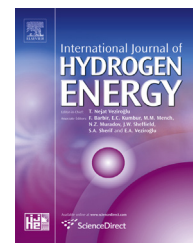


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Review Article

Molten carbonates for advanced and sustainable energy applications: Part II. Review of recent literature

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ABSTRACT

Unprecedented interest for clean and sustainable energy innovation has recently stimulated a return of attention on molten alkali carbonate salts not only for traditional use as electrolyte and high temperature reaction media but also as innovative energetic material for advanced applications in hybrid fuel cell systems and high-temperature CO₂ gas separation processes. The main focus of this literature review is on examining novel and emerging molten carbonate applications in energy sectors beyond the well-assessed and mature domain of the Molten Carbonate Fuel Cells. In general, a number of advanced processes and highly functional materials are currently under investigation involving molten carbonates in a key role, suggesting a high potential of these salt systems for the future development of sustainable energy technologies. Current research activities can be grouped into three main energy research areas related to generation/conversion/storage of energy, materials and manufacturing processes, hot gas processing and gasification technologies. As already analyzed in Part I of this work, notable features of molten carbonates include their chemical stability, safety and optimal performance under a wide range of moderate (500–600 °C) and moderate-to-high temperature (600–800 °C) conditions. Thanks to these peculiar aspects, molten carbonate processes can be ideally integrated with solar energy sources for maximum sustainable level of use and with broad development prospects in the storage of solar energy and solar-to-chemical conversion systems. This view is confirmed, for example, by a series of extensive studies that has recently investigated novel solar-to-chemical energy conversion strategies based on a molten carbonate electrolysis process for solar production of fuels and other important chemical products, including iron and cement. In the last part of this work, several directions and opportunities for future research and studies on molten carbonates are suggested.

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Introduction

Application of Molten Alkali Carbonate (MAC) salts in various key sectors of sustainable energy development is a research area of growing interest, although still relatively overlooked. In the last years, interest for MAC salt research is slowly expanding beyond the traditional area of Molten Carbonate Fuel Cells (MCFCs) [1] to embrace many important and advanced areas of modern energy research, including the broad and complex area of sustainable energy as witnessed by a stream of journal articles and book chapters (see, for instance [2–4]) that have been published on the theme over the past few years. The recent launch of a new series of biennial international workshops (IWMC, International Workshop of Molten Carbonates and Related Topics) is a further sign on the growing attention for molten carbonates in the emerging arena of sustainable and advanced energetic technologies.

Thus, by way of example, the unique ability of MAC salts to naturally absorb CO₂ makes them very interesting systems for capture and chemical conversion of CO₂ via molten carbonate electrolysis as suggested by Cassir and co-workers [5]. As a further example, the possibility of using MAC salts as efficient electrolytes for converting, storing and harvesting the renewable energy produced by high temperature solar power sources such as Concentrating Solar Power (CSP) plants is another field of research with a tremendous potential growth. For example, according to a series of recent studies conducted at The George Washington University [6–10], solar-integrated molten carbonate electrolysis processes seem to have a much future promise for a really sustainable production of fuels, chemicals and commodity products, including strategic commodities like iron and cement.

Thus, as a contribution to move beyond the traditional view that molten salts belong to a general class of complex, reactive or corrosive chemical systems, Part I of this study [11] has in detail analyzed the most relevant MAC salt properties, notably from a sustainability point of view and shown to be largely superior with respect to other common molten salts in providing an efficient, benign and stable high temperature liquid chemical system. Our analysis supports the view of molten carbonate salts as a good choice for implementing a potentially sustainable molten salt technology with high application versatility and functionality under a wide range of moderate-to-high temperatures. MAC salts are being primarily investigated as electrolyte, reaction and synthesis media, although other emerging application areas include their uses as solar thermal storage material or as highly functional material for advanced composite high-ionic conductors in gas separation membranes or hybrid fuel cell systems. The current body of literature dealing with novel energy uses of molten carbonates is not vast and it is also dispersed on many different energy-related areas of current or potential future interest. Review studies covering all the current research activities are not available in literature. Therefore, it is purpose of Part II of this study to fill this gap offering a broad coverage across all the ongoing research activities, in which MAC salts are involved, with exclusion of MCFC research, which is nowadays a well mature field of activity.

Molten alkali carbonates for sustainable energy applications

Fig. 1 presents a summary of recent research activities involving sustainable use of molten carbonates that, for sake

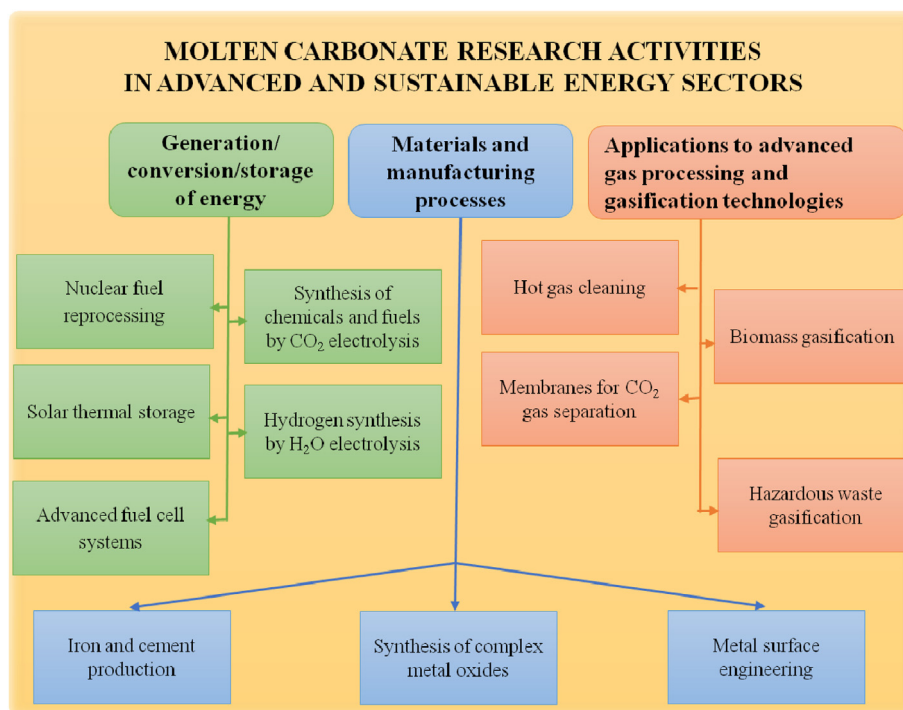


Fig. 1 – Overview of current studies and research activities on molten alkali carbonates in the energetic field.

of simplicity, has been split into three broad application categories. Each main research area will be analyzed hereafter in its own separate chapter.

Generation, conversion and storage of energy

Nuclear fuel reprocessing

A number of publications has recently concerned with nuclear applications of MAC salts. In general, nuclear waste treatment by molten salts has become a research priority due to recent introduction of sustainable concepts even in the nuclear power industry [12]. In this context, the reconversion of spent nuclear fuels by molten salt pyrochemical methods is actively studied to replace the current hydrothermal technology with the goal of minimizing waste production and reducing fuel cycle costs [13]. Decisive advantages of molten salts are related to their good solvent properties for nuclear fuel dissolution, sufficiently large electrochemical window and resistance to radiolysis degradation. Electrolytic separation of actinides from fission products (e.g., lanthanides) in molten alkali chloride mixtures represents the core process of most current pyrochemical recycling methods [14,15]. The possibility of using MAC salts to realize a simpler and safer pyrochemical scheme without involving electrolytic separation steps has been extensively studied by Griffiths and his group for several years (see Fig. 2) [16–19]. According to their studies, uranium fuel can be easily separated from lanthanides by selective precipitation taking advantage that actinides are converted to insoluble salts in binary or ternary eutectic MAC salts by simple air bubbling, whereas lanthanides do not precipitate under these conditions. Lanthanides can be later removed by adding phosphate salts since these salts, except alkali phosphates, are insoluble in most molten salts,

including carbonates. Numerous aspects of the molten carbonate reprocessing method have been studied and published by the authors during a period of more than 10 years from 1997 to 2008. However, it seems that more decisive improvements will be needed for a practical use of their proposed method in a such extremely complex field as the nuclear molten salt reprocessing one. A number of critical issues can be identified. Optimizing phosphate precipitation processes requires deep knowledge of the reactions involved. For practical reasons, most precipitation studies were performed in chloride melts so that detailed information on the phosphate precipitation characteristics is available only for chloride melts, but not for carbonates, including the effect of minimum excess of phosphate for complete precipitation, settling time, nature and form of the precipitates. Secondly, decisive experiments with transuranium elements were not performed in carbonate melts. Thirdly, the lanthanide phosphates are separated by precipitation in a similar way to uranates. However, up to a 3% concentration of lanthanides is reported to remain in solution after the precipitation instead of ppm levels of uranates [17], which probably requires more frequent salt cleaning and handling of large quantities of the carbonate melt compared to other concurrent pyrochemical methods. Furthermore, complete removal of Cs cation, which is a severe nuclear fuel contaminant, could be obtained in chloride melts, but not in carbonates [17].

Apart from these practical considerations, an interesting chemical effect has been discovered and reported during these studies, which may be relevant for other potential uses of MAC salts and possibly for introducing new ones. It is related to the fact that the oxidizing capability of carbonate melts can be dramatically increased by small additions of nitrate salt: the addition of a few percent of KNO_3 to air-

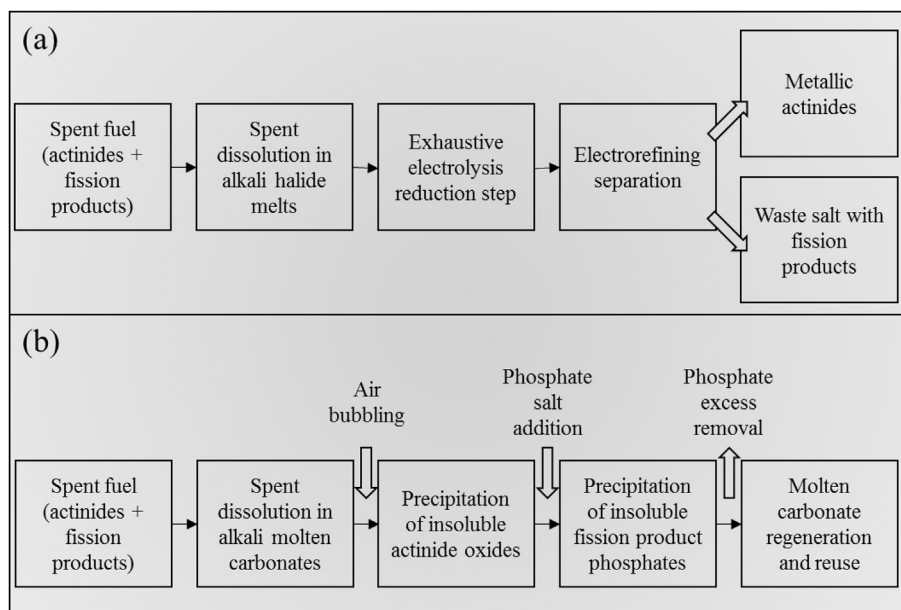


Fig. 2 – Pyrochemical separation methods of lanthanide fission products from actinides: (a) conventional separation method based on electrolysis in molten halide media; (b) alternative separation method based on precipitation partitioning in molten carbonates.

sparged MAC salts was in fact sufficient to achieve a rapid and complete conversion of uranium oxide fuel into uranate salt [19]. As already seen in Part I of this study, Griffiths has ascribed this effect to the fact that adding nitrate maximizes the concentration of superoxide and peroxide anions that can stably exist in MAC salts, thus explaining the observed exceptional oxidizing capability of the mixed nitrate-carbonate melts towards uranium oxide.

