STEP, Efficient solar syntheses: A comprehensive approach to decreasing the concentration of atmospheric carbon dioxide

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ABSTRACT

The Solar Thermal Electrochemical Process (STEP) was introduced to provide a complete solution to lowering carbon dioxide in the atmosphere (1). STEP utilizes a synergy of thermal and electrochemical energy to drive endothermic processes at increased efficiencies and high rates. STEP is a versatile technique that applies thermal energy to concentrated reactants to decrease the energy of endothermic electrolysis reactions. By elevating reactant temperature using solar thermal energy, the voltage needed to drive the endothermic electrolysis reactions can be tuned to allow for sub-bandgap sunlight that was previously discarded by photovoltaics1 This process has been shown experimentally for processes ranging from the initial water splitting experiment to bleach production, iron metal production, cement, and carbon dioxide reduction. STEP can achieve in excess of 50% solar energy conversion efficiency. Utilizing different molten salt mediums, these processes have been shown to occur at very low energy and to maintain current densities (A cm^{-2}) sustaining high process rates. STEP utilizes chemical and solar thermal concentrations to adjust the tuning potentials of endothermic electrolysis processes to allow more efficient conversions. 1. STEP: A solar chemical process to end anthroprogenic global warming. J. Phys. Chem. C, 113, 16283, 2009.

Keywords: solar synthesis, sustainability, climate change, green chemistry

1 Background

Anthropogenic release of carbon dioxide and atmospheric carbon dioxide have reached record levels. Along with control of fire, iron production is one of the founding technological pillars of civilization, but is a major source of CO_2 emission. In industry, iron is still produced by the carbothermal greenhouse gas intensive reduction of iron oxide by carbon-coke, and a carbon dioxide free process to form this staple is needed. In a similar manner, society consumes use a large amount of cement, and the cement industry releases ~9 kg of CO_2 for each 10 kg of cement produced. Cement production accounts for 5-6% of all anthropogenic carbon dioxide emissions. An alternative to this CO_2 intensive process is needed, as well as alternatives to produce bleach, aluminum, fuels and all societal staples without releasing carbon dioxide to the atmosphere.

2 STEP - using the sun to produce societal staples & remove CO_2

In 2009 we introduced the theory of the STEP generation of energetic molecules: A solar chemical process to end anthropogenic global warming. From 2010 to the Licht group has presented experimental validation of the STEP process, including the direct conversion of atmospheric carbon dioxide into valuable graphite, and other individual new chemistries to synthesize a growing portfolio of societal staples at over 50% solar energy efficiency and without carbon dioxide emission. The solar thermal electrochemical production (STEP) process is capable of the production of societal staples with little or no carbon footprint, and can directly capture & convert carbon dioxide from the air that can be stored as useful graphite. In STEP the efficient formation of metals, fuels, cement, chlorine, and carbon capture is driven by solar thermal heated endothermic electrolyses of concentrated reactants occurring at voltage below that of the room temperature energy stored in the products. As an example, CO_2-free

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STEP iron production, occurs from the new chemistry of solar driven iron ore (hematite) reduction in molten carbonate. As another example, CO_2 is reduced to either fuels, or storable carbon, at solar efficiency higher than the best solar cells. This is due to a synergy of efficient solar thermal absorption and electrochemical conversion at high temperature and reactant concentration. Water is efficiently split to H_2 by molten hydroxide electrolysis, and chlorine, sodium and magnesium from molten chlorides. STEP cement uses a novel molten electrochemistry for the production of calcium oxide (lime from limestone) [1-17].

The Solar Thermal Electrochemical Production of energetic molecules converts solar energy at high efficiency. Rather than electricity, a variety of useful chemicals, including solar fuels and iron without CO_2 emission, are produced by this STEP process. A synergy of solar thermal and solar-electric and other renewable energy electronic charge transfer, forms an alternative higher efficiency solar energy conversion process. For example, STEP can split CO_2 with >50% solar efficiency.

The STEP approach for solar energy conversion [1] is based on our theory and experimental observation [2-17], that even a semiconductor with bandgap smaller than the water splitting potential ($E(H_2O)$=1.23V at 25°C) can split water at elevated temperature. Hence, silicon (band-gap 1.1 eV) was used to directly form hydrogen fuel from water at elevated temperature in a novel molten alkali hydroxide electrolyzer. As represented in Fig. 1 STEP generalizes the advantage of this energy conversion process to the endothermic formation of all useful, energetic molecules, is and includes STEP cost effective production of hydrogen, iron fuels and carbon capture.

