PN-III-P1-1.1-TE-2019-1456

Contract TE 166/2020

Metal-ceramic nanocomposites: next-generation thermal energy storage materials (MOST)

Director: Dr. Raul-Augustin MITRAN

01/11/2020 - 31/10/2022

Summary:

Currently, the only “green” technology which can replace polluting coal or gas power plants for continuous energy generation is Concentrated Solar Power. This can be coupled with thermal energy storage, typically using molten salts. However these materials have limited operating temperature range, leading to decreased plant efficiency. The MOST project aims to study innovative metal – porous ceramic composites for high temperature energy storage. The materials will act as shape-stabilized phase-change materials (PCM), using both latent and sensible heat storage. Latent heat storage at elevated temperatures improves the heat to electricity conversion efficiency, yielding lower cost per kWh. This approach is based on a concept demonstrated by the team in 2015, involving the maximization of heat storage agent through nanoconfinement into porous oxide matrices. The projects aims at both fundamental studies of metal/semi-metal nanoconfinement into porous inorganic matrices and applicative research aiming to increase the TRL of these materials to at least 2. A laboratory demonstration of gram-scale synthesis of a nanocomposite PCM with at least 50% wt. metal and shape-stability will be carried out.

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 for elevated temperatures (>200 °C), based on nanoconfinement effects. Furthermore, the project activities are aimed at both applicative and fundamental research, increasing the team international visibility and capacity for further collaborative projects with industry and academia, as well as addressing the important challenge of mitigating anthropogenic carbon emissions associated with energy generation..

Main objective

The main objective of the project is the establishment of a young, independent research team focused on the nanoconfinement of elemental phase change materials (PCMs) inside porous inorganic matrices such as porous alumina and silica for thermal energy storage applications. Keeping in line with the European Research Council's mission, the proposed theme is a frontier research activity, containing both fundamental and applicative research elements. The goal of the applicative project part is establishing all relevant aspects pertaining to the laboratory synthesis and demonstration of PCMs using metals and/or semi-metals as the active heat storage component. A Technology Readiness Level (TRL) of 2 for this class of materials will be also attained. The goal of the fundamental research is to investigate the physico-chemical processes specific to the nanoconfinement of elemental PCMs inside porous oxide matrices.

Team

Raul-Augustin Mitran
Mihaela Deaconu
Cristina-Maria Vladut
Ana Maria Brezoiu
Simona Ionita
Daniel Lincu
Bogdan Trica
Jeanina Cusu Pandele

Budget

No.	**Category**	**2020**	**2021**	**2022**	***Total***
1	Personnel	20000	57150	47621	*124771*
2	Logistics	23120	216128	13874	*253122*
	2.1. Capital	0	191956	0	*191956*
	2.2. Consumables	22600	18368	13000	*53968*
	2.3. Subcontracting	520	5804	874	*7198*
3	Travel	0	3839	11517	*15356*
4	Indirect costs	8500	15800	14351	*38651*
5	**Total**	**51620**	**292917**	**87363**	***431900***

Stage 1 : Initial studies on obtaining metal – oxide nanocomposites

The goal of this stage was investigating the possibility of obtaining metal – oxide nanocomposites starting from porous oxide matrices. To this end, a library of 10 mesoporous titania – silica (TiO_2 – SiO_2) matrices as well as 1 alumina (Al2O3) matrix were obtained and characterized. The possibility of adsorbing a metal salt followed by reduction was also investigated.

Stage 1 results consists of :

a) Obtaining a mesoporous oxide library with 11 materials having different pore size, shape, volume and arrangement.

b) Studying the adsorption and reduction of a metal salt with the goal of obtaining metal – oxide nanocomposites which could act as heat storage materials.

Stage 2 : Fundamental studies on metal – oxide nanocomposites

The goal of this stage was to systematically investigate synthesis conditions and the resulting properties of various metal – oxide systems. Three types of synthesis strategies were investigated: - the impregnation of metal salt precursors followed by reduction through various methods, the direct synthesis of metal – oxide composites and metal impregnation into porous oxide matrices. The nanoconfinement effects on the thermal energy storage properties of the nanomaterials was also investigated.

