Options to dissociate CO_2 and H_2O for sustainable sunlight-to-fuel pathways: Comparative assessment of current R&D hurdles and future potential

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Abstract

The IPCC's 5th assessment report has heightened the urgency of steep reductions in atmospheric CO_2 concentrations. The transportation sector contributes 22% of global CO_2 emissions from fuel combustion. Solar-to-fuel technologies thus offer tremendous potential to contribute significantly to such reductions. Engineering offers a multitude of pathways to produce liquid hydrocarbon fuels starting from CO_2 and H_2O. In these pathways, downstream processes such as fuel synthesis are generally well understood and often commercially available. In contrast, upstream processes such as the dissociation of CO_2 and H_2O are usually less mature (exception: low temperature water electrolysis). Here, we first analyze recent research on various CO_2 and H_2O dissociation technologies and then assess their future potential to be used at scale. The dissociation technologies range from thermolysis, to thermochemical cycling, low and high temperature electrolysis, photo-electro-chemical splitting, and artificial photosynthesis. In addition to the state-of-the-art of these technologies, we compare their inherent disadvantages and advantages as well as key future R&D requirements. For completion, other steps of the pathways, namely CO_2 capture, providing water, and fuel synthesis, are addressed briefly as well. We conclude with a discussion of the relative future potential of the various pathways and an R&D outlook.

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Introduction

Background and Motivation

IPCC's 5th assessment report has further heightened the urgency of steep reductions in atmospheric CO_2 concentrations versus business as usual (IPCC, 2014). Principally this can be achieved by removal from the atmosphere (negative emissions) and/or by rendering those carbonaceous processes that currently (net) contribute to atmospheric CO_2 carbon-neutral. In the latter category, hydrocarbon fuels used in the transportation sector (road, sea, rail, air) pose a particular challenge: Their advantageous energy density makes them difficult to replace (with e.g., electricity). And their CO_2 emissions from large vehicles or jet engines are difficult to capture directly at source because doing so would likely add prohibitive weight to the vehicle/aircraft (Dahlgren et al., 2010).

Yet fuels burned for transportation contribute significant portions (22%) to global total CO_2 emissions from fuel combustion (IEA, 2013). Rendering transportation fuels carbon-neutral therefore bears enormous potential towards above reduction goals. Indeed, science and hundreds of years of practical experience of the oil and gas industry have given us a sheer endless number of pathways to enrichonce emitted CO_2(and water)back into synthetic hydrocarbons suitable as fuels(Graves et al., 2011b). So long as this enrichment uses low-carbon energy, resulting fuels would be (nearly) carbon-neutral with regards to atmospheric emissions (Figure 1). In other words fuels, with a (near) zero life cycle carbon footprint (Ciroth and Meinrenken, 2014, Draucker et al., 2011, Meinrenken et al., 2011, Meinrenken et al., 2012, 2014, Meinrenken and Lackner, 2014, Meinrenken, 2015).

Focus of Comparative Assessment

We focus our assessment on any photo- and/or electro-chemical processes to make synthetic fuels, including artificial photosynthesis. However we exclude any pathways that require living organisms (plants, algae, micro-organisms, etc.) as these represent a separate set of technological challenges and/or other life cycle considerations such as use of fertile land.

Within the full pathway illustrated in Figure 1, we further narrow our focus only on the gas dissociation steps. Upstream capturing of CO_2 and downstream fuel synthesis are assessed only for those pathways that integrate those steps into the dissociation itself (*Methods*). Other processes are not the focus of the comparative assessment because none of these would represent a major technological obstacle to the particular pathway's overall feasibility. Instead, only a brief overview is given in *Methods*.

Figure 1: Carbon-Neutral Fuel Process and Focus Areas (Shaded) of This Assessment
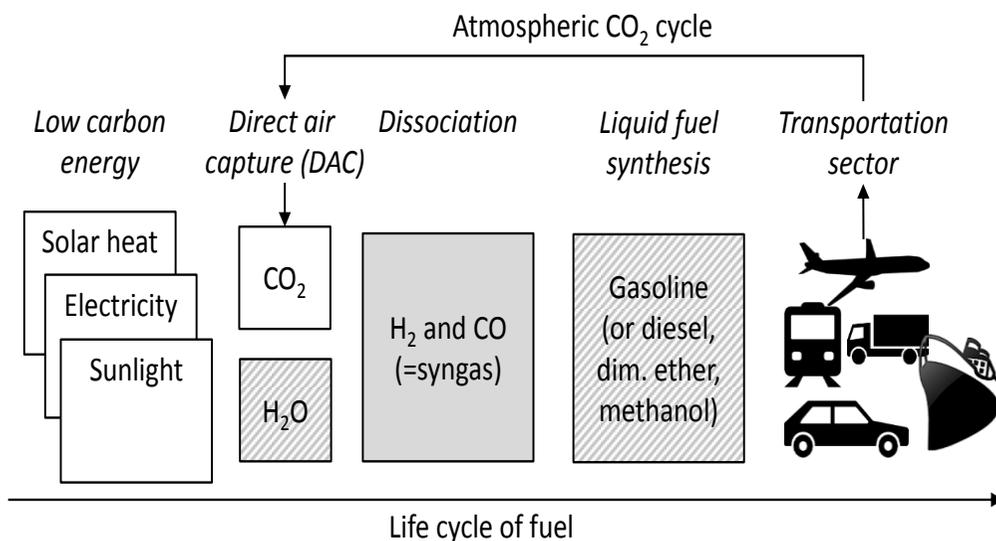
In assessing the various dissociation options, we seek a balance between providing a high level overview of the broad range of technological options while also providing in-depth analysis of their current state-of-the-art, remaining R&D needs, inherent (dis-)advantages and thus future potential.

