



ScuDo

Scuola di Dottorato ~ Doctoral School

WHAT YOU ARE, TAKES YOU FAR



Doctoral Dissertation
Doctoral Program in Materials Science and Technology (32th Cycle)

Thermochemical energy storage with salt hydrate composites: from materials design to lab-scale reactor validation

Sergio Salviati

* * * * *

Supervisor
Prof. Alberto Fina

Summary

The development of improved heat management technologies is a mandatory step in the mitigation of greenhouse gases emissions. In particular, innovative Thermal Energy Storage (TES) systems can introduce significant improvements in energy production and usage. Already developed TES technologies include the storage of sensible heat in high thermal capacity materials (i.e. water) or the use of latent heat of phase change materials. Thermochemical energy storage is an innovative TES approach that focuses on the sorption/desorption reaction of a gas/solid system and inorganic salt hydrates are known as valuable candidates for the application of this technology. When these materials are heated, they produce water with a dehydration reaction. The salt is maintained dry by keeping it isolated from the environment, thus storing heat for a theoretically unlimited period. Heat is then delivered to the environment by rehydrating the material. The main advantages of this technology are i) a high energy storage density and ii) the possibility to trigger the energy release independently on ambient conditions, thus offering efficient solutions in applications such as seasonal storage in household and waste heat recovery in industrial processes. Since salt hydrates present limitations such as low cyclability, corrosivity, slow hydration/dehydration kinetics and low thermal conductivity, they may be enclosed in a porous matrix to form composite materials. These compounds are then included in thermochemical reactors, designed to fulfill the heating needs of a considered application.

In this PhD thesis, $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ and $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$ were selected after a careful literature screening and evaluated as thermochemical materials. While all of them were found suitable for thermochemical energy storage, only $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$ was exploited for the preparation of composites due to its fastest sorption and desorption rates and chemical stability up to at least 50 hydration/dehydration cycles. A wet impregnation process was used for materials preparation, using expanded graphite as porous conductive matrix, as well as including polyelectrolytes or cellulose nanofibers as binders. A decrease in the salt grains size on the graphite lamellae compared to state of the art salt/graphite composites was obtained, coupled with an energy storage density higher than expected due to the active contribution of the binders to the storage process. Freeze-drying procedure was also applied as an alternative preparation route, obtaining porous structures with sorption kinetic increased by 50% with respect to the pristine salt. Further studies on the binders' sorption/desorption reactions showed a strong effect of their concentration on performance. An optimal binder/graphite weight ratio of 0.5/1 was identified. Higher concentrations lead to hindrance phenomena in water mass transfer from the salt hydrate.

Composite powders were then pressed into tabs to obtain a modular and scalable design. The presence of hygroscopic binders resulted in an increase in sorption kinetics and mechanical stabilization compared to salt/graphite

composites. The tabs were also exploited in a lab scale open thermochemical reactor including a 0.3 l material bed, obtaining an output power in the range of a few tens of mW/g. Different closed reactors were also evaluated, comparing a state of the art system to a design in which evaporator and condenser are formed by two physically uncoupled surfaces, obtaining a better control on water condensation. A thermo-fluidodynamics model was also developed and validated on a closed reactor to predict heat and water mass transfer phenomena. Condensation surfaces can also be defined in the model with the identification of saturated humidity volumes.

Overall, this thesis evaluated the performance of salt/graphite/binder thermochemical materials and different reactor concepts, demonstrating the possibility of efficient improvements in thermochemical salt hydrates towards their application in heat storage systems.