Electrocatalytic Reduction of Nitrogen and Carbon Dioxide to Chemical Fuels: Challenges and Opportunities for a Solar Fuel Device

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Abstract

Aspects of the electrochemical reduction of nitrogen and carbon dioxide at molecular and heterogeneous catalysts are discussed. We focus on recent advances in the field and discuss some of the remaining challenges in the production of solar fuels from N₂ and CO₂ with a direct, integrated solar fuel device.

Keywords: solar fuels, artificial photosynthesis, electrocatalysis, carbon dioxide reduction, nitrogen reduction

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1. Introduction

A solar fuel is a chemical compound synthesized using solar radiation that stores protons and electrons as energy currency units within its chemical bonds. **Artificial photosynthesis of a solar fuel is a light-driven photoelectrochemical reaction through which the fuel is synthesized.** To attain efficient artificial photosynthesis, a suitable catalyst is necessary to facilitate reaction of the photo-generated electrical excitations with the source of the chemical components of the fuel: water (for protons), with added carbon dioxide (for C-solar fuels) or nitrogen (for N-solar fuels). Efficient photocatalysis is often obtained by interfacing a light-harvesting unit with a catalyst of satisfactory performance, motivating the development of catalysts under device-relevant electrochemical conditions in the absence of solar illumination.

Methods for the photoelectrochemical water splitting and consequent production of hydrogen (H₂) are the subject of current major research efforts [1-5]. For the purpose of implementing H₂ as a viable fuel alternative for mobile and stationary applications, the cumulative cost of its production, storage and delivery must compete against current fuel options that have the advantage of an established infrastructure [3].

Alternatives to H₂ as fuel have been proposed [5-8], however the methods for their efficient production from abundant sources have not reached the level of technologic implementation. Water oxidation (anodic reaction) is generally assumed to be the proton source for widespread deployment of solar fuels technology, while significant progress in catalyst development will be required to determine suitable cathodic reactions and target fuels. The present review highlights some of the C and N -fuel forming, electrode-driven catalytic reactions that may be performed to enable artificial photosynthesis. We also discuss possible metrics of catalytic efficiency and some of **the current obstacles** in technological implementations.

1.1. CO₂ Reduction in Nature: The Photosystems

Photosystems I and II are enzyme complexes that allow plants to carry out chemical reactions by harnessing energy from light. These membrane-bound units are responsible for the production of adenosine triphosphate (ATP) and sugars for storage of energy, which involves the oxidation of water as a proton and electron source [9, 10] :

This reaction occurs in Photosystem II where the protons released in the membrane drive ATPase to produce ATP *via* a proton gradient [11]. The electrons produced in the reaction are driven to Photosystem I where NADPH is produced. This reducing cofactor is then used to convert CO₂ into carbohydrates as storage units of energy in chemical bonds (Scheme 1), resulting in a net chemical reaction described by Eq. 2.¹

Water oxidation occurs at an active site, the Oxygen-Evolving Complex (OEC) also known as the Water-Oxidizing Complex (WOC), which consists of a Mn_4CaO_5 cluster. The structure of this active site is a Mn_3Ca cubane held together by five oxygen bridges with four terminal water molecules and an a dangling manganese external to the cubane core [12, 13]. The mechanism for water oxidation remains under discussion and has been reviewed elsewhere [14].

Scheme 1. Depiction of photosynthetic reactions.[15]

Artificial photosynthesis can proceed by reducing CO_2 with electrons generated via light absorption and conversion in a semiconductor (photocathode), coupled to a photoanode which oxidizes water (Eq. 1) to provide both the electron source to the cathode and solvated protons for the CO_2 reduction reaction. Current research in electrochemical CO_2 reduction catalysis focuses on coupling a reduction event of CO_2 with a proton from the solvent medium. This research strategy enables catalyst science applicable to component-level development of artificial photosynthesis and does not require light absorbers and water oxidation; some recent efforts are highlighted in Section 2.1.

1.2. N_2 Reduction in Nature: Nitrogenase

Nitrogenase is an enzyme that converts N_2 to ammonia under mild conditions (Eq 3) even though dinitrogen is normally inert, having a strong NN triple bond. Its conversion to a fuel in biological systems is contingent upon release of chemical energy from the hydrolysis of ATP [16].