Target Fuels

Arguably the most practical near-time fuels are gasoline, diesel, kerosene, and methanol. They feature high energy density (at manageable explosiveness) and ease of use (liquid, low corrosiveness). They could be used "drop-in", i.e. to fuel existing internal combustion engines hybrids(Meinrenken and Lackner, 2015), or fuel cells, for road, rail, air(Meinrenken and Lackner, 2011, 2012, 2014)as well as in smartgrid-related micro-grid electricity generation via traditional generators (Zheng and Meinrenken, 2013, Zheng et al., 2014a, b, Zheng et al. 2015).

This drop-in feature enhances their commercial viability because no new or modified infrastructure is required downstream of fuel production.However, they are not necessarily the best fuels in the future. For example, advanced electrolysis cells could synthesize dimethyl ether (CH_3OCH_3) which is liquid at only moderate pressures and a clean burning fuel once engines would be properly optimized.

Methods

Taxonomy of Process Pathways

We organize the pathways into three principal groups, according to the energy source that each pathway employs to dissociate CO_2 and/or H_2O.

This taxonomy has the advantage of showing each pathway's flexibility with regards to the source of primary energy: For example, the electricity to power electrolysis could be supplied by low-carbon sources such as solar thermal, solar photovoltaic, or wind. Table 1 gives an overview of 8 distinct pathways, each of which is covered separately in *Results*. Except for pathways E1b, E2b, and P2 (which feature integrated fuel synthesis), our comparative assessments in *Results* focus only on the dissociation of CO_2 and/or H_2O into intermediary compounds CO and/or H_2, not upstream or downstream processes of the pathway (Figure 1).

Table 1: Process Pathways to Sustainable Liquid Hydrocarbons[i]

Energy source	Technology	Inputs	Dissociation	Fuel conversions	Final fuel
Heat					
H1	Thermolysis	H_2O CO_2	Yielding H_2 and CO	Methanol Synthesis or Fischer-Tropsch	Drop-in fuel *[ii]*
H_2	Thermochemical cycles	H_2O CO_2	Yielding H_2 and CO	Methanol Synthesis or Fischer-Tropsch	Drop-in fuel *[ii]*
Electricity					
E1a	Low temperature electrolysis	H_2O CO_2	Yielding H_2 (option: simultaneous CO)	Optional RWGS *[iii]* and methanol synthesis or Fischer-Tropsch	Drop-in fuel *[ii]*
E1b	Low temperature electrolysis	H_2O CO_2	Single cell yields H_2 and CO simultaneously and integrates hydrocarbon synthesis *[iv]*		Drop-in fuel *[ii]*
E2a	High temperature electrolysis	H_2O CO_2	Yielding H_2 or CO or both simultaneously	Optional (R)WGS and methanol synthesis or Fischer-Tropsch	Drop-in fuel *[ii]*
E2b	High temperature electrolysis	H_2O CO_2	Single cell yields H_2 and CO simultaneously and integrates hydrocarbon synthesis *[v]*		Dimethyl ether or CH_4
Light					
L1	Photo-electro-chemical (PEC)	H_2O CO_2	Yielding H_2	RWGS followed by Methanol Synthesis or Fischer-Tropsch	Drop-in fuel *[ii]*
L2	Artificial photosynthesis	H_2O CO_2	Integrated oxidation and reduction		Methanol *[vi]*††

[i] Underlined processes indicate portions of pathway assessed herein. [ii] Drop-in-fuel refers to gasoline, diesel, kerosene, or methanol.[iii] (R)WGS = (reverse) water gas shift reaction. [iv]Very early development stage. [v] Pressurized solid-oxide fuel cells (SOEC) under development. [vi] Immediate output typically assumed to be methanol but other hydrocarbons may be possible.

Sub-processes other Than CO_2 and/or H_2O Dissociation

Water

Large-scale implementation of any pathway will require water to provide the hydrogen atoms that are incorporated into the fuel.

Technology to desalinate sea water (a near abundant source) is commercially available today and would add little to the fuel's total cost: Desalinated water is typically produced for less than US$ 1 per m^3 (Fritzmann et al., 2007) which corresponds to US$ ~0.001 for the equivalent amount of hydrogen atoms in a liter of synthetic gasoline. Still, actual water consumption can exceed the amount of water incorporated into the fuel. For example, in the scenario by Dahlgren et al., the amount of water to support the moisture swing in the air capture devices is ~20 times that required for electrolysis, or US$ ~0.02 per liter of fuel (Dahlgren, Graves et al., 2010). Another proposed source of water is the atmosphere, e.g. (Olah and Aniszfeld, 2008).

Such an approach could extract both CO_2 and H_2O from ambient air, thus providing a highly location-independent feedstock for hydrocarbons.

CO$_2$ Capture from Point Sources or via Direct Air Capture (DAC)

Except for artificial photosynthesis that aims to have CO$_2$ capture from ambient air built-in, all pathways discussed here require pure CO$_2$ as an input. Various methods to capture CO$_2$ from large industrial plants have been well documented (Thambimuthu et al., 2005). While this option can be considered carbon-neutral so long as the CO$_2$ would otherwise not be captured and permanently stored (i.e., carbon capture and storage, CCS), it cannot be considered sustainable long term because fossil fuel power plants may either be standard-equipped with CCS or cease to operate altogether. Another non-atmospheric CO$_2$ source is geothermal vents (Shulenberger et al., 2007). This too would comprise a net increase in atmospheric CO$_2$.

