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Developed materials for thermal energy storage: synthesis and characterization

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Abstract

Heat storage or thermal energy storage is one of the key technologies towards an efficient use of renewable energy resources, particularly the thermochemical heat storage looks promising, but the progress has not yet been succeeded. Therefore our research group focuses on the development of a heat storage system called “thermal battery” for private households and industry applications. On the one hand especially thermochemical reactions have a high potential for high energy density and long term storage. On the other hand the used materials in particular hygroscopic salts are related to disadvantages such as agglomeration, storage capacity loss over cycling or slow reaction kinetics. Those disadvantages are caused by deliquescence and by the occurrence of side reactions, among other effects. We combined the optimization of mixing of salt hydrates and impregnation of carriers to overcome these disadvantages. This paper reports on synthesis of thermochemical materials and comparison of the material properties energy density and effective thermal conductivity.

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Keywords: thermochemical heat storage, composites, mixtures, impregnation, water vapor pressure, thermal conductivity

1. Introduction

Thermal energy storage is one of the key technologies towards an efficient use of renewable energy resources. Hereby thermochemical heat storage promises higher storage density as sensible or phase change heat storage. Based on reversible chemical reactions long term storage becomes possible. Many challenges are associated with potential thermochemical heat storage materials. Hygroscopic salt hydrates have a high kinetic water uptake but tend to agglomeration. This deliquescence reduces the water uptake rate and cycle stability of the storage material. In order to overcome this disadvantage many studies have

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been performed.[1] The Impregnation of the salt hydrates into porous matrices prevented deliquescence and improved the diffusion of water vapor into the material.[2] The Controlling of the water vapor access into the material prevents in micro scale the deliquescence, too.[IRES2012] However, this procedure is not manageable in macro scale because of the heterogenic reactions occurring in the storage bulk. Salt mixtures of metal chlorides and sulfates showed high cycle stability beside deliquescence.[1] This paper reports on the synthesis of thermochemical materials and the comparison of the material properties energy density and effective thermal conductivity.

Nomenclature

| | |
|------|-------------------------------------|
| ACF | activated carbon foam |
| ENGB | compacted expanded natural graphite |
| ENGP | expanded natural graphite powder |

2. Experiments

Hydration levels of used pure salts were confirmed by TGA – measurements.

2.1. Sample preparation

Salt-porous-carrier composites were synthesized by impregnating host matrices with molten salt (soaking) and a saturated aqueous salt solution (wet impregnation) under vacuum (10 mbar) and at atmospheric pressure. The impregnation time varied between seconds and minutes. For all experiments anhydrous CaCl_2 (AppliChem Company), $\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$ (AppliChem Company) and KCl (Merck) were used. The host matrices activated carbon foam media ACF (Blücher GmbH), compacted expanded natural graphite ENGB (SGL Group) and expanded natural graphite powder ENGP (SGL Group) were first preheated to remove residual water and then impregnated and finally dried. The mixed salts of CaCl_2 and KCl were crystallized from a solution of their basic salt components in pure water. The mixing ratios depend on the compound expected to form and are calculated by molecular weight of the involved salts.

2.2. TGA/DSC –Measurements

Thermogravimetric analysis and heat flux measurement was performed using a simultaneous TGA/DSC 1 device from Mettler Toledo to investigate the water sorption properties and the long-term thermal stability of the host matrices upon modification. The gas flow was controlled by a gas box, providing 2 independent mass flow controllers connected to the TGA/DSC control. We used silica gel-dried nitrogen as purge gas at a flow rate of 50 mL/min. In addition to the purge gas flow, we used a separate nitrogen flow, humidified via a tempered gas bubbler flask as the reaction gas during hydration. The hydration measurements were done at 25 °C at a water vapor pressure of 20 mbar. The dehydration was done with a heating rate of 3 K/min up to 200 °C at atmospheric pressure. Salt mixtures were measured with a heating rate of 5 K/min in two steps up to 200 °C. The mass of samples were 10 - 20 mg. Integration of the hydration heat fluxes over time was done manually using the Mettler Toledo STARE Software 11.00a.

2.3. Thermal conductivity measurements

First of all thermal conductivity of salt samples was measured in the range of 100 °C to 200 °C with 50 mL/min nitrogen flow and bed thermal conductivity was calculated using the calorimetric method [3]. The heating rate of 10 °C/min has been chosen because of the results according to the literature or provider data. Heat conductivity enhancement is clearly shown in the following table.