Advanced fuel cell systems

The “electricity directly from coal” is a very old and fascinating concept dating back to the last decade of the 19th century [20]. Although direct conversion to electricity could place the basis for an effective clean coal power technology, the research has been largely frustrated by a lack of developmental progress for many years due to issues such as poor coal electrochemical reactivity, ash accumulation, sulfur contamination and materials corrosion [21,22]. However, the relatively rapid improvement in molten carbonate and solid oxide fuel cell technologies over the past two decades has contributed to solve some technical challenges related to design and operational aspects of early types of solid-fed fuel cells [23] and stimulated a significant return of research interest on this topic as highlighted by numerous journal articles ([21,24–45]), book chapters ([2,3,46,47]) and review studies ([29,48–53]) that have been published over the past few years. Recent works carried out by Cooper, Selman and co-workers on carbon particulate reactivity in molten carbonates have been a further stimulus to the new research interest [41,42,54].

Based on the electrolyte type, modern-day versions of carbon-air fuel cells (aka Direct Carbon Fuel Cells, DCFCs) can be classified into four main fuel cell types [50], i.e. aqueous hydroxide, molten hydroxide, molten carbonate and solid oxide fuel cells. More recently, a new DCFC concept, the

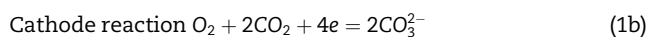
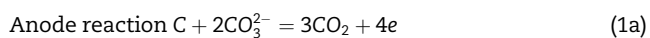
Hybrid-DCFC has been introduced in 2007 by Irvine and his group of the St Andrews University. The Hybrid-DCFC consists essentially of a solid oxide electrolyte fuel cell, which include a fine dispersion of carbon anode particles into a molten electrolyte above its percolation limit to ensure both higher carbon reactivity and electrical connectivity [55,56]. Classification is further complicated by the fact that carbon particles can be also dispersed in conductive fluid metallic media in the anode chamber, which can be considered another variant of solid oxide DCFCs [50].

In spite of encouraging results obtained over the past years, it is to be noted that the applicability of DCFC systems remains severely limited by some unresolved issues with respect to both fundamental and technological aspects. Although a detailed analysis of all issues affecting current DCFC systems is well outside the purpose of this work, the problem of sluggish carbon electro-oxidation reactivity, which is generally considered one of the main impediments for practical DCFC development, will be discussed here in some detail.

To enhance carbon particle contact and its electrochemical reactivity the most efficient way of using carbon fuels is to prepare slurries by mixing coal or carbon particles of various origin (biomass, petcoke, etc.) with a molten alkali electrolyte of hydroxide or carbonate salt ([23,44,53]). Several efforts have been made for further enhancing carbon reactivity and wettability in molten salts, including surface treatments of carbon fuels [57], pyrolysis pre-treatments [35], use of catalysts ([31,33,43]) and preparation of highly active carbons [58].

Although molten hydroxides are characterized by higher ion conductivity, better electrochemical activity to carbon and can operate at lower temperatures [44,59], MAC electrolytes are more attractive in DCFC systems due to their long-term chemical stability and invariant composition in presence of CO₂, which is the main by-product of carbon electro-oxidation reactions [45].

Anode and cathode reactions in a typical molten carbonate DCFC system can be expressed as follows:



The actual anode reaction may become more complicated at temperatures above than 750 °C, where carbon corrosion is thermodynamically possible [53], according to the well-known Boudouard equilibrium:



Recent experimental studies have clearly demonstrated that optimal conversion efficiency combined with a sufficiently high carbon reactivity is found in the range 700–750 °C, where the effects of carbon corrosion are still tolerable [34]. Since carbonate ions readily dissociate at the DCFC temperatures, oxide ions are presumed to play a key role in the carbon electro-oxidation mechanism. A simplified reaction mechanism involving oxide ion has been recently proposed by Cooper et al. [21], which consists of five steps including adsorption, electrochemical discharge and desorption as reported in Fig. 3.

The adsorption of the second oxide ion (step (3)) is believed to be the rate determining step (rds), based on the fact that this step involves a reaction between a negatively charged oxide ion and an electronegative CO_{ads} site that should be hindered by strong charge repulsion effects. Minor variations of this mechanism have been later proposed by Li and co-workers,

which includes the possibility that rds may shift from the adsorption step (3) to electrochemical discharge steps (step 2 or 4) under different operating conditions [24]. Due to the complexity of oxide chemistry in molten carbonates, some authors have also observed that the overall reaction rate is probably governed by concentration of all the oxygen-containing anions present in the melt, with a possible role for carbonate anions [56] and oxygen anionic species [60,61] in addition to the oxide ions. By analogy to what happens in the case of the more basic molten hydroxide electrolytes, in which oxygen anionic species are well known to play a key role, it has been recently suggested that carbon anodic oxidation in molten carbonates might follow a similar mechanism with peroxide, superoxide and percarbonate species, playing a decisive, yet largely overlooked, role [53,59,61]. However, it can be noted that the effect of oxygen anionic species on carbon reactivity in MAC salts has not yet received the due attention in literature.

The progress in understanding of carbon reaction mechanisms has also led most recent research to focus on lowering the DCFC operation temperature below 700 °C, which could be a key towards the design of more efficient and sustainable molten carbonate DCFC processes [32,62,63]. With temperature operations below 700 °C, in fact, efficiency losses due to carbon corrosion could be kept at a minimum, while maintaining the advantage that MAC salts are low in corrosivity and toxicity with respect to the hydroxide electrolyte counterpart. As a remarkable example, a novel type of hybrid-DCFC with an improved anode structure and with a low internal cell resistance at 650 °C has been recently developed. This hybrid cell achieved a peak power density of 113 mWcm⁻² at 650 °C and using an activated carbon fuel. In comparison, a more conventionally structured hybrid cell achieved only 3.0 mWcm⁻² in the same conditions [27].

In definitive, DCFC is still an early stage of development with a number of complex challenges that are more difficult to solve than in other types of fuel cells [48]. Besides reaction kinetics, major issues waiting for practical solutions include materials corrosion and degradation, anode chamber structure, carbon fuel processing, handling of carbon fuels for continuous operation [38], stack fabrication and technology up-scaling.

A second important area of research is directed to the study of alkali carbonates in both solid and liquid state for the development of composite electrolyte materials to be used in advanced concepts of fuel cells and high temperature CO₂ separation membranes [64–69]. Thanks largely to a decade and more of research efforts by Zhou and co-workers (see Ref. [70] and references therein), composite electrolytes formed by mixing small amounts of alkali carbonate salts with a solid oxide-ion conducting phase is nowadays one of the fastest expanding area of SOFC-related fuel cell research. In particular, composite electrolytes using doped ceria oxides (usually, gadolinia- or samaria-doped ceria) have been demonstrated to possess high ion conductivity and multi-ion transport (H^+ , O^{2-} and CO_3^{2-}) properties [71,72] providing an excellent fuel cell performance of 300–1100 mW/cm² in the 300–600 °C range [73–75], thus opening up new perspectives for the development of low temperature hybrid SOFC technologies. With respect to conventional electrolytes based on single-phase

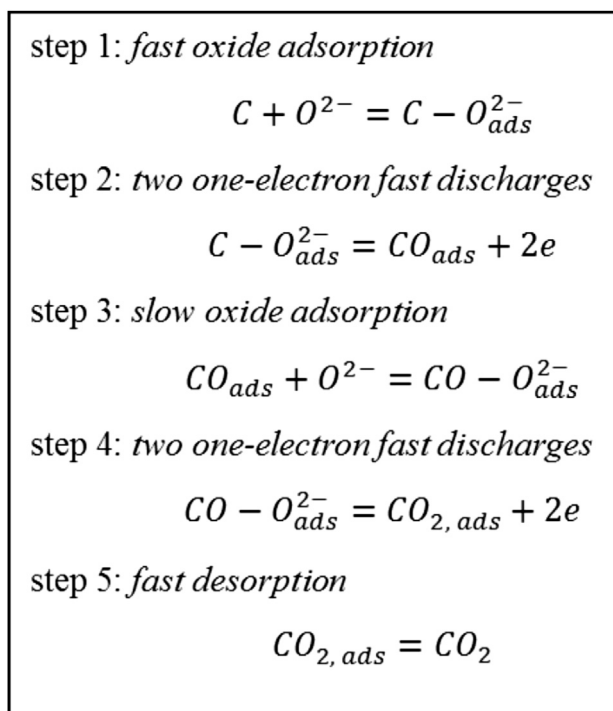


Fig. 3 – Multi-step reaction scheme for the carbon electro-oxidation mechanism in molten carbonate salts as proposed by Cooper [21].

doped ceria oxides, the ionic conductivity of the doped ceria phase appears to increase dramatically through the addition of the second phase of carbonate salt up to $>10^{-1} \text{ S cm}^{-1}$ at 600°C , which has been regarded as indication that a superionic phase transition has possibly occurred due to coupling effects by the two phases [76–79]. Although there are questions about the exact nature of the coupling mechanism [80], ceria-carbonate composites seem to exhibit typical liquid-like superionic conductivity characteristics, even at temperatures below the carbonate salt bulk melting points. As a general rule, this behavior is not in contrast with that commonly observed in many composite materials, in which a microscopic liquid-like structure at phase interface is supposed to promote high interfacial conduction between one moderate ion conducting phase and one insulating phase or one different conductor phase resulting in the so-called “composite effect enhancement” [81–83].

Work published by different research groups has also evidenced that superionic conduction of ceria-carbonate composites is largely affected by the composition and structure of the carbonate phase [84–86]. The role of various alkali cations (usually Li, Na and K) has been analyzed in single or binary cation mixtures and in various carbonate/ceria phase ratio compositions. Thus, for instance, the effect of cation salt composition on electrical properties and fuel cell performance of composite ceria/20 wt. binary carbonate electrolytes with different melting points has been investigated in the $500\text{--}600^\circ\text{C}$ range [84]. The authors report that fuel cells with ceria/(Li-Na) $_2\text{CO}_3$ composite electrolytes shows only slight performance improvement in comparison to ceria/(Li-K) $_2\text{CO}_3$, but the improvement was much more significant if compared to ceria/(Na-K) $_2\text{CO}_3$ electrolytes. These results were consistent with the electrolyte conductivity behavior measured in separate experiments. Sharp conductivity jumps in the same temperature region, i.e. $500\text{--}600^\circ\text{C}$, had been observed only for composites containing the low-temperature melting (Li-Na) $_2\text{CO}_3$ and (Li-K) $_2\text{CO}_3$ carbonate eutectics, but not with the high-temperature melting (Na-K) $_2\text{CO}_3$ carbonate eutectic. Although these results could indicate that superionic conduction should be related to the melting temperature of bulk carbonate, however, very recent studies suggest that other liquid-like mechanisms should come into play at a nanoscale structure dimension in the pre-melting region of the carbonate salt [70,87–90]. Thus, studies on nano-structured core-shell ceria-carbonate composites containing single Na_2CO_3 or binary (Li-Na) $_2\text{CO}_3$ eutectic mixtures show that ionic conductivity increases rapidly in the $300\text{--}400^\circ\text{C}$ range, which is in correspondence with a sharp increase in structural disorder of the carbonate phase [70,89,90]. As a result, a superionic phase is supposed to exist at the phase interface between the ceria matrix and the thin regions of liquid-like/disordered carbonate layers enclosing the ceria nanoparticle surfaces. Space charge regions with much higher defect concentrations might easily form thanks to the nanoscale dimension of the interface enabling fast ionic conduction even at temperatures significantly below melting of bulk carbonate. By way of example, a 0.05 S cm^{-1} conductivity has been observed at 450°C for a nanocomposite electrolyte consisting of Mg^{2+} and Sr^{2+} co-doped ceria and (Li-Na) $_2\text{CO}_3$ eutectic mixtures [89], which is five times higher than the value 0.01 S cm^{-1} at 481°C ,

reported for a similar ceria-(Li-Na) $_2\text{CO}_3$ electrolyte but with the difference of a microcomposite structure [91]. These core-shell ceria nanostructures are also reported to exhibit impressive stability and can apparently tolerate high temperature treatments without losing the nanosize dimension, which seems to be due to the stabilizing effect of carbonate shell structure [70]. Although ceria-carbonate nanocomposite undoubtedly represent an intriguing and exciting research topic, more studies on long-term stability are required to support their application in practical fuel cell devices. Since ceria-carbonate composites exhibit tunable conductivity properties in terms of proton, oxide or carbonate ion conductivity, depending on the specific gas conditions, they are potential candidates also for other advanced energy applications including as hydrogen sensor, electrochemical hydrogen and ammonia synthesis [87,92–95] and CO_2 separation processes (see Fig. 4). Due to its importance for various sustainable industrial applications, the use of ceria-carbonate composites for CO_2 gas separation processes will be discussed separately in a next section.