Figure 1. Fe-Mo Nitrogenase active site exhibits an interstitial C atom at the center [17].

Recent structural studies on the active site of nitrogenase reveal an unusual interstitial carbon at the center of a mixed Mo and Fe cluster. (Figure 1) The central electronic density was initially assigned to a N,[18] but it has now been reassigned as a C in more recent studies, making the enzyme the first example of a biological organometallic catalyst, to the best of our knowledge. The mechanism of N_2 reduction at the FeMo active site remains elusive to date; however, several studies highlight functional models in Section 2.2.

1.3. Evolutionary Links? Nitrogenases Reduce Oxidized Carbon Substrates

Most interestingly, nitrogenase has been shown to react with carbonaceous substrates as well as with N_2 . It can reduce a wide variety of acetylenic, allenic and heteroallenic substrates, [19] the most notable of which is CO_2 , the reduction of which leads to a 2e^- reduced product: CO and H_2O [20].

In a remarkable advance, vanadium nitrogenases have now been shown to convert CO to a mixture of ethylene, ethane and propene in the absence of N_2 , thus suggesting a possible evolutionary connection between the nitrogen and carbon cycles [21]. We remain forward-looking to such a connection being observed, as it may lead to insights into the repurposing of CO_2 -reducing catalyst motifs towards N_2 -reducing systems.

2. Research Status

In this section, we highlight some recent aspects of N and C solar fuel electro-catalysis and molecular transformations shown to occur via sequential proton/electron addition steps.

2.1. CO_2 reduction

2.1.1. Thermodynamic Considerations in Electrocatalytic CO_2 Reduction

The thermodynamic potentials of CO_2 reduction[22, 23] to C_1 -products at pH 7 under aqueous conditions (1 atm, 25°C , 1 M solutes) suggest that coupled multi-electron, multi-proton steps

can be performed at less cathodic potentials (Equations 4-7) than discrete one electron processes (Eq 8). This effect has been attributed to the large reorganizational energy required for the reduction of CO₂ to a bent anion radical.

2.1.2. Heterogeneous Electrocatalysis Highlights

Pioneering work by Horii [25] *et al.* followed up by Sakata and coworkers[26] has provided a comprehensive account of heterogeneous electrocatalysis of CO₂ reduction on metallic surfaces and of particular interest, product distributions at both 20 and 0 °C. Much research is currently focused on the discovery of high-selectivity, low-overpotential CO₂ reduction electrocatalysts with the ultimate goal of device integration. However, a concerning trend in the available data is the sensitivity of the observed product distribution favoring the less desirable hydrogen evolution reaction as being preferred at higher temperatures, thus detracting from CO₂ reduction at the electrode surface. We foresee future research efforts in catalysis at device-relevant temperatures that address the issue of energy losses by solar heating.

Work on Cu[27] and Ag[28] has been recently revisited by Jaramillo and coworkers bringing forth a wealth of knowledge regarding product selectivity at different applied potentials by using highly sensitive analytical techniques.

2.1.2.1. Selectivity for Methane on Cu Surfaces[29, 30]

In contrast with the high-activity, low-selectivity behavior reported for Cu catalysts under ambient conditions, Cu surfaces have been shown to act as selective heterogeneous electrocatalysts for the conversion of CO₂ to methane at low temperature (-30 °C) [29, 30]. To the best of our knowledge, this is the first report of such a selectivity trend. This work raises the question whether a low-temperature prototype could be an alternative for such selective conversions.

Some of the produced methanol, being a 2e⁻ reduction product away from methane, may perhaps be reduced to methane under such conditions. Productive CO₂ chemistry arising from the solvent has been noted with solvent variation by Fujita and coworkers [31].

2.1.2.2. CO reduction over nanocrystalline copper[32, 33]

In an important advance by Kanan and coworkers,[33] the formation of ethanol, acetate and propanol as products of CO reduction was observed at specially-prepared Cu surfaces.

The particular advance arises from the catalytic formulation. The active electrocatalyst is nanocrystalline copper derived from Cu_2O . This is an exciting development, as the mechanisms of C-C bond formation at heterogeneous surfaces, particularly highly active Cu surfaces have not yet been fully understood, and creates an opportunity to develop *direct* alkane synthesis from CO_2 [34].

