed has also significantly increased the direct methanol formation from CO_2 and H_2. Among various catalyst systems studied so far for this reaction, the copper-zinc oxides doped with ZrO_2, Ga_2O_3, and SiO_2 have been found to be best[4]. It has been identified that methanol is formed on a metallic Cu surface of these catalysts, and the activity of these catalysts was found to be directly proportional to the surface area of this active metallic Cu. In a study, it was found that the catalytic activity of methanol synthesis was found to be independent of the CuO surface area[4]. Yet in another study, Cu^+ sites were found to be the active sites in this reaction. When compared with a pure oxidized Cu (100), a mixture of metallic Cu (100) plus oxidized Cu (100) exhibited an order of magnitude higher activity for this reaction[4]. The Cu(I) sites formed out of the oxidation of Cu have been found to stabilize carbonate, formate, and methoxide reaction intermediates during methanol formation. These observations were further substantiated by near-infrared-visible absorption study of Cu^+-O-Zn matrix[4].

From the above discussion, it can be understood that the activity of direct formation of methanol by the catalytic hydrogenation of CO_2 is not only influenced by active catalytic sites but also by the support material. For the first time, Cu supported on CuO/ZnO with 30/70 weight ratio produced a methanol yield of 3.63×10^{-5} kg per square meter of the catalyst per hour at 250°C under a pressure of 75 atm., whereas, pure Cu produced a yield of less than 10^{-8} kg per square meter of the catalyst per hour[4]. Since, ZnO is a wurtzite n-type semiconductor, besides oxygen vacancies, it also contains an electron pair which are believed to serve as an active sites for methanol formation. According to a theory, the electron pair in Zn^+ creates cation and anion lattice vacancies, which are responsible for improved adsorption and transformation of CO_2 as well as the enhancement of Cu dispersion on the catalyst support. The formate intermediate was found to adsorb at the interface between Cu and ZnO or Cu-O-Zn. By employing the mixtures of $Cu/SiO_2 + ZnO/SiO_2$ as catalysts for this reaction, it was found that ZnO actually creates Cu-Zn active sites and the morphology of Cu does not change during the reaction. Further, ZnO is believed to stabilize many active sites by absorbing the impurities presenting in the synthetic gas stream as even a small amount of sulphur could poison the Cu catalyst if ZnO is not there as a support[11].

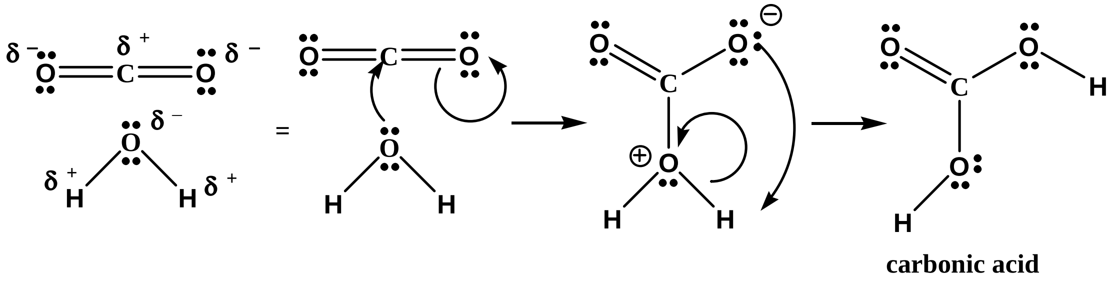
In addition to the catalyst composition, the reaction conditions were also found to influence the reaction activity, product yields and catalyst life. As both catalytic hydrogenations of CO and CO_2 into methanol are exothermic reactions, methanol conversion was found to be increased upon increasing the reaction pressure and decreasing the reaction temperature (as per Le Chartelier's principle). Since, the equilibrium constant decreases with increase in temperature, a low temperature condition is preferred for methanol formation[11]. On the other hand, increasing reaction temperature could increase the reaction rates for CO and CO_2 hydrogenations. Nevertheless, methanol formation has been found to be sensitive to optimal temperature ranges over different catalysts. Higher reaction temperatures could also rapidly reduce the activity and shorten the catalyst lifetime by promoting the sintering process and agglomeration of Cu on the catalyst surface. Catalysts also tend to undergo deactivation faster at high pressures again by the enhanced sintering process. A search for ideal catalyst system that is very active under low pressures and low temperatures with long life time is still going on[4,11].

The most advanced method for the production of methanol from CO_2 is being followed by a leading Japanese chemical company, Mitsui Chemicals Inc.[7]. This company is producing H_2 from water using renewable solar energy and then reducing CO_2 into methanol using thus produced H_2. Carbon Recycling International (CRI) Inc., also developed a process for converting CO_2 into methanol with the help of Nobel Laureate George A. Olah[7]. This company is located in Iceland and it has a capacity to produce around 2 million liters of methanol per year. The H_2 for this reaction also produced by electrolysis using energy produced from renewable sources mainly geothermal, hydro, and wind.

Although the Sabatier and F-T processes are still being practiced today, the electrochemical reduction of CO_2 appears to a better process than those of historical thermo-chemical processes[14,19]. In contrast to these thermo-chemical processes, which are normally operated in extreme reaction conditions such as high pressures (>75 bar pressure) and high temperatures (>250°C), the electrochemical processes are normally performed under ambient conditions. Since, either H_2 or aqueous electrolyte is the source of the H^+ in aqueous-electrolyte based electrochemical reduction of CO_2 to liquid fuels, there are no side products other than water that could harm the environment. The other advantages of electrochemical processes are the better chemical efficiency and higher physical yield of products compared with the amount of side-products formed. By employing suitable electrode and catalytic systems, Faradaic efficiencies could be increased to a great extent in electrochemical cells. A reaction with high Faradaic efficiency means lower over-potential (energy) requirement to complete the reaction. The efficiencies of electrochemical CO_2 reduction products can be further improved by additional understanding of underlying mechanisms in this process.