A long term sustainable (albeit currently more experimental) option is direct capturingof CO$_2$ from ambient air (DAC). Per unit of fuel, DAC would neutralize the CO$_2$ emissions during subsequent combustion of the fuel. DAC was first studied in the 1940s using an alkaline absorbent as a means to obtain CO$_2$-free air (Spector and Dodge, 1946). Today four main approaches are pursued: (1) sodium hydroxide spray to bind CO$_2$ and thus wash it out of the air (Keith et al., 2006); (2) solid state amine-based anionic exchange resins to adsorb and subsequently desorb CO$_2$ via a moisture swing (Lackner et al., 2012); (3) thermo-chemical cycling processes(Nikulshina et al., 2009); and (4) amine-based nanofibrillated cellulose to adsorb and subsequently desorb CO$_2$via a temperature swing (Gebald et al., 2011).

Fuel Conversions

As indicated in Table 1, pathways without integrated fuel conversion require the following technologies to convert their immediate outputs to target fuels gasoline, diesel, kerosene, or methanol (see (Graves, Ebbesen et al., 2011b) for details and further references):

- <u>Reverse</u> water gas shift reaction (<u>R</u>WGS): A portion of H_2 is used to convert CO_2 to CO

- WGS: A portion of CO is used to convert H_2O to H_2

- Fischer-Tropsch: Once H_2 and CO are obtained, ideally at 2:1 stoichiometric ratio (syngas), this well established process can synthesize gasoline, diesel, and kerosene

- Methanol-to-gasoline: If methanol is the immediate output, as has been suggested for some versions of artificial photosynthesis or low temperature electrolysis (Table 1), it could be used either as a final product or converted further via e.g., methanol-to-gasoline.

None of these technologies cause large drops in overall efficiencies that would render infeasible any particular pathway that depends on them(Graves, Ebbesen et al., 2011b). For example, efficiencies of the Fischer-Tropsch process – measured as the chemical energy of the incoming syngas vs. that of net gasoline output – are usually well above 50% (and higher if the waste heat from the exothermic process is captured/re-used and therefore counted as additional energy output).

Results

Pathway H1 – Thermolysis

Technology

Thermolysis refers to dissociating H_2O and CO_2 at extremely high temperatures, by the direct use of heat, i.e. under possible presence of catalysts but without any actual other reactants.

While literature mentions a temperature range of 2000–2500 °C for H_2O thermolysis (Kogan et al., 2000, Perkins and Weimer, 2004, Steinfeld, 2005), the thermodynamics of CO_2 and H_2O dissociation govern that thermolysis occurs fully only at temperatures exceeding 3000 and 4000 °C, respectively.

The heat required for thermolysis could be supplied by concentrated solar furnaces or a variety of electric furnaces. Alternatively, combustion of fuels in an oxygen or chlorine atmosphere have been discussed, but for thermolytic fuel production this would be self-defeating since more fuel would be consumed for heat generation than could be produced by thermolysis using the generated heat (Graves, Ebbesen et al., 2011b).

Current State of the Art

Jensen et al. have developed a CO_2 thermolysis chamber driven by concentrated sunlight. The absorption spectrum of CO_2 is shifted at higher temperatures (Macheret et al., 1995, Macheret et al., 1996, Gillespie et al., 1997, Meinrenken et al., 1997)such that in this particular chamber the CO_2 is partlyphotolyzed by the solar irradiation itself(Reed J. Jensen et al., 2000). The observed peak conversion of solar energy to chemical energy was 5%, with an expected 20% for a mature system (Traynor and Jensen, 2002). While the demonstrated yield is low, the system also produced unutilized high temperature heat which could be used to drive a steam turbine, giving an additional 25% efficiency for electrical energy (Traynor and Jensen, 2002)which could be used to produce more CO or H_2 via electrolysis. If these goals could be met, the total conversion efficiency would be nearly 50%, suggesting a promising process.

However, the majority of energy output from the system is not in the form of thermolysis products but rather electricity, which could have been produced more cheaply (Graves, Ebbesen et al., 2011b).

Key R&D Challenges &Inherent (Dis-)Advantages

Owing to the high temperatures, the product gases, H_2 and O_2, must be separated effectively at high temperature or rapidly quenched (to avoid recombination) and then separated at lower temperature. Furthermore, recombination reduces both the efficiency and the converted fraction of H_2O or CO_2. Unfortunately, 2500 °C also represents a crucial upper limit in system design because high temperature ceramics such as zirconia begin to decompose at higher temperatures (Graves, Ebbesen et al., 2011b).

The expensive materials required as well as the complicated gas handling/separations and heat management may outweigh the advantages from high efficiency. The concentrated sunlight resulted in about 2400 °C in the chamber, indicated by the partially melted zirconia rod at the focal point (Traynor and Jensen, 2002). The stability of materials can also be strained by thermal shocks due to intermittency of the solar heat source (e.g. rapid transients in sunlight due to clouds). Despite some promising results, due to the severe temperature, materials, and separation requirements for direct solar thermolysis, development of an economically viable process seems unlikely in the near future (Perkins and Weimer, 2004).