Solar thermal storage

Thanks to a wider thermal stability than nitrates, some investigations have recently explored the possibility of using alkali carbonate mixtures for high temperature thermal storage in Concentrating Solar Power (CSP) plants [96–99]. Extending thermal storage above 700°C is an important goal of current solar research, since it could allow the practical use of Brayton or Rankine power cycles to increase the thermal-to-electricity conversion efficiency. In-depth information about thermal stability of standard ternary carbonate eutectic (i.e., $32.1\text{Li}_2\text{CO}_3\text{--}33.4\text{Na}_2\text{CO}_3\text{--}34.5\text{K}_2\text{CO}_3$ wt%) has been recently provided through thermo-analytical studies conducted up to 1000°C in gas atmospheres of CO_2 , air and argon [97]. The results clearly indicate that thermal stability strongly depends on the gas atmosphere. Thermal decomposition starts at ca.

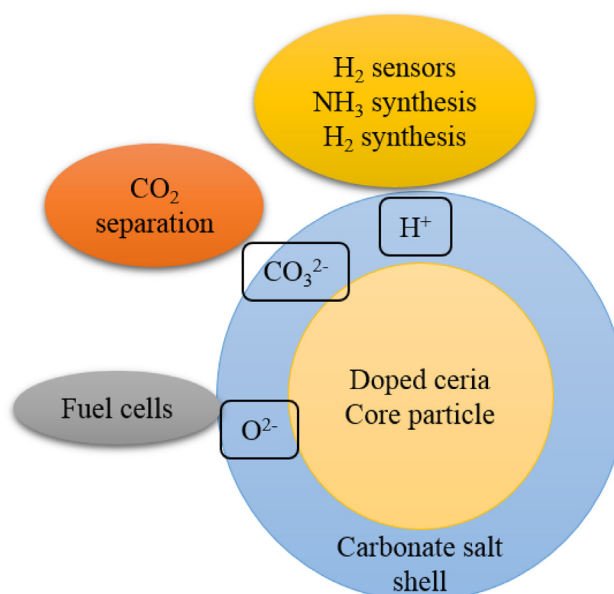


Fig. 4 – Advanced energy applications of ceria-carbonate salt composites. Figure adapted from Ref. [87].

700 °C when the salt is heated under air or argon atmosphere, whereas no sign of decomposition was observed up to 1000 °C under CO₂ atmosphere. Basic thermo-physical properties of several ternary (Li/Na/K) carbonate compositions such as melting point, specific heat and decomposition temperatures have been extensively reviewed by Wu et al. [96]. These authors report the beginning of extensive decomposition at ca. 800 °C in air, which is in good agreement with the above mentioned paper. The work also reports that specific heat is strongly affected by salt composition. Results indicate that K₂CO₃-rich ternary mixtures show the highest specific heat values with a maximum found for the 40K₂CO₃-40Li₂CO₃-20Na₂CO₃ wt% composition, whose specific heat is 4.90 J/g-K. This is a more than three times as much of the binary NaNO₃-KNO₃ “solar salt” mixture (i.e., 1.54 J/g-K).

Latent heat storage using phase change materials (PCM) is a perspective technology of storing solar thermal energy at much reduced storage volume under isothermal operation conditions. Past research had shown that ternary MAC salts could be used as better PCM materials than nitrates showing no significant supercooling effects over many storage charging/discharging cycles at around their melting point (i.e., 395–400 °C) [100]. On this basis, the potential of 36 kinds of ternary MAC salts as PCM materials has been recently reviewed with the purpose to optimize the salt composition in terms of latent heat properties [101]. Latent heat is largest for mixtures containing 40 weight % of Li₂CO₃ (the maximum of 1.97 J/g is found for the 40Li₂CO₃-30Na₂CO₃-30K₂CO₃ wt% composition), which means that optimal composition of ternary MAC salts for solar thermal storage depends on the intended use as either in sensible [96] or latent heat storage systems [101]. Very recently, mixtures of carbonate salts and solid powders were also investigated to produce carbonate-based PCM materials with good physical, chemical stability and high thermal conductivity. Interesting results have been lately reported for PCM composite materials formed by mixing an eutectic salt of lithium and sodium carbonates with MgO powder that forms a microstructural skeleton and with graphite flakes or carbon nanotubes as thermal conductivity enhancers [102].

The potential of MAC salt-based composites for use as thermal storage fluid in solar chemical reactor technology has also gained some attention. Thus, for instance, in order to ensure stable temperature operation even under intermittent insolation, a new absorber/reformer system was conceived and described in Refs. [103–105] for use in solar natural gas reforming processes, which includes a double-walled tubular reactor and a heat storage reservoir of 80 wt% Na₂CO₃-20 wt% MgO composite contained in the annular space between the walls. Choice of the salt-ceramic composite rather than a simple carbonate salt medium was mainly dictated by considerations on the high thermal conductivity of MgO as compared to Na₂CO₃ (7.7 vs 1.84 W/m-°C).

Synthesis of chemicals and fuels by CO₂ electrolysis

Capture, storage, chemical valorization and recycling of CO₂ into useful chemical products is a bridging technology approach for continuing to use fossil fuels but in a sustainable way. In particular, chemical valorization of CO₂ is hot and ever-expanding area of current sustainable chemical

research. In this context, last decade has seen a growing interest for the use of molten carbonate electrolysis as a practicable and convenient approach for electrochemical reduction and conversion of CO₂. Basically, two different approaches for development of molten carbonate electrolysis of CO₂ are under investigation. A long-established and more conventional line of activity is directed to the study of molten carbonate electrolysis for production of electrolytic carbon materials. A second and newer direction of research is mainly directed to investigating molten carbonate electrolysis for synthesis of carbon monoxide in view of producing syngas, which is nowadays a strategic feedstock for production of methane or liquid synthetic fuels from renewable energy sources.

Carbon deposition in molten carbonates has been studied for a long time (see, for instance [106,107]). From early literature it is known that carbon can be readily electrodeposited from carbonate melts or, in more general terms, from molten salts that contain carbonate anions. Moreover, carbon deposition is inhibited in carbonate melts that do not contain lithium cations, in which the prevalent cathodic process becomes the alkali metal formation [106].

However, in the new energy scenarios, carbon deposition from molten carbonates have recently gained new attention as a sustainable route for chemical conversion of CO₂ into a variety of high-tech carbon products ranging from the well crystalline graphite to strongly disordered carbons and nanostructures (tubes, rings, fibers, quasi-spherical particles) [108–114]. These carbon materials hold good promise for technologically important applications either in industrial electrochemistry (e.g. carbon anodes for electrolysis processes) or in energy storage and conversion devices such as in Li-ion batteries and supercapacitors [108] as well. Thus, for instance, quasi-spherical nanocarbon particles have been recently found to exhibit promising performance as anode material in Li-ion batteries since reversible capacity is three times higher than that obtained with conventional graphite electrodes [108–110]. These carbon powders have been prepared in eutectic ternary MAC salt by cathodic reduction at 450 °C under CO₂ atmosphere resulting in particles with size in the 40–80 nm range. An exceptionally high specific surface area (1315 m² g⁻¹) has been obtained for powders deposited at a voltage of -6.0 V and then dried at 600 °C under vacuum. High crystallinity and minimal incorporation of metallic or ionic lithium in the carbon lattice could be obtained by keeping the electrolysis potential more negative than -2.4 V [110].

Due to ease of carbon formation in molten carbonates, the possibility of using a molten carbonate electrolysis process for electrochemical storage of solar energy has been recently evaluated by some authors [113–115]. Converting the deposited carbon back to electricity via anodic re-oxidation in the same molten carbonate salt could allow to easily realize a seasonal storage closed cycle. The basic idea, illustrated in Fig. 5, is to use electricity and CO₂ to store solar energy (charge cycle) in form of carbon during the summer and to produce electricity for winter uses by re-oxidizing the deposited carbon (discharge cycle).

A recent work that is worth mentioning summarizes the results of over 50 years of research on the electroreduction

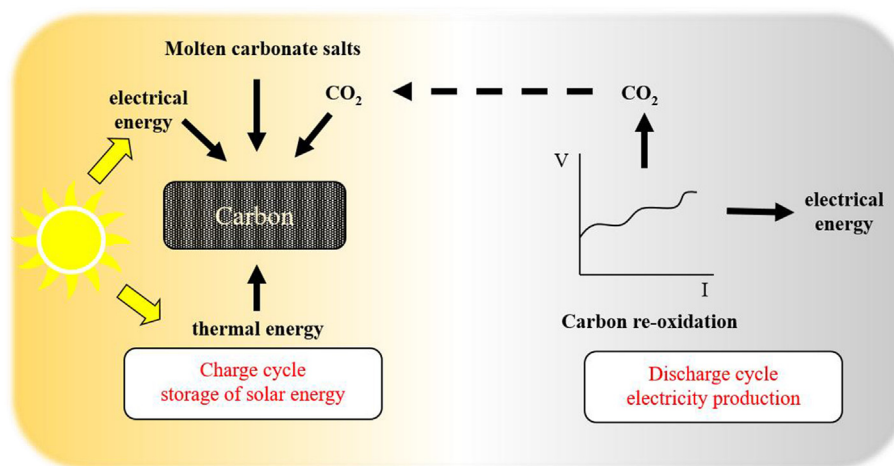


Fig. 5 – Closed electrochemical storage cycle of solar energy based on a molten carbonate electrolysis process of CO₂ to form solid carbon and its anodic re-oxidation to CO₂ to release electricity as proposed in Ref. [115].

mechanism of CO₂ in molten carbonates, which is an important aspect for the optimal design and development of modern carbon materials with advanced structures and functional properties [114].

Reduction of CO₂ in molten salt electrolytes takes place via a direct or an indirect route, depending mostly on the nature of the molten salt, solubility of CO₂ and temperature. In particular, solubility of CO₂ in MAC salts is not very high [5]. Thus, it comes as no surprise that a large body of experimental evidence indicates that reduction mechanism of CO₂ in MAC salt electrolytes proceeds indirectly through a carbonate reduction path.

Moreover, three possible reaction pathways have been proposed for the indirect CO₂ reduction mechanism, although most authors agree on the fact that carbon form prevalently through a direct reduction of carbonate involving the transfer of four electrons as:



The oxide produced in the reaction may promptly react with the CO₂ in the atmosphere to regenerate the carbonate ions:



Other authors suggest alternatively that the transfer of four electrons takes place via a two-step process involving the hypothetical CO₂²⁻ ion as intermediate:



According to some other authors, alkali metal cations are the effective species involved in the electrochemical reduction process and not the carbonate anions. Carbon formation is thus believed to take place through an indirect chemical reduction of carbonate ions via a prior electrochemical reduction of alkali metal cations M⁺ to metal M as:



Nevertheless, these results may indicate that various reaction mechanisms are possible and that the mechanism can vary depending on the experimental conditions chosen for the reaction. This seems reasonable since it has been noted that many electrolysis variables including, for instance, melt temperature, electrolysis potential, molten carbonate and gas atmosphere compositions may dramatically affect the carbon formation in MAC salts [115].