CO_2 SPECIATION

The dissolved CO_2 in aqueous electrolyte exists in three to four different forms or species that include CO_2 gas ($CO_{2(g)}$), liquid (solvated) CO_2 ($CO_{2(liq)}$), carbonic acid (H_2CO_3), bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}), whose concentrations vary with aqueous electrolyte pH[20,21]. As it is very difficult to distinguish $CO_{2(liq)}$ and H_2CO_3, they are usually considered as one. At 25°C, about 90 cm^3 of CO_2 dissolves in 100 mL water ($C_l/C_g = 0.8$) (eq. 6 and Scheme 1). The formation of H_2CO_3 takes place by the nucleophilic addition of H_2O to CO_2. As carbon atom in the CO_2 molecule pos-



Scheme 1 : Formation of carbonic acid from water solvated CO_2 molecule.

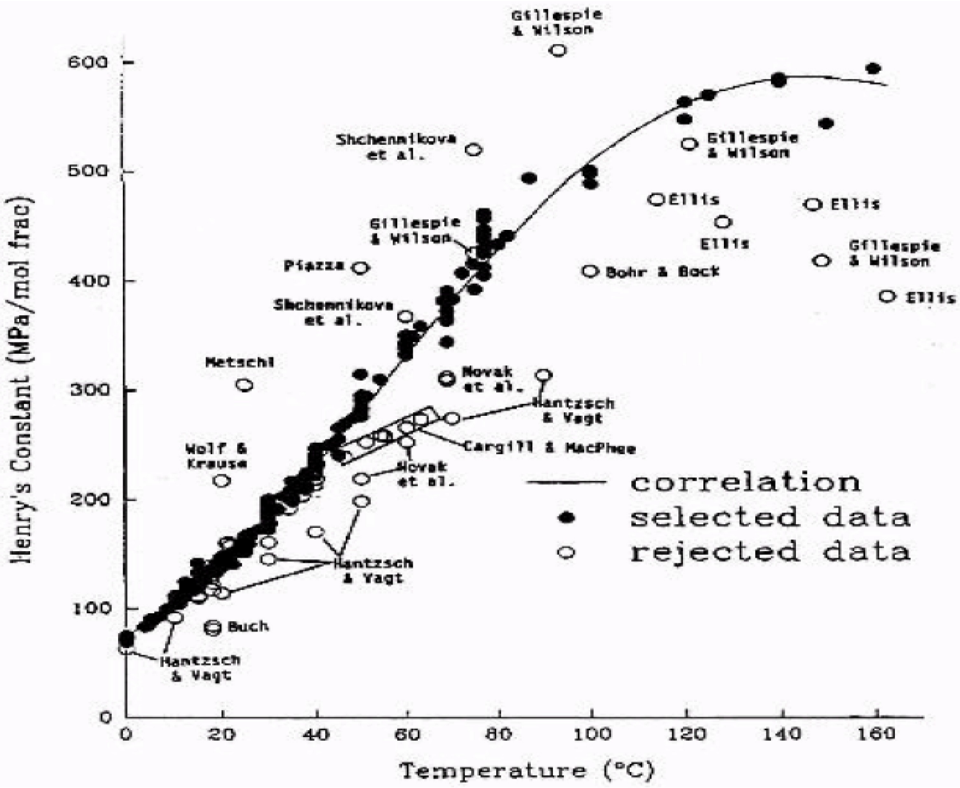


Figure 3 : Henry's constant for CO_2 in water (adapted from[22]).

sesses slightly positive charge, and as oxygen atoms possess slightly negative charge due to the prevalent differences in electro-negativity of these two atoms, a lone pair of electrons of oxygen atom of water molecule nucleophilically attacks the carbon atom in the CO_2 molecule leading to the formation of carbonic acid after a few rearrangements of electrons and protons (Scheme 1)[20,21].

$$CO_{2(gas)} \leftrightarrows CO_{2(aq)},\ [CO_{2(aq)}] = K_H P_{CO_2},$$
$$pK_H = 1.464\ (P\ in\ atm.) \qquad (6)$$

The reaction of converting CO_2 into carbonic acid is a simple dissolution process, which is governed by Henry's law. This latter law states that the CO_2 concentration in the solution is proportional to the partial pressure of CO_2 in the gas phase that is in contact with the solution phase (eq. 7), where ρ_{CO_2} is the partial pressure of the gas in the bulk atmosphere (Pa), K is a constant, and X_{CO_2} is the equilibrium mole fraction of CO_2 solute in liquid phase. According to Carrol and Mather, a form of Henry's law can be used for modelling the solubility of CO_2 in water for pressures up to about 100 MPa (Figure 3)[20-22].

$$\rho_{CO_2} = K \times X_{CO_2} \qquad (7)$$

The solubility of CO_2 is also a temperature dependent parameter as can be seen from the date of TABLE 2[23]. Normally, the dissolution of CO_2 decreases with increasing temperature of the solution. Equilibrium is established between the dissolved CO_2 and H_2CO_3 (eq. 8). This reaction is kinetically slow as its equilibrium constant (K_r) is only about 1.7×10^{-3}. At equilibrium, only a small fraction (ca. 0.2-1%) of the dissolved CO_2 is actually converted to H_2CO_3. Most of the CO_2 remains as solvated molecular CO_2[20,21]. TABLE 3 lists the equilibrium constants for CO_2 dissolution and acid dissociation constants (pKa values) at 25°C and zero ionic strength (I = 0)[20,21,23]. The variation of pKa values with temperature is shown in TABLE 4[23]. H_2CO_3 is a weak acid that dissociates in two steps (eqs. 9 & 10). As the rate of hydration of dissolved CO_2 (eq. 8) is slow (about 0.1 second), it is possible to separate this step from the much faster (10^{-6} sec) dissociation of H_2CO_3 into H^+ and HCO_3^- (eq. 9). If any cations are present in the electrolyte, these carbonate anions will react with them to form insoluble carbonates. For example, sea water contains Ca^{2+} and Mg^{2+}, which lead to the formation of limestone ($CaCO_3$) and $MgCO_3$ upon reactions with CO_2. The

TABLE 2 : Solubility of CO_2 at a partial pressure for CO_2 of 1 bar[23].