2.1.2.3. Virtual Hydrogen Storage and Electrocatalytic CO_2 Reduction: Formate Battery[35, 36]

A fuel cell is a device that releases the chemical energy stored in the chemical bonds and it is in a sense the opposite of a fuel-forming device. A common device that has been shown to effect the efficient energy-release from energy-rich chemical bonds is the hydrogen fuel cell. As such, the storage of H_2 is a central area of modern research [37] as hydrogen has been shown to act as an efficient, high-energy fuel with only water as the byproduct of the energy-release steps. The large-scale implementation of this technology is however, plagued with safety, cost and infrastructure issues and these aspects have been discussed elsewhere.[38]

For the purpose of this discussion, we would like to emphasize the concept of Virtual Hydrogen Storage [35] originally described by Crabtree [39], where the electrocatalytic reduction of CO_2 has now taken a central role as a hydrogen storage molecule [36] .

As such, we would like to briefly describe the operation of such a device. The endergonic side of a hydrogen fuel cell has hydrogen being oxidized to protons and electrons at an electrode-bound catalyst. The protons and electrons are transported through a medium, usually a membrane to the exergonic side of this fuel cell, where they react to reduce O_2 at a catalyst at the cathode. The overall energy output of this device depends on the efficiency of the catalysts, the overpotentials and even specific cell components for non-faradaic losses related to resistive and *in operando* degradation processes.

In a Virtual Hydrogen Storage device, the fuel oxidized at the anode side is an organic molecule with oxidizable CH bonds [40-42]. The oxidation of such a chemical entity releases the protons and electrons necessary for the cathode side of the cell and at the same time generates a stable, desaturated organic molecule side-product. This spent fuel can then be hydrogenated (regenerated), by running the electrochemical cell in reverse, thus turning the fuel-consuming device into a fuel-forming device, similar to a battery, where energy is released and stored in a cyclic fashion in operation/charging cycles.

An important advance in the field of electrochemical CO₂ reduction is the report of the first aqueous formate/bicarbonate battery. [36] The design by Bi and coworkers reported the use of a strained Pd nanoparticle catalyst that can effect the oxidative release of protons and electrons from formate to generate carbon dioxide, which under the operation conditions speciates as bicarbonate under the aqueous basic conditions instead of leaving the system as CO₂ gas. The spent fuel, in this case CO₂ and more specifically bicarbonate under the basic conditions can be regenerated to produce formic acid by running the cell in the reverse direction. Under these “recharging” conditions the Pd nanoparticles that operated as an oxidation catalyst in the energy-release cycle operate as a cathodic catalyst to regenerate the spent fuel: bicarbonate into formate, thus realizing an operational Rechargeable Hydrogen Battery with the use of CO₂ as a hydrogen storage molecule.

2.1.3. Electrode-driven Molecular Catalysis for CO₂ Reduction

The distinct advantage of molecular catalysis is the ability to modulate the electronics of the ligand framework of metal complexes by rational structural design. It has been therefore possible to tune the electron "richness" of the metal center and consequently, the redox potentials accessible to the putative catalyst [43, 44]. Once the potentials of the catalytic process are determined, a light-driven conversion of this type may become a realistic goal by interfacing the system with a photoelectrode [23].

Table 1. Selected Molecular Catalysts for the Electrolytic Reduction of CO₂.

Entry	Catalyst	Potential	Conditions	Products
1[45]	[Co ^{III} N ₄ H(Br) ₂] ⁺ ^a	-1.88 V <i>vs</i> Fc/Fc ⁺	20 % H ₂ O/MeCN	CO, H ₂
2[46, 47]	Mn(bpy-Bu)(CO) ₃ Br ^b	-2.2 V <i>vs</i> SCE	1.4 M CF ₃ CH ₂ OH/MeCN	CO
3[48-50]	Re(bpy)(CO) ₃ Br ^b	-1.49 V <i>vs</i> SCE	9 : 1 DMF ^c /H ₂ O	CO
4[51, 52]	[Ni(cyclam)] ²⁺ ^d	-1 V <i>vs</i> NHE	0.1M KNO ₃ pH 4.1	CO

