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Overview on CO_2 valorization: challenge of molten carbonates

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The capture and utilization of CO_2 is becoming progressively one of the significant challenges in the field of energetic resources. Whatever the energetic device, it is impossible to avoid completely the production of greenhouse gas, even parting from renewable energies. Transforming CO_2 into a valuable fuel, such as alcohols, CO, or even C, could constitute a conceptual revolution in the energetic bouquet offering a huge application domain. Although several routes have been tested for this purpose, on which a general panorama will be given here, molten carbonates are attracting a renewed interest aiming at dissolving and reducing carbon dioxide in such melts. Because of their unique properties, molten carbonates are already used as electrolytes in molten carbonate fuel cells; they can also provoke a breakthrough in a new economy considering CO_2 as an energetic source rather than a waste. Molten carbonates' science and technology is becoming a strategic field of research for energy and environmental issues. Our aim in this review is to put in evidence the benefits of molten carbonates to valorize CO_2 and to show that it is one of the most interesting routes for such application.

Keywords: CO_2 valorization, electrolysis, molten carbonates, carbon monoxide, carbon

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The Problematic of CO_2 and Its Valorization

Global warming due to rising levels of greenhouse effect gases, such as atmospheric carbon dioxide, and energy consumption are the major challenges in the energetic field. Decreasing carbon dioxide emissions is a key issue but not the only one; thus, it is becoming compulsory to capture and reuse this gas in an efficient mode as a new source of fuels. There are different approaches to this stimulating problem.

Some Facts

Carbon dioxide is in the heart of fundamental processes over millions of years on Earth. It allows stocking solar energy through synthesis, and it is a key molecule for producing fossil fuels and, thus, it is an indicator of the consumption of energy from fossil fuels. Of course, the negative effect of CO_2 in the atmosphere is dramatic and contributes to a significant increase in the temperature of our planet, which is becoming alarming. Concentration of this gas is nowadays increasing by more than 2 ppm per year, reaching 400 ppm against 280 ppm in the preindustrial era. The challenge is to store and to transform the CO_2 into valuable chemicals and fuels along with a better understanding of the physicochemical properties and behavior of CO_2. This would be an extraordinary input in the development of sustainable energy.

Key Molecule in a New Energetic Economy

Carbon capture and storage (Sequestration) (CCS) is a potential method to allow the continued use of fossil-fueled power stations while preventing emissions of CO_2 from reaching the atmosphere.

Gas and coal (and biomass)-fired power stations can respond to changes in demand more readily than many other sources of electricity production, hence the importance of retaining them as an option in the energy mix (Boot-Handford et al., 2014).

Various technologies for the capture of CO_2 from fossil fuel-fired power plants are available. The four different capture methods are post-combustion, pre-combustion, oxy-combustion, and chemical looping combustion. Each technology has its own advantages and disadvantages and is at different stages of development (Spigarelli and Komar Kawatra, 2013). Recently, molten carbonates are emerging as challenging electrolytes for CO_2 capture (Cassir et al., 2012). In effect, molten carbonate fuel cells (MCFCs) can be used as CO_2 separator and concentrator while producing electricity from hydrocarbons fuels. According to calculations and some tests, using MCFC for carbon capture, the resulting SPECCA (Specific, Primary Energy Consumption for CO_2 avoided), is about 0.5 MJ kg^{-1} CO_2, which is well below the value obtained with conventional post-combustion removal based on amines (Suguira et al., 2003; Cassir et al., 2012).

A Large Panel of Transformation Media

In 2010, 12 carbon dioxide valorization recovery methods were identified by the Alcimed Company, whose activity lies at the interface of science and marketing (**Figure 1**).

CO_2 can be valorized with three main routes. The "No transformation" route will not be described in this review as it is out of the scope of this article. With a "Chemical CO_2 conversion" route, it is technically possible to use CO_2 as a carbon source for the synthesis of commodity products, from simple CO to liquid fuels and high-molecular-weight polymers (Hu et al., 2013). The electrochemical deposition route will be more detailed being our principal focus.

Biologic Transformation

Microalgae

Microalgae, due to their photosynthetic activity, could be used to capture and valorize the CO_2. Microalgae have the ability of fixing CO_2 directly from waste streams such as flue gas as well as using nitrogen from the gas as a nutrient. Before microalgae can be converted into fuels, the biomass content has to be harvested and dried. The conversion can be carried out through thermochemical or biochemical conversion. The products synthesized depend on the algae or bacteria variety chosen and also on the operating conditions. Pharmaceutical industry already uses this route to produce food supplements (spirulina, β-carotene, etc.). Biofuels (biodiesel precursors, ethanol) are emerging. The US start-up SOLIX[1] has initiated commercialization of biofuel from CO_2 proceeding from combustion smokes.

Biocatalysis

It is the use of biochemical agents, as enzymes, to stimulate a chemical reaction and, thus, obtain products by using less drastic operating conditions than in heterogeneous or homogenous catalysis. Inspired by nature, a large body of research has been devoted to new materials catalyzing CO_2 functionalization in either electrochemical or chemical ways. In 2009, the US start-up Carbon Science[2] has produced liquid fuels thanks to a prototype. The demonstration prototype uses Carbon Science innovative biocatalytic process to break down CO_2 and water and then combines carbon and hydrogen to form methanol, a liquid fuel. Enzymes from microorganisms transform CO_2 and H_2O to methane, methanol, and butanol. CO_2 can be captured by a biologic agent and then electroconverted to bicarbonate and formate (Karthikeyan et al., 2014).

Chemical Transformation

Energetic Value Product

Photonic energetic power source route

In the photonic energetic power source route, carbon dioxide reacts with photogenerated electrons in order to create an anion radical as intermediate species (Hu et al., 2013). Photoelectrochemical reduction of CO_2 requires photoelectrocatalysts combining a

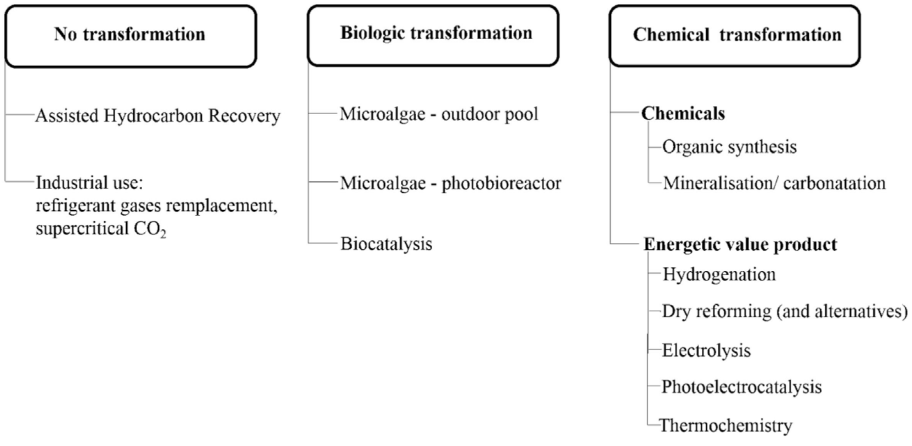

FIGURE 1 | Summary of the 12 CO_2 valorization recovery methods (Thybaud and Lebain, 2010).