Pathway H2 – Thermochemical Cycles

Technology

Thermochemical cycles split concentrated H_2O (or CO_2) via a series of thermally driven chemical reactions. This is possible at much lower temperatures than with thermolysis. Product separation is simpler and often inherent in the cycles' reaction steps, with one step yielding the H_2 (or CO) and a separate one the O_2. Cycles can be driven by nuclear reactor heat (Petri et al., 2006, Yildiz and Kazimi, 2006) or concentrated sunlight (Perkins and Weimer, 2004, Steinfeld, 2005, Kodama and Gokon, 2007). Two-step cycles are usually based on reducing a metal oxide while evolving the O_2 in the first step, and in the second step oxidizing the metal or lower-valence metal oxide by reaction with H_2O (or CO_2) thereby producing H_2 (or CO). The first step requires temperatures up to 2000 °C depending on the cycle, usually envisioned from concentrated solar heat because it can provide such temperatures. Cycles with three or more steps are possible, often at lower temperatures (1000 °C) (Graves, Ebbesen et al., 2011b).

Current State of the Art

Possibly the best-known 2-cycle is the ZnO/Zn cycle (Perkins and Weimer, 2004). However, as in direct water thermolysis, the gaseous Zn and O_2 require quenching to avoid recombination. The H_2O (or CO_2) splitting step also faces challenges, including the formation of a passivating layer of ZnO, which reduces the reaction rate (S. Abanades and Flamant, 2006, Loutzenhiser et al., 2009).

Seeking to overcome these issues, similar two-step cycles favor gas–solid separations and/or lower temperatures. Recent investigations have focused on cycles

using modified ferrites (substituted with Co, Ni, or Mn) or ceria-based materials as the oxidation–reduction media for dissociation of H_2O to yield H_2(S. Abanades and Flamant, 2006, Hiroshi Kaneko et al., 2007, Diver et al., 2008, H. Kaneko et al., 2008, Miller et al., 2008, Stéphane Abanades et al., 2010, William C. Chueh and Haile, 2010, H. Kaneko et al., 2010), CO_2 to yield CO (Miller, Allendorf et al., 2008, Loutzenhiser, Galvez et al., 2009, William C. Chueh and Haile, 2010), or both to yield syngas (Shin et al., 2004, Miller, Allendorf et al., 2008, W. C Chueh and Haile, 2009, Loutzenhiser, Galvez et al., 2009, William C. Chueh and Haile, 2010, Stamatiou et al., 2010b, a). These materials can be reduced at lower temperature (<1500 °C) and both the oxidized and the reduced phases remain solid, as with the basic ferrite cycle.

In a major step forward from related work at Sandia National Laboratories (known as Sunlight-to-Petrol, or S2P), Chueh et al. report using a solar cavity-receiver reactor to combine the oxygen uptake and release capacity of cerium oxide and facile catalysis at elevated temperatures to thermo-chemically dissociate CO_2 and H_2Osimultaneously (William C. Chueh et al., 2010). Stable and rapid generation of fuel was demonstrated over 500 cycles. Solar-to-fuel efficiencies of 0.7% to 0.8% were achieved and shown to be largely limited by the system's scale and design rather than by chemistry. Authors cite as essential to their demonstration a simple and scalable reactor design using porous ceria directly exposed to concentrated solar radiation. This enabled high-temperature heat transfer to the reaction sites, as required for performing both steps of the cycle. A thermodynamic analysis of efficiency based solely on the material properties of CeO_2 indicated that values in the range of 16% to 19% are attainable, even in the absence of sensible heat recovery (William C. Chueh and Haile, 2010). This is in line with estimates of practical net solar-to-chemicals conversion efficiencies in the range of16–25%,dependingonthe process (Perkins and Weimer, 2004).

Key R&D Challenges and Inherent (Dis-)Advantages

While relatively simple and elegant, any thermochemical cycling faces a number of obstacles: (1) expensive materials (or equivalently, short material lifetimes) to withstand high temperatures, rapid temperature transients and/or corrosive chemical intermediates; (2) difficult separations of the chemical intermediates; (3) energy losses across multiple steps from heat exchange; and (4) undesired side reactions.

This frequently leads to tradeoffs that must be managed and optimized: While having more steps lowers required temperatures (thus easing heat tolerance requirements for materials), more steps also mean lower overall efficiency, often require corrosive materials, and generally more complex heat management (Graves, Ebbesen et al., 2011b).

To enable an efficient and economical process, any thermochemical cycling requires particularly good thermal management. With this in mind, research in solar thermochemical cycles also includes the design and development of efficient heat recuperating solar collectors. Rotary reactor systems have been developed to mechanically transport the reactants and to optimize heat exchange between the oxidation and reduction steps (Hiroshi Kaneko, Miura et al., 2007, Diver, Miller et al., 2008, Miller, Allendorf et al., 2008, Schunk et al., 2008).

With respect to ceria-based materials specifically, if the microstructure may be redox-stable, the high temperature of the reduction step can lead to coarsening of the microstructure. Grain growth (and corresponding loss of activity) was observed in porous ceria reduced at 1500 °C – but only during the first 100 cycles, whereafter the performance was stable for hundreds of cycles (William C. Chueh and Haile, 2010).

Despite the initial performance loss, the high long-term durability suggests that ceria-based materials are a promising thermochemical cycle redox medium. Looking forward, it appears that other ceria-based materials enable even lower temperature cycles. For example, Cr-doped ceria was recently reported to be significantly reduced at only 465 °C and reoxidized at 65 °C (Singh and Hegde, 2009).

Along with these advantages, ceria-based materials often feature igh molecular weights, which can be a disadvantage (Graves, Ebbesen et al., 2011b). The solar-to-heat conversion efficiency is limited by re-radiation losses and the heat-to-chemicals conversion efficiency is limited by thermodynamics (Fletcher and Moen, 1977, Stéphane Abanades et al., 2006), with further energy losses from heat recuperation and from separation and quench steps. Practical efficiencies for the net solar-to-chemicals conversion have been estimated in the range of 16–25% (depending on the exact process (Perkins and Weimer, 2004)), placing it in similar, if not higher territory as photo-voltaic-powered electrolysis. However, the economic benefits from the slightly higher efficiency of a thermochemical process may easily be outweighed by the economic cost of exotic materials, leading to an overall similar cost structure between the two approaches (Graf et al., 2008).