5[53]	$[\text{Co}^{\text{I}}\text{L}]^{+e}$	-1.34 V <i>vs</i> SCE	CH_3CN^f	CO and H_2
5[54]	$[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+b}$	-1.5 V <i>vs</i> SCE	DMF / H_2O 1/1	HCOO^- and CO
6[55]	$\text{TPPFeCl}^g, \text{FeTDHPPCl}^h, \text{FeTDMPPCl}^i$	-1.7 V <i>vs</i> SCE	DMF 0.1 M n-Bu ₄ NPF ₆ , H_2O	CO, HCOO^-
7[31]	CoTPP^c	-1.9 V	Butyronitrile, n-Pr ₄ NClO ₄	CO, HCOO^-
8[56]	$[(\eta^5\text{-Me}_5\text{C}_5)\text{M}(\text{bpy})\text{Cl}]$ M=Ir, Rh	-1.6 V	CH_3CN , 0.1M Bu ₄ NClO ₄ , 20% H_2O	HCOO^- , H_2 , very little CO
9[57]	$[\text{Pd}_2(\text{CH}_3\text{CN})_2(\text{eHTP})](\text{BF}_4)_2$ <i>j</i>	-1.3 V	DMF 0.1 M n-Bu ₄ NBF ₄ , HBF ₄	CO
10[58]	$[\text{Pd}(\text{triphosphine})(\text{CH}_3\text{CN})](\text{BF}_4)_2$	-1.4 V	DMF 0.1 M n-Bu ₄ NBF ₄ , HBF ₄	CO, H_2

1 *a.* N₄H = 2,12-dimethyl-3,7,11,17-tetraazabicyclo-[11.3.1]-heptadeca-1(7),2,11,13,15-pentaene
 2 *b.* Bpy: 2,2' bipyridine; *c.* DMF: N,N'-dimethylformamide *d.* cyclam: 1,4,8,11-
 3 tetraazatetracyclodecane *e.* L: 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-
 4 diene *f.* pulse radiolysis experiment *g.* TPP: tetraphenylporphyrin, *h.* TDHPP: 5,10,15,20-
 5 tetrakis(2',6'-dihydroxyphenyl)-porphyrin, *i.* TDMPP: 5,10,15,20-tetrakis(2',6'-
 6 dimethoxyphenyl)-porphyrin; *j.* eHTP: $[(\text{Et}_2\text{PCH}_2\text{CH}_2)_2\text{PCH}_2\text{P}(\text{CH}_2\text{CH}_2\text{PEt}_2)_2]$
 7

8 Table 1 summarizes several of the current state-of-the art molecular electrocatalysts for the
 9 reduction of CO₂. Since the field has a long history and exciting new developments appear quite
 10 often, we restrict the discussion to some highlights. Entry 1 by Lacy *et al*[45] is one of the first
 11 Co-based molecular electrocatalytic systems for the reduction of CO₂, as most of the previous
 12 reports in of similar coordination compounds demonstrated activity for the hydrogen evolution
 13 reaction (HER) [59-61]. It is worth noting that the system is supported by a redox-active ligand
 14 which is involved in the reduction process [62]. Ligand participation in the CO₂ reduction
 15 chemistry has also been discussed in the chemistry related to M(bpy-Bu)(CO)₃Br (M=Mn, Re)
 16 [46, 63]. Parasitic dimerization reaction in the reduction of the Mn catalyst of entry 2 has been
 17 avoided by using a bulky bipyridine ligand in a recent report by Sampson *et al* [64]. Entries 2,3,4
 18 and 9 remarkably show CO as main product of the electrolysis.

19 The selectivity between HER and the formation of CO and HCOO^- remains a challenge as
 20 several of the systems have been shown to produce variable amounts of both reduction products.

So far, there seem to be no reported electrocatalytic processes involving a metal-based molecular electrocatalyst that performs a transformation of CO₂ to products more reduced than by 2 H⁺ and 2 e⁻.

2.1.4. Using Organic "Cofactors" for the Selective Conversion of CO₂ to Chemical Fuels

The use of substoichiometric amounts of certain organic molecules as catalysts or mediators for chemical processes defines the field of organocatalysis [65]. At the same time, it is directly reminiscent of such transformations in nature, where cofactors and coenzymes are essential in biological pathways [66]. Such organic-mediated transformations with regards to the electrochemical conversion of CO₂ to chemical fuels have been reviewed by Hu and coworkers [67]. The work highlights the use of tetraalkylammonium salts [68], ionic liquids [69], and pyridinium derivatives [70] that have been successfully shown to act as mediators in the photo- and electrochemical reduction of CO₂ to products such as CO and methanol.