The STEP process distinguishes sunlight that is energy sufficient to drive photovoltaic charge transfer, and applies solar thermal energy to heat and decrease the energy of enodothermic electrolysis reactions. This process **captures sunlight with conversion efficiency** greater than either photovoltaic or solar thermal electric processes, through the use of the global (visible + thermal) sunlight. Energy sufficient, visible, sunlight drives photovoltaic charge transfer, and available heat, infrared sunlight, and excess visible sunlight, heats, and decreases the energy of, an electrolysis reaction.

In the STEP process, rather than electrical generation, solar energy directly provides the chemical products needed by society. This original process is derived for the solar generation of energetically rich chemicals, including chlorine, metals, hydrogen and to proactively convert anthropogenic CO_2 generated in burning fossil fuels towards the formation of energy rich hydrocarbons, including solar synthetic diesel. As one STEP example, carbon dioxide is inherently highly stable and noncombustible. This thermodynamic stability creates a very high activation energy, *until now, the process of efficient CO_2 conversion had been considered a difficult, if not impossible, task* [5]. However, **STEP** conversion can recycle and remove CO_2 at ampere level currents and at 34 to over 50% solar efficiency.

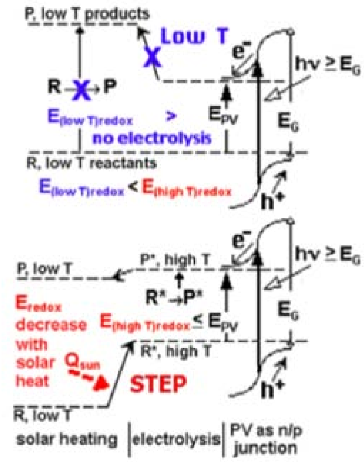

Figure 1: **Top**: a conventional, efficient photovoltatic generates a voltage too low to drive many useful electrochemical reactions, such as water or carbon dioxide splitting, or the indicated generic redox transfer, at ambient temperature. **Bottom**: The **STEP** process uses solar thermal energy to drive down the required electrolysis. This forms an energetically allowed pathway to drive charge transfer.

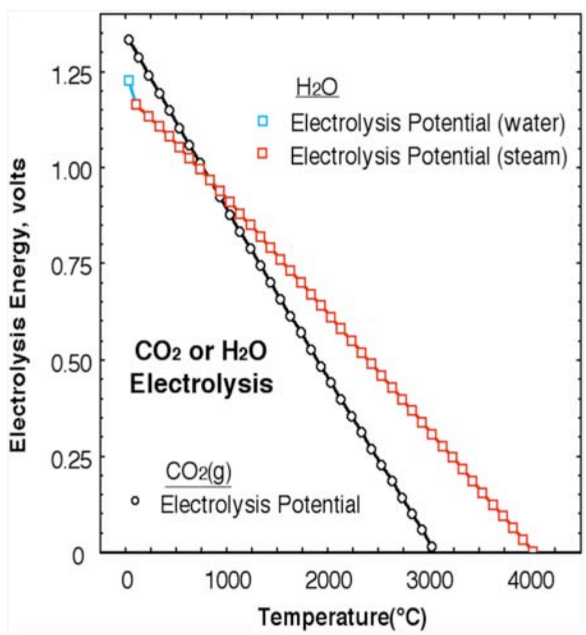

Figure 2: Example of decrease in splitting energy ($V_{electrolysis}$) with increase of temperature for both CO_2 & H_2O. Sunlight provides an efficient heating source to these lower energies.