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[1] http://www.solixbiosystems.com/

[2] http://www.carbonsciences.com/view_news.php?id=41

semiconductor and a molecular catalyst. Lim et al. reported the use of four types of semiconductors: p-Si, p-GaAs, p-InP, and p-GaP. Metallic molecular catalysts used are mostly based on nickel, cobalt, ruthenium, and rhenium, whereas enzymes (dehydrogenase and pyridine) are the non-metallic molecular catalysts (Lim et al., 2014). CO_2 photoelectrocatalysis is feasible in gaseous phase or in aqueous solvent. In gaseous phase, the photocatalysts directly react on carbon dioxide and steam to produce synthetic or oxygenated hydrocarbons. Water dissociation and carbon dioxide reduction are realized at the same time. On the contrary, in the other system, water dissociation is physically separated from CO_2 reduction because the photocatalysts are integrated in a photoelectrochemical reactor. CO_2 and steam direct photocatalysis produces hydrocarbons and alcohols such as methanol, methane, carbon monoxide, and other compounds of alkene type or paraffin. Different photocatalytic CO_2 reduction systems exist, one of them is the photoactive metal-organic frameworks (MOFs) (Wang et al., 2015). MOFs' porosity facilitates CO_2 adsorption and, thus, increases the photocatalytic efficiency. Different photocatalysts have been investigated for their performance in photocatalytic CO_2 reduction (TiO_2, $BiVO_4$, $BiWO_6$, Zn_2GeO_4). Present investigations are developing less toxic catalysts. The challenge is to develop efficient photocatalysts that can reduce CO_2 under visible light, because currently most of them are only active in the UV region, and to design an efficient harnessing solar radiation reactor (optical fiber, monolith photoreactors, etc.) (Das and Wan Daud, 2014).

In atmospheric conditions, in a dielectric barrier discharge, syngas is produced, either by the conversion of a mixture of CO_2 and CH_4 or by CO_2 reduction in water (Ozkan et al., 2015).

Solar energy could be stored as formic acid which is electrochemically generated from CO_2; it is a viable solar fuel pathway. White et al. accomplished this transformation by semi-optimized indium-based electrolyser stack powered by a photovoltaic panel. They separated light absorption and CO_2 reduction through the use of a commercial solar panel (White et al., 2014).

Another route to valorize the CO_2 is the use of plasma. Plasma permits to reform CO_2 by methane, providing a highly efficient fuel compared to thermocatalytic methods. But it is not commercially viable due to the higher energy plasma input. Carbon nanofibers along with syngas (H_2 + CO), traces of methanol, and some hydrocarbons (C_2H_2, allene) were produced by CO_2 reduction by plasma-assisted *in situ* decomposition of water. Mahammadunnisa et al. reported, for the first time, the simultaneous activation of carbon dioxide and water in a catalytic non-thermal plasma dielectric barrier discharge reactor operated under ambient conditions. Three different conditions were applied (plasma alone without catalyst, plasma with NiO/γ-Al_2O_3, or plasma with Ni/γ-Al_2O_3). The higher CO_2 conversion was due to synergy between plasma excitation of CO_2 molecule and catalytic action of NiO catalyst. Nickel-based catalysts are promising for H_2 and syngas production. Plasma alone is good for syngas formation. But for the reduction of CO to methane, NiO catalyst facilitates the conversion of CO into methane (Mahammadunnisa et al., 2013).

Ionic Liquids

Ionic liquids' (ILs) physicochemical properties make them very attractive for the CCS. Once separated from the atmosphere or exhaust flue, there are two options for the carbon dioxide: chemical transformation into useful products or into a form suitable for long-term storage. Long-term CO_2 storage is not perfect because the CO_2 absorption in ILs is reversible (increase in the viscosity leading to CO_2 and absorption rate diffusion restriction). Electrochemical transformation of carbon dioxide is achieved by direct electroreduction at noble metals, or at carbon electrodes (with a substantial overpotential for the last one); thus, yielding carbon dioxide radical anion ($CO_2^{\bullet-}$), which then typically dimerizes in $C_2O_4^{2-}$ or disproportionates in CO and CO_3^{2-}. Also electroreduction could be achieved in more active metals, such as transition-based metal centers (Ni, Fe, Pd, Ru, Re, Rh) complexed with various ligands such as porphyrins, bipyridines, or phosphines; thus, yielding a variety of reduction products, most commonly carbon monoxide and onward products such as formic and oxalic acid but also extending to methanol and methane (hydrogen evolves at the same potentials required for CO_2 reduction). CO_2 electroreduction in RTILs (room temperature ionic liquids) allows long-term storage and produces valuable useful chemicals. The choice of RTILs and reaction conditions greatly influences the reduction products. Also, lower potential routes are available for CCS, which are indirect electrochemical reduction routes. The formation of peroxodicarbonate $C_2O_6^{2-}$ by oxygen reduction to superoxide in RTILs is an example. Among hydrogen, nitrogen, and carbon monoxide, carbon dioxide and water have the highest solubility in an ionic liquid (C_4C_1-iPF_6) at 25°C. CO_2 is the most soluble in fluorinated IL. CO_2 can be collected from the ILs by pressure decreasing. Optimizing the design of the appropriate RTILs, as well as the electrode material, is compulsory to enhance the absorption and the reduction of CO_2 (Rees and Compton, 2011).

CO_2 Electrochemical Reduction in Aqueous Solutions

This process has been studied since the late 90s on metallic electrodes in aqueous solutions. It is depicted in **Figure 2.** The main products of CO_2 reduction are methane, ethylene, formate, carbon monoxide, and some alcohols (methanol, ethanol, and propanol). Copper is the most studied electrode, able to give a large panel of products (hydrocarbons and other products such as alcohols at a high current efficiency) when compared with other metals. Indeed, metals are divided into four groups for the CO_2 aqueous electrochemical reduction. Group 1 (Hg, Pb, Bi, In, Sn, Cd, Tl) binds the $CO_2^{\bullet-}$ intermediates and gives formate (or formic acid) as a product. Group 2 (Au, Ag, Zn, Ga, Pd) yields CO as the major product. Group 2 binds the $CO_2^{\bullet-}$ intermediate to varying degrees, but cannot reduce CO. Copper is the only commonly studied (for the CO_2 reduction) metal that falls into group 3. Copper binds the $CO_2^{\bullet-}$ intermediate and reduces the CO to higher reduction products such as hydrocarbons (methane, ethylene, etc.) and alcohols. The last group (Ni, Fe, Pt, and Ti) does not reduce CO_2 directly, strongly binding hydrogen to produce hydrogen only.

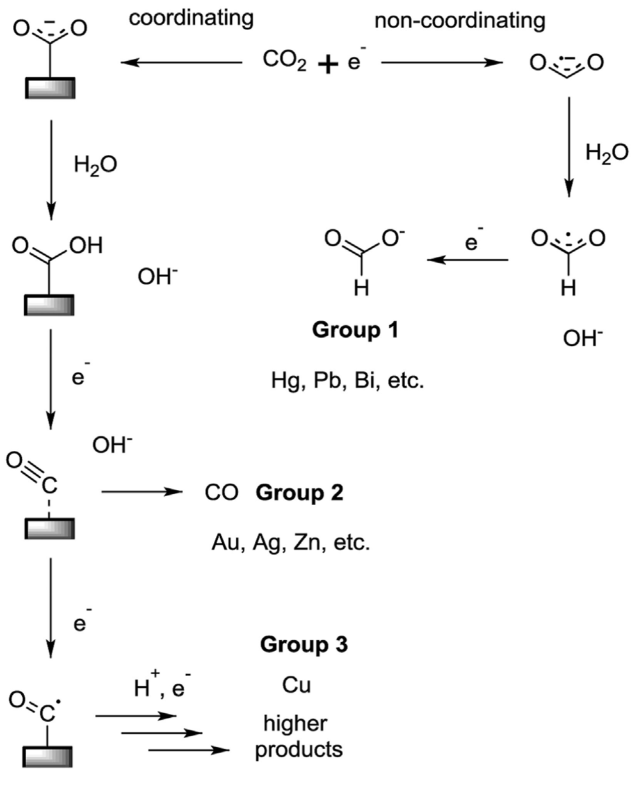

FIGURE 2 | Mechanism for electrochemical CO_2 reduction on metal surfaces in water (Jones et al., 2014).

