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Contract TE 95/2018

Nanoconfinement in mesoporous Silica: Towards next generation Energy storage Materials (STEMA)

Director: Dr. Raul-Augustin MITRAN

02/05/2018 - 30/04/2020

Summary:

The most promising "green" energy generation and storage technology which can economically replace coal and gas at scale is concentrated solar power (CSP). The STEMA project aims to increase the heat storage capacity for this technology with ~50% by developing new solid, shape-stabilized phase change materials through the nanoconfinement of molten salts (such as alkali nitrates and halides) in mesoporous silica matrices. This innovative approach is based on a concept demonstrated by the project team in 2015, involving the maximization of the weight fraction of the active heat storage component through impregnation inside the silica mesopores and in the interparticle spaces, while yielding shape-stability (preservation of macroscopic solid form upon active component phase transition) through capillary forces. The project aims at laboratory demonstration of a novel material with 220J/g heat storage over 100 °C range, an increase of ~50% over state-of-the-art. In contrast with current approaches based only on sensible heat storage, this project will utilize both latent and sensible heat storage mechanisms, increasing the storage capacity and operating temperature range which will yield increased efficiencies and decreased cost per kWh for CSP. Fundamental research pertaining to this promising research field will also be carried out, with the aims of investigating the physico-chemical processes taking place upon molten salt nanoconfinement (adsorption/desorption, crystallization, stability and chemical reactions).

The project proposes a multidisciplinary approach and aims to consolidate the research team position as a leader in the field of shape-stabilized phase change materials with high storage potential, based on nanoconfinement effects. Furthermore, the project activities are aimed at both applicative and fundament research, increasing the team international visibility and capacity for further collaborative projects with industry and academia.

Main objective

The main objective of the STEMA project is the establishment of a young, independent research team focused on the nanoconfinement of molten salts and other high temperature energy storage substances inside mesoporous silica for thermal energy storage applications. Specifically, the project aims at investigating both fundamental and applicative aspects pertaining to the synthesis and application of composite phase change materials for high temperature thermal energy storage using mesoporous silica matrices.

Team

Project director: Raul-Augustin Mitran

Members:
Mihaela Deaconu
Cristina-Maria Vladut
Ana Maria Brezoiu
Lucian Buhălţeanu
Jeanina Pandele Cusu
Oana Cătălina Mocioiu
Daniela Cristina Culita

Budget

No.	Category	2018	2019	2020	*Total*
1	Personnel	64.050,00	96.075,00	32.025,00	*192.150,00*
2	Logistics	43.950,00	126.400,00	20.000,00	*190.350,00*
	2.1. Equipments	16.000,00	111.100,00	4.750,00	*131.850,00*
	2.2. Consumables	22.450,00	10.000,00	14.050,00	*46.500,00*
	2.3. Subcontracting	5.500,00	5.300,00	1.200,00	*12.000,00*
3	Travel	4.500,00	22.500,00	0,00	*27.000,00*
4	Indirect costs	13.500,00	20.000,00	7.000,00	*40.500,00*
5	**Total**	**126.000,00**	**264.975,00**	**59.025,00**	***450.000,00***

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Stage 1 : Fundamental study of molten salts nanoconfinement inside mesoporous silica

The goal of this stage was carrying out fundamental research pertaining to molten salt nanoconfinement. The activities were aimed at obtaining suitable mesoporous silica matrices with different textural parameters, testing the molten salt adsorption and desorption from these matrices and studying the crystallization process under nanoconfinement.

Stage 1 results consists of :

a) Obtaining a mesoporous silica library with 13 materials having different pore size, shape, volume and arrangement. The pore diameter was varied from **6 to 35 nm**, while the pore volume was varied between **0.8 – 2.4 cm^3/g**. Furthermore, Al doping of the silica matrix was investigated.

b) Testing 3 salt adsorption methods: melt impregnation, incipient wetness impregnation and solution adsorption.

c) Studying the molten salt desorption from the mesoporous silica-salt composites. Salt desorption and degradation can greatly affect the lifetime of composite PCMs. The salt behavior at elevated temperature as well as in contact with water was investigated.

d) Molten salt-mesoporous silica composite synthesis and crystallization under nanoconfinement study. 21 composites were obtained and characterized. The nanoconfined salt phase shows reduced melting point in comparison with the bulk phase. Both nitrate - and halide – based salts were employed.