Temperature (°C)	0	10	20	30	40	50	80	100
Solubility (cm^3 CO^2/g of water)	1.8	1.3	0.88	0.65	0.52	0.43	0.29	0.26

TABLE 3 : Equilibrium constants for CO_2[23].

Log of equilibrium constant	25°C, I = 0
$[CO_2] = K_H P_{CO_2}$	–1.464
$[HCO_3^-][H^+] = K_{a1} [CO_2]$	–6.363
$[CO_3^{2-}][H^+] = K_{a2} [HCO_3^-]$	–10.329
$[OH-][H^+] = K_w$	–13.997

TABLE 4 : Selected values of equilibrium constants extrapolated to I = 0[23].

Temperature (°C)	$pK°_H$ (mol/kg atm)	$pK°_{a1}$ (mol/kg)	$pK°_{a2}$ (mol/kg)	pK_W (mol/kg)	$pK°_{SO}$ (mol/kg)
30	1.521	6.336	10.290	13.83	8.53
35	1.572	6.317	10.250	13.68	8.58
37	1.591	6.312	10.238	13.62	8.60
40	1.620	6.304	10.220	13.53	8.63
45	1.659	6.295	10.195	13.39	8.69

$$CO_{2(g)} \rightleftharpoons CO_{2(liq)} \xrightleftharpoons{+H_2O} H_2CO_3 \xrightleftharpoons{+H_2O} HCO_3^- + H_3O^+ \xrightleftharpoons{+H_2O} CO_3^{2-} + H_3O^+ \xrightleftharpoons{+\,Ca^{2+}} CaCO_3 \downarrow$$

Scheme 2 : Reactions of different forms of CO_2.

formation of these deposits usually drives reaction equilibriums more towards right resulting in acidification of the water (eqs. 11 & 12). The three reaction steps can be grouped together as shown in Scheme 2[20,21,23].

$$\mathbf{CO_{2(liq)} + H_2O_{(l)} \leftrightarrows H_2CO_{3(liq)} (K_r = 1.7 \times 10^{-3})} \qquad (8)$$

$$\mathbf{[CO_{2(aq)}] \leftrightarrows H^+ + HCO_3^- ([H^+][HCO_3^-] = K_{a1}[CO_{2(aq)}])}$$
$$\mathbf{(pK_{a1} = 6.363 \text{ at } 25°C \ \& \ I = 0)} \qquad (9)$$

$$\mathbf{HCO_3^- \leftrightarrows H^+ + CO_3^{2-} ([H^+][CO_3^{2-}] = K_{a2}[HCO_3^-])}$$
$$\mathbf{(pK_{a2} = 10.329 \text{ at } 25°C \ \& \ I = 0)} \qquad (10)$$

$$\mathbf{Ca^{2+} + CO_3^{2-} \leftrightarrows CaCO_3\downarrow (S = 4.96 \times 10^{-9};}$$
$$\mathbf{S = \text{solubility constant})} \qquad (11)$$

$$\mathbf{Mg^{2+} + CO_3^{2-} \leftrightarrows MgCO_3\downarrow (S = 6.82 \times 10^{-6})} \qquad (12)$$

If one considers the room temperature is below 40°C (for example in Hyderabad, India), at this temperature, the Henry coefficient for CO_2 in water is about 220 MPa/mole fraction[20,21]. At 1 bar pressure of CO_2 over the aqueous electrolyte, the mole fraction of CO_2 in water would be about 0.00045 (= 0.1 MPa/220 MPa/mole fraction). Since, at 40°C, the molar density of water is about 55.18 (= 992.2/18.02), the concentration of dissolved CO_2 in the electrolyte can be 25.077 mM/L (= 0.00045 × 55.18) that is equal to 1.510×10^{22} (25.077 × Avogadro number, 6.023×10^{23}) CO_2 total species (H_2CO_3 + HCO_3^- + CO_3^{2-})[20,21].

The distribution of different CO_2 species in aqueous electrolyte as a function of electrolyte pH under 1 bar CO_2 pressure below 40°C and ionic strength of zero (I = 0) can be derived using two acid dissociation constants of carbonic acid ($K_{a1} = 4.97 \times 10^{-7}$ and $K_{a2} = 6.03 \times 10^{-11}$), which can be generated from their corresponding pKa values (pK_{a1} = 6.304 and pK_{a2} = 10.220)[20,21]. The basic equations required to calculate the distribution of CO_2 species can be derived from the equilibrium reactions of carbonic acid dissociation (eqs. 11 & 12), which can be reorganized as shown in eqs. 13 & 14[20,21]. If the total initial concentration of carbonic acid is assumed as C_T (= $[H_2CO_3]$ + $[HCO_3^-]$ + $[CO_3^{2-}]$), then the concentrations of $[H_2CO_3]$, $[H_2CO_3]$ and $[CO_3^{2-}]$ can be calculated using eq. 15 to 19.