The pH of the solution impacts the CO_2 solubility as well as the first CO_2 reduction competition reaction, the hydrogen evolution reaction. The selection of the electrolyte is also a very important parameter for electrochemical reduction of carbon dioxide (Gatrell et al., 2007; Hori, 2008; Oloman and Li, 2008). Many researchers found that lower temperatures suppress hydrogen evolution and increase CO_2 reduction efficiency (Lote, 2014). High-pressure CO_2 electrolysis (till 60 atm) could be the most feasible method for achieving a commercial electrochemical process. The high current density and efficiency observed in this case on different electrodes are comparable with those obtained with high-temperature solid oxide electrolysers.

Molten Carbonates: Strategic Electrolytes

Physicochemical Properties

The interest of molten carbonates proceeds from their unique chemical and physical properties described by many authors (Yuh et al., 1995; Janz and Lorenz, 1961; Ward and Janz, 1965; Kojima et al., 2008; Lair et al., 2012). First of all, they cover a large domain of temperatures according to their nature and combinations, roughly from 450°C to more than 1,000°C. They are constituted either by single alkali carbonates, such as Li_2CO_3, Na_2CO_3, and K_2CO_3, with melting points of 730, 901, and 858°C, respectively, or more commonly by eutectic mixtures, Li_2CO_3–K_2CO_3 (62–38 mol% and 42.8–57.2 mol%), Li_2CO_3–Na_2CO_3 (52–48 mol%), Li_2CO_3–Na_2CO_3–K_2CO_3 (43.5–31.5–25 mol%), or Na_2CO_3–K_2CO_3 (58–42 mol%) with lower melting points, respectively, 488, 499, 501, 397, and 710°C (Janz and Lorenz, 1961; Sangster and Pelton, 1987). Their conductivities are another major feature depending on the nature of the alkali cation, knowing that smaller ions imply higher conductivity: for Li_2CO_3, Na_2CO_3, and K_2CO_3, the values are, respectively, 5.4, 2.8, and 2 S cm^{-1} at 900°C (Tanase et al., 1987).

The self-ionization constant of a molten carbonate is characterized by the equilibrium:

$$M_2CO_3(l) \Leftrightarrow M_2O(s) + CO_2(g) \qquad (1)$$

With (l), (s), and (g) as the liquid, solid, and gas phase, respectively.

This equilibrium can be simplified in terms of a simple ionic form, and considering a molten carbonate as a strong electrolyte, the equilibrium can be given in an ionic form:

$$CO_3^{2-} \Leftrightarrow O^{2-} + CO_2 \qquad (2)$$

The oxoacidic concept derives from this equilibrium, where O^{2-} is an electron pair donor which is associated with an oxoacid CO_2 and forms an oxobase CO_3^{2-} (Flood and Forland, 1947; Yamada and Uchida, 1994). The oxoacidity can be fixed by imposing a carbon dioxide partial pressure or by adding oxides in the melt. High partial pressures of CO_2 represent, for instance, highly oxoacidic media.

Present Applications

Fuel Cells

Molten Carbonate Fuel Cells

If molten carbonate media have gained their reputation, it is surely due to their use in MCFCs that have nowadays reached an advanced state of maturity and a first step toward commercial market entry (Cassir et al., 2012). In the last 3 years, more power has been produced by MCFCs, between 70 and 100 MW/year, than with any other fuel cells, including polymer electrolyte membrane fuel cells (PEMFCs), used for transport and, in particular, electric vehicles. The global cell reaction in an MCFC is the following:

$$H_2 + \frac{1}{2}O_2 + CO_2(\text{cathode}) \rightarrow H_2O + CO_2(\text{anode}) \qquad (3)$$

CO_2 formed at the anode is recycled and consumed at the cathode. The fuel introduced in the anode compartment is H_2, resulting from natural gas conversion usually by reforming. The anode reaction is:

$$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^- \qquad (4)$$

The oxidant introduced at the cathode side is constituted by a mixture of air and CO_2. The cathode reaction is:

$$\frac{1}{2}O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-} \qquad (5)$$

Hybrid Direct Carbon Fuel Cell

Direct oxidation of carbon in a fuel cell is an old dream of the industrial revolution where cities were polluted by CO_2 emission. Nevertheless, due to advances in electrochemical kinetics, it is only in the recent years that impressive progress has been realized in direct carbon fuel cells (DCFCs), which is an important issue the important resources in carbon spread all over the world. In a DCFC, a carbon fuel (pyrolysis of biofuels, farming products, etc.) is oxidized at the anode with an energy produced per unit volume four times higher than with methane (Zecevic et al., 2004). In such devices, molten carbonates may have two roles, either directly as the electrolyte or as a carrier of carbon fuel, acting also as an electrochemical mediator for the oxidation process, in the anode reservoir of a hybrid direct carbon fuel cell (HDFC), with a solid oxide electrolyte (Irvine et al., 2006; Pointon et al., 2006; Nabae et al., 2008).

Hybrid Fuel Cells (MCFC/SOFC)

Another kind of hybrid fuel cells presenting a growing interest is constituted by an electrolyte combining solid oxides with molten carbonates (Benamira et al., 2011, 2012). Oxide ions are mostly responsible for the conductivity in the oxide phase and carbonates in the carbonate phase. These composites form highly disordered interfacial regions between the oxide phase and the carbonate phase (Zhu et al., 2010).

Carbon, Capture and Storage, CCS in Molten Carbonates

The molten carbonate fuel cell system can be considered as a CO_2 separator and concentrator because CO_2 can be transferred from the cathode to the anode stream while producing electricity from fuels at the anode side. CO_2 can be extracted from the flue gas of a combined cycle power plant while generating electricity, avoiding loss in plant efficiency and consequent increase in primary energy consumption. It is clear that MCFC is an interesting device for CCS, but its effectiveness still has to be proven against the other present technologies for CO_2 emission mitigation (Spigarelli and Komar Kawatra, 2013). Theoretically, MCFCs can reach 90% CO_2 separation efficiency while producing electricity at high generation efficiency. In fact, some systems are under investigation and seem to have interesting features (Suguira et al., 2003; Wade et al., 2007). Small power plants of 10–20 Mton CO_2 per year are feasible and can find more immediate implementation. Nevertheless, although the potential market is enormous, the present capacity for producing MCFCs at the level of larger power plants of more than 100 Mton CO_2 per year is not yet possible.