Pathway E1a&b – Low Temperature Electrolysis

Technology

Low temperature electrolysis cells – alkaline electrolysis cell (AEC) and proton exchange membrane electrolysis cells(PEMEC) – use a pure stream of water to produce hydrogen at the cathode (or consume pure CO_2 at the same time to simultaneously produce CO).

Current State of the Art

AECs are commercially employed in industry. The maximum demonstrated cell stack size is 3.4 MW(DPHFC, 2009). The capital cost for an alkaline electrolyzer stack and system has been estimated at US$ 7.5 to US$ 9 per GJ of H_2 produced (HHV), assuming high capacity factor operation and at an operating point that yields 75-85% efficiency(DPHFC, 2009, Graves, Ebbesen et al., 2011b).

Although the technology is not yet as firmly established as for alkaline electrolysis, small PEMEC plants for industrial applications are available on the market,and the maximum demonstrated cell stack size is 45 kW(DPHFC, 2009).

Key R&D Challenges and Inherent (Dis-)Advantages

In all electrolysis cells (low and high temperature), the fuel and the oxygen are produced at opposite sides of the electrolysis cell, so there is no need for subsequent separation, as is the case with some of the other dissociation methods.

Whereas AECs and PEMECs as well as below high temperature cells can all be used to electrolyze H_2O to yield H_2 (as well as to simultaneously electrolyze CO_2 and H_2O), AECs and PEMECs cannot electrolyze CO_2 alone because their electrolytes conduct only hydrogen-containing ions. In other words, the particular cell type affects which subsequent fuel conversion reactors will be needed to produce the desired target fuel (*Table 1*).Variations on the cell chemistry to produce syngas or hydrocarbons directly at the cathode have been demonstrated, but not at economically feasible operating points. Such cells are at a very early stage of development(Graves, Ebbesen et al., 2011b).

An advantage of AECs is that they are off-the-shelf technologies, proven to be reliable in commercial applications. In contrast to high temperature cells, they do not require any additional heat management components. Hence they can most likely be deployed as installations with a smaller footprint than that of high temperature cells. This head start notwithstanding, looking forward, low temperature electrolysis cells may be fundamentally limited to lower reaction rates than those of high temperature cells and hence higher capital costs (below).

Already in today's AECs, no precious metals are used, and the nickel-based electrodes or similar inexpensive catalysts are expected to be used in future cell designs.Future developments aim to improve the operating points by elevating the operating temperature to 100-200 °C or even higher (DPHFC, 2009). Elevated temperature brings the possibility of faster degradation, however. Alternative electrode materials are also being developed with the goal of improving reaction rates(Graves, Ebbesen et al., 2011b).

PEMECs at present have a lower market penetration, probably because they are more expensive than AECs, largely due to the use of more expensive materials: PEMECs contain expensive noble metals (typically Pt particles) in their electrodes, which provide enhanced reaction rates due to their high electro-catalytic activity, but not enough to compensate for the material expense and bring down the capital cost. The rarity of these materials also limits the ability of PEMECs to meet large scale fuel production. Therefore, R&D mainly focuses on reducing the fraction of precious metals or to eliminate them entirely by replacing them with new base-metal catalysts, while maintaining high electro-catalytic activity.

Pathway E2a&b – High Temperature Electrolysis

Technology

Molten carbonate electrolysis cells (MCECs) and solid oxide electrolysis cells (SOECs) are operated at elevated temperatures (typically >600 °C), in order for their electrolytes to conduct ions at feasible rates. To electrolyze H_2O, both cells use (pure) steam as input. When electrolyzing CO_2 (separately or simultaneously in the same cell), SOECs require CO_2 to be supplied as a concentrated stream, whereas some types of MCECs can absorb CO_2 from more dilute streams (Kaplan et al., 2010). Current State of the Art

SOECs were studied for H_2 production since the late 1970s (Graves, Ebbesen et al.). Recently there been a surge of active research, and the maximum demonstrated cell stack size is 15 kW(DPHFC, 2009). Using the latest developments of solid oxide fuel cell technology, very high electrolysis performance has been demonstrated – H_2O electrolysis at–3.6 A/cm^2 at the thermoneutral voltage (Søren H. Jensen et al.), which is an order of magnitude higher than that of commercial AECs and PEMECs. In other words, such high current densities are attainable at close to 100% electricity-to-fuel efficiency, with zero net electrolysis reaction losses and the only losses being heat transfer losses (therefore feasibly ~90%).

Compared with SOECs, MCECs have been studied less. Recently, CO_2 electrolysis using MCECs has been reported in two different studies (Kaplan, Wachtel et al., 2010, Licht et al., 2010). The cells showed performance similar to that of low-temperature cells – lower than has been demonstrated with SOECs – but these were proof-of-concept studies and optimization of the cell design may well yield significant performance improvements.

Key R&D Challenges and Inherent (Dis-)Advantages

High temperature cells are typically less mature than low temperature cells. But they promise lower capital and operating costs via faster reaction rates and lower cell voltages while maintaining a similar operating lifetime and manufacturing cost(Graves et al., 2011a).