$$K_{a1} = \frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]} \left(\approx \frac{[H_3O^+][HCO_3^-]}{[CO_2 + H_2CO_3]}\right.$$
$$\left.\approx \frac{[H_3O^+][HCO_3^-]}{[CO_2]_{liq}}\right) \qquad (13)$$

$$K_{a2} = \frac{[H_3O^+][CO_3^{2-}]}{[HCO_3^-]} \qquad (14)$$

$$C_T = \frac{[H_3O^+]^2[CO_3^{2-}]}{K_{a1}K_{a2}} + \frac{[H_3O^+][CO_3^{2-}]}{K_{a2}} + [CO_3^{2-}] \qquad (15)$$

$$\Rightarrow [CO_3^{2-}] \left(1 + \frac{[H_3O^+]}{K_{a2}} + \frac{[H_3O^+]^2}{K_{a1}K_{a2}}\right) \qquad (16)$$

$$\Rightarrow [CO_3^{2-}] = \frac{K_{a1}K_{a2}C_T}{[H_3O^+]^2 + K_{a1}[H_3O^+] + K_{a1}K_{a2}} \qquad (17)$$

$$[HCO_3^-] = \frac{K_{a1}[H_3O^+]C_T}{[H_3O^+]^2 + K_{a1}[H_3O^+] + K_{a1}K_{a2}} \qquad (18)$$

$$[H_2CO_3] = \frac{C_T[H_3O^+]^2}{[H_3O^+]^2 + K_{a1}[H_3O^+] + K_{a1}K_{a2}} \qquad (19)$$

The distribution curves obtained upon plotting the values of [H_2CO_3], [HCO_3^-] and [CO_3^{2-}] vs. solution pH values through 0 to 14 are shown in Figure 4[20-22]. Above pH 10 and below pH 4, the solutions contain mainly CO_3^{2-} and H_2CO_3/CO_2, respectively. Near pH 7, all three species HCO_3^-, CO_2^{2-} and H_2CO_3 present in the solution. Depending upon the experimental procedures (and time scales), the above equilibria may lead to substantial changes in the CO_2 partial pressure above a solution and in the concentration(s) of dissolved species. For example, in stoichiometric (neutralization) reactions, either solvated or molecular CO_2 gas reacts with monoethanolamine during separation of CO_2 from the exhaust flue gas of thermal power plants when it is passed through an aqueous solution of monoethanolamine (80 vol.%) (eq. 20) or with epoxides in copolymerization reactions[11]. However, in electrochemical CO_2 reduction reaction, any one of the three CO_2 species (H_2CO_3, HCO_3^- or CO_3^{2-}) can undergo reduction depending on the solution pH leading. As reduction of already negatively charged HCO_3^- and CO_3^{2-} ions is normally difficult, the electrochemical CO_2 reduction experiments are preferentially conducted in electrolytes with pH d”6 so that the neutral carbonic acid [H_2CO_3] species undergo reduction relatively easily. However, at this pH, CO_2 reduction reaction competes with hydrogen evolution reaction (HER). Since, above pH 2, the concentration of CO_2 species is always much higher than that of H^+ concentration (Figure 5), a suitable CO_2 reduction catalyst should enhance the CO_2 reduction reaction over HER[19-21].

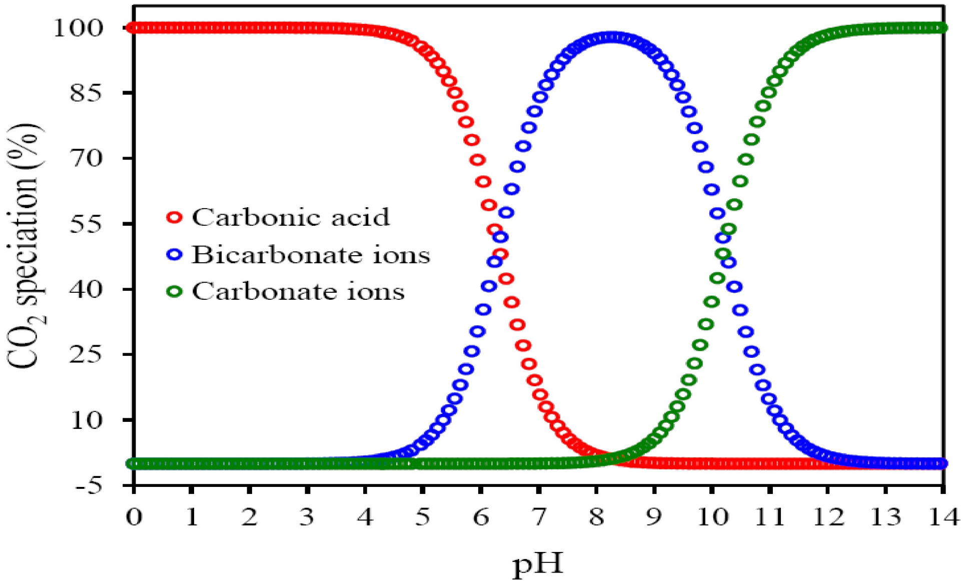


Figure 4 : CO_2 speciation vs. solution pH (adapted from[23]).

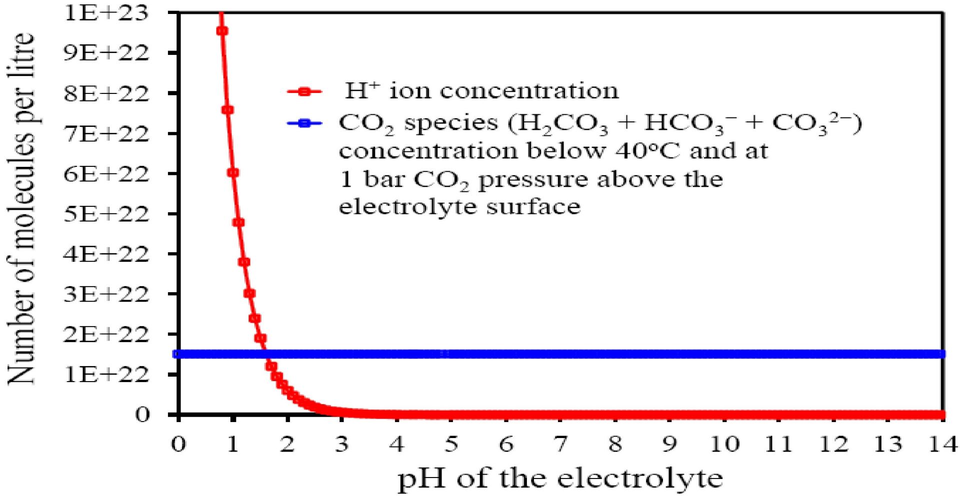


Figure 5 : Variation of H^+ and CO_2 species concentration as a function of solution pH (adapted from[23]).