High-Temperature CO_2 Electrolysis

General Features

It is well known that high-temperature electrolysis requires less electrical energy but higher thermal energy; however, as thermal energy is cheaper, electrolysis processes are favored at high temperature (Chery et al., 2015). This question is crucial in water steam electrolysis, which is thoroughly investigated in solid oxide electrolysers (Bradley et al. 2004). Recently, it has been shown that CO_2 electrolysis is also feasible in such devices. Bidrawn et al. have shown that an SOE system operating under CO–CO_2 atmosphere exhibited a total cell impedance of 0.36 $\Omega\ cm^2$, its efficiency is similar to that of water electrolysis (Bidrawn et al., 2008). The feasibility of such processes in ceramic electrolysers has been investigated in view of NASA's future exploration of Mars, aiming at converting CO_2 from the Mars atmosphere into life-supporting oxygen and oxidant/propellant fuel (Washman, 2003). The reduction of CO_2 into CO, at typically 800–900°C, can be associated to water electrolysis into H_2 in a so-called co-electrolysis process producing syngas: $H_2 + CO$. The durability of these types of electrolysis devices is still under study. In any case, it would be interesting to explore the same electrochemical approach at lower temperatures to avoid the drastic corrosion of the materials. Molten carbonates with lower operation temperatures, from 600 to 650°C, and allowing a high solubility of CO_2 within the molten electrolyte, are very interesting candidates to combine the benefits of high temperature, but not too high, with the reactivity of CO_2 in a liquid medium.

Electrolysis in Molten Carbonates

Before introducing molten carbonates, it should be outlined that electroreduction of CO_2 into C has been evidenced in molten chlorides, i.e., NaCl–KCl eutectic; the reduction mechanism has been studied by cyclic voltammetry at a gold electrode, showing a three-step reaction, the first one involving a radical intermediary species, CO_2^{2-}; the second formation of CO; and the third elemental carbon (Novoselova et al., 2007, 2008; Ijije et al., 2014). The production of C by electroreduction of CO_2 in LiCl–Li_2O or $CaCl_2$–CaO has also been depicted by other authors (Otake et al., 2013).

In the last decade, there is a growing and significant attention on electrolysis processes in molten carbonates with different goals, from water electrolytic transformation into hydrogen, which can also be extended to water and CO_2 coelectrolysis yielding syngas, to CO_2 electroreduction into C or CO in view of producing CH_4 as a second step. The main attractiveness of such melts is their capability of solubilizing carbon dioxide, from single alkali molten carbonates to a variety of carbonate eutectics (Claes et al., 1996, 1999; Chery et al., 2014). **Table 1** shows some solubility data extracted from the literature, showing a relatively high solubility. Nevertheless, it is clear that the values obtained depend on the technique used and on the experimental procedure. In view of the important applications of CO_2 in molten media (capture and valorization), a new set of reliable data is urgently required.

CO_2 properties in molten carbonates have been analyzed early in the literature. Peelen et al. have given some useful characteristics on the CO_2/CO redox system in Li–K carbonate eutectic, finding a simple charge transfer and evaluating the square root of the diffusion constant and the solubility $S\sqrt{D}$ (Peelen et al., 1997). Claes et al. have found by a manometric technique that CO_2 solubility was higher than predicted, attributing this fact to the production of $C_2O_4^{2-}$ by the reaction of CO_2 with the carbonate melt (Claes et al., 1996, 1999). Other authors have also detected the reduction of CO_2 directly or as a rate-limiting species in oxygen reduction (Yamada et al., 1995). Nevertheless,

TABLE 1 | Solubility of CO_2 in molten carbonates.

Determination technique	Molten carbonate eutectics	T (°C)	Solubility × 10^{-2} (mol l^{-1} atm^{-1})	Reference
Elution	Li–K	806	21.2	Kanai et al. (2013)
Manometry	Na–K	800	18.3	Claes et al. (1996)
Elution	Li–Na–K	701	20.2	Kanai et al. (2013)
Potentiometric titration	Li–Na–K	700	9.5	Claes et al. (1999)
Impedance spectroscopy	Li–Na–K	700	12	Broers (1969)

processing this molecule into valuable fuels by electrolysis is a more recent challenge. The literature pointing out the feasibility and interest of electroreduction of CO_2 in molten carbonates into elemental C or CO is recent and significant, but is lacking a systematic approach and rigorous data (Groult et al., 2003, 2006; Kaplan et al., 2002, 2010; Le Van et al. 2009; Yin et al., 2013; Chery et al., 2014, 2015; Ijije et al., 2014). Kaplan et al. and Groult et al. were the first in conceiving the conversion of CO_2 in molten carbonates into energy-storage materials (Groult et al., 2003; Kaplan et al., 2002). These authors obtained carbon nanopowders by electrochemical reduction of CO_2 in Li–Na–K carbonates at 450°C, a relatively low temperature, on nickel and glassy carbon. The amorphous carbon obtained had a high specific surface area (450–850 m^2 g^{-1}) and was tested for lithium-ion intercalation in view of its application in batteries (Groult et al., 2006). Ge et al. used an inert platinum anode and a tungsten cathode CO_2 into amorphous carbon and oxygen in molten LiCl–Li_2CO_3 salt at 700°C (Ge et al., 2015). Yin et al. also used the ternary carbonate eutectic at 500°C, with a Ni cathode and a SnO_2 anode, captured and converted carbon dioxide into a carbon material, exhibiting high BET surface areas of more than 400 m^2 g^{-1}; SnO_2 anode was found efficient for oxygen production (Yin et al., 2013). In similar conditions, but optimizing the electrolysis cell voltage and over a temperature range of 450–650°C, Tang et al. obtained carbon powder at 450°C with a low energy consumption of 35.6 kWh, a current efficiency of 87.86%, and under a cell voltage of 3.5 V (Tang et al., 2013). Over the production of carbon in molten salts, Ijije et al. developed a review including electrolysis in molten chlorides and molten carbonates (Ijije et al., 2014).

Another route was tested by Kaplan et al. focusing on the conversion of carbon dioxide into carbon monoxide by continuous electrolysis in Li_2CO_3 at 900°C using a titanium cathode and graphite anode; these authors obtained current densities superior to 100 mA cm^{-2} (Kaplan et al., 2010). Licht and his coworkers (Licht, 2009, 2011; Licht et al., 2011, 2013) explored the concept of a large-scale development of CO_2 electrolysers combining the production of CO or C with solar thermal energy. Evidence was given on the feasibility of producing valuable molecules, such as CO and C, with a solar efficiency reaching 50% using the so-called STEP (Solar Thermal Electrochemical Production) process. **Figure 3** shows the capability of driving three in series molten carbonate electrolysis (Li_2CO_3) with only the maximum power point photovoltage of one Spectrolab CPV (Licht et al., 2011). According to the electrolysis temperature, either C ($T < 900$°C) or CO ($T > 950$°C) is formed.

Apart from CO_2 electrochemical reduction, another important rising application of molten carbonates is water electrolysis yielding hydrogen and oxygen. Hu et al. have very recently given the proof of concept of such approach. CO_2 valorization can also be combined with water transformation into H_2 through coelectrolysis of CO_2 and CO in order to produce syngas (Hu et al., 2014). Another possible goal with a significant importance in the present energetic field would also be the production of CH_4 through methanation reactions ($CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$; $CO + 3H_2 \rightarrow CH_4 + H_2O$). High-temperature electrolysis of CO_2 is probably one of the very promising routes for valorizing this molecule into CO. This benefit could be enhanced by water electrolysis leading to the combination between CO and H_2. The possibility of producing graphite, used also as a fuel in the direct carbon fuel cell (DCFC), is then possible as well.