Attaining higher performance is one key R&D challenge. Recently, new materials have been developed that can provide sufficient conductivity in the intermediate temperature range (200 – 600 °C), which may open up a new window of operation.Another challenge is to demonstrate sufficient durability, especially at high current densities. Although low or negligible degradation has recently been demonstrated at lower current densities(Sune D Ebbesen et al., 2010, Sune Dalgaard Ebbesen and Mogensen, 2010), high current density operation currently results in faster degradation (Knibbe et al., 2010, Graves, Ebbesen et al., 2011a). Also, system design including heat management, and reliability through unexpected events such as gas supply failures, must be demonstrated. Finally, as with MCECs, no rare elements like Pt are needed for SOECs.

To optimize integration with subsequent fuel synthesis, both MCECs and SOECs can electrolyze H_2O and CO_2, either separately or simultaneously in the same cell. If H_2O and CO_2 are supplied together, syngas is produced directly from the cell with the same performance as electrolyzing H_2O and CO_2 separately. This is advantageous as it avoids the need for subsequent (R)WGS (*Methods*). However, when an MCEC is applied for H_2O electrolysis, one CO_2 molecule must be transported from cathode to anode for each H_2 molecule produced, which places additional hurdles on the technology (requires separation of the CO_2 from the O_2 at the anode).

Finally, currently high temperature cells cannot be used to produce liquid hydrocarbon fuels directly at the cathode because liquid hydrocarbons are not stable at such a high temperature. However, pressurized SOEC systems are under development with the goal to produce gaseous hydrocarbons like methane or dimethyl ether (DME) directly as well as to further improve the operating point (Søren Højgaard Jensen et al.).

Pathway L1 – Photo-Electro-Chemical (PEC)

Technology

In photo-electro-chemical-dissociation of H_2O (PEC, or photo-electro-catalytic), light absorbing semiconductors are combined with electro-catalysts to enable splitting of water using energy from photons. This eliminates the need for an external electricity source (Turner et al., 2008, Holladay et al., 2009). A PEC cell has as a semiconductor photoelectrode immersed in an aqueous solution (as either its anode or cathode). The photoelectrode collects photons creating excited electrons which electrolyze water molecules at the interface with the aqueous electrolyte. At the interface, the electrode can be coated with an electro-catalyst that enhances the electrolysis reaction. Research focuses on a multitude of electrodes, including semiconductor oxides such as TiO_2, $CaTiO_3$, $SrTiO_3$, and composite oxides tailored to yield appropriate band gaps, and multi junction cells with two or more semiconductor layers, e.g., Si as one layer and a second layer (e.g., GaInPN, $CuGaSe_2$) protecting it from corrosion (Graves, Ebbesen et al., 2011b).

Current State of the Art

With a tandem electrode configuration of two semiconductor layers, p-GaInP$_2$ and GaAs, 15% solar-to-chemical efficiency (H$_2$) has been reported (Khaselev and Turner, 1998), which is around half the reported photovoltaic efficiency for this combination (without water splitting). A similar cell with Si and Al$_{0.15}$Ga$_{0.85}$ as semiconductor layers yielded even higher efficiency when RuO$_2$/Pt electro-catalysts were added (22%, close to the reported photovoltaic efficiency) (Licht et al., 2000). An alternative PEC cell may be formed by suspending the semiconductor as tiny particles in solution and optionally loading the particles with catalysts (Nozik, 1980, Hashimoto et al., 2005). However, in such a powder suspension, the produced H$_2$ and O$_2$ gases more easily recombine than in the electrode-based system, because the H$_2$ and O$_2$ production sites are located so close to each other (Hashimoto, Irie et al., 2005).

Key R&D Challenges and Inherent (Dis-)Advantages

In theory, integration of the light absorption and H$_2$ dissociation steps should enable higher efficiency by reducing the losses in transporting electricity from the PV cell to the electrolysis cell, eliminating current collectors, and interconnections between devices. In practice, however, several characteristics of the photoelectrode must be satisfied simultaneously: (1) The electronic band gap must be low enough for efficient photon collection from the solar spectrum (<2.2 eV), and high enough such that the excited electrons have enough energy to split water (>1.23 eV or typically at least 1.6–1.7 eV for sufficient rates); (2) the band edges must straddle the water electrolysis redox potentials; and (3) the photoelectrode must be stable and resistant to corrosion in the aqueous electrolyte (Turner, Sverdrup et al., 2008). These constraints rule out most inexpensive, conventional PV materials.

However, a photoelectrode of similar photoconversion efficiency as conventional PV would actually be required if PEC were to hold an advantage over a PV-electrolysis system made up of separate units (Graves, Ebbesen et al., 2011b).

In summary, while demonstrated at bench top level, an integrated photo-electric process to split H_2O does simply not appear scalable at present. No single, sufficiently durable material has yet been found that satisfies above stringent constraints (Turner, Sverdrup et al., 2008).

Pathway L2 – Artificial Photosynthesis

Technology

Most plants and some bacteria are photoautotroph, i.e., they have the capability to use light as an energy source and carbon from in-organic CO_2, to create organic carbon compounds for their own subsequent use as structural materials and for their metabolism. The well known redox reaction for this (oxygenic) photosynthesis is seductively simple:

$$2n\ CO_2 + 2n\ H_2O\ _{Light} \rightarrow 2\ (CH_2O)_n + n\ O_2$$
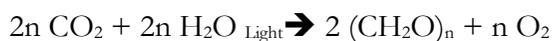
However, just as the reverse reaction – humans, animals, and plants breathing the resulting oxygen and glucose back into water and CO_2 (via the citric acid cycle) – is anything but simple, the actual implementation of photosynthesis in nature is tantalizingly complex: (i) Chlorophyll in photosynthetic reaction centers absorbs part of the visible sunlight (preferentially red and blue, hence its green appearance) and this results in a proton gradient across the chloroplast membrane; (ii) a portion of this energy is stored in adenosine triphosphate (ATP); (iii) the remainder is invested to

oxidize water; and finally (iv) the thus freed electrons and ATP are used to capture CO_2 from ambient air and reduce it to organic compounds, in a sequence known as the Calvin cycle and involving Rubisco as one of the key catalysts (Renger, 2008). Artificial photosynthesis seeks to mimic this process – albeit in a dead rather than alive system – integrating absorption of CO_2 from ambient air, H_2O & CO_2 dissociation, and fuel conversion into a single reactive unit.

