INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2016) 1–8

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

Full Length Article

Molten carbonates for advanced and sustainable energy applications: Part I. Revisiting molten carbonate properties from a sustainable viewpoint

S. Frangini [a,*], A. Masi [a,b]

[a] DTE-PCU-SPCT, ENEA CR Casaccia, 00123, Rome, Italy
[b] DAFNE, University of Tuscia, Via San Camillo de Lellis snc, 01100, Viterbo, Italy

ARTICLE INFO

Article history:
Received 26 October 2015
Accepted 7 December 2015
Available online xxx

Keywords:
Molten salts
Molten alkali carbonates
Electrolyte
Reaction media
Sustainable energy

ABSTRACT

In addition to the traditional fuel cell field, recent research on molten alkali carbonates is increasingly directed towards their use as efficient reaction medium or for the preparation of highly functional materials in advanced, low fossil-carbon and sustainable energy applications. The expansion of renewable energy use, and particularly of solar power, appears to be a major driving force behind the new wave of molten carbonate studies. However, since the relevant molten carbonate literature in the new field of sustainable energy is still relatively small, this work is an attempt to stimulate further and more systematic investigations on molten carbonates by revisiting some of their characteristic properties from a modern and sustainable perspective. In particular, this work is specifically focused on molten carbonate properties that are important for uses as electrolyte or reaction media. Specific properties that have been considered as major indicator of technological sustainability include safe melt chemistry, thermal and moisture stability, high electrical conductivity combined with low metallic corrosiveness, ease to regenerate, tunable acid-base and redox properties, and catalytic activity in gasification and partial oxidation reactions. From this analysis it can be concluded that molten carbonates are very stable systems under a wide range of chemical conditions and mild to moderate temperature ranges, giving the possibility of designing ideal reaction and electrolyte media for advanced chemical/electrochemical processes related to production, storage, conversion and efficient uses of renewable energy, particularly of solar energy, in future low-carbon energy scenarios.

Introduction

High temperature molten salt technology is a strategic sector of the modern-day industry [1]. An almost endless list of industrial processes today exploit the unique functional properties of molten salts such as thermal and radiolysis stability, non-flammability, low vapor pressure, ionic and thermal conductivity, heat transfer, solvent capability and

* Corresponding author. Tel.: +39 06 30483138; fax: +39 06 30486357.
E-mail address: stefano.frangini@enea.it (S. Frangini).

http://dx.doi.org/10.1016/j.ijhydene.2015.12.073
0360-3199/

catalytic activity. Extractive metallurgy was historically the first sector to make a large-scale use of molten salts for the electrolytic production of light metals like aluminum and magnesium during the Industrial Revolution of the nineteenth century. With the later advent of easy oil energy at the turn of the new century, molten salts further expanded their crucial role in the more demanding metallurgical processes of stainless steels and corrosion-resistant alloys. Only in the last few decades, the interest for non-metallurgical uses of molten salts, in particular as heat transfer and thermal storage fluids, has steadily increased being driven by the arise of first molten salt nuclear reactor [2] and solar power plant programs [3].

In this context, several molten salt systems including molten alkali carbonates (MACs) were actively studied as thermal storage media in the seventies and eighties [4,5]. During this period, the high versatility of MAC properties attracted a broader attention for their use in other energy-related technologies, including coal gasification [6], waste disposal [7], gas cleaning [8,9], CO_2 concentration [10] and fuel cells [11,12]. Unfortunately, most of the above mentioned research programs saw a substantial decline of interest over the time, because of various technical and economic constraints impeding their further implementation and leading to a concurrently declining interest also for the study of MAC salts. The only remarkable exception was in the emerging fuel cell field, where the study of alkali carbonate electrolytes continued to grow fast, being driven by the high promise of fuel cells to become the power source of choice in a sustainable energy future. In particular, the world oil crisis of the seventies sparked outstanding research efforts to develop molten salt fuel cells with the result that today the Molten Carbonate Fuel Cell (MCFC) is an available technology in the power marketplace [13]. This interest has generated over the past two decades a copious amount of technical and scholarly literature focusing almost exclusively on the study of functional properties and performance of molten carbonates as MCFC electrolytes. Thus, apart from fuel cells, practical use of alkali molten carbonates is today confined in a few niche energy applications. For example, ternary mixtures of alkali carbonate salts, known under the Cartecsal™ trade name, are being used in the nuclear power industry for cleaning and processing of uranium-containing alloys [14,15].