Although the proof of concept of high-temperature electrolysis processes in molten carbonates has been proven up to a certain level, chemistry and electrochemistry of molten carbonates is complex and requires a deeper understanding, scarcely existing in the present literature, in order to optimize the materials and operation conditions, from the nature and conductivity of the electrolyte to the electrocatalytic properties of the electrodes. Thus, it is compulsory to select the carbonate melt and the precise running conditions according to the required process. For example, succeeding in preparing CO or C, at lower potentials and temperatures (avoiding deterioration of the materials and the cell), is beneficial from an energetic point of view and requires a thorough comparison of the main molten carbonate eutectics. In this sense, we have focused our efforts in two recent articles on a thorough analysis of the electrochemical behavior of CO_2 in different molten carbonate eutectics, from a thermodynamic predictive approach and an experimental one (Chery et al., 2014, 2015). Some significant results concerning this approach will be given.

Figure 4 depicts a potential oxoacidity diagram of the ternary molten carbonate eutectic at two temperatures. The full comprehension of such diagrams with an explanation of all the selected conditions can be found in the literature (Chery et al., 2015). All the potentials are referred to Li_2O/O_2 system. The oxoacidity domain is limited on the oxoacidic side by a $P(CO_2)$ pressure, arbitrarily taken as 1 atm. (higher pressures can be also selected) and on the oxobasic side by the precipitation of the less soluble oxide among the three alkali cations of the melt: Li_2O. The oxidation limit of the diagram is always due to the oxidation of oxide ions into molecular oxygen in this specific case (or other species such as peroxide or superoxide ions under different melts and conditions). The direct reduction of CO_2 into elemental carbon may occur only at relatively oxobasic media, with $P(CO_2) < 10^{-3}$ atm, which is not realistic under

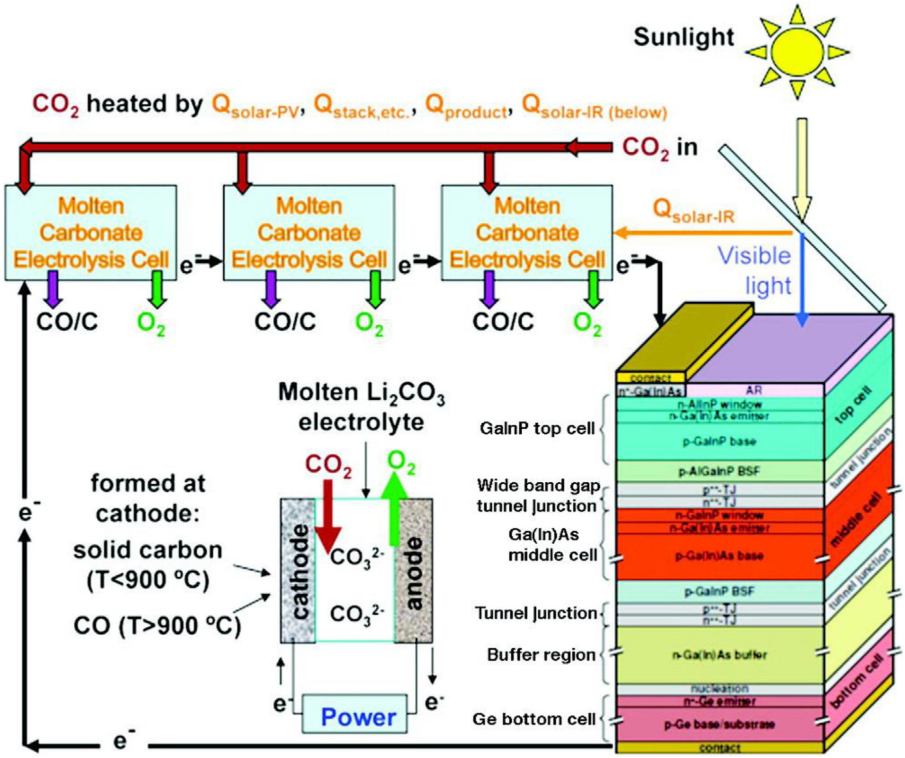

FIGURE 3 | STEP carbon capture in which three molten carbonate electrolysis in series are driven by a concentrator photovoltaic. The maximum power point photovoltage of one Spectrolab CPV is sufficient to drive three in series carbon dioxide splitting 950°C molten Li_2CO_3 electrolysis cells (Licht et al., 2011).

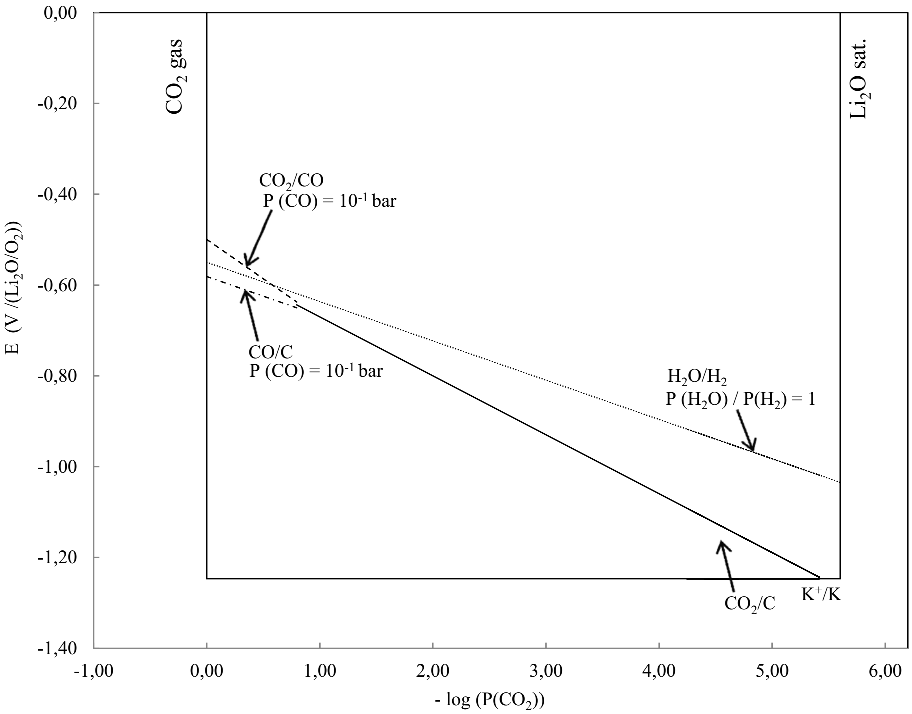

FIGURE 4 | Influence of the temperature on the Li–Na–K (43.5–31.5–25 mol%) eutectic at 600°C for a H_2O/H_2 ratio in pressure of 1 bar and a CO pressure of 10^{-1} bar.

