

Why cesium doping improves the hydration of potassium carbonate as thermochemical storage material

Introduction

In the Paris Agreement from 2015 it is recognized that there is an urgent threat of climate change [1]. To meet the objective in the Paris Agreement a transition has to be made from a fossil fuel based society to a renewable energy based society. Renewable energy sources are inherently accompanied with fluctuations in supply and therefore storage is particularly crucial for large scale implementation of renewable energy. A major part of renewable energy is based on solar energy, which often offers its highest peak during periods of low demand i.e. high solar irradiation in summer and high heat demand in winter is an example of a mismatch in energy supply [2].

Focusing on the total energy consumption in Northern European countries, 41% can be contributed to the built environment. Of which the largest part can be contributed to thermal energy for residential purposes, making residential thermal energy consuming 25% of the total energy use [3]. So advancement in this specific sector may contribute significantly in the reduction of energy use.

A promising heat storage concept is based on thermo-chemical heat storage. Wherein sorption energy is used to store heat in a reversible chemical reaction. Sorption is defined as the fixation or capture of a gas or vapor (sorbate) by a solid or liquid (sorbent) [4]. A promising class of thermo-chemical materials are the salt hydrates, based on their high energy density. From an extensive review of 563 hydrate reactions, K_2CO_3 is selected as the most promising material for domestic heat storage based on the temperature operating window, stability, price and safety [5].

From a kinetics study as performed by Sögütöglü it is shown that close to equilibrium conditions hydration of K_2CO_3 is kinetically hindered and a hydration/dehydration reaction is only observed after an induction period [6]. This behavior is called metastable behavior and is caused by a nucleation energy barrier where surface energy has to be overcome to make a transition from a local minimum in free energy to a global minimum [7].

To overcome this meta-stable behavior and to improve kinetics in the whole range of operating conditions, doping is used to enhance the material performance. By doping is meant the introduction of small amounts of alien ions in the crystal structure of the base material. With the goal to promote nucleation and thereby improve kinetics of the base material potassium carbonate.

In this work potential doping candidates are selected based on ion substitution rules in ionic crystal structures. Taken into account a crystallization method from solution the selected dopants materials are the carbonates salts of group 1 elements Lithium, Sodium, Rubidium and Cesium. Further work focusses on the screening and characterization of the effect of the doping on the metastable behavior of potassium carbonate and on the effect on kinetics in general.

It is shown that Cesium doping has an effect on both the hydration and dehydration onset points., thereby reducing the meta-stable zone width and increasing the temperature operating window. Moreover the deliquescence onset point is shifted substantially to a lower RH. The dopant increases the kinetics also beyond the meta-stable zone and thereby decreasing the full conversion time significantly. It is shown that the doping effect is cyclic stable up to 80 cycles. Finally it is shown that the effect is caused by promoting the formation of a wetting layer which is a prerequisite for the phase transition.

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