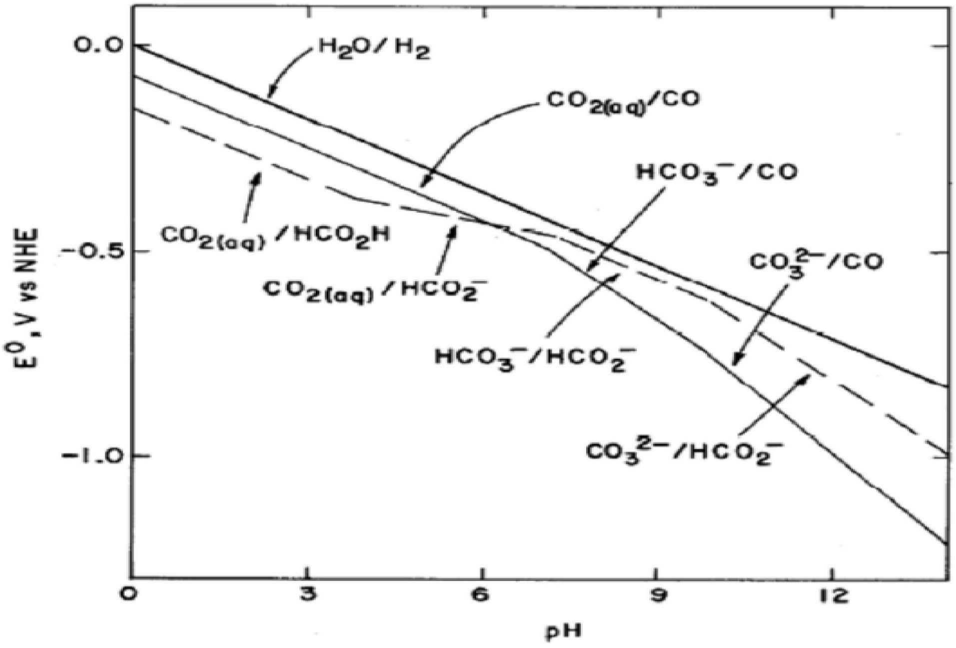


Figure 6 : E° values (vs. normal hydrogen electrode, NHE) for two electron reduction of H_2O and CO_2 as a function of pH and dominant forms of reactants and products. The following standard state conventions are used: H_2O, liquid; H_2 and CO, gas (i.e., 1 atm. pressure); CO_2, HCO_2H, HCO_2^-, HCO_3^-, and CO_3^{2-}, aqueous (i.e., 1 M) (adapted from[24]).

$$CO_2 + HOCH_2CH_2NH_2 \rightarrow HOCH_2CH_2NH_2^+CO_2^- \text{ (Zwitterion)} \qquad (20)$$

ELECTROCHEMICAL CO_2 REDUCTION

The CO_2 electro-catalytic reduction reactions are reversible when compared with anodic reactions that normally occur in fuel cells. CO_2 reduction reactions store electrical energy in the form of chemical energy in chemical bonds of the formed fuel chemicals[11]. In thermodynamics, the Gibbs free energy of CO_2 reduction is always positive at medium and high pH range, hence, the theoretical potentials are negative[19]. Thus, CO_2 reduction requires electrical energy input. In kinetics, the electrochemical reduction of CO_2 require over-potentials >1.0 V to get reasonable amounts of reduced products. In an aqueous electrolyte, the H_2O also undergoes reduction and releases H_2 is a major by-product[14]. Thus, water reduction is in always competition CO_2 reduction reactions in electrochemical cells. Certain metals such as Hg which possesses high H_2 overvoltage (over-potential) can suppress HER, but lead to the formation of only formate ions ($HCOO^-$) again at very high over-potentials. Involvement of appropriate catalytic systems can promote the reaction rates, and directs the selective pathways, hence, with minimum excess energy requirements to facilitate the formation of desired CO_2 reduction products. Furthermore, the free-energy change for CO_2 reduction is a function of electrode and the electrolyte pH (TABLE 5)[19]. Figure 6 summarizes the data presented in TABLE 5 in a graphic form[24]. As can be seen the reactivity of CO_2 reduction is very low, however, the equilibrium potentials of CO_2 reduction reactions are not very negative when compared with HER in aqueous electrolyte solutions under standard conditions (eqs. 21-28). The water oxidation reaction that occurs at anode surface in electrochemical cells is shown in eq. 29. The primary reactions that occur on the surface of electrode in an aqueous solution at 25°C, vs. standard hydrogen electrode (SHE or normal hydrogen electrode, NHE) are as follows[24]. The single electron reduction of CO_2 to $CO_2^{\bullet-}$ (eq. 30) occurs at −1.90 V. This step has also been considered to be a rate determining step (RDS) in the CO_2 reduction processes. According to Nernst equation, the

TABLE 5 : Half-reactions of CO_2 in aqueous electrochemical cells[24].