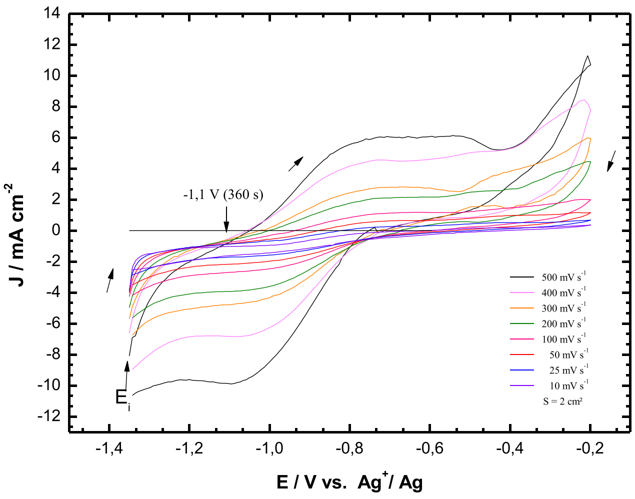

FIGURE 5 | Cyclic voltammograms of CO_2 reduction at a gold electrode in Li–Na–K at 600°C after a short pre-electrolysis of 360 s at −1.1 V vs. Ag^+/Ag under 100% CO_2. Surface area of 2 cm².

high partial pressures of CO_2 required for the desired application. At higher values of $P(CO_2)$, thermodynamically the most favorable phenomenon is the electroreduction of CO_2 into CO, this tendency being increased at $P(CO_2) = 1$ atm. The second reduction step, occurring at lower potentials, is the reduction of CO into C. This is only one example of how thermodynamic diagrams allow predicting the conditions in which the electrochemical processes might occur. Of course, useful in high-temperature electrochemistry (where reactions are favored thermodynamically), this vision does not take into account kinetics, which can be analyzed through cyclic voltammetry, electrochemical impedance spectroscopy. **Figure 5** shows cyclic voltammograms relative to CO_2 in the same ternary eutectic at a gold flag electrode at 600°C, under $P(CO_2) = 1$ atm. The three-electrode setup associating the gold working electrode with a gold auxiliary electrode and an Ag^+/Ag reference was fully described in the literature (Chery et al., 2014). A slight pre-electrolysis, carried out during 360 s at −1.1 V vs. Ag^+/Ag, was found to be important for conditioning the working gold electrode. The potential scan was initiated from the pre-electrolysis potential up to −0.2 V vs. Ag^+/Ag and then reverses until reaching −1.35 V vs. Ag^+/Ag. The reduction peak around −1.1 V vs. Ag^+/Ag depicts the global reduction of CO_2 into CO ($2CO_2 + 2\,e^- = CO + CO_3^{2-}$). This peak is at least a combination of two reactions: the first forming an unstable species which is up to now undetermined: CO_2^-: $2\,CO_2 + 2\,e^- = 2\,CO_2^-$ (Peelen et al., 1997), CO_2^{2-} (Novoselova et al., 2008), $C_2O_5^{2-}$ (Sangster and Pelton, 1987), or $C_2O_4^{2-}$? The second step is the reduction of the unstable species into CO, i.e., $2\,CO_2^- = CO + CO_3^{2-}$. The oxidation roughly shows a peak around −0.8 V vs. Ag^+/Ag, which is probably the reoxidation of CO, and another around −0.5 V vs. Ag^+/Ag, which might be attributed to the reoxidation of adsorbed CO. More insight is given in the literature (Chery et al., 2014), but no sharp conclusion can be given on the mechanistic process. According to the evolution of the CO_2 peak with the scan rate, the reduction potential is slightly moved toward negative potentials, showing a rapid to quasi-rapid system. It should be noted that the same system when using another electrolyte, for instance Li–K, appears slower (Chery et al., 2014). Thus, the properties of the system depend on the nature of the electrolyte and, of course, the electrocatalytic properties of the electrode. Analysis of the reduction peak also shows that it is diffusion-limited.

Conclusion

Among the different techniques used for the valorization of carbon dioxide, electrochemical reduction through electrolysis processes has an important position because it is a relatively low-cost technique that is beginning to be associated with renewable energies, such as solar. Moreover, the variety of electrolytic media plays in favor of this approach. High-temperature electrolysis, either with solid oxides or molten salts, appears as interesting from an electrocatalytic and energetic viewpoint. As the MCFCs electrolytes state of art, molten carbonates are able to capture and dissolve CO_2; thus, they are very favourable media for transforming this greenhouse effect gas into valuable chemicals and/or fuels. A rational use of molten carbonates requires a perfect control of the properties and reactivity on CO_2 in such melts, in order to optimize the electrolysis process, making it more efficient and less expensive. This field is very attractive from both scientific and technological sides. It is one of the significant challenges in the energetic and environmental field.

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References

Benamira, M., Ringuedé, A., Albin, V., Vannier, R.-N., Hildebrandt, L., Lagergren, C., et al. (2011). Gadolinia-doped ceria mixed with alkali carbonates for SOFC applications: I- a thermal, structural and morphological insight. *J. Power Sources* 196, 5546–5554. doi:10.1016/j.jpowsour.2011.02.004

Benamira, M., Ringuedé, A., Albin, V., Vannier, R.-N., Hildebrandt, L., Lagergren, C., et al. (2012). Gadolinia-doped ceria mixed with alkali carbonates for SOFC applications: II – an electrochemical insight. *Int. J. Hydrogen Energy* 37, 19371–19379. doi:10.1016/j.ijhydene.2011.10.062

Bidrawn, F., Kim, G., Gorre, G., Irvine, J. T. S., Vohs, J. M., and Gorte, R. J. (2008). Efficient reduction of CO_2 in a solid oxide electrolyser. *Electrochem. Solid-State Lett.* 11, B167–B170. doi:10.1149/1.2943664

Boot-Handford, M. E., Abanades, J. C., Anthon, E. J., Blunt, M. J., Brandani, S., Mac Dowell, N., et al. (2014). Carbon capture and storage update. *Energy Environ. Sci.* 7, 130. doi:10.1039/C3EE42350F

Bradley, J., Irvine, J. T. S., and Lakeman, J. B. (2004). Electricity producing fuel cell or battery device. *Brit. Patent Appl.* GB0426879.3, WO2006061639.

Broers, G. H. J. (1969). *Survey of Basic Research on Fuel Cells with Fused Carbonate Electrolytes*. Appeldoorn: Central Technisch Instituut TNO.

Cassir, M., McPhail, S., and Moreno, A. (2012). Strategies and new developments in the field of molten carbonates and high-temperature fuel cells in the carbon cycle. *Int. J. Hydrogen Energy* 37, 19345. doi:10.1016/j.ijhydene.2011.11.006

Chery, D., Albin, V., Lair, L., and Cassir, M. (2014). Thermodynamic and experimental approach of electrochemical reduction of CO_2 in molten carbonates. *Int. J. Hydrogen Energy* 39, 12330. doi:10.1016/j.ijhydene.2014.03.113

Chery, D., Lair, V., and Cassir, M. (2015). CO_2 electrochemical reduction into CO or C in molten carbonates: a thermodynamic point of view. *Electrochim. Acta* 160, 74–81. doi:10.1016/j.electacta.2015.01.216

Claes, P., Moyaux, D., and Peeter, D. (1999). Solubility and solvation of carbon dioxide in the molten $Li_2CO_3/Na_2CO_3/K_2CO_3$ (43.5:31.5:25.0 mol-%) eutectic mixture at 973 K I. Experimental part. *Eur. J. Inorg. Chem.* 4, 583–588. doi:10.1002/(SICI)1099-0682(199904)1999:4<583::AID-EJIC583>3.3.CO;2-P