In a recent report, Xiang *et al* have shown the conversion for CO₂ and formate to methanol at a glassy carbon electrode surface with the use of an organic cofactor, mercaptopteridine [71]. Analyses of the liquid phase illustrate the presence of carbamate derivatives of the cofactor during operation. This observation raises the possibility of further systematic CO₂ binding studies stemming from these exciting results and likely optimization of the modest faradaic efficiencies (10-23%).

2.2. Nitrogen Reduction

2.2.1. Thermodynamic Considerations in Electrocatalytic Nitrogen Reduction

Nitrogen reduction as a solar fuel-forming reaction has received considerably less attention. The thermodynamic reduction potentials for several of the possible reduction products are given in the equations below at pH 0.

Of particular interest, hydrazine forming solar-driven reactions would possibly allow access to the generation of a high-value liquid fuel with uses as rocket propellant [75] among others. Ammonia and hydrazine are the two most interesting products, and significant work has been done on their electrochemical synthesis [76-78] but to date no such electrode-driven electrocatalytic N₂-reduction transformation has been reported.

2.2.2. The Haber Process [79] and Heterogeneous Electrocatalysis Highlights

In the commercial Haber-Bosch process, catalytic hydrogenation of nitrogen over an iron oxide catalyst at elevated temperatures and pressures leads to the formation of ammonia[80-82]. Essential to food production at the core of fertilizer industry, the scale of ammonia production is 450 million tonnes annually and consumes a significant amount of the world's natural gas production for its H₂ source [82] .

The mechanism of this reaction occurs *via* adsorption of an inert N₂ molecule (Eq 13) at an iron oxide surface at high temperature (at least 400 °C) and pressures (200 to 300 atm). The adsorbed N₂ gets split into atomic N (Eq 14). At the same time H₂ gas gets similarly adsorbed and split into atomic species at the catalyst surface (Eq 15 and 16). The adsorbed N atom combined with three H atoms in three steps (first NH is formed, then NH₂) to reach an adsorbed ammonia molecule (Eq 17) which then desorbs (Eq 18) to release ammonia gas. The scission of the N₂ triple bond has been determined to be the slow, rate-determining step.

Given the societal implications of this highly important reaction, several alternatives for N₂ reduction are being sought. In more recent developments, The Kellogg Advanced Ammonia Process allows for the reaction in Eq 3 to occur at lower pressures over a Ru catalyst with carbon support [83, 84]. Efforts in establishing N₂ cycle electrocatalysis [85] reactions have been reviewed, but no routes rivaling the Haber and Kellogg processes have yet emerged.

Table 2. Highlights in efforts towards electrocatalytic N₂ reduction.

Entry	Cathode Material	Temperature	Pressure	Conditions	Comments
1[77]	Ru	90 C	1 atm	0.1 M H ₃ BO ₃ -1.02 V to -1.10V Water Oxidation as the anodic	Hydrazine was not detected, NH ₃ from a dissociative

				reaction, N ₂ stream at cathode	mechanism, H ₂ also observed
2[86]	Pt/C in an electrolysis cell	Room temperature	1 atm	Ammonia synthesized from air and water <1% efficiency*	Protons and electrons from water in an MEA 1.6V
3[87]	Ru/Ag	450 – 700 C	1 atm	Steam and N ₂	Solid polymer electrolyte fuel cell

Acetylene has been proposed as an N₂ model system and a recent investigation reports on its reduction to ethylene and ethane over Mo thin films [88].

In a striking recent report summarized in Entry 2, an artificial ammonia synthesis was achieved from air and water under ambient conditions in a fuel cell equipped with a Pt/C cathode. Given the harsh conditions and the heavy use of fossil fuels in the Haber and Kellogg processes, this is a major advance.

2.2.3. Molecular Catalysis for N₂ reduction

Molecular catalysts for the reduction of N₂ with Fe complexes has been reviewed [89]. We now briefly highlight just a few of the breakthroughs in the field of N₂ reduction. Firstly, a redox-active ligand facilitated N-N bond cleavage in 1,2-diaryldiazines on a vanadium complex. Multi-electron multi-proton transformations will likely be facilitated by such ligand reactivity in the coming years. ² An alternate strategy for such multi-electron, multi-proton reactivity is the use of multi-nuclear complexes providing several accessible redox states. This strategy was validated by Betley and coworkers [90] and remains an active area of research.