An important aspect to consider is that carbon deposition in MAC salts is a high energy consumption process requiring, for instance, over than 1.7 V at 600 °C, according to thermodynamic considerations [115]. However, Licht and collaborators have very recently published an interesting article showing that the electrolysis energy needed to convert CO₂ to carbon may be strongly minimized if the electrolysis is conducted in a Li₂CO₃ salt or alternatively in a eutectic binary Li/Na carbonate melt with an excess presence of Li₂O. For instance, at 750 °C, the carbon deposition reaction was observed to occur with high Faradaic efficiency and at potentials well below 1 V, giving raise to compact, storable and energetic pure carbon products [9]. Since carbon deposition occurred at potentials significantly less than predicted by thermodynamics and oxygen gas was the only product of the anodic reaction, an alternative stoichiometry for the carbon formation reaction has been proposed by the authors postulating an active role of Li₂O in the CO₂ electro-reduction.

At 750 °C, the energy consumption for carbon production from MAC salts with Li₂O excess has been estimated to be as 9.6 kWh per Kg C, which could mean a cost of less than \$2 per Kg C. Needless to say, much further research is needed for validating these promising results and for a full understanding of the proposed reaction mechanisms.

The thermal re-oxidation behavior of the electrolytic carbon has been also the subject of some research. Anomalous low combustion temperatures in the range 310–450 °C have been found for carbon deposited in Li₂CO₃–K₂CO₃ mixtures at various temperatures and voltages [115]. This unusual

thermal behavior of carbon has been ascribed to its peculiar nanostructure and to the catalytic effects of the alkali metal cations that are present in the electrolytic carbon. Based on this behavior, the electrolytic carbon deposited from molten carbonates has been proposed as a solid fuel for advanced combustion technologies, such as, for instance, to make slurries for internal combustion engines [114].

Since molten carbonate electrolysis for carbon production is highly energy-consuming, several authors have recently shifted their attention on the use of molten carbonate electrolysis for turning CO_2 into CO, which may be carried out at much less reducible electrolysis potentials than carbon deposition, representing thus a more promising approach for CO_2 valorization [5]. Kaplan et al. have used very high temperatures, i.e. 900 °C, to conduct continuous electrolysis experiments showing high conversion efficiency using a molten Li_2CO_3 carbonate as electrolyte, corrosion-resistant Ti materials for the container and the cathode and a graphite anode [116]. More recently, the possibility of using carbonate eutectic mixtures to carry out a CO_2 electroreduction at much lower temperatures has been evidenced by Cassir and co-workers in a series of articles [5,117–119]. Since also water is reducible in molten carbonates (see next paragraph and Ref. [120]), benefits could be further enhanced by electrolysis of CO_2 in presence of steam for a possible co-production of CO and H_2 . Both experimental and thermodynamic studies have been conducted to identify convenient reaction conditions and temperatures for CO_2 electro-reduction. CO formation is promoted by high temperature, high CO_2 partial pressure and low CO partial pressure, whereas low temperature, high CO_2 partial pressure and high CO partial pressure should be preferred, if the aim is to produce carbon. Theoretical conditions for co-electrolysis have been also examined by the same authors. Gibbs free energy analysis indicates that CO_2 electrolysis is slightly more energy-demanding than that of H_2O until 800 °C and that co-electrolysis can be conveniently performed in the range 700–900 °C, where the Gibbs free energies become comparable. Interestingly, thermodynamic analysis with potential-oxoacidity diagrams predicts the possibility of using Li-containing molten carbonates to carry out co-electrolysis even at temperatures lower than 700 °C, although this is possible only under very special reaction conditions. In particular, high $\text{H}_2\text{O}/\text{H}_2$ ratio must be used to avoid that only reduction of water would take place at lowered temperatures. For instance, at 550 °C the predicted $\text{H}_2\text{O}/\text{H}_2$ ratio for syngas production in Li–Na carbonate eutectics is 1000 [117,119], which is not easy to realize in practice.

The electroreduction process of CO_2 into CO has been also experimentally studied in Li–K and Li–Na carbonate eutectics by cyclic voltammetry and micro-electrolysis techniques [117]. The authors report that CO_2 can be electro-reduced into CO at moderate electrolysis potentials (ca. 1.3 V vs Ag^+/Ag reference electrode) for temperatures from 575 to 650 °C, although the whole process appears complex and relatively slow even under pure CO_2 atmosphere. A multistep reaction mechanism has been postulated involving not well identified soluble intermediate species, which agrees well with the conclusions of earlier studies [121].

Hydrogen synthesis by H_2O electrolysis

MAC salts have also been investigated for exploring unconventional ways of producing hydrogen via molten salt electrolysis. Successful attempts to generate hydrogen by steam electrolysis in mixed hydroxide/carbonate electrolytes or in pure alkali carbonate eutectics have been recently reported in various studies [10,120,122,123]. Mixed hydroxide/carbonate melts with melting points below 400 °C have been used by Licht and co-workers to generate H_2 or co-generate H_2 and carbon fuels at various temperatures from 480 to 700 °C [10]. Electrolytes containing carbonate as minor component (15 mol%) and hydroxide as major component (85 mol%) supported facile water electrolysis forming H_2 as the only fuel product. Conversely, electrolytes containing carbonates as the major component (85 mol%) supported simultaneous reduction of H_2O to H_2 and of CO_2 to carbon from 480 °C onwards. The electrolyte composition has been optimized to minimize the significant corrosion of the Ni anode that had been observed in mixed electrolytes containing potassium and sodium cations. Efficient co-generation of H_2 and carbon with a negligible anode corrosion effects has been obtained for electrolysis conducted in a mixed LiOH and ternary Li/Ba/Ca carbonate at 620 °C.

A series of recent studies on water electrolysis based on a reversed MCFC technology concept and state-of-the-art MCFC components has been conducted at KTH, Sweden [122,123]. A 3 cm² button cell has been found to exhibit a better electrochemical performance in electrolysis mode than in a fuel cell mode in a temperature range of 600–675 °C, mainly due to the NiO oxygen electrode performing much better in electrolysis mode. On the contrary, the Ni hydrogen electrode shows higher polarization losses in electrolysis mode at all temperatures and water contents investigated (10–30 mol%). Kinetic and reaction mechanisms on the Ni hydrogen electrode have been also studied in Ref. [123] suggesting the participation of CO_2 as reactant with production of CO directly at electrode or indirectly through a reverse gas shift reaction, which is highly possible above 600 °C.

The alternative possibility of a molten carbonate electrolysis process at temperatures below 550 °C for a fully solar-powered H_2 production has been the object of recent studies at ENEA [120]. Although bicarbonate species are often neglected in molten carbonate studies, focus has been given to the role of bicarbonate anion species as stable and effective proton sources for the cathodic hydrogen at temperatures below 550 °C. Electrochemical studies in a ternary carbonate eutectic by steady polarization tests and cyclic voltammetry have pointed out that the best conditions for conducting MAC electrolysis is at around 500 °C, where a bicarbonate reduction mechanism is largely dominant and H_2 production takes place faster than at the near-immediate higher temperatures. Since the anodic reaction results in carbonate decomposition with production of O_2 gas mixed with CO_2 , it is possible to conceive a solar-powered molten carbonate electrolysis coupled with an oxycombustion process to capture the CO_2 from the electrolysis anode off-gas and thus realize a CO_2 -closed and carbon neutral cycle scheme of electrolytic H_2 production by partial CO_2 recirculation (see Fig. 6).

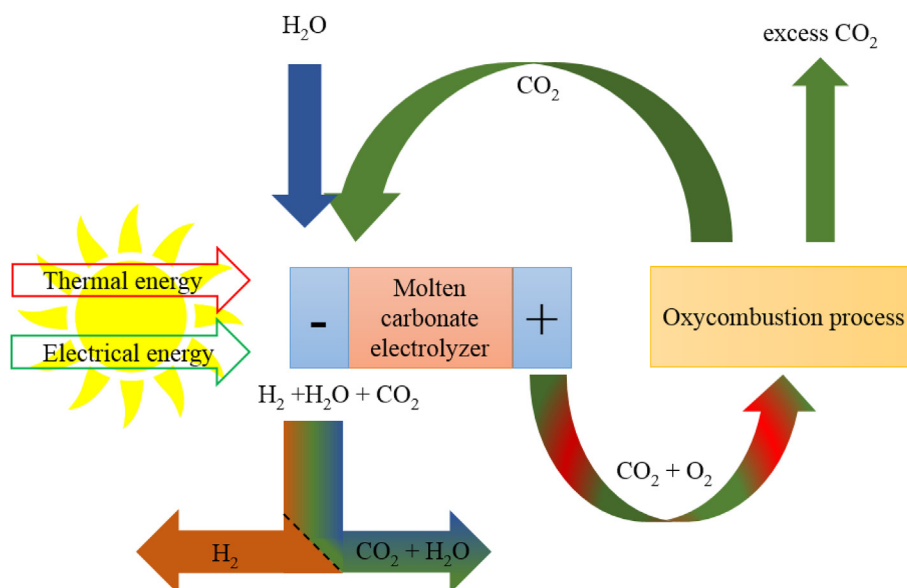


Fig. 6 – Conceptual scheme to realize a CO_2 -closed cycle of solar H_2 production by coupling molten carbonate water electrolysis and oxycombustion processes as proposed in Ref. [120].

Materials and manufacturing processes

Iron and cement production

As already mentioned in the Introduction, molten salt electrolysis is at the heart of a series of novel processes proposed by Licht and co-workers for the CO_2 -free production of important commodity products and fuels in a cost-effective and highly sustainable way. These processes are designed to be powered only by solar energy, to combine maximum reduction of CO_2 emission with high rate and high process efficiency [124]. The name of solar thermo-electrochemical processes (STEP) has been given to these totally solar-driven molten salt electrolysis processes to underline the fact that the solar energy is being exploited in two different forms, both as thermal energy and as visible light, which respectively provide heat and photovoltaic electric energy to power the process as clearly seen in Fig. 7. In the

Figure emphasis is given to the so-called thermoneutral voltage as defined in connection to enthalpy change. This is because electrolysis for industrial uses is being generally conducted at this characteristic voltage (Fig. 7-(a)), which represents an ideal operating condition to achieve practical current densities under an adiabatic isothermal operation mode (no heat input is required). However, the availability of a sustainable external source of thermal energy like solar energy may be used to reduce significantly the electrical energy demand of electrolysis well below the thermoneutral voltage, resulting in a strong increase of theoretical efficiency in electricity-to-chemical energy conversion ($>100\%$) (Fig. 7-(b)). Among various studied molten salts, MAC salt has been identified as the most suitable electrolyte to implement a cost-effective and sustainable electrolysis process for producing two fundamental commodities like iron and cement [7,8,124–127].