Claes, P., Thirion, B., and Glibert, J. (1996). Solubility of CO_2 in the molten carbonate Na_2CO_3-K_2CO_3 (42 mol%) eutectic mixture at 800°C. *Electrochim. Acta* 41, 141. doi:10.1016/0013-4686(95)00278-M

Das, S., and Wan Daud, W. M. A. (2014). Photocatalytic CO_2 transformation into fuel: a review on advances in photocatalyst and photoreactor. *Renew. Sustain. Energ. Rev.* 39, 765–805. doi:10.1016/j.rser.2014.07.046

Flood, H., and Forland, T. (1947). The acidic and basic properties of oxides. *Acta Chem. Scand.* 1, 592–604. doi:10.3891/acta.chem.scand.01-0781

Gattrell, M., Gupta, N., and Co, A. (2007). Electrochemical reduction of CO_2 to hydrocarbons to store renewable electrical energy and upgrade biogas. *Energy Convers Manag.* 48, 1255–1265. doi:10.1016/j.enconman.2006.09.019

Ge, J., Hu, L., Wang, W., Jiao, H., and Jiao, S. (2015). Electrochemical conversion of CO_2 into negative electrode materials for Li-ion batteries. *ChemElectroChem.* 2, 224–230. doi:10.1002/celc.201402297

Groult, H., Kaplan, B., Komaba, S., Kumagai, N., Gupta, V., Nakajima, T., et al. (2003). Lithium insertion into carbonaceous anode materials prepared by electrolysis of molten Li-K-Na carbonates. *J. Electrochem. Soc.* 150, G67–G75. doi:10.1149/1.1531490

Groult, H., Kaplan, B., Lantelme, F., Komaba, S., Kumagai, N., Yashiro, H., et al. (2006). Preparation of carbon nanoparticles from electrolysis of molten carbonates and use as anode materials in lithium-ion batteries. *Solid State Ionics.* 177, 869–875. doi:10.1016/j.ssi.2006.01.051

Hori, Y. (2008). "Electrochemical CO2 reduction on metal electrode," in *Modern Aspects of Electrochemistry*, Vol. 42, eds C. G. Vayenas, R. E. White, and M. E. Gamboa-Aldeco (New York: Springer), 89.

Hu, B., Guild, C., and Suib, S. L. (2013). Thermal, electrochemical, and photochemical conversion of CO_2 to fuels and value-added products (review). *J. CO_2 Utilization.* 1, 18–27. doi:10.1016/j.jcou.2013.03.004

Hu, L., Rexed, I., Lindbergh, G., and Lagergren, C. (2014). Electrochemical performance of reversible molten carbonate fuel cells. *Int. J. Hydrogen Energy* 39, 12323–12329. doi:10.1016/j.ijhydene.2014.02.144

Ijije, H. V., Lawrence, R. C., and Chen, G. Z. (2014). Carbon electrodeposition in molten salts: electrode reactions and applications. *RSC Adv.* 4, 35808–35817. doi:10.1039/C4RA04629C

Irvine, J. T. S., Bradley, J. L., Lakeman, J. B. (2006). A fuel cell, WO2006061639-A2.

Janz, G. J., and Lorenz, M. R. (1961). Electrical conductance cell assembly for precise measurements with carbonates, oxides, and fluorides up to 1000°C. *Rev. Sci. Instrum.* 32, 130–133. doi:10.1063/1.17172

Jones, J. P., Surya Prakash, G. K., and Olah, G. A. (2014). Electrochemical CO_2 reduction: recent advances and current trends. *Irs. J. Chem.* 54, 1451–1466. doi:10.1002/ijch.201400081

Kanai, Y., Fukunaga, K.-I., Terasaka, K., and Fujioka, S. (2013). Mass transfer in molten salt and suspended molten salt in bubble column. *Cheml. Engineering Sc.* 100, 153–159. doi:10.1016/j.ces.2012.11.029

Kaplan, B., Groult, H., Barhoun, A., Lantelme, F., Nakajim, T., Gupta, V., et al. (2002). Synthesis ans structural characterization of carbon power by electrolytic reduction of molten $Li_2CO_3Na_2CO_3K_2CO_3$. *J. Electrochem. Soc.* 149, D72–D78. doi:10.1149/1.146464884

Kaplan, V., Wachtel, E., Gartsman, K., Feldman, Y., and Lubomirsky, I. (2010). Conversion of CO_2 to CO by electrolysis of molten lithium carbonate. *J. Electrochem. Soc.* 157, B552–B556. doi:10.1149/1.3308596

Karthikeyan, C., Rajeswari, S., Maruthamuthu, S., Subramanian, K., and Rajagopal, G. (2014). Biogenic ammonia for CO_2 capturing and electrochemical conversion into bicarbonate and formate. *J. CO_2 Utilization.* 6, 53–61. doi:10.1016/j.jcou.2014.03.004

Kojima, T., Miyazaki, Y., Nomura, K., and Tanimoto Density, K. (2008). Surface tension, and electrical conductivity of ternary molten carbonate system Li_2CO_3-Na_2CO_3-K_2CO_3 and methods for their estimation. *J. Electrochem. Soc.* 155, F150–F156. doi:10.1149/1.2917212

Lair, V., Albin, V., Ringuedé, A., and Cassir, M. (2012). Theoretical predictions vs. experimental measurements of the electrical conductivity of molten Li_2CO_3-K_2CO_3 modified by additives. *Int. J. Hydrogen Energy* 37, 19357–19364. doi:10.1016/j.ijhydene.2011.09.153

Le Van, K., Groult, H., Lantelme, F., Dubois, M., Avignant, D., Tressaud, A., et al. (2009). Electrochemical formation of carbon nano-powders with various porosities in molten alkali carbonates. *Electrochim. Acta* 54, 4566–4573. doi:10.1016/j.electacta.2009.03.049

Licht, S. (2009). STEP (solar thermal electrochemical photo) generation of energetic molecules: a solar chemical process to end anthropogenic global warming. *J. Phys. Chem. C* 113, 16283–16292. doi:10.1021/jp9044644

Licht, S. (2011). Efficient solar-driven synthesis, carbon capture, and desalinization, STEP: solar thermal electrochemical production of fuels, metals, bleach. *Adv. Mater.* 23, 5592–5612. doi:10.1002/adma.201103198

Licht, S., Cui, B., and Wang, B. (2013). STEP carbon capture – the barium advantage. *J. CO_2 Utilization.* 2, 58–63. doi:10.1016/j.jcou.2013.03.006

Licht, S., Wang, B., and Wu, H. (2011). STEP—a solar chemical process to end anthropogenic global warming. II: experimental results. *J. Phys. Chem. C* 115, 11803–11821. doi:10.1021/jp111781a

Lim, R. J., Xie, M., Sk, M. A., Lee, J.-M., Fisher, A., Wang, X., et al. (2014). A review on the electrochemical reduction of CO_2 in fuel cells, metal electrodes and molecular catalysts. *Catal. Today.* 233, 169–180. doi:10.1016/j.cattod.2013.11.037

Lote, D. A. (2014). Literature Survey on Electrochemical Reduction of CO_2. *Int J. Electronic Electrical Eng.* 7, 341–346. International Research Publication House.