Catalytic conversion of nitrogen to ammonia was recently achieved *via* chemical means with a discrete Fe organometallic complex, thus setting the stage for the involvement of first-row metals in N₂ reduction [91]. To date, no such electrode-driven transformation has been reported, though it may soon be possible, given the precedent.

2.2.3.1. Molybdenum Reduction Chemistry[92]

In pioneering studies, Schrock and coworkers have shown the stepwise reduction of a single-site Mo-N₂ adduct stabilized by a trisaminoamide to Mo-NH₃ (**6**) and interfaced it with a catalytic process [93, 94]. As several stepwise successive reduction processes (by addition of protons and single-electron reducing agents such as cobaltocene) have been stoichiometrically achieved as

depicted in Scheme 2, it is likely that soon an electrode-driven process will be implemented in the future and that turnover will occur in the presence of applied potential in protic media.

Scheme 2. N_2 reduction via sequential H^+/e^- steps with a tripodal Mo catalyst (1). [92]

Catalytic activity for the conversion of N_2 to ammonia with the trisamidoamide N_2 adduct (1) has been achieved with pentamethylchromocene ($CrCp^*_2$) as a $1e^-$ reducing agent operating at -0.9V vs. NHE [92].

Yoshizawa and coworkers have also shown productive conversion of N_2 to ammonia with a series of Mo pincer complexes supported by a PNP ligand (2,6-bis (di-*tert*-butylphosphinomethyl) pyridine) [95]. In a recent report, De Bruin and coworkers highlight light-driven conversions of N_2 to ammonia as a possible route for the sustainable, scalable production of ammonia [96].

2.2.3.2. Mononuclear Iron Reduction Chemistry[91, 97, 98]

Peters and coworkers have made significant advances in the field of N_2 reduction to highly reduced products such as ammonia [91, 97, 98]. The series of tripodal complexes on Fe have generated a series of studies that report N_2 adducts that in the presence of protons and electrons can turnover to synthesize ammonia in modest yields. These are the first reports of such transformations occurring at a first-row metal center [91]. Catalytic N_2 reduction with boryl

triphosphine tripodal ligands with Fe-N₂ complexes was also achieved [91, 98] and most recently a report of N₂ reduction catalysis with tripodal ligands with a central C atom- akin to the interstitial carbon was made available[97].

2.2.3.3. Dinuclear Iron Chemistry[99]

An important contribution in the field of N₂ reduction comes from research by Holland and coworkers [99]. A dinuclear molecular Fe complex was reported to reduce N₂ to form two nitrides (N³⁻) in the presence of a K reductant. (Scheme 3a) This nitride was shown to release ammonia upon exposure to H₂ at room temperature in toluene (Scheme 3b). The nitride complex was also shown to react with protons to release ammonia.

Although not at the stage where catalysis has been achieved, a wealth of spectroscopic insight can be gained by understanding the N-H forming reactions of this remarkable Fe system[100].

Scheme 3. Dinuclear Fe complexes for the reduction of N₂ to a nitride [99].

3. Technical Challenges of a Solar Fuel Device [8]

In a solar-driven device for water splitting, the anode reaction consists of the oxidation of water, releasing the protons and electrons necessary in the fuel-forming reaction occurring at a cathode. The protons are transported through a membrane to the cathode side, whereas the electrons travel to the cathode through the external circuit. This particular design is limited by the overpotentials for the catalysts for both anode and cathode, cell resistance, losses at solid state junctions, etc.

The lifetime of such a device is also an issue that is usually addressed at an advanced stage of technological development, but perhaps should be included in the testing procedures for the catalysts.

3.1 Challenges Difficult to Identify Without a Specific Device Design

Figure 2. Schematic representation of a solar-fuel-forming electrolyzer.