Stage 2 : DT-PCMs technology concept formulation

The goal of this stage was formulating the dual thermal response phase change material concept through applicative research. The activities were aimed at establishing a matrix structure – composite thermal properties theoretical model, followed by optimization of the matrix and composite synthesis and testing of the materials properties.

Stage 2 results consists of :

a) Obtaining a structure-properties model which links the mesoporous silica properties (pore diameter and pore size) and molten salt parameters (thickness of non-melting layer) to the resulting DT-PCMs thermal properties (melting point, nanoconfined phase enthalpy, total enthalpy). A methodology for constructing this model was proposed and investigated.

b) Optimization of mesoporous silica synthesis was carried out in order to obtain matrices with total pore volume of at leas 1 cm^3/g and pore diameters of at least 10 nm. Two classes of mesoporous materials were investigated and optimized, yielding **6 matrices** with the desired properties.

c) Optimization of molten salt adsorption was carried out by variation of different process parameters (concentration, volume, impregnation method etc.) The best method was then employed to obtain **4 DT-PCMs** containing the optimized silica matrices.

d) The thermal storage properties of the optimized materials were tested. The best results show a latent total heat storage of **~180 J/g** as well as good sensible heat storage (specific heat of **0.74 ± 0.07 J/gK and 1.13 ± 0.15 J/gK**, before and after melting of the active heat storage phase, respectively).

Stage 3 : Achieving TRL 2 for DT-PCMs

The goal of this stage was reaching TRL 2 for the dual thermal response phase change materials. The activities were aimed at optimization of the PCM composite, multi-gram synthesis and establishing the relevant thermal and process properties.

Stage 3 results consists of :

a) Optimization of the phase change materials was carried out with respect to the amount of heat storage phase and shape-stability at temperatures above the salt melting point. The maximum molten salt amount was experimentally optimized at 92.5% wt.

b) Multi-gram (10g) synthesis of the optimized material was carried twice. A maximum yield of 92.4 %.

c) The thermal storage properties of the optimized materials were tested. The best results show a latent total heat storage of **171.5 ± 10.7 (J/g)**. The specific heat capacity, thermal stability, stability under repeated thermal cycles was also investigated. The optimized DT-PCM is stable up to 670 °C and it has a heat storage capacity of **241.7 ± 5.6 J/g** over a 100 °C temperature range and s total heat storage capacity of **548.2 ± 22.8 J/g**.