Over the past years rising concerns over energy and environment are placing strong pressure for a process chemistry redesigned on more sustainable principles resulting in increased research activities for those technologies that have both the potential of lower energy consumption and environmentally benign properties. As a part of this broader sustainable scenario, interest for energy applications of MAC salts has begun to creep up again after decades of languishing research [16]. Very interestingly, the new emerging areas of storage and conversion of energy has opened up new directions for molten carbonate research not only as efficient, safe and sustainable reaction media, but also as component for the preparation of highly functional solid materials in advanced energy devices. For instance, carbonate-ion conducting solid electrolytes consisting of a molten carbonate phase and solid ceria oxide phase are today actively studied for hybrid high temperature fuel cell [17] and gas separation membrane applications [18].

Chemical and physico-chemical properties of MAC salts make them unique among the various classes of high temperature molten ionic systems based upon oxo-anion, halide or pseudo-halide salts in terms of safety, chemical stability and environmental benignity. Potential exists that a wider use of MAC salts can help to design more sustainable high temperature molten salt media and therefore explain, at least in part, the recent interest among researchers for the development of novel and sustainable molten salt processes specifically based on the use of MAC salts.

However, it is also felt that these long known properties of carbonate salts could not simply justify all the observed new research activities on these salts. A much more decisive factor is likely related to the vigorous recent development of renewable energy sources that could promote wide sustainability of MAC salt-based applications and technologies. In fact, the rather wide working temperature range of MAC salts, which stems from mild to moderate temperatures (500–800 °C), opens up the possibility of easy integration with solar-derived sources of electrical and thermal energy, thus offering a lot more options for a versatile design of MAC salt processes with expected strong reduction of energy intensity and environmental impact. At the same time, operations at such wide temperature range allows to potentially exploit a large spectrum of different chemical/electrochemical reactions, especially in conversion, storage and efficient use of energy technologies such as fuel cells, electrolysis, gas separation and clean-up, CO_2 chemical utilization and capture, material processing.

This paper is intended to be the first of a two-part paper series. General aspects of MAC salt chemistry and properties of relevance for use of molten carbonates as sustainable functional media will be highlighted in this work. A subsequent work (Part II) will focus on reviewing recent research published in energy applications of MAC salts, including research on advanced functional materials using molten carbonates as key component.

MAC salt properties and sustainability

This work will focus on chemical and physico-chemical properties of primary importance for a sustainable technological use of MAC salts. Comprehensive compilation of molten carbonate physical and physico-chemical properties can be found in Ref. [11].

Alkali molten carbonates are high temperature ionic salts with melting temperatures above 700 °C and boiling points exceeding 1300 °C. In general, MAC salt media are characterized by a suite of attractive properties such as high thermal and chemical stability, insignificant vapor pressure, high ionic conductivity and low metallic corrosiveness. Moreover, several properties including the acid-base chemistry can be finely tuned through slight change in temperature, gas atmosphere, alkali cation composition and special additive formulation [11]. Table 1 identifies major advantages (and also some limits) for a sustainable use of MAC salts as electrolyte or chemical reaction media. Some of these properties will be analyzed in more detail in the following paragraphs.

A general view on the potential of MAC salts as effective media for high temperature processes can be readily obtained

Please cite this article in press as: Frangini S, Masi A, Molten carbonates for advanced and sustainable energy applications: Part I. Revisiting molten carbonate properties from a sustainable viewpoint, International Journal of Hydrogen Energy (2016), http://dx.doi.org/10.1016/j.ijhydene.2015.12.073