pH	Half-reaction	E° (V)	H^+/H_2; E° (V)
0	$CO_{2(g)} + 2H^+ + 2e = CO_{(g)} + H_2O$	−0.12	−0.00
7	$HCO_3^- + 3H^+ + 2e = CO(g) + 2H_2O$	−0.48	−0.41
9	$HCO_3^- + 3H^+ + 2e = CO(g) + 2H_2O$	−0.66	−0.53
11	$CO_3^{2-} + 4H^+ + 2e = CO(g) + 2H_2O$	−0.87	−0.65

theoretical equilibrium potentials decrease with increasing solution pH[24].

$$\mathbf{CO_2 + H_2O + 2e^- \rightarrow HCOO^- + OH^-}$$
$$\mathbf{(E_o = -0.43\ V\ vs.\ SHE)} \tag{21}$$

$$\mathbf{CO_2 + H_2O + 2e^- \rightarrow CO + 2OH^-}$$
$$\mathbf{(E_o = -0.53\ V\ vs.\ SHE)} \tag{22}$$

$$\mathbf{CO_2 + 6H_2O + 8e^- \rightarrow CH_4 + 8OH^-}$$
$$\mathbf{(E_o = -0.25\ V\ vs.\ SHE)} \tag{23}$$

$$\mathbf{2CO_2 + 8H_2O + 12e^- \rightarrow C_2H_4 + 12OH^-}$$
$$\mathbf{(E_o = -0.34\ V\ vs.\ SHE)} \tag{24}$$

$$\mathbf{CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O}$$
$$\mathbf{(E_o = -0.38\ V\ vs.\ SHE)} \tag{25}$$

$$\mathbf{2CO_2 + 9H_2O + 12e^- \rightarrow C_2H_5OH + 12\ OH^-}$$
$$\mathbf{(E_o = -0.33\ V\ vs.\ SHE)} \tag{26}$$

$$\mathbf{3CO_2 + 13H_2O + 18e^- \rightarrow C_3H_7OH + 18OH^-}$$
$$\mathbf{(E_o = -0.32\ V\ vs.\ SHE)} \tag{27}$$

$$\mathbf{2H_2O + 2e^- \rightarrow 2OH^- + H_2\ (E_o = -0.41\ V\ vs.\ SHE)} \tag{28}$$

$$\mathbf{3H_2O \leftrightarrows 1.5O_2 + 6H^+ + 6e^-\ (E_o = 1.23\ V\ vs.\ SHE)} \tag{29}$$

$$\mathbf{CO_2 + e^- \rightarrow CO_2^{\bullet-}\ (-1.90\ V\ vs.\ SHE)} \tag{30}$$

Considering their low equilibrium potentials, thermodynamically, the CO_2 reduction products of methane and ethylene (eqs. 23 & 24) should form at less cathodic potentials than HER (eq. 28), however, kinetically this does not occur. This suggests that the former reactions need additional high over-potential energies when compared with HER. Similarly, the electrochemical reduction of CO_2 to methanol and methane also require high electrode over-potentials, which make these processes uneconomical as the amount of energy consumed during these products formation is much larger than the energy stored in them. Two-electron reduction reactions that occur at pH 7 and 25°C vs. SHE are shown in eqs. 31 & 32. Both H_2O and CO_2 reductions are very difficult via. one-electron processes, since the one-electron reduction products, H atom and $CO_2^{\bullet-}$ (formate radical), are extremely energetic species[24]. By using pulse-radiolytic methods, Schwarz and Dodson have determined E° for $CO_2/CO_2^{\bullet-}$ couple to be –1.9 V vs. NHE in water, and the intrinsic barrier for this one-electron reduction was estimated to be ca. 0.6 V. The $CO_2^{\bullet-}/CO_2^{2-}$ potential has been estimated to be about –1.2 V vs. NHE[24]. One-electron reduction potentials at pH 7 and 25°C vs. NHE are also shown in eqs. 33 & 34. In the H_2O/H_2 reaction, certain metal hydride complexes provide catalytic routes. In the CO_2/CO or HCO_2^- reaction, catalysis by metal complexes involve coordination of CO_2 or its insertion of CO_2 into a metal hydride bond to yield formate species by consuming a minimum over-potential (or kinetic) energy.

$$\mathbf{2\ H_2O_{(l)} + 2\ e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}}$$
$$\mathbf{(E° = -0.41\ V\ vs.\ SHE)} \tag{31}$$

$$\mathbf{CO_{2(l)} + H_2O_{(l)} + 2\ e^- \rightarrow HCO_2^-{}_{(g)} + 2OH^-_{(aq)}}$$
$$\mathbf{(E° = -0.31\ V\ vs.\ SHE)} \tag{32}$$

$$\mathbf{H^+ \overset{-2.7V}{\overline{\qquad\quad}} H^\bullet \overset{+0.03V}{\overline{\qquad\quad}} H^-} \tag{33}$$

$$\mathbf{CO_2 \overset{-1.9V}{\overline{\qquad\quad}} CO_2^{\bullet-} \overset{-1.2V}{\overline{\qquad\quad}} CO_2^{2-}} \tag{34}$$

Despite studying electrochemical reduction of CO_2 for more than a century, neither a electrode material nor a catalytic system is identified or developed for exclusive reduction of CO_2 into liquid fuels without allowing HER[11]. In electrochemical CO_2 reduction process, theoretically, water undergoes oxidation at anode and releases electrons, protons and molecular oxygen. These protons and electrons are consumed in CO_2 reactions or in HER at cathode. In these reactions, the product formation is a combination of the reduction reaction at the cathode and the oxidation reaction at the anode[19]. The large thermodynamic and kinetic energy requirements associated with electrochemical CO_2 reduction reactions demand use of certain efficient catalytic systems to suppress HER and to speed up utilization of all generated protons and electrons at anode only in CO_2 reduction reactions at cathode. In general, the electrochemical processes developed so far either have poor thermodynamic efficiency (i.e., high over-potential), low current efficiency, low selectivity and slow kinetics, or poor stability[19].