Stage 2 results consists of :

a) Obtaining 20 nanocomposites (impregnation/reduction) through 4 reduction methods.
b) The synthesis of 20 nanocomposites through direct synthesis with 3 types of oxide matrices (alumina, silica, zinc oxide)
c) The study of 10 impregnation syntheses.
d) Physico-chemical characterization and model of the nanoconfinement effects on the thermal properties of the materials.

Stage 3 : Optimization of metal-oxide PCMs

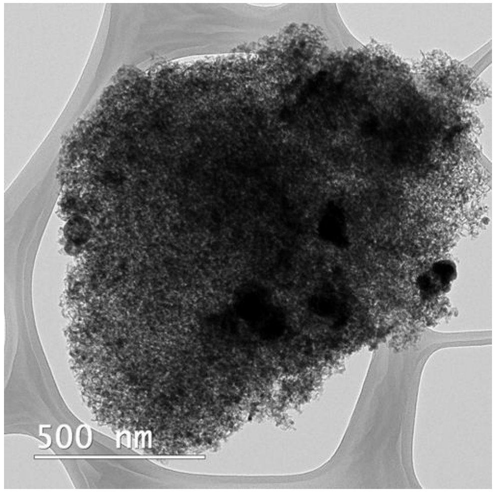
The goal of this stage was to optimize two synthesis pathways for obtaining metal-oxide PCMs. Both mesoporous silica – bismuth and zinc oxide – bismuth systems were studied and the synthesis conditions were optimized in terms of thermal energy storage properties. A multi-gram (~5 g) scale-up of the first optimized system was carried out.

Stage 3 results consists of :

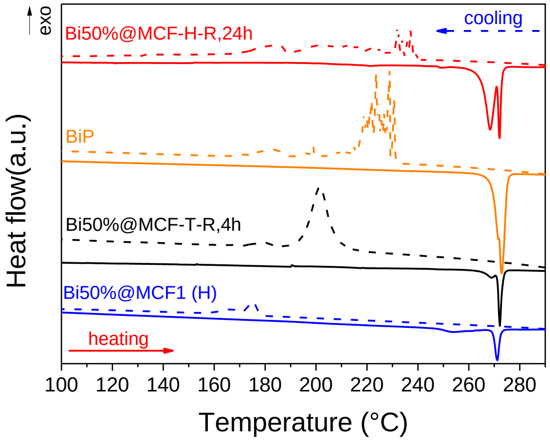
a) 2 Synthesis methods optimized (mesoporous silica/bismuth and zinc oxide/bismuth PCMS).

b) A structure – thermal properties model was developed.

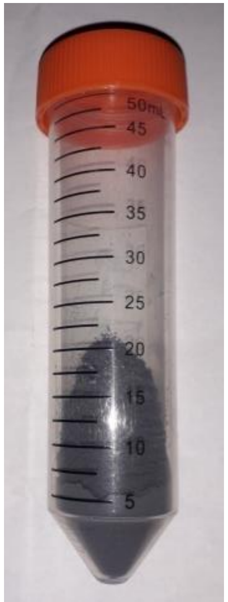
c) A multi-gram PCM containing 50% wt. metal was obtained.(TRL 2 stage achieved)



TEM analysis of silica-metal PCMs



DSC analyses



Scaled-up sample

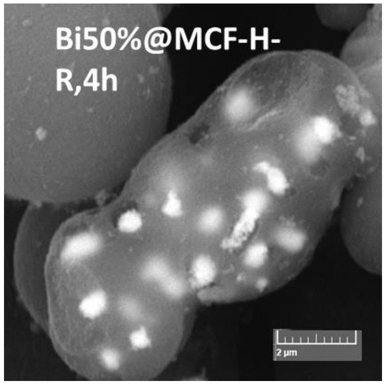
UEFISCDI INNOVATION AND CREATIVITY
EXECUTIVE AGENCY FOR HIGHER EDUCATION, RESEARCH, DEVELOPMENT AND INNOVATION FUNDING