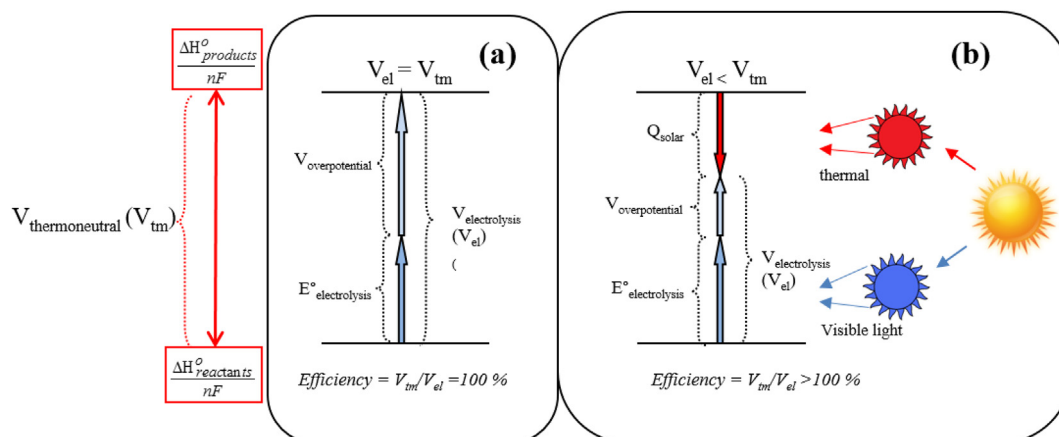


Fig. 7 – STEP-electrolysis process showing utilization of solar energy in form of heat and sunlight for higher electric conversion efficiency.

For what is concerned with the STEP iron process [8,125–127], it should be noted that the development of electrolysis processes for iron (aka iron electrowinning) had moved intensive research in the past but with a progressively declining interest over the years since electrochemical processes are generally deemed as not sufficiently competitive to replace the traditional high efficient, yet heavy polluting carbothermal ironmaking process [128,129]. However, in view of recent emphasis given to sustainability, there is some new attention on alternative iron production based on electrowinning processes. STEP iron production can be seen as a variant of historically employed methods of iron electrowinning in molten salts (see, for instance, Introduction in Ref. [130] for a brief early work history in the field), which substantially differs from earlier works since MAC salts are being used instead of molten halide salts. Advantage lies in the fact that a MAC salt is a much less corrosive electrolyte than halides, while showing a comparable dissolving capability for iron ores such as hematite, Fe_2O_3 , and magnetite, Fe_3O_4 . The dissolving properties of molten carbonates for iron ores seems to be a rather unexpected result based on what known from literature. However, Licht reports that iron ore solubility can be greatly enhanced at temperatures higher than 750°C using pure Li_2CO_3 or lithium-containing carbonate eutectic mixtures [126], which means that the lithium addition seems necessary for enabling fast dissolution of iron ores in molten carbonate salts probably through lithiation reactions of the iron oxide as postulated by Licht.

High temperatures strongly decrease the energy demands for molten carbonate iron electrowinning. For instance, at 800°C , the authors report that 1.6 V is needed to sustain a current density of 500 mA/cm^2 in iron ore-saturated lithium carbonate, whereas the same current density requires only 0.7 V at 950°C [126]. The corresponding room-temperature thermodynamic electrolysis potential is ca. 1.3 V, which makes clear how much electrical energy savings can be obtained when an external source of heat such as thermal solar is available. As reported in Ref. [8], the iron deposit appears compact and dense. No evidence of deleterious dendritic growth is observed, especially when silicate and aluminate impurities are present in the carbonate melt. Considering the high cost of lithium, a really sustainable iron electrolysis process should be designed without using lithium. Thus, a lithium-free molten carbonate electrolyte for a more sustainable iron production has been lately suggested by other authors [131]. By observing that iron oxides and in general all transition metal oxides show limited solubility in eutectic $\text{Na}_2\text{CO}_3\text{--K}_2\text{CO}_3$ mixtures [127], the authors of this work propose a different iron electrolysis scheme. In their approach low solubility of iron ores in eutectic $\text{Na}_2\text{CO}_3\text{--K}_2\text{CO}_3$ mixtures is exploited for using them as solid stable electrodes. Electroreduction of the solid iron oxide electrodes to metal iron could be then realized at 750°C under high current efficiency and low energy consumption conditions. According to authors' view, there is no obstacle in extending the method for sustainable production of other important transition metals such as Ni, Co and Mn.

The possibility of using molten carbonate electrolysis as a potentially sustainable process for a CO_2 -free production of cement products has been also investigated by Licht and co-

workers. According to the proposed reaction mechanism, CaO lime forms as indirect product during a CO_2 electrolysis process in molten mixed $\text{Li}_2\text{CO}_3\text{--CaCO}_3$ carbonate mixtures (STEP cement) [7]. Electrolysis products are oxygen at anode and solid carbon (at $T < 800^\circ\text{C}$) or carbon monoxide (at $T > 800^\circ\text{C}$) at cathode. CO_2 consumption during the electrolysis has the effect to decompose the CaCO_3 into the CaO lime. Unlike CaCO_3 , CaO is highly insoluble in Li_2CO_3 -containing electrolytes and readily precipitates at the cell bottom due to its higher density.

The process leaves the electrolyte unchanged because Li_2O does not precipitates but reacts with CO_2 in the gas atmosphere to reform Li_2CO_3 . STEP cement can be produced also in lithium-free eutectic sodium-potassium carbonates, taking advantage of the fact that CaCO_3 behaves as a strongly inhibitor of metal corrosion but only if added to lithium-free carbonate electrolytes. However, the STEP cement process seems more energetically favorable when conducted in Li_2CO_3 -containing carbonates requiring, for instance at 750°C , less than 1 V against 1.9–2.2 V needed in lithium-free carbonates, under a fixed 100 mA/cm^2 current density.

Although intriguing, these studies reflect only work performed at a laboratory stage of process. Much more information on engineering and scaling-up aspects is required before the full potential and conceptual advantages of these processes can be transformed into an effective and practicable strategy to a future solar production of iron and cement products.

Synthesis of complex metal oxides

Use of molten carbonates as a source of oxide ions for a facile and sustainable synthesis of complex perovskite ceramic oxides or polyanion compounds via molten salt flux methods has recently gained interest.

Salt fluxing may be seen as a special solid-state synthesis technique in which the molten salts are used as additives to promote the rates of solid state reactions and not as reaction media. In a salt fluxing synthesis the amount of salt added to the reactant system is therefore very small, typically a few percent of the total weight, so that fluxing can be considered as a suitable methodology for designing sustainable and quasi solvent-free synthesis strategies. As the mechanism of fluxing reactions is not controlled by diffusing processes as in an ordinary solvent medium, salt fluxing is ideal to prepare single crystals or powders with special shapes and sizes or very complex oxide structures, including polyatomic oxides. In particular, molten carbonate fluxes are long used for growth of complex oxide systems and structures.

Recent research has emphasized on the use of carbonate fluxing as best way for single crystal synthesis of many of the perovskite oxides that are related to the complex 2H hexagonal family and denoted by a general formula $\text{A}_{3n+3m}\text{A}'_n\text{B}_{3m+n}\text{O}_{9m+6n}$, where A is mainly an alkaline earth cation, whereas A' and B can be almost any element from the periodic table such as alkali, alkaline earth, transition or main group elements [132,133]. Because of their complex composition and structure, hexagonal perovskites have been attracting an ever-increasing interest for energy advanced applications due a large variety of complex and unusual properties that they exhibit including magnetic,

superconductivity, ferroelectricity and ionic conductivity properties, just to mention a few. Renewed interest for carbonate flux growth is also due to the ability of molten carbonates to generate perovskite compounds and structures that would not be otherwise easy to prepare. Thus, by way of example, after several years of frustrating efforts, carbonate fluxing has recently demonstrated as the only possible method to synthesize large single crystals of the $2\text{H Sr}_6\text{Co}_5\text{O}_{15}$ oxide phase, which is an interesting material with potential applications in advanced thermoelectric devices [134]. Very large single crystals of oxygen-deficient $\text{Sr}_6\text{Co}_5\text{O}_{15}$ oxide of about 10 mm long and 2 mm in diameter have been obtained after 1 week treatment at 920°C by using a K_2CO_3 salt flux to which small amounts of transition metal oxides had been added. In particular, the role of Cr_2O_3 additions in promoting large crystal formation has been investigated by the authors. It is suggested that Cr_2O_3 stabilizes the high oxidation states of cobalt ions in the perovskite structure by enabling high melt basicity through formation of soluble chromate species. Incorporation of Cr in the perovskite was not observed. Other works report that Na_2CO_3 salt can substitute K_2CO_3 as effective fluxing agent for 2H perovskite single crystal growth like in $\text{Ca}_3\text{CaPtO}_6$ [135], $\text{Ca}_3\text{NaIrO}_6$ [136], $\text{Ca}_3\text{NaRuO}_6$ [136], $(\text{Na}_{0.55}\text{Nd}_{2.45})\text{NaRhO}_6$ [133], although K_2CO_3 is in general a more desirable option to avoid alkali cation incorporation into the crystal lattice since K^+ cation is too large to interact with 2H perovskite structures. For this reason, K_2CO_3 is far more widely used for crystal growth of 2H perovskite oxides that do not contain alkali cations in the crystal composition such as, for example, $\text{Sr}_4\text{Fe}_{0.73}\text{Rh}_{2.27}\text{O}_9$ [137], $\text{Ba}_{11}\text{Rh}_{10}\text{O}_{30}$ [138], $\text{Ba}_{1.1170}\text{Ni}_{0.1170}\text{Rh}_{0.8830}\text{O}_3$ [139], $\text{Ca}_3\text{CuRhO}_6$ [140] compositions, among many others.

Other researchers have shown that molten carbonates are also effective flux media for the synthesis of perovskite oxide powders belonging to the simple cubic-related trivalent ABO_3 structure family (where $\text{A} = \text{La}$ and $\text{B} = \text{Al, Cr, Fe, Co, Ni}$) [141]. In this case, the authors have used low-melting carbonate mixtures of various chemical composition as flux agents with the eutectic (Li/Na) carbonate being proved as the most effective for rapid synthesis of pure phase ABO_3 perovskite oxides at 650°C . An acidic CO_2 gas atmosphere has been found as the most appropriate for rapid formation of perovskite oxides since solubility of reactants and particularly of the lanthanum oxide is significantly promoted by the CO_2 gas.

A very similar molten carbonate flux method has been later proposed by the same research group for the synthesis of novel silicate-based polyanion compounds as novel materials to be used in Li-ion batteries. In an attempt to develop more sustainable types of Li-ion batteries, molten carbonate fluxing has been used for a facile synthesis of new polyanion cathode materials based on abundant and less toxic resources such as lithium iron silicate ($\text{Li}_2\text{FeSiO}_4$) [142] and lithium manganese silicate ($\text{Li}_2\text{MnSiO}_4$) [143] cathodes and much lower in cost than the actual LiCoO_2 cathodes. Reaction temperatures of 500°C and gas atmosphere of CO_2/H_2 (100/3 v/v) have been found the most idoneous for a pure phase synthesis of both the silicates. Electrochemical performance of these materials show some promising properties in terms of discharge capacity, efficiency and capacity retention, although further

improvements are warranted before considering them as effective cathode alternatives in Li-ion batteries.

Metal surface engineering

In recent years, the use of molten carbonate baths to develop novel coating and surface modification processes on a more sustainable basis has attracted some attention. For instance, molten carbonates has been found as optimal carbonaceous medium to design an alternative and sustainable electro-carburization process of mild steels for producing thick carbon-hardened cases (up to 600 μm) using a CO_2 atmosphere rather than the highly noxious CO -rich gas atmospheres as in more conventional processes [144].

Two different salt mixtures, namely a Na_2CO_3 - NaCl (molar ratio = 4:1) and a Li_2CO_3 - K_2CO_3 (molar ratio = 1:1) composition, have been analyzed and compared as carbon source medium. The experiments have showed that the Li_2CO_3 - K_2CO_3 is more effective than the Na_2CO_3 - NaCl mixture for producing carbon-hardened cases. This has been attributed to a distinctly higher carbonate activity of the Li_2CO_3 - K_2CO_3 electrolyte, thus resulting in faster electro-carburization reactions. Results also showed that electro-carburization becomes faster with increasing the electrolysis voltage, although cell voltages higher than 2 V resulted in a lower current efficiency due to excessive graphite deposition and onset of parasitic cathodic reactions producing noxious CO gas.