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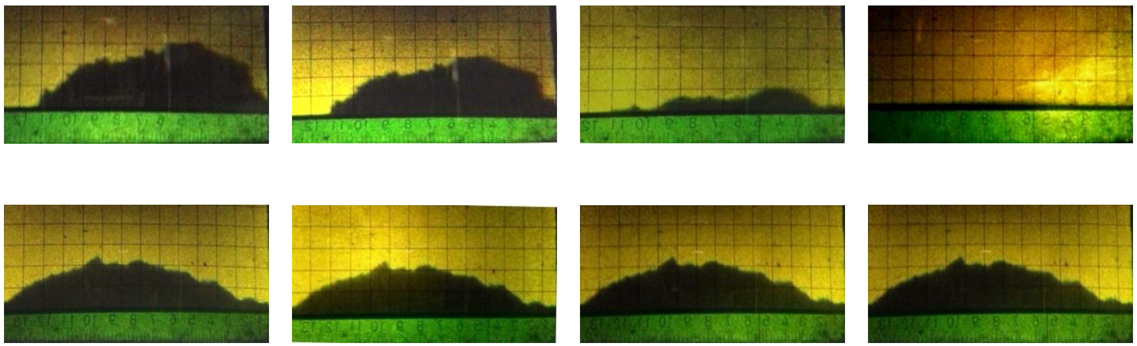
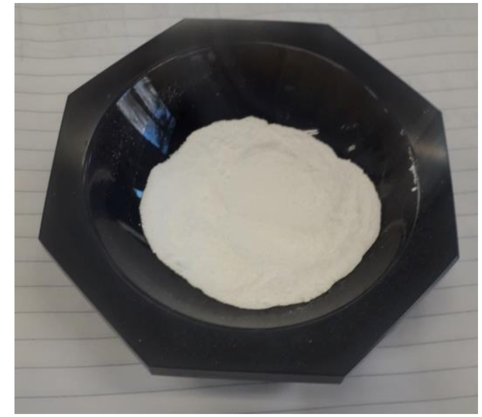
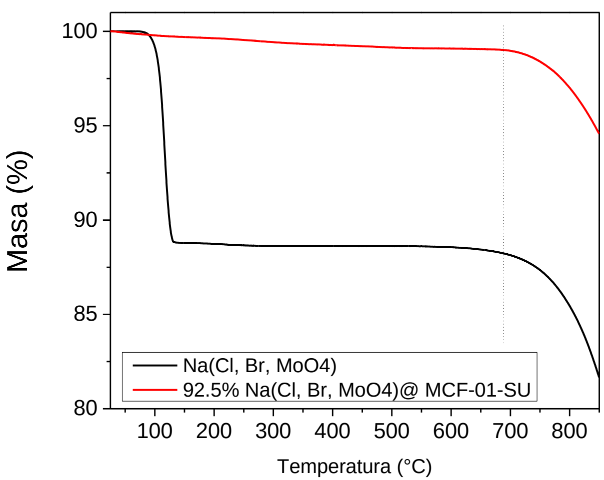
Stage 3 : Selected results

	25 °C	450 °C	525 °C	600 °C
Molten salt				
90% Molten salt & 10% MSN				

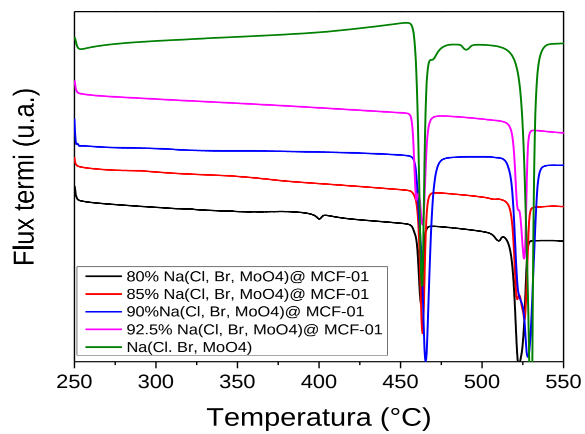




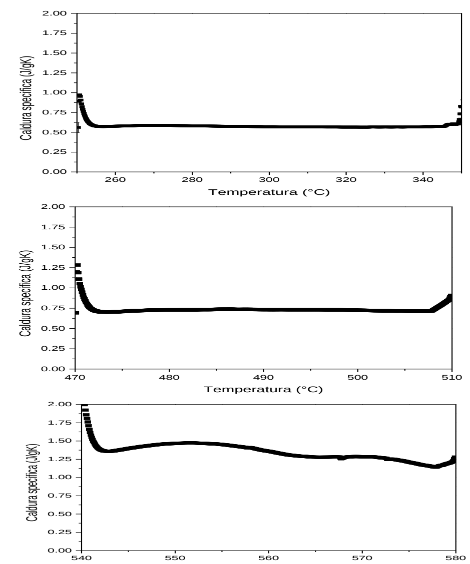
10 g synthesis of optimized PCM



High thermal stability



High latent heat & dual thermal response



Good sensible heat storage

Results - ISI articles published / accepted for publication during the project:

1. Raul - Augustin Mitran*, Daniela Berger, Cristian Matei - Phase Change Materials Based On Mesoporous Silica, Current Organic Chemistry, 22 (2018) 2644-2663, DOI: 10.2174/1385272822666180827125651 (**Impact factor = 2.193**)
2. R.-A. Mitran*, S. Petrescu, S. Şomăcescu, O.C. Mocioiu, L. Buhălţeanu, D. Berger, C. Matei, Nanocomposite phase change materials based on NaCl–CaCl2 and mesoporous silica, Journal of Thermal Analysis and Calorimetry, 138 (2019) 2555-2563. DOI: 10.1007/s10973-019-08489-x (**Impact factor = 2.731**)
3. C. Matei, L. Buhălţeanu, D. Berger, R.-A. Mitran*, Functionalized mesoporous silica as matrix for shape-stabilized phase change materials, International Journal of Heat and Mass Transfer, 144 (2019) 118699. DOI: 10.1016/j.ijheatmasstransfer.2019.118699 (**Impact factor = 4.947**)
4. R.-A. Mitran*, D. Lincu, L. Buhălţeanu, D. Berger, C. Matei, Shape-stabilized phase change materials using molten $NaNO_3$ – KNO_3 eutectic and mesoporous silica matrices, Solar Energy Materials & Solar Cells 215 (2020) 110644. DOI:10.1016/j.solmat.2020.110644 (**Impact factor= 6.984**)
5. R.-A. Mitran*, D.C. Culita, I. Atkinson, Thermal stability enhancement of mesoporous SBA-15 silica through nanoconfinement of ceria nanoparticles, Microporous and Mesoporous Materials, 306 (2020) 110484. DOI: 10.1016/j.micromeso.2020.110484 (**Impact factor= 4.551**)

6. R.-A. Mitran*, D. Lincu, S. Ioniţă, M. Deaconu, V.V. Jerca, D. Berger, C. Matei, High temperature shape – stabilized phase change materials obtained using mesoporous silica and NaCl – NaBr – Na_2MoO_4 salt eutectic, Solar Energy Materials & Solar Cells (2020) (**Impact factor= 6.984**) *accepted for publication*

Results

Patent applications:

1. Raul - Augustin Mitran, "Nanocomposite materials for thermal energy storage at high temperatures containing mesoporous silica and inorganic salts"(„Materiale nanocompozite pentru stocarea energiei termice la temperaturi ridicate ce conţin de silice mezoporoasă şi săruri anorganice”), OSIM, 133504, 30.07.2019

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Results

International conference presentations:

1.Raul-Augustin MITRAN, Oana Cătălina MOCIOIU, Jeanina PANDELE-CUŞU, Lucian BUHĂLȚEANU, Simona PETRESCU - Nanocomposite phase change materials using mesoporous silica for elevated temperature applications, 12th European Symposium on Thermal Analysis and Calorimetry (ESTAC12), Brasov, Romania, 27-30 Aug. 2018 (http://estac12.org/estac12/topics.html)

2. Raul-Augustin MITRAN, Breaking the wall of solar energy storage, Falling Walls Lab Romania, Cluj-Napoca, Romania, 8 Jun. 2018 (https://www.falling-walls.com/lab)

3. R.A. Mitran, D. Lincu, S. Ioniţă, D. Berger, C. Matei, Composite phase change materials containing molten Li-Na-K nitrates and mesoporous silica",9th International Conference of the Chemical Societies of the South-East European Countries , Targoviste, Romania, 8-11 May 2019 (http://events.icstm.ro/index.php/ICOSECS/9)

4. R.A. Mitran, D. Lincu, V.V. Jerca, D. Berger, C. Matei, High Temperature Nanocomposite Phase Change Materials Containing Mesoporous Silica Matrices, 15th International Symposium "Priorities of Chemistry for a Sustainable Development - PRIOCHEM", Bucharest, Romania, 30.10 - 1.11. 2019. (http://priochem.icechim.ro/en_index)

5. R.A. Mitran, D. Lincu, S. Ioniţă, D. Berger, C. Matei, "Nanocomposite phase change materials using molten salts and mesoporous silica matrices", 21st Romanian International Conference on Chemistry and Chemical Engineering, Constanta, Romania, 4-7 September 2019. (http://riccce21.chimie.upb.ro/)