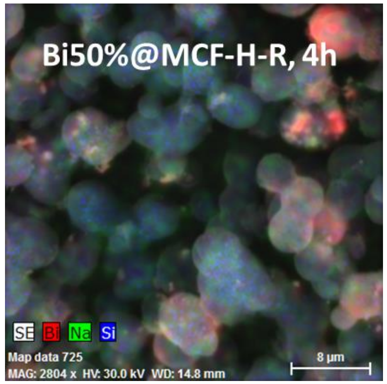
MINISTERUL EDUCAȚIEI ȘI CERCETĂRII ȘTIINȚIFICE

ACADEMIA ROMANA - INSTITUTUL DE CHIMIE FIZICA ILIE MURGULESCU

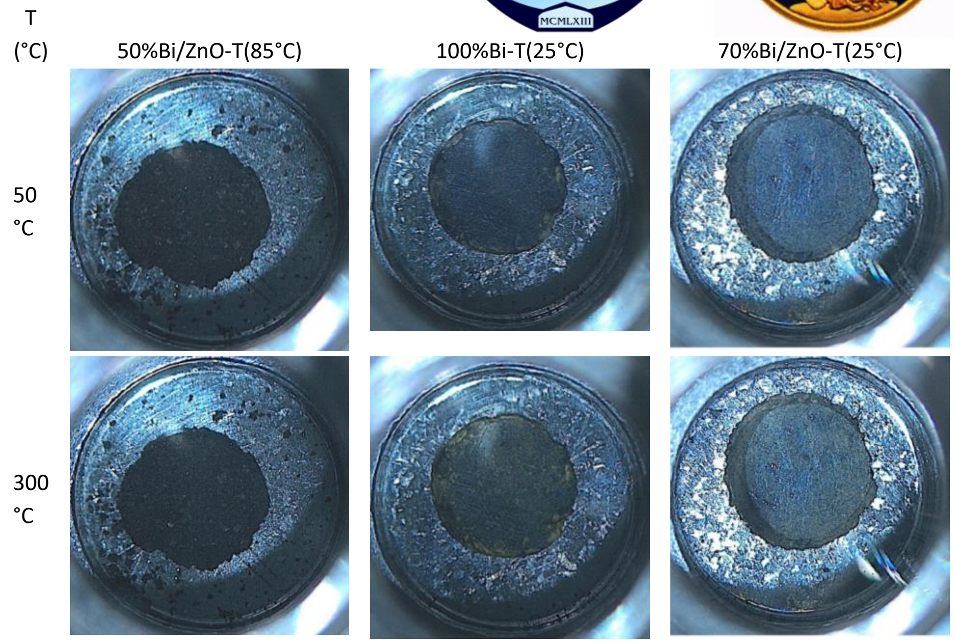
ACADEMIA ROMANA

Representative results

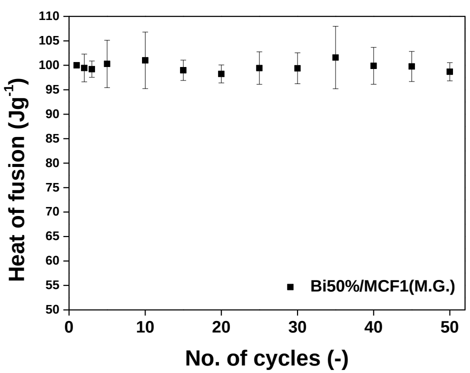




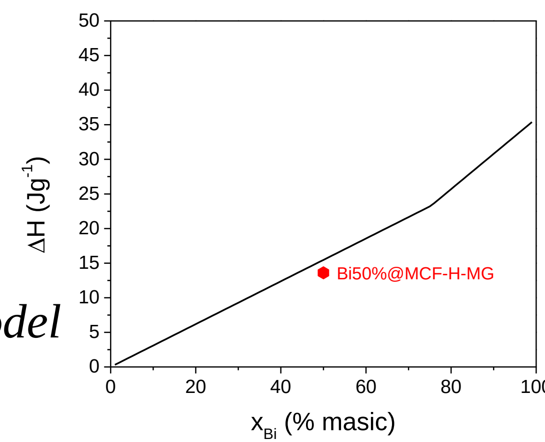
SEM analysis showing the nanoconfined Bi particles (white spots) inside the silica matrix (left) and elemental distribution (right)



Optical microscopy coupled with DSC showing the shape stability above the metal melting point for zinc oxide/ metal PCMs