In a device configuration of a Proton Exchange Membrane (PEM)-separated electrolysis cell, the protons and electrons generated from the oxidation of water would be needed to reduce CO_2 or N_2 , ideally under atmospheric conditions (Figure 2). A CO_2 or N_2 -reducing device would be unlikely to have the same geometry/ electrode arrangement as a hydrogen-producing one, with optimal device architecture requiring consideration of product extraction and separation. For device architectures relying on membrane separation of fuel products and evolved O_2 , membrane compatibility and fuel crossover will require substantial material development. Some advancements on this front have come from the related technologies, such as membranes of direct alcohol fuel cells [101]. A device concept that does not include integrated light capture has been reported for ammonia electrolysis from N_2 , in which elevated temperature affords the use of a solid electrolyte to separate fuel and O_2 streams [87].

Under conditions of aqueous operation concentration and speciation of the substrate will be a limiting factor. Under neutral to basic conditions, CO₂ will partition in the aqueous phase as bicarbonate or carbonate, whereas in acidic media, its solubility is very low.

3.2. Uniform Metrics of Assessment of Electrocatalytic Processes

Difficulties in defining descriptors of catalytic activity arise from the myriad catalyst interrogation conditions. As a consequence, a recent effort in the benchmarking of dark catalysis[102] for water splitting electrocatalysis, puts forth a series of metrics for the investigated electrocatalysts. The activity of a molecular catalyst is difficult to benchmark and compare side-by-side with a heterogeneous catalyst, unless the molecular species is directly immobilized to an electrode surface and the catalyst is interrogated under non-diffusional conditions. Efforts in identifying kinetic models for overpotential determinations under diffusional conditions have been made [103-105].

In the context of non-H₂ solar fuels dark catalysis for the reduction of CO₂ and N₂, it would be beneficial to define a similar set of activity metrics as discussed in the following sections.

3.2.1. Long-Term Stability under Operating Conditions

Depending on the limitations of the device design and the nature of the products observed in the fuel-forming process, catalyst interrogation requires an optimized set of conditions. Under these conditions, long-term catalyst operation is a crucial measurement. In the academic literature, this aspect is often not addressed, thus vital information for device integration remains unavailable. A minimum test of a hundred hours of catalyst operation would be beneficial for assessing the intermediate-duration stability and selectivity of a given catalyst [102].

3.2.2. Overpotential

The issue of determination of catalyst overpotential for non-H₂ solar fuel electrocatalysts is twofold.

Firstly, in order to determine overpotential at a given current density, the thermodynamics of the reaction under study need to be understood. This brings forth the central issue of product selectivity, as choosing a single product under standard conditions is the most direct method of establishing a well-defined thermodynamic potential to reference against. For a multi-product-forming process, the operational overpotential of a catalyst is poorly defined, requiring the electrochemical potential to be reported with respect to a reference potential with the understanding that that higher potential (less cathodic polarization) corresponds to higher efficiency.

Secondly, as previously mentioned, a certain current density for catalyst operation needs to be chosen to adequately compare different catalysts and their operating potential. For heterogeneous electrocatalysis of the oxygen evolution reaction, 10 mA cm^{-2} was chosen as a benchmark current density as this value corresponds to a 10% solar to current conversion under non-concentrated solar illumination [102]. Given the purpose of referencing to an illuminated area, the geometric surface area was chosen instead of the specific surface area or areal density of catalytically active sites. Determining these latter quantities is challenging [106, 107] but is necessary for calculating turnover frequency, which when paired with a well-defined overpotential provides the most meaningful basis for fundamental comparison of different catalysts.

3.2.3. Catalytic Activity - Selectivity and Rates

As previously mentioned, the selectivity of the electrocatalytic process for non- H_2 fuels is an important metric. Since many products can form during electrocatalytic reduction, a uniform method for determining and quantizing the formation of liquid and gas phase products is necessary in combination with traditional current-voltage measurements. The combination of such techniques will allow for the determination of the Faradaic efficiency for each product as a function of applied potential, leading to greater understanding of the catalytic mechanisms associated for a given electrocatalyst.

3.3. Parasitic Processes Compromise Device Activity

3.3.1. O_2 reduction

Current systems for the reduction of CO_2 require anoxic media due to fairly negative applied potentials. Electrochemical reduction of O_2 is a well-studied [108], proton-dependent reaction as a relevant transformation in fuel cell chemistry and is the thermodynamic reverse of water oxidation, as depicted in Scheme 4. Reducing CO_2 in the presence of O_2 is desirable from a technology viewpoint, but depending on the target fuel, the operational overpotential for O_2 reduction at least 1 V larger and places extreme requirements on catalyst selectivity.