INFLUENCE OF IONIC LIQUIDS IN ELECTROCHEMICAL CO_2 REDUCTION REACTIONS

Recently, the department of energy (DOE), USA has concluded that the major obstacle that is preventing efficient conversion of CO_2 into several energy-bearing products is the lack of efficient catalytic systems[25,26]. Hence, DOE has called for research that investigates systems to reduce the over-potentials associated with

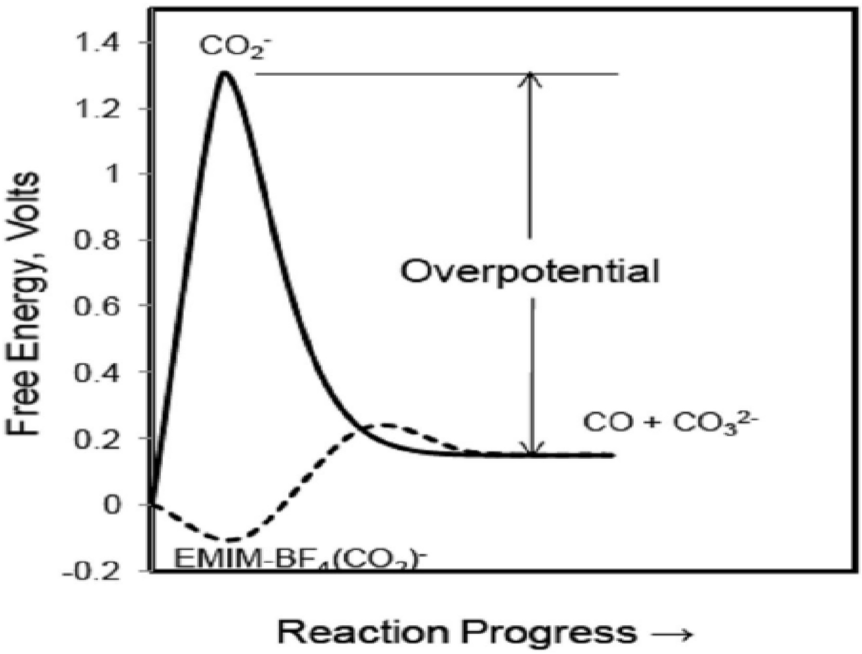


Figure 7 : Hypothesis for how and ionic liquid or amine could lower the over-potential for the CO_2 reduction (adapted from[25]).

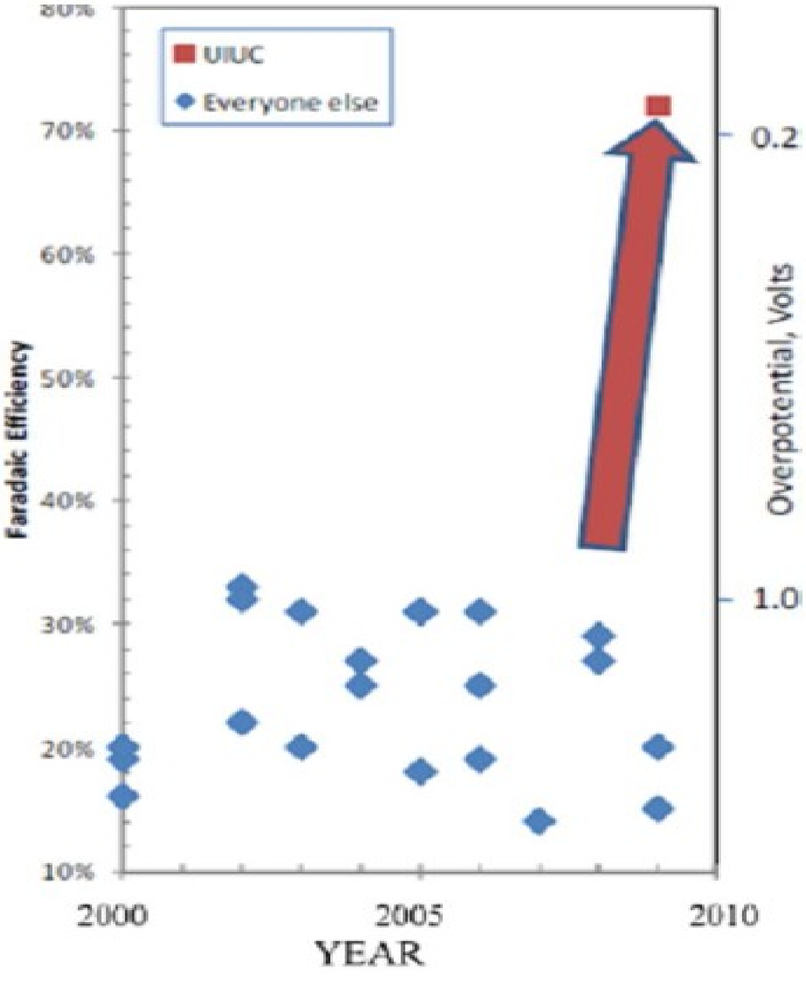
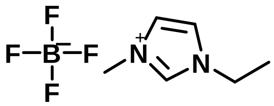


Figure 8 : Comparison of over-potential and Faradaic efficiency values (adapted from[25]).

CO_2 conversion while maintaining high current efficiencies[25,26]. The large over-potentials has been identified to be due to the formation of a high energy one electron reduced intermediate $CO_2^{\bullet-}$ with a standard redox potential of –1.9 V vs. SHE during electrochemical CO_2 reduction process. In a study, a room temperature ionic liquid (RTIL) comprising 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF_4) (eq. 35) was employed to reduce the over-potential associated with the formation of $CO_2^{\bullet-}$ intermediate that forms during reduction of CO_2 into value added chemicals in a electrochemical cell[25]. In this case, first, EMIM-BF_4 RTIL converts CO_2 into $CO_2^{\bullet-}$ intermediate, which is then catalyzed over a transition metal cathode to form useful products mainly CO. In this process, CO was formed at –250 mV vs. SHE compared to –800 mV in the absence of EMIM-BF_4 RTIL. These results indicate that CO_2 conversion to CO can occur without the large energy loss associated with a high over-potential.