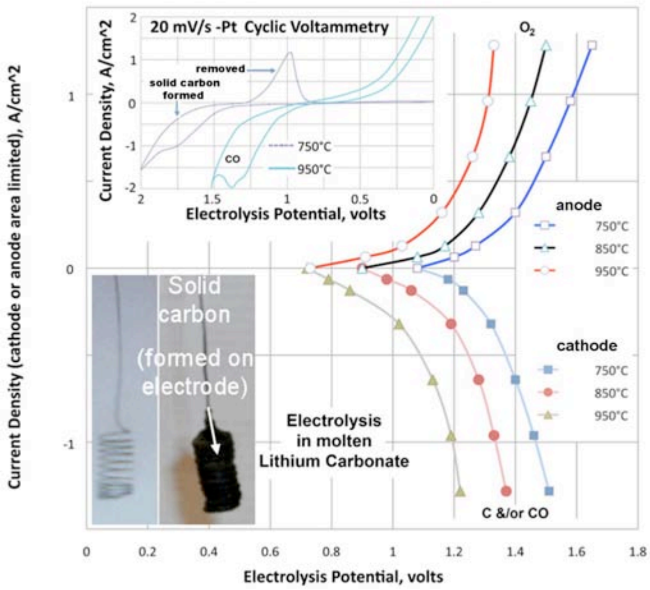

Figure 3: CO_2 is easily captured as solid carbon at 750°C, or at 950°C as carbon monoxide using a molten Li_2CO_3 electrolysis cell powered by sunlight.

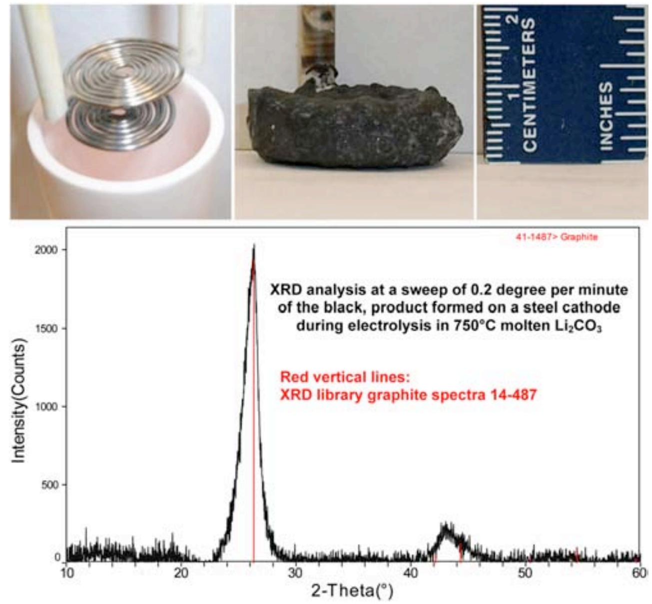

Figure 5: Ni (air electrode) & steel (lower coil) are immersed in molten salt. Thick carbon forms on the steel (middle photo) after 4 A hour of CO_2 electrolysis. XRD verifies this product is graphite.

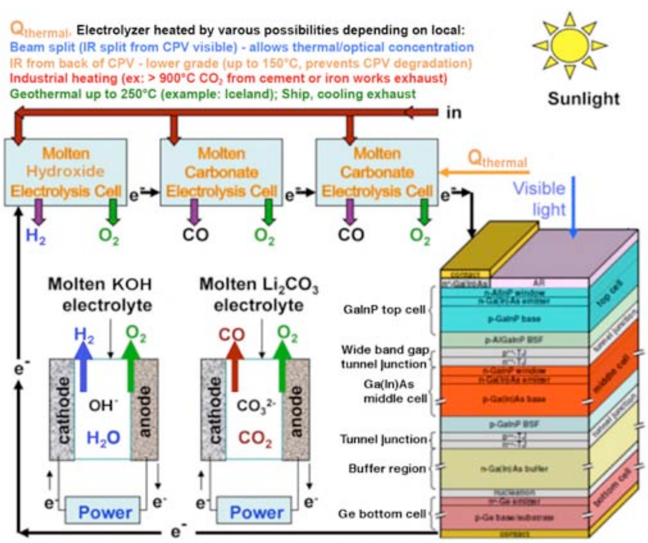

Figure 4: STEP system that converts CO_2 and water to fuel. STEP uses solar thermal energy to drive otherwise energy forbidden pathways of electrolysis. Atmospheric CO_2 can split to form fuel, such as syn gas $CO + H_2$, or graphite. The graphite is both a valuable product and is easily stored for future generations.

Figure 6: STEP R&D is conducted at indoor and outdoor state-of-the art facilities to advance solar CO_2 removal at George Washington University's Science & Technology Campus.

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