Thermal reliability of the scaled-up sample



Structure thermal properties model results versus scaled-up sample

Results – published ISI articles

1. 1. R.-A. Mitran, S. Ioniţă, D. Lincu, D. Berger, C. Matei, A Review of Composite Phase Change Materials Based on Porous Silica Nanomaterials for Latent Heat Storage Applications, Molecules, 26 (2021) 241. (Impact factor= 4.927)
2. 2. D. Lincu, S. Ioniţă, O.C. Mocioiu, D. Berger, C. Matei, R.A. Mitran, Aluminum doping of mesoporous silica as a promising strategy for increasing the energy storage of shape stabilized phase change materials containing molten $NaNO_3$: KNO_3 eutectic mixture, Journal of Energy Storage, 49 (2022) 104188. (Impact factor = 8.907)
3. 3. R.-A. Mitran, D. Lincu, D. Berger, C. Matei, FDU-12 cubic mesoporous silica as matrix for phase change materials using bismuth or stearic acid, Journal of Thermal Analysis and Calorimetry, (2022) DOI: 10.1007/s10973-022-11588-x. (Impact factor = 4.755)

ISI article accepted for publication

4. Daniel LINCU, Simona IONIŢĂ, Bogdan TRICĂ, Daniela C. CULITA, Cristian MATEI, Daniela BERGER, Raul-Augustin MITRAN, Bismuth-mesoporous silica-based phase change materials for thermal energy storage, Applied Materials Today, (2022) accepted for publication (Factor impact = 8.663).

National patent applications:

1. D.F. Lincu, R.A. Mitran, “Materiale nanocomposite metal-oxid mezoporos pentru stocarea energiei termice la temperature ridicate” (“Nanocomposite metal-oxide materials for high temperature thermal energy storage”), OSIM 135118 A0, 30.07.2021.

EXECUTIVE AGENCY FOR HIGHER EDUCATION, RESEARCH, DEVELOPMENT AND INNOVATION FUNDING

MINISTERUL EDUCAȚIEI ȘI CERCETĂRII ȘTIINȚIFICE

Results – Invited/Keynote conference presentations

1. R.A. Mitran, Thermal Energy Storage Nanomaterials Based on Mesoporous Silica Matrices, 23rd International Conference "New Cryogenic and Isotope Technologies for Energy and Environment" EnergEn 2021 , Băile Govora, Romania, 27-29.10.2021.

Conference presentations :

2. Daniel Lincu, Raul-Augustin Mitran, Simona Ioniță, Mihaela Deaconu, Cristian Matei, Daniela Berger, Mesoporous silica-based phase change materials for thermal energy storage, 17th International Symposium "Priorities of Chemistry for a Sustainable Development", PRIOCHEM, 27-29. 10.2021, Bucuresti, România
3. Daniel Lincu, Simona Ionită, Mihaela Deaconu, Ana Maria Brezoiu, Raul Augustin Mitran, Cristian Matei, Daniela Berger, Phase change materials based on porous silica, The Fourtenth Conference for Young Scientists in Ceramics, 20-23.10.2021, Novi Sad, Serbia.
4. Raul-Augustin Mitran, Daniel Lincu, Simona Ioniţă, Daniela Berger, Cristian Matei, Stocarea energiei termice la temperaturi ridicate folosind nanocompozite pe bază de silice mezoporoasă, Conferinţa Cercetării Științifice din Academia Română (CCSAR-2021), 22-23 noiembrie 2021, Bucureşti, România.
5. Daniel Lincu, Raul-Augustin Mitran, Simona Ioniță, Mihaela Deaconu, Florica Papa, Cristian Matei, Daniela Berger, Mesoporous Silica–Metal Composites for Thermal Energy Storage, 20th International Balkan Workshop on Applied Physics and Materials Science, IBWAP 2022, 12-15. 07.2022, Constanţa, România
6. Cristina Vladut, Daniel Lincu, Daniela Berger, Bogdan Trica, Cristian Matei, Raul-Augustin Mitran, Molten metal – zinc oxide composites for high temperature thermal energy storage, Ceramics in Europe 2022, 10-14.07.2022, Cracovia, Polonia