(35)

Like strong acids (H_2SO_4, HNO_3, HCl, etc.), RTILs also completely dissociate into ions and are not diluted by any bulk solvent. Further, because of their poor vapour pressures at room temperature unlike acids such as HCl, RTILs are thermally and electrically quite stable. RTILs consists a bulky organic cation (e.g., imidazole) and an organic/inorganic anion (e.g., tratrafluoroborate, hexafluorophosphate). Further, owing to their poor coordinating nature, they are highly polar solvents without coordinating strongly to solutes. Due to their low volatile nature, RTILs are environmentally friendly unlike certain organic solvents, which possess significant vapor pressures. Furthre, RTILs do not need any supporting electrolyte in electrochemical reactions as they themselves can act like supporting electrolytes and bear up to 3-6 V charge[25].

Interestingly, owing to their ionic characteristics, RTILs stabilize the intermediate $CO_2^{\bullet-}$ in situ during CO_2 reduction reaction by columbic complexation. This stabilization considerably lowers the electrode potential required for CO_2 reduction. The activation energy (over-potential) needed to form the EMIM$^+$-CO_2^- intermediate has been found to be lower than the one required to form $CO_2^{\bullet-}$ in the absence of stabilization by RTIL. Figure 7 shows the reduction in over-potential due to involvement of RTIL[25]. In the presence of EMIM$^+$-BF_4^-, CO_2 reduction starts at as low as –250 mV vs. SHE and this RTIL has reduced about 80% of over-potential required for CO_2 reduction. Figure 8 shows the calculated Faradaic efficiency of a RTIL involved process with other processes reported in the literature for CO_2 reduction over a period of 10 years[25]. As CO_2 cannot survive in basic solution, neutral to slightly acidic media is employed for electro-chemical reduction of CO_2. The HER is a strong function of solution pH, and the equilibrium potential decreases with increase of pH. Under slightly acidic conditions, HER is thermodynamically more preferred reaction over reduction of CO_2[19]. In aqueous medium, CO_2 undergoes reduction to various products and releases hydroxide ions (eqs. 21-27). Due to the release of hydroxide ions during CO_2 reduction reactions, the pH near to the surface of the electrode is different from the equilibrium value as the rate of neutralization between the hydroxide anion and CO_2 is considerably slow in aqueous solution under ambient conditions[27]. For this reason, electrolytes such as $KHCO_3$ or K_2HPO_4 are normally employed to facilitate CO_2 reduction reactions smoothly as these supporting electrolytes supply anions with buffering action, there by nullify the effect of pH change at the electrode surface due to the release of hydroxide ions (eqs. 36 & 37)[25]. The supporting electrolytes such as, KCl, $NaClO_4$, K_2SO_4, etc., do not have the ability to release protons, hence to exhibit buffer action to nullify the effect of pH change by the formed hydroxide ions during CO_2 reduction reactions. It can be inferred from these results that EMIM-BF_4 has several useful characteristics for reducing CO_2 at relatively less negative potentials and low temperatures in non-aqueous medium such as acetonitrile[25].

$$OH^- + HCO^{3-} \leftrightharpoons H_2O + CO_3^{2-} \qquad (36)$$

$$OH^- + HPO_4^{2-} \leftrightharpoons H_2O + PO_4^{3-} \qquad (37)$$

In a recent study, an electro-catalytic system was reported to reduce CO_2 to CO at over-potentials below 0.2 V[28]. This system relies on an ionic liquid electrolyte to lower the energy of the $(CO_2)^-$ intermediate, most likely by complexation, and thereby lower the initial reduction barrier. The silver cathode then catalyzes the formation of CO at 1.5 V, just slightly above the minimum (i.e., thermodynamically predicted equilibrium) voltage of 1.33 V. This system continued producing CO for at least 7 hours at Faradaic efficiencies greater than 96%[28]. Yet in very latest study, an inexpensive bismuth-carbon monoxide evolving catalyst (Bi-CMEC) was reported for reducing CO_2 to CO in conjunction with ionic liquids with appreciable current density at over-potentials below 0.2 V[29]. This catalyst is selective for CO production operating with a Faradaic efficiency of approximately 95%. This activity is on far with those historically observed over expensive silver and gold cathodes[29].

In a very recent study, CO_2 was reduced at lower over-potentials on Cu electrodes resulted from the reduction of thick Cu_2O films[30]. These Cu electrodes reduced CO_2 at 0.5 V less over-potentials than that of pure polycrystalline Cu does to form CO at a higher rate than H_2O reduction at current densities > 1 mA/cm^2 and over-potentials of <0.4 V. This is a higher level of activity than all previously reported metal electrodes evaluated under comparable conditions. Further, these electrodes were found to be stable for several hours, whereas, the polycrystalline Cu electrode exhibited deactivation within 1 hour time under identical conditions[30].

CONCLUSIONS

Conversion of carbon dioxide into chemical fuels like methanol and ethanol using renewable energy such as sunlight can i) greatly contribute to solve the CO_2 associated global warming problem, ii) become a renewable and sustainable way of energy generation, and iii) becomes one of the best ways of storing energy for future generations. From the above discussions, it can be concluded at present there is no catalytic system that can efficiently reduce CO_2 in electrochemical cells with desired speed, stability and selectivity towards any particular product. Understanding the CO_2 speciation and underlying mechanisms in the electrochemical CO_2 reduction in ionic liquids would greatly help in designing effective electrochemical systems and catalysts to convert waste stream CO_2 into value added chemical fuels.

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