Scheme 4. Diagram for the stepwise reduction of O₂. Thermodynamic reduction potentials shown.

Ideally, in a CO₂ device, the CO₂ source would be the atmosphere, thus atmospheric operation and O₂ tolerance will pose a real challenge, as the potentials necessary for the fuel production would need to be positive of those necessary for the reduction of O₂.

3.3.2. Co-evolution of Hydrogen and Other Fuels[1]

The hydrogen evolution reaction (HER) is a cathodic process in a solar water splitting device. This reaction happens at an electrocatalyst that enables the reaction of protons and electrons to form H₂ gas:

For several of the known CO₂ reduction catalysts, the reduction of protons to H₂ [109] also occurs during catalyst operation. In the case of the molecular catalyst in Table 1 entry 1, [Co^{III}N₄H(Br)₂]⁺ electrocatalyst, H₂ forms together with CO. Although a parasitic process in the context of the development of selective processes, H₂/CO mixtures are known as syngas and are used in the Fisher-Tropsch process to produce alkanes [110-113].

3.4. Operating conditions

In order to define the operating conditions of a solar fuel device, an explicit device design needs to be established. Since one of the bottlenecks in developing such a device is the identification of a suitable electrocatalyst that performs the selective conversion of CO₂ or N₂ into a fuel, such an electrocatalyst would need to be tested under some general device-relevant operation conditions.

The issue of substrate availability to maintain a reasonable current density is dependent on the nature of solvent, temperature, pressure, flow if applicable.

In aqueous solution at pH 7, the concentration of dissolved CO₂ is 33 mM (25 °C), almost an order of magnitude lower than its solubility in some ionic organic media [114-116].

In an attempt to increase CO₂ concentration in aqueous media, low temperatures and high pressure conditions were shown to provide higher currents in electrolysis measurements which correlated increased selectivity for hydrocarbon products rather than the common 2 e⁻ reduction products CO and formic acid. Under high pressure conditions, the catalytic rate of the HER is lessened in favor of the CO₂RR, remarkably even for metal surfaces with low-overpotentials for HER [25, 117, 118]. Perhaps a non-aqueous prototype is likely to provide the necessary substrate solubility properties for sustained operation.

3.4. Incompatibilities with device components

The nature of the chemical products resulting from the reduction process is likely corrosive and component function will likely be compromised during operation.

Carbon monoxide formation may be a limiting factor in CO₂ reduction- surface poisoning. Ammonia and hydrazine are basic and likely corrosive as well as incompatible with acidic membranes. A solution would be an anion conducting membrane or perhaps a membrane-less device, which would have the issue of headspace mixing and explosive mixtures of O₂ with fuels.

3.5. Alternate proton sources

Overpotential of the oxidation of water may be a limiting factor in establishing a fully functional solar fuel device. For the purposes of a proof-of-principle design, perhaps lower potential oxidation such as halide oxidation, will allow for some fundamental studies to be achieved. Halide oxidation is one of the important aspects of Dye-sensitized solar cell photovoltaics [119-121]. A device design based on this premise is depicted in Scheme 5.

Scheme 5. Dye-sensitized photoelectrosynthesis concept for the reduction of CO₂ to a fuel [122].

In this design, after oxidation of water to oxygen and 4 H⁺ and 4 e⁻ at an anode/chromophore assembly, the protons travel through a proton exchange membrane (PEM) to arrive at the cathode chamber. A reduction catalyst interfaced with a NiO photocathode receives electrons upon light excitation. The reducing equivalents would then be used to convert the CO₂ to a fuel.

Such an integrated device would certainly be a major advancement in the field, but to date, it remains an interfacial challenge.

4. Conclusions

The ability to use inert molecules such as N_2 and CO_2 as reactants in the renewable generation of chemical energy has long been established in nature, such processes being at the core of N_2 -fixation and the light-driven conversion of CO_2 into sugars *via* photosynthetic mechanisms. Analogous artificial light-driven processes remain a technological feat to date and will likely be the subject of many more years of research. As knowledge progresses, we will soon develop the ability to produce chemical fuels by identifying catalyst compositions that operate at low overpotentials and device-relevant temperatures, thus allowing us to interface our selective chemical process with a light-capturing semiconductor interface.

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