3. Results and discussion

The pure calcium chloride shows higher release of water as uptake, caused in the mentioned delinquency behaviour. (Table 1) The mixing of calcium chloride and potassium chloride gave a heterogeneous picture. The salt mixtures showed completeness rehydration depending on the amount of calcium chloride. The measurements of the reaction enthalpies the results of enthalpy were not clear. Results show that the impregnation success is related to the host matrix and the impregnating medium. The composite based on ACF has with 63 wt-% the lowest salt content in comparison to the samples with ENGB and ENGP as host matrices (Table 1). Due to its open pore structure ACF tends to lose calcium chloride during impregnation and drying. Expanded natural graphite impregnated with molten salt (Ca-ENGB-S, Ca-ENGB-S1) have a slightly higher salt content than those impregnated with aqueous salt solutions (Ca-ENGB-W, Ca-ENGP-W). All samples show good water sorption behaviour, Ca-ENGP-W has a more stable water sorption behaviour than the other composites. In general the water uptake is about 30-40 % higher than the water release. Despite a high salt content of 90 wt-%, samples impregnated with molten salts have a lower water sorption than those impregnated with an aqueous salt solution. The more salt is confined to the matrix surface and into the matrix pores the lower is the diffusivity of the water vapour during hydration and dehydration due to partial pore blocking and thus the total energy density of the composite is decreased.

Table 1. Water release and uptake – mass and enthalpy (ACF and ENG showed no sorption properties)

| Material | Water release | | Water uptake | |
|---------------------------|---------------|-------|--------------|-------|
| | (g/g) | (J/g) | (g/g) | (J/g) |
| CaCl ₂ | 0.71 | 2203 | 0.62 | 1375 |
| KCl | 0.02 | -* | 0.01 | -* |
| KCl + 2 CaCl ₂ | 0.69 | 1302 | 0.70 | 1260 |
| KCl + CaCl ₂ | 0.45 | 1111 | 0.49 | 1572 |
| 2 KCl + CaCl ₂ | 0.42 | 838 | 0.52 | 969 |
| Ca-ENGB-W | 0.35 | 1038 | 0.50 | 1397 |
| Ca-ACF-S | 0.16 | 701 | 0.24 | 645 |
| Ca-ENGB-S | 0.29 | 910 | 0.44 | 1222 |
| Ca-ENGB-S1 | 0.27 | 624 | 0.44 | 1160 |
| Ca-ENGP-W | 0.45 | 1268 | 0.50 | 613 |

The impregnation of calcium chloride in ACF or ENG improved the heat conductivity. Different impregnation ratios of calcium chloride and ENG or ACF were synthesized. Impregnated samples with higher amount of calcium chloride showed less heat conductivity as samples with less amount of calcium chloride (Table 2).

Table 2. Thermal conductivity measurements using DSC

| Materials | Mass | Bulk | Specific | Thermal | Literature values of thermal conductivity |
|-----------|------|------|----------|---------|---|
|-----------|------|------|----------|---------|---|

| | (mg) | density (kg/m ³) | energy (J/g) | conductivity (W/m·K) | (W/m·K) |
|----------------------------|------|---------------------------------|-----------------|-------------------------|--|
| ACF | 53.7 | 537 | 3.8 | 0.55 | 0.15 – 0.5 [4]; 0.36 [6] |
| ENG | 2.3 | 23 | 93.8 | 4.78 | 3 – 10 [5] |
| CaCl ₂ | 49.7 | 497 | 2.5 | 0.54 | 0.1 – 0.5 [3] [7] |
| ACF-CaCl ₂ -V | 64.9 | 649 | 2.7 | 1.03 | n.a. |
| ENG-CaCl ₂ -1:1 | 8.5 | 85 | 21.1 | 1.64 | 1.7 (d=550Kg/m ³); 1.66 (d=450Kg/m ³) [6] |
| ENG-CaCl ₂ -1:2 | 4.6 | 46 | 35.7 | 0.74 | 1.51 (d=550Kg/m ³); 1.23 (d=450Kg/m ³) [6] |

4. Conclusion

We have showed new results of our experiments of mixing calcium chloride with potassium chloride and impregnation of calcium chloride in matrices as ACF or ENG. The synthesized composites showed improved dehydration and hydration behavior, and heat conductivity. We will use the modified salt mixture to impregnate porous materials to obtain a stable thermochemical storage material with high energy density. Further we will focus on the development of better mixing methods to create salt hydrate mixtures of other salt hydrates too.

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