In a different work, Kaplan et al. [145] have produced a thick and protective coating layer of titanium carbide onto metallic titanium substrate by electro-reduction of a molten Li_2CO_3 electrolyte at 900°C . Titanium carbide layers have been observed to form prevalently in the initial stages of the electro-reduction process, during which the carbon diffuses within the Ti electrode surface resulting in a rapid formation of a up to 10 μm thick TiC carbide layer. In spite of high bias voltages (carbon production begins at -3 V), carbon accumulation on the Ti surface could be largely avoided during the first 5–20 min of treatment, which is possibly due to the fact that any carbon formed on the electrode surface would immediately react with the TiO_2 layer initially present on the Ti surface, according to:



Carbon deposition starts only after that the initial TiO_2 surface layer is being completely consumed by the above reaction. However, prolonged treatments do not lead to further increase in TiC layer thickness. The suitability of TiC coated titanium as novel inert, non-consumable anodes in molten carbonate electrolysis processes has been also tested. Thus, outstanding electrochemical properties of TiC coated titanium anodes have been reported during electrolytic conversion experiments of CO_2 into CO in a pure Li_2CO_3 melt at 900°C . These electrodes appear far more efficient than conventional graphite anodes by supporting current densities 3.5 times higher. In addition, TiC coatings exhibit no appreciable anodic corrosion or degradation, whereas in comparison graphite suffer from anodic swelling and mechanical disintegration due to fast Li intercalation reactions [116].

Since carbonate melts have proven to be a powerful medium for the synthesis of perovskite oxides, a novel molten carbonate conversion coating treatment has been recently developed by the authors of this work with the purpose of producing protective and electrically-conductive lanthanum-based perovskite oxide layers onto stainless steel substrates [146–148]. This surface “ceramization” process is specifically conceived to enable electrical and electrochemical applications of stainless steels in high temperature corrosive environments, including current collectors of fuel cells. Basic melt conditions are required to form perovskite layers via chemical conversion reactions taking place at around 600 °C between the iron component of the stainless steel and lanthanum dissolved in the basic salt as soluble LaO^+ species [149]. Two very different reaction mechanisms, namely dissolution-precipitation and precursor-template route synthesis may be involved resulting in thick or thin perovskite layer formation. The exact formation depends on the melt basicity as illustrated in Fig. 8. Thus, for instance, under high melt basicity, initial dissolution of iron oxides is seen to take place in the carbonate salt followed by their subsequent precipitation/crystallization as LaFeO_3 particles at the steel surface. Since carbonate melt basicity assumes a key role in changing iron oxides from almost insoluble to highly soluble species, these results support and extend previous findings by Licht [126] in showing that iron oxides may indeed become very soluble in molten carbonates if appropriate melt basicity conditions are chosen. Perovskite conversion coatings have been applied to various stainless steels with austenitic and ferritic structure and with a Cr content ranging from 13 to 18 wt%. Results of corrosion tests conducted on austenitic 18Cr and ferritic 13Cr type steels in MCFC environments suggested that such perovskite conversion coatings could potentially offer lifetime protection to MCFC current collectors, regardless structure and Cr content of the stainless steel substrate [146,147].

Applications to advanced gas processing and gasification technologies

Hot gas cleaning

Some recent studies have reported on the use of molten carbonates as high-temperature liquid sorbents to solve specific and important cleaning or separation gas problems. Development of hot gas desulfurization systems is one challenging topics of current research for cleaning and upgrading of fuel gases. Most current research in this sector is focused on the development of novel gas cleaning materials that combine both sorbent and catalytic properties to optimize energy use and lowering processing/cleaning temperatures. The gas cleaning ability of molten carbonates is a long known property that has been studied in the past alone or in combination within other important processes like coal gasification. From these pioneering studies, regeneration step of used carbonates invariably emerged as the most critical point of the whole cleaning/gasification process. Starting from these premises, regeneration studies have attracted some new attention in literature [150–152]. In particular, Raharjo has reinvestigated in detail the regeneration process of molten carbonate salts used to remove sulfur from syngas [152]. By using an eutectic binary $43\text{Na}_2\text{CO}_3$ - $57\text{K}_2\text{CO}_3$ salt composition, a complete removal of large concentrations (1000 ppmv) of pollutant sulfur species (H_2S , COS) in a N_2 -based gas stream had been obtained in bench-scale experiments over a wide range of high temperature conditions starting from above the eutectic carbonate melting point (>700 °C) up to 900 °C. The authors report that easy regeneration of molten salts is possible by simply using CO_2 as regeneration agent. Na_2S and K_2S sulfides could be converted back to their original carbonate salts at temperature range of 300–600 °C with optimal regeneration temperature being found at ca. 300 °C, where around 80% sulfides were

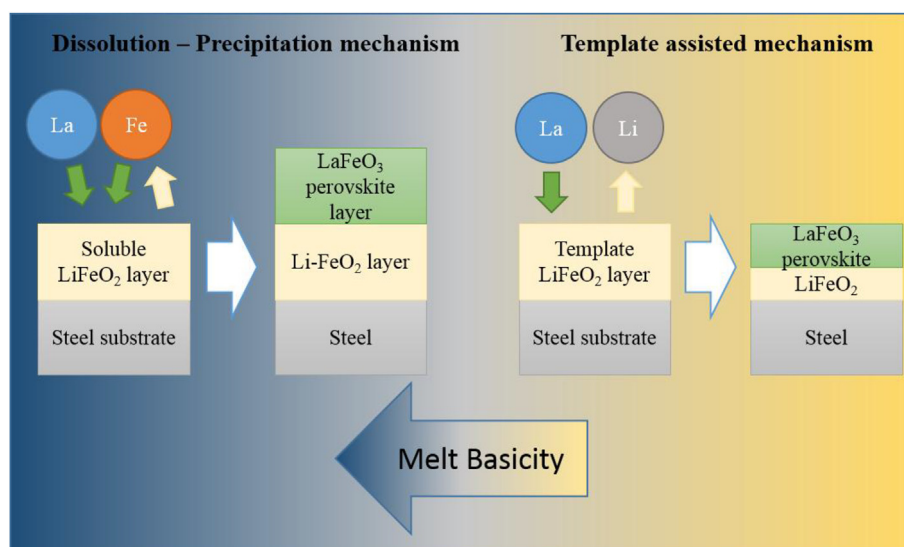


Fig. 8 – Conversion coating formation of lanthanum-iron perovskite surface layers onto stainless steel substrates as a function of molten carbonate basicity: high-melt basicity-dissolution-precipitation mechanism and lower melt basicity-template-assisted mechanism.

regenerated to their alkali carbonates. In an attempt to enhance the overall process efficiency, an improved procedure for spent molten carbonate regeneration has been illustrated in a subsequent paper [151]. Results suggest that spent carbonates could be more optimally regenerated under a temperature range of 400–500 °C by adding steam to improve the regeneration ability of CO₂. With a CO₂/steam ratio of 1:2, around 95% of alkali sulfides could readily be converted back to alkali carbonates demonstrating thus high potential of MAC salts to work as effective liquid sorbent systems with high sulfur capture capabilities and ease of regeneration (see Fig. 9).

Using molten carbonates for deep H₂S cleaning purposes has recently been also investigated by other researchers [150]. The chemistry and performance of a Na₂CO₃ salt sorbent under simulated syngas containing 350 vppm of H₂S has been studied from 800 to 1000 °C in bench-scale experiments. At temperatures lower than 1000 °C, the desulfurization capability of the carbonate salt is significantly affected by the concentration of CO₂ in the syngas. At 900 °C, desulfurization is highly inefficient in presence of high CO₂ concentrations. However, adding carbon elements such as char and tar to the molten carbonate can newly raise the capture ability of H₂S at very high levels, i.e., ca. 90%. This happens because carbon decreases the CO₂ concentration in the syngas according to the already-seen Boudouard equilibrium (Eq. (2)).

Scaled-up experiments have been also conducted to validate the process efficiency from CO₂-rich gases containing large amounts of H₂S. For this purposes, molten carbonate purification has been applied to sewage sludge pyrolysis gas with 6800 vppm H₂S and brown coal gasification gas with 1200 vppm H₂S. In both the cases, purified gases contained less than 0.1 vppm H₂S, confirming thus that molten carbonates are very suitable systems for deep desulfurization applications of pyrolysis-derived gases. However, much lower sorption performance is expected with fermentation or byproduct gases from chemical plants that contain CO₂ but not char or tar compounds.

Membranes for CO₂ gas separation

The current interest for CO₂ capture technologies have also opened up new directions for molten carbonate research in high temperature membrane separation technology in an attempt to exploit the unique chemistry properties of MAC salts.

Pioneering work on CO₂ separation from hot flue or fuel gases had been built based on MCFC fuel cell membrane technology, exploiting the fact that a MCFC system, while producing electricity, works also as a selective membrane, resulting in a net CO₂ transport from the cathode to the anode side. In an attempt to improve separation performance of a fuel cell carbonate membrane, Winnick was the first to study a MCFC fuel cell operating in a reversed mode, namely with the application of an electrochemical gradient to realize an electrochemical separation pump working in a closed circuit, i.e., with no fuel added to the anode (see Fig. 10) [153]. Further studies evidenced that an electrochemical molten carbonate pump has several advantages in design and reliability over a fuel cell separation mode making it suitable for capturing CO₂ from air also in special applications like space flight [154,155]. However, these early electrochemical molten carbonate pumps suffered of major troubles like poor selectivity and permeability along with a low stability under severe flue gas conditions, thus leading to a progressive interest decline over the time. Interestingly, the possibility of capturing CO₂ through MCFC devices running in normal fuel cell mode has newly gained some attention in recent works [156–162].

Using MCFC systems adapted to be fed with clean flue gases emitted from gas turbine plants is an interesting method for realizing retrofitting CO₂ capture schemes combined with electricity production. Results show that recovery of CO₂ from gas turbine flue gases, which has a very low CO₂ concentration (<4%) is possible, but with high energy penalty. Significant losses in fuel cell efficiency and electricity production should be taken into account, in fact, under the MCFC process conditions that are needed to maximize the CO₂ separation effects with such diluted flue gases [156]. According to more recent studies, recovery of CO₂ from more concentrated flue gases (>10%) such as those emitted by

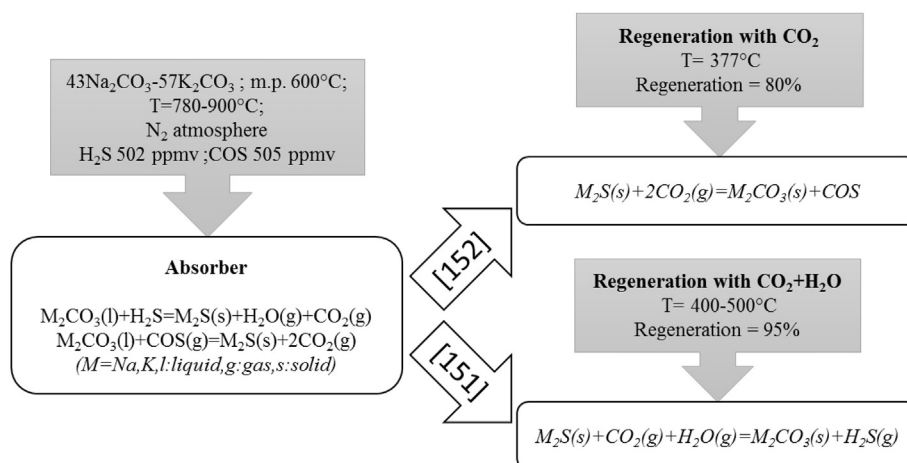


Fig. 9 – Molten carbonates as high temperature liquid sorbents with high sulfur capture capability and easy to regenerate with CO₂ [152] or with CO₂+steam [151].