Current State of the Art

Research that seeks to mimic this (oxygenic) photosynthesis usually defines a target architecture of four distinct steps: (1) light absorption or harvesting; (2) charge separation across a membrane; (3) using accumulated positive charges to oxidize water; and (4) using resulting negative charges for reductive chemistry to produce the fuel (Cogdell et al., 2010). As a default assumption, this fuel is usually assumed to be methanol although the exact target fuel of artificial photosynthesis is not yet certain and quite probably flexible.

In this framework, the target architecture for steps (1) and (2) – often referred to as the light reactions of photosynthesis – is quite similar to the processes as they occur in nature: Light antennas combined with a kind of molecular scaffolding (reaction centers) to enable electron transfer. In contrast, the target architecture for the subsequent dark reactions departs from the natural blueprint and essentially seeks to substitute alternatives (e.g., no involvement of ATP) and the quest to mimic and improve the infamous Rubisco has been all but given up (Portis and Parry, 2007, Cogdell, Brotosudarmo et al., 2010).

The reason for this departure is four-fold (reviewed in (Cogdell, Brotosudarmo et al., 2010)).

First, the light reactions occur without molecular motion and the associated proteins do not actually partake in any reactions – they are not very alive one might say and thus easier to copycat. In contrast, the proteins in the dark reactions actively participate in the catalytic mechanisms, thus posing a far greater challenge for mimicry since knowing their static structure alone (e.g., via X-ray crystallography) does not suffice as a blueprint to imitate them. Second, some scientists point out that, in natural photosynthesis, the dark reactions, in particular the respective proteins' affinity to CO_2 in ambient air, are actually far from optimal and thus offer a promising area to increase photosynthesis' overall efficiency. Third, the natural proteins are often deemed not robust enough for use in systems that will function for years with only limited damage/repair. Lastly, it should be noted that the fuel of the natural system – usually glucose – works well for animals (and plants) that have the proper catalysts to burn it efficiently but would be rather less useless for e.g., the transportation sector.

Key R&D Challenges and Inherent (Dis-)Advantages

Despite tremendous progress over the past decades, ongoing R&D in artificial photosynthesis is still tackling issues of fundamental understanding of some of the underlying mechanisms. In contrast to all other pathways reviewed herein, these issues have so far prevented any working implementation of the end-to-end process or even some of its components, including at lab scale.

Some of the many remaining R&D challenges in artificial photosynthesis are (Cogdell, Brotosudarmo et al., 2010):

- For the light reactions, identify pigments that can absorb and undergo photochemistry in higher bands of the energy spectrum, thus possibly boosting overall efficiency (generally artificial photosynthesis seeks a factor 10 improvement in solar to carbohydrate efficiency over current photosynthesis in plants)
- For the dark reactions, produce new catalysts capable of fixing CO_2 (from dilute sources) into a suitable fuel
- Improve overall robustness of all proteins in the end-to-end system, particular their sensitivity to photo damage (or, alternatively, mimic even the part of the natural process that continuously self-repairs damaged components in a living system)
- Nano-to-macro integration: All pathways covered herein face R&D challenges with regards to system integration as they scale up. Still for artificial photosynthesis this task faces an extra twist, namely the integration from units designed to function at nano-scale to large structures that deliver fuel at macro scale. For example, as yet, most of the artificial light absorbing antenna mimics have not been organized into the large arrays that will be needed for a scalable device (Escalante et al., 2008, Cogdell, Brotosudarmo et al., 2010)

From an input/output perspective, artificial photosynthesis (AP) comes close to an ideal system: It integrates not only the CO_2 absorption but also the fuel synthesis into a single system. And it avoids the disadvantages of having to sustain a life system that unduly competes for fertile land and water. AP thus seeks the best of both worlds, biomass on one hand and inert, chemistry-based systems on the other.

This integration should bring distinct advantages via overall efficiency gains and cost savings. For example, no separate system is required to capture and concentrate CO_2 (as is the case for all other pathways assessed herein) and no separate

reactors need to be maintained for downstream fuel conversions (as is the case for some other pathways). Further, no auxiliary systems are required for complicated heat management and shuffling liquids and gases back and forth between various system components. The integration, however, comes with a possible downside as well. Artificial photosynthesis is inflexible with regards to alternative sources of primary energy input – a disadvantage vis-a-via electrolysis-based approaches.

Another often cited advantage of artificial photosynthesis comes with a caveat. In artificial photosynthesis, much higher ratios of solar-to-harvestable hydrocarbon energy are expected than with biomass because plants actually metabolize much of the produced hydrocarbons for their own use (US DoE, 2009). However, even artificial photosynthesis cannot work without at least some of such "maintenance costs" – experts anticipate significant ongoing repair costs e.g., from photo damage. Indeed, continued research into artificial photosynthesis that is capable of self-repairing has been proposed (Cogdell, Brotosudarmo et al., 2010).