Mahammadunnisa, S., Reddy, E. L., Ray, D., Subrahmanyam, C., and Whitehead, J. C. (2013). CO_2 reduction to syngas and carbon nanofibers by plasma assisted in situ decomposition of water. *Int. J. Green Gas Controm.* 16, 361–363. doi:10.1016/j.ijggc.2013.04.008

Nabae, Y., Pointon, K. D., and Irvine, J. T. S. (2008). Electrochemical oxidation of solid carbon in hybrid DCFC with solid oxide and molten carbonate binary electrolyte. *Energy Environ. Sci.* 1, 148–155. doi:10.1039/B804785E

Novoselova, I. A., Oliynyk, N. F., and Volkov, S. V. (2007). "Electrolytic production of carbon nano-tubes in chloride-oxide melts under carbon dioxide pressure," in: *Hydrogen Materials Science and Chemistry of Carbon Nanomaterials SE*, eds T. N. Veziroglu, S. Zaginaichenko, D. Schur, B. Baranowski, A. Shpak, V. Skorokhod, et al. (Springer), 459–465. [Internet]. doi:10.1007/978-1-4020-5514-0_57

Novoselova, I. A., Oliynyk, N. F., Voronina, A. B., and Volkov, S. V. (2008). Electrolytic generation of nano-scale carbon phases with framework structures in molten salts on metal cathodes. *Z. Naturforsch A Phys. Sci.* 63, 467–474. doi:10.1515/zna-2008-7-814

Oloman, C., and Li, H. (2008). Electrochemical processing of carbon dioxide. *ChemSusChem* 1, 385. doi:10.1002/cssc.200800015

Otake, K., Kinoshita, H., Kikuchi, T., and Suzuki, R. O. (2013). CO_2 gas decomposition to carbon by electro-reduction in molten salts. *Electrochim. Acta* 100, 293–299. doi:10.1016/j.electacta.2013.02.076

Ozkan, A., Dufour, T., Arnoult, G., De Keyzer, P., Bogaerts, A., and Reniers, F. (2015). CO_2-CH_4 conversion and syngas formation at atmospheric pressure using a multi-electrode dielectric barrier discharge. *J. CO_2 Utilization.* 9, 74–81. doi:10.1016/j.jcou.2015.01.002

Peelen, W. H., Hemmes, K., and de Wit, J. H. (1997). CO_2 reduction in molten 62/38 mole% Li/K carbonate mixture. *Electrochim. Acta* 43, 763–769. doi:10.1016/S0013-4686(97)00141-2

Pointon, K. D., Lakerman, B., Irvine, J. T. S., Bradley, J., and Jain, S. (2006). The development of a carbon air semi fuel cell. *J. Power Sources* 162, 750–756. doi:10.1016/j.jpowsour.2005.07.023

Rees, N. V., and Compton, R. G. (2011). Electrochemical CO_2 sequestration in ionic liquids; a perspective (minireview). *Energy Environ. Sci.* 4, 403–408. doi:10.1039/C0EE00580K

Sangster, J. M., and Pelton, A. D. (1987). "Critical Coupled Evaluation of Phase Diagrams and Thermodynamic Properties of Binary and Ternary Alkali Salts Systems," in *Special Report to the Phase Equilibria Program* (Westerville, OH: American Ceramic Society), 4–231.

Spigarelli, P. B., and Komar Kawatra, S. (2013). Opportunities and challenges in carbon dioxide capture (review). *J. CO_2 Utilization.* 1, 69–87. doi:10.1016/j.jcou.2013.03.002

Suguira, K., Takei, K., Tanimoto, K., and Miyazaki, Y. (2003). The carbon dioxide concentrator by using MCFC. *J. Power Sources* 118, 218–227. doi:10.1016/S0378-7753(03)00084-3

Tanase, S., Miyazaki, Y., Yanagida, M., Tanimoto, K., and Kodama, T. (1987). "Numerical formulation of electrical conductance data of molten alkali carbonates", in *Progress Batteries & Solar Cells*, 6th Edn, eds A. Kozawa, H. Shimotake, and E. Voss (Cleveland, OH: JEC Press), 195.

Tang, D., Yin, H., Mao, X., Xiao, W., and Wang D. H. (2013). Effects of applied voltage and temperature on the electrochemical production of carbon powders from CO_2 in molten salt with an inert anode. Electrochim Acta. 114, 567–73. doi:10.1016/j.electacta.2013.10.109

Thybaud, N., and Lebain, D. (2010). *Panorama des voies de valorisation du CO_2. Report of the French Agency*. ALCIMED, ADEME "Agence de l'Environnement et de la Maîtrise de l'Energie". http://www.ademe.fr/sites/default/files/assets/documents/72052_rapport_ademe_version_finale.pdf

Wade, J. L., Lackner, K. S., and West, A. C. (2007). Transport model for a high temperature, mixed conducting CO_2 separation membrane. *Solid State Ionics.* 178, 1530–1540. doi:10.1016/j.ssi.2007.09.007

Wang, C.-C., Zhang, Y.-Q., Li, J., and Wang, P. (2015). Photocatalytic CO_2 reduction in metal–organic frameworks: a mini review. *J. Mol. Struct.* 1083, 127–136. doi:10.1016/j.molstruc.2014.11.036

Ward, A. T., and Janz, G. J. (1965). Molten carbonate electrolytes: electrical conductance, density and surface tension of binary and ternary mixtures. *Electrochim. Acta* 10, 849–857. doi:10.1016/0013-4686(65)80048-2

Washman, E. D. (2003). *Electrolytic Reduction of CO_2 to O_2 and CO for ISRU with High Conductivity Solid Oxide Electrolytes.* NASA Report Contract No. NAG 10-303.

White, J. L., Herb, T. J., Kaczur, J. J., Majsztrik, W. P., and Bocarsly, A. B. (2014). Photons to formate: efficient electrochemical solar energy conversion via reduction of carbon dioxide. *J. CO2 Utilization.* 7, 1–5. doi:10.1016/j.jcou.2014.05.002

Yamada, K., Nishina, T., and Uchida, I. (1995). Kinetic study of oxygen reduction in molten Li_2CO_3-Na_2CO_3 under pressurized conditions. *Electrochim. Acta* 12, 1927–1932. doi:10.1016/0013-4686(94)00328-X

Yamada, K., and Uchida, I. (1994). In-situ formation process of $LiCoO_2$ in the molten lithium-potassium carbonate eutectic at 923 K. *Chem. Lett.* 2, 299–302. doi:10.1246/cl.1994.299

Yin, H., Mao, X., Tang, D., Xiao, W., Xing, L., Zhu, H., et al. (2013). Capture and electrochemical conversion of CO_2 to value-added carbon and oxygen by molten salt electrolysis. *Energy Environ. Sci.* 6, 1538–1545. doi:10.1039/C3EE24132G

Yuh, C., Johnsen, R., Farooque, M., and Maru, H. (1995). Status of carbonate fuel cell materials. *J. Power Sources* 56, 1–12. doi:10.1016/0378-7753(95)80001-W

Zecevic, S., Patton, E. M., and Parhami, P. (2004). Carbone air fuel without a reforming process. *Carbon N. Y.* 42, 1983–1993. doi:10.1016/j.carbon.2004.03.036

Zhu, L., Wang, Y., Fang, Z., Sun, Y., and Huang Q. (2010). An effective heat dissipation method for densely packed solar cells under high concentrations. *Solar Energy Mater Solar Cells*. 94, 133–140. doi:10.1016/j.solmat.2009.08.014

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