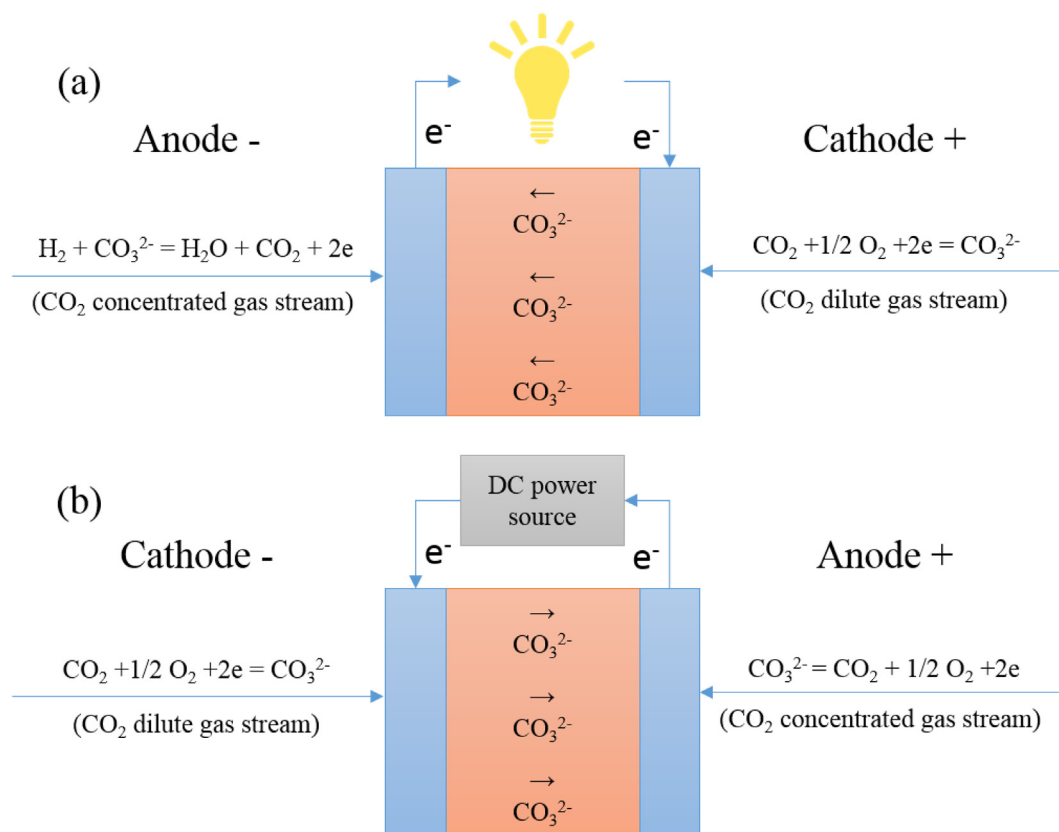


Fig. 10 – Basic principles of an electrochemical molten carbonate membrane for high temperature CO₂ separation: (a) membrane operating in fuel cell mode with a simultaneous production of electricity and (b) membrane operating in an electrochemical pumping mode with no added fuel to the anode.

lignin-fired or coal-fired plants could significantly reduce the energy penalty and capture costs of MCFC separation systems, although important technical issues such as sulphur or particulate removal have not been included in process analysis and separation costs [160–162].

The recent arise of new membrane systems totally independent from electricity has provided new tools to improve stability and performance of molten carbonate membranes for CO₂ separation becoming a rapidly growing area of investigation. A new concept of dual-phase molten carbonate-based membrane in which CO₂ separation can be realized with the driving force of a CO₂ partial pressure gradient and not with electricity has been first introduced by Lin in 2005 (Fig. 11(a)) [163]. Initial investigations have focused on using the molten carbonates as the ion conducting phase mixed with an electronic conducting metallic phase such as stainless steel [163] or silver [164]. Dual metal-carbonate membranes have proven high flux CO₂ permeation properties at temperatures above 450 °C. However, problems arise for their practical applications because a high CO₂ permeation can be obtained only with a simultaneous permeation of O₂, which means that these membranes could be applied for production of CO₂–O₂ mixtures rather than for pure CO₂ separation. Secondly, these membranes are prone to ion transport blockage due to oxidation or degradation stability of the metallic phase at high temperatures [165,166]. These problems have been recently addressed by Huang et al. for dual

metal-carbonate membranes containing silver [166]. Since sintering and wettability loss with the molten phase are the main degradation issues of the silver, a surface-modified silver-molten carbonate membrane has been prepared by coating the surface of the silver porous matrix with a thin layer of γ -Al₂O₃ before impregnation with the molten carbonate phase. According to the authors, this surface-modified silver-carbonate membrane is much more resistant to silver degradation and promotes a prolonged and stable CO₂ and O₂ permeation operation at 650 °C.

While dual metal-carbonate membranes are adequate for CO₂ (and O₂) separation from an oxidizing stream such as a flue gas emitted by conventional power plants, several studies have clearly shown that ceramic-carbonate composites that are studied as fuel cell electrolytes could be useful to improve membrane stability and enable CO₂ separation without the concomitant transport of O₂ [165,167–173]. Thus, attention of several research groups has been increasingly directed towards the development of dual-ion conducting electrolyte membranes suitable for pre-combustion applications and composed of a molten carbonate phase and an oxygen ion conducting or a mixed ion-electron conducting oxide phase to capture CO₂ from flue or fuel gas atmospheres. The rationale behind all this is that combining a carbonate-ion conductor with an oxide-ion conductor is possible to obtain a net CO₂ transport across the membrane provided that the two types of ions move in opposite directions (Fig. 11(b)) [169]. Although

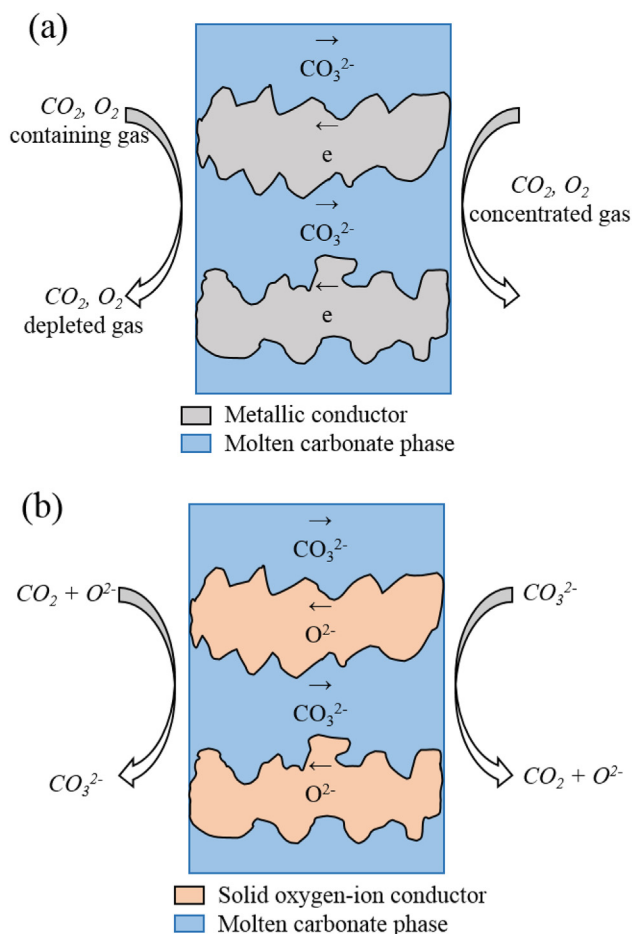


Fig. 11 – Basic principle of a dual-phase separation membrane using molten carbonates as liquid phase and a solid (a) electronic or (b) oxide ion conductor for chemical CO₂ separation in (a) O₂-containing gases and in (b) flue or fuel gases.

several design and synthesis aspects of ceramic-carbonate membranes need to be more definitely assessed (see, for instance [173,174]), promising results have been already reported for separation of CO₂ in non-oxygen containing gases. In particular, dual phase membranes containing a mixed ion-electron oxide conductor show a very interesting hybrid behavior. These membrane allow the simultaneous permeation of CO₂ and O₂ at high oxygen partial pressures, similarly to the metal-carbonate membranes, but only CO₂ at low oxygen partial pressures [171].

Flux values of CO₂ in the range 10^{-4} – 10^{-3} mol m⁻² s⁻¹ have been reported between 600 and 800 °C for several types of dense and thick (thickness > 1 mm) membranes, such as La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-x}(LSCF)-eutectic (Li/Na/K) carbonate [165], gadolinia doped ceria (CGO)-eutectic (Li/Na/K) carbonate [169], B_{1.5}Y_{0.3}Sm_{0.2}O_{3-x}(BYS)-eutectic (Li/Na/K) carbonate [167], yttria stabilized zirconia (YSZ)-eutectic (Li/Na/K) carbonate [169], La_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_{3-δ}-(Li,Na)₂CO₃-LiAlO₂ [171] and La_{0.85}Ce_{0.1}Ga_{0.3}Fe_{0.65}Al_{0.05}O_{3-δ}-carbonate [175]. Membranes based on ternary eutectic (Li/Na/K) carbonate salts show higher and remarkable permeation stability due to

minimal chemical reactivity with any type of ceramic oxide phase [169], although binary eutectic Li/Na carbonates are also efficient salt systems [176]. In particular, samarium-doped ceria-carbonate membranes have been tested under highly demanding conditions. Long-term excellent membrane stability has been reported in the range 700–900 °C at high gas pressure (up to 5 atm) and for extended periods of time (up to 35 days) in a simulated syngas showing only minimal decomposition of the ceramic phase in presence of hydrogen [177]. Optimization of structure and thickness of the solid phase is also an important factor for improving membrane flux at levels required for practical applications. A high CO₂ flux of ca. 10^{-2} mol m⁻² s⁻¹ has been reported at 650 °C for a samarium doped ceria (SDC)-eutectic (Li/Na) carbonate membrane with an improved microstructure of the solid phase, which consists of a dense network of interconnected 3D ionic channels [176]. Other authors have reported that a high CO₂ flux can be obtained by fabrication of dense asymmetric thin film structures using a ternary eutectic (Li/Na/K) as the carbonate phase infiltrated into a yttria stabilized zirconia (YSZ) ceramic phase [170]. This asymmetric dual-layer structure consists of a 10 μm thickness dense layer membrane supported on a large pore substructure made of a ceramic material that is not-wettable by molten carbonates (Fig. 12). With this structure, the membrane is reported to achieve a CO₂ flux of ca. 4×10^{-3} mol m⁻² s⁻¹ at 650 °C, which is 5–10 times higher than that an analogous thick YSZ-carbonate membrane.