Discussion

Assessing Current Capabilities and Future Potential

The pathways assessed in *Results* span a spectrum of current technological readiness and represent a diverse set of remaining R&D challenges. This creates very divergent future outlooks. To better illustrate this spectrum, we chose to focus on just three of the pathways and illustrate an approximate future trajectory side by side. Figure 2 places each pathway on a time trajectory (horizontal axis) along 4 major maturity stages (outlined on vertical axis).

Figure 2: Status-Quo, Time Line, and Future Promise of Major Pathways
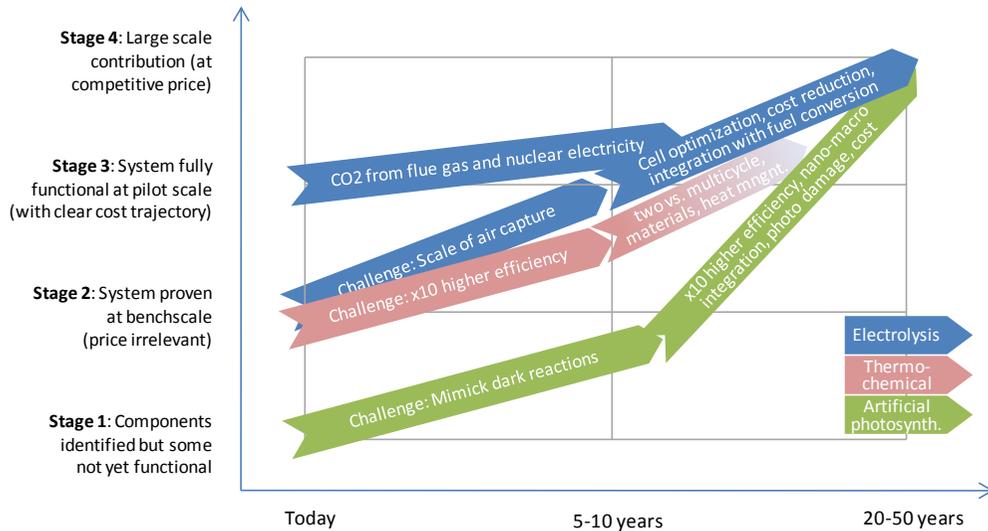
Artificial Photosynthesis (Currently Stage 1, Future 4)

From a policy perspective, artificial photosynthesis may well be the candidate with the most odds but quite possibly highest rewards. Still, the fact that at present it simply does not work means enormous future challenges. Even basic components towards a system working at bench scale have been estimated to be available within 10+ years only (Cogdell, Brotosudarmo et al., 2010). However, after such a period of catching up, the potential for large scale and low price is tremendous: The fully integrated design combined with general advances in mass manufacturing promises particularly low cost (unless these are offset by the need for rare materials or extensive repair/material turnover to overcome photo damage and other degradation).

Perhaps the biggest boon for artificial photosynthesis is its overall attractiveness as a vision. The advances it will bring to fundamental science – albeit

difficult to measure monetarily – and the spillover effects themselves (for catalyst research, hydrogen production, and nano/macro integration) are so attractive that artificial photosynthesis will likely continue to attract significant R&D funding. And this itself represents aninherent advantage to success vis-a-vis the other pathways.

Thermochemical Cycling (Currently Stage 2, Future 3+)

Especially with the more recent work employing ceria-based materials (William C. Chueh, Falter et al., 2010), thermochemical cycling to dissociate H2O and CO2 has been shown to clearly work. Once extracted from the reactors, the syngas can be fed into existing, well established fuel conversion technologies (Methods). Efficiencies (<1%) are currently an order magnitude below a reasonable threshold to produce significant output per occupied land, so scale up is currently not an option. However, increases to well above 10% are expected (William C. Chueh, Falter et al., 2010). This then shifts focus to the challenge of material and heat management. Here, the inherent opportunity to exploit optimization strategies between 2-step and multi-step cycling appears particularly promising. However, generally large temperatures and often corrosive materials seem to indicate a probably long and bumpy road until thermochemical cycling can contribute at significant scale. Finally, thermochemical cycling can benefit from few synergies with other technologies or markets (except for the direct sale of hydrogen into specialist markets).

Electrolysis (currently stage 3, future 4)

At present, electrolysis enjoys a clear head-start in the race to produce sustainable hydrocarbons.

Especially when reverting to CO2 from concentrated sources (to circumnavigate a not yet pilot-scale ready DAC, Methods) and relying on low-carbon

electricity, electrolysis could enable a fully sunlight-to-fuel system even today (Graves, Ebbesen et al., 2011b). Looking further into the future, electrolysis could be fully integrated with the subsequent fuel conversions, likely further reducing cost.

Outlook

In a presentation on the world's energy predicament (Chu, 2007), former US energy secretary Stephen Chu laid out a time table for fusion that he considers optimistic based on past and future R&D: Pre-pilot stage in a few decades, and first plants coming onto the grid only in the last quarter of this century (and growth from thereon). Despite these rather sobering prospects, the R&D funds invested in fusion internationally are orders of magnitude above what is invested into artificial photosynthesis or any other pathway to sustainable hydrocarbons. This points to a much higher reward that is expected in case of success.

In contrast, even if solar-powered hydrocarbon production becomes commercially competitive, its potential to solve the world's energy dilemma will ultimately remain limited. Even at today's population and energy needs per capita, landuse concerns already drive researchers towards efficiencies of at least 10% to be sustainable (Cogdell, Brotosudarmo et al., 2010). Therefore, solar-based pathways do not allow too much room for growth. Maybe at that time (next turn of the century) fusion will be available to deliver some of the primary energy needed to synthesize even more hydrocarbons – if indeed they have not been replaced altogether.

Acknowledgments

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