Biomass gasification

Molten Salt Oxidation (MSO) is a thermal, non-flame process that has been actively studied during the seventies for coal gasification as well as destruction of propellants or other reactive wastes that are difficult to treat. After initial

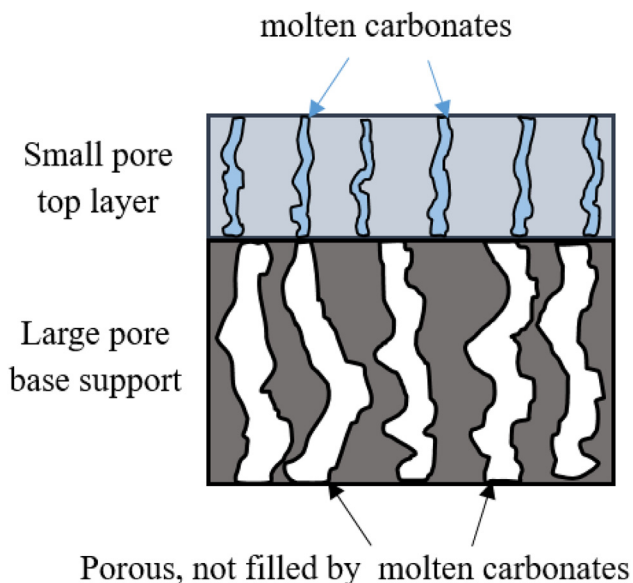


Fig. 12 – Schematic illustration of a dual-phase/dual ion-conducting molten carbonate dense membrane with an asymmetric thin film structure for improved CO₂ separation from flue or fuel gases.

enthusiasm, research interest on MSO has progressively declined due to various unresolved design and experimental challenges. Recently, MSO has attracted new attention in an attempt to develop a more sustainable alternative to the traditional gasification and pyrolysis processing methods. However, a primary goal of modern research in this sector is to introduce sustainability principles into the gasification processes, which may be achieved by innovative process design along with a replacement of fossil fuels like coal or petroleum with biomass or waste feedstocks. In this context, there is an increasing appreciation on the possible role of molten salt processes for a more sustainable design of coal gasification processes due to minimal tar and char residue production and virtual absence of gaseous contaminant and particulate matter emissions. As a further advantage, chemical thermodynamics also predicts that the ash may form liquid phases with molten salts, thus avoiding formation of solid slags in the reactor. Thus, several research initiatives have been launched in these last years in order to unlock potential benefits of molten salt processes.

In particular, the role of MAC salts (but also of other molten salts like zinc chlorides, alkali metal halides and nitrates [178]) for advanced production of H_2 and syngas from coal [179–181] or from biomass is currently one active area of the current molten carbonate research [178,182–192]. It is worth noting that, although the potential benefits of molten carbonates for biomass gasification are being increasingly recognized, many investigations have not so far scaled up beyond the laboratory scale. This clearly indicates the much more basic research is needed before practical application of molten carbonates in biomass gasification could be practically exploited.

Different from halides, MAC salts do not show a strong catalytic effect for demolition of large and complex molecules (e.g. biomasses, plastic wastes) unless a suitable gasifying agent is used [182]. On the other hand, since molten carbonate represents also an oxygen-containing medium, molten carbonate pyrolysis processes are always accompanied by oxidation reactions making it very difficult to determine exact reaction mechanisms in this medium. As a general rule, moderate-to-low amounts of residual char have been reported to form during molten carbonate pyrolysis of biomasses or organic wastes. For example, MAC salts consisting of an eutectic mixture of sodium and potassium carbonates have been recently investigated for conducting fast pyrolysis experiments (heating rates up to 100 K/s) of pure cellulose at 850 and 915 °C. Although cellulose-to-syngas conversion is greatly accelerated by MAC salts, however, conversion reaction to gas did not go to completion leaving a 2% char residue in the salt after the treatment at 915 °C, which rapidly increases at 6% with only a small drop in temperature, at 850 °C [184].

Use of molten carbonates in combination with gasifying agents (i.e. gasification) has proven to be a far more effective approach for achieving almost complete solid-to-gas conversion of a large variety of structurally complex feedstocks like plant biomasses, switchgrass, corn stover and activated carbon [185,186]. Tenfold increase in the rate of gasification of cellulose or carbon has been demonstrated in presence of molten carbonates with gasifying agents [186]. Most effective molten carbonate gasification processes uses CO_2 and steam as gasifying agent system, which is usually realized under

bubbling fluidized bed configurations for a maximum conversion efficiency [191]. For instance, the molten carbonate gasification of wastepaper with CO_2 gas bubbling has been explored at temperatures between 650 and 750 °C and with different mixtures of Li_2CO_3 , Na_2CO_3 and K_2CO_3 salts [191]. Especially when Li_2CO_3 is included in the salt mixture, carbonate salts are highly effective to fully decompose wastepaper into H_2 and CO gaseous products. The liquid carbonate salt has been found to have an enhanced catalytic effect on the Boudouard reaction (i.e., $C + CO_2 = CO$), thus resulting in a high CO production. The total absence of higher hydrocarbon products is supposed to be due to a specific effect of the small lithium cation that can easily penetrate into the $\beta(1,4)$ glycosidic bond, promote an intimate contact with molten salt and the gasifying agent and thus catalyze effective breakdown of glucose monomers into gaseous products. In a follow-up paper, a number of additional aspects have been evaluated by comparing wastepaper gasification results under both CO_2 and steam bubbling conditions [188]. Moving on more complex biomass sources, Sugiura et al. have reported a study on the CO_2 gasification of rice and sludge from a sewage plant with a Li/K eutectic carbonate mixture [187]. Temperature as high as 750 °C is demanded for conducting rapid and efficient CO_2 gasification and thus obtain CO and H_2 near their chemical equilibrium from both the rice and sludge. However, gasification of rice is more promising since it contains a sufficiently high moisture content that it is useful to avoid carbon deposition (soot) in the reactor.

Hazardous waste gasification

Because MSO provides an effective in-situ scrubbing of gaseous contaminants including acid gases, molten media processes using MAC salts have been also recently re-investigated with the purpose of destroying or transforming noxious industrial wastes like contaminated or hard-to burn wastes (organic chemicals, municipal refuses, plastics, wastes of electronic industry, radioactive and special military wastes) into harmless chemicals or clean gaseous fuels [193–196]. For a faster and more effective gasification of complex wastes, most of the studies use steam or air as gasifying agent rather than CO_2 . An interesting study is reported by Yang [196], who has studied a clean destruction process of chlorine-containing organic wastes based on the use of a two-stage molten carbonate gasification reactor under various operating conditions (temperature, gas feed rate and gas residence time). Complete destruction of chlorobenzene and trichloroethylene has been obtained using excess air as gasifying agent and a binary eutectic Li/Na carbonate salt as processing fluid in both the reactors. Although various harmful chlorinated, non-chlorinated organic species and HCl still exit from the primary MSO reactor at 700 °C, these species could then be completely destroyed with the second stage reaction at 900 °C. Other studies have recently investigated the use of molten carbonates to convert the plastic fraction of electronic waste materials containing bromine or chlorine into clean fuel gases [189,195]. A particular mention deserves the work of Zhang et al. [189]. These authors report that ternary eutectic MAC salts show a strong catalytic effect for hydrogen production by steam gasifying a phenolic circuit board at 625 °C. The use of molten carbonate salts include also the possibility of

designing processes with very rapid heating rates ($>10\text{ }^{\circ}\text{C/s}$). Rapid heating is a key process parameter in the process studied by Zhang since it greatly promotes pyrolysis fragmentation reactions of the plastic fraction thereby accelerating the conversion of tar and char into gaseous products. In a very similar paper, steam gasification of activated carbon in presence of mixed carbonate salts has been studied at $700\text{ }^{\circ}\text{C}$ finding that presence of carbonate salts is highly effective for an almost complete conversion of solid carbon into H_2 and CO_2 [195]. Results also show that fluidity of carbonates and potassium content are two important factors for an accelerated steam gasification.

MAC salts have been also considered for effective destruction of military ammunition and chemical warfare agents. According to Griffiths and co-workers [194], MSO processes using MAC salts are particularly efficient and do not produce noxious emissions from demolition of explosives, propellants and chemical warfare agents such as Sarin gas and arsenicals. Rapid fragmentation and destruction efficiencies of almost 100% have been reported in molten carbonates containing small amounts of nitrate ions. The effect of nitrate addition for increasing the oxidizing power of molten carbonate salts under air bubbling conditions has been already discussed in the Part 1 of this work and will be here not repeated. Besides technological aspects, it is worth mentioning that during these studies the authors have also studied in some detail the catalytic mechanisms of molten carbonates in the oxidation reactions. According to them, the catalytic action of molten carbonates should be related to the content of active oxygen species (i.e., mostly superoxide and peroxide anions) dissolved in the melt, rather than to the direct action of the carbonate anion species, as widely believed yet in a much less precise way. Molten carbonates are usually classified as neutral, non-oxidizing salts, but the results of Griffiths and coworkers indicate clearly that small additions of nitrates can be used as powerful oxide buffers to produce a strongly oxidizing carbonate medium with unusual catalytic and functional properties.

Concluding remarks and opportunities for further research

Consistent evidence has been provided in this review on the fact that recent molten carbonate research is moving away from the traditional area of high temperature fuel cells towards more cutting-edge fields of energy research that are related to the sustainable development, thus well adapting to the new societal contexts and challenges. MAC salts are non-polluting, low-corrosive and relatively inexpensive salts thus offering important advantages not only for the design of chemical/electrochemical sustainable processes but also as advanced functional materials. For reasons of convenience, the two types of applications will be considered separately.

Concerning the use of molten carbonates in sustainable process development, a general observation can be made. From analysis of literature, it appears that process intensification, which is an important aspect of sustainability concept in the modern-day chemical industry, has been neglected in molten carbonate studies, although there are clear indications

that significant reduction of size, temperature and energy requirements can be achieved with the use of molten carbonate electrolytes or reaction media as compared to more conventional processes. The use of MAC salts as a key to process intensification undoubtedly warrant further studies and analysis, since focus on this aspect could offer further application opportunities for molten carbonates.

More specifically, according to literature and major research trends, electrolysis is emerging as the key process to exploit at the highest level possible the unique and versatile properties of MAC salts thus offering the greatest opportunities in developing a future and sustainable molten carbonate technology for advanced applications in various sectors of the energetic field, especially if combined with solar energy sources.

In particular, molten carbonate electrolysis processes are easy to integrate with high-temperature solar energy sources, based on both temperature and energetic considerations. From the literature analysis emerges clearly that a broad spectrum of applications for electrochemical storage of solar energy and solar-to-chemical energy conversion can be envisaged by using molten carbonate processes and technologies. In particular, the potential of solar-integrated molten carbonate electrolysis processes for sustainable large-scale production applications has been extensively analyzed in a series of studies conducted at The George Washington University. A demonstration on small-scale of the impressive versatility of molten carbonate electrolysis processes for synthesis of carbon and hydrogen fuels or basic commodities like iron and cement without release of any CO_2 has been provided in these studies, under the condition that both solar thermal and photocurrent energy are used to fully power the whole electrolysis process. Needless to say, much more research is required on large-scale demonstrations prior to making more definitive conclusions on these radically-new processes.

Hydrogen production and CO_2 electrolysis are two research sectors with large potential growth for synthetic fuel production by renewable energy. In this context, development of water and CO_2 electrolysis technologies in molten carbonate electrolytes could similarly benefit from an integrated design of molten carbonate electrolysis with solar energy. These topics have not yet fully explored in research literature, although well worth of further research and developments. In particular, there is a strong need to go beyond the current proof-of-concept studies and examine more practical electrolysis aspects related to effective feasibility, cell configuration, materials stability, technology implementation and costs.

On the basis of the literature survey, there are also promising chemical applications of molten carbonates, especially for biomass gasification, which is a research topic rapidly growing in importance in the last years. In fact, molten carbonate chemical processes seem to offer great potential advantages particularly for the development of sustainable gasification processes characterized by minimal tar and char residues, absence of solid slags and particulate matter.

Incorporation of MAC salts into solid ionic conductors have recently opened up new strategies and routes for preparation of advanced functional materials in the energy field. This

survey clearly supports the view that molten carbonates provide unique opportunities for the design of structure-complex functional composite materials with advanced and unique super-ionic conductor properties. In particular, many studies have been conducted on solid oxide-carbonate ceramic composites as highly promising materials to realize ionic and super-ionic conducting membrane systems with task-specific and multi-ion transport properties. Studies on these composite membranes have focused on advanced energy applications mainly for hybrid fuel cell and CO₂ separation processes, although other interesting applications have begun to appear in the very recent literature such as in ammonia and hydrogen synthesis or as hydrogen sensor. There is little doubt that the sector of ionic and super-ionic composite conductors may provide new and exciting opportunities for research and applications of molten carbonates as key energetic material in the next future.

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