Proceedings of the 15th International Green Energy Conference IGEC2023-321~326 (invited) July 10-13, 2023, Glasgow, UK

Special Session: Advances in green refrigeration and cold storage technologies

Session Description:

Global climate change and emissions are tightly intertwined. Our last decade was the warmest on record, and we are all aware by now of our need to reduce human activity-related emissions to slow global warming. Unfortunately, warming has increased Europe's reliance on cooling. This has resulted in its emergence to the forefront of areas targeted for decarbonisation. This special session is organized by the CO-COOL consortium is a large international collaboration aiming to develop improved cooling technologies that leverage either renewable electricity/heat or waste heat to keep people and spaces cool without warming our planet. This special session is devoted to the latest development and R&D achievements in the topic of green refrigeration and cold storage, with particular interests in composite sorbents and composite phase materials for cooling energy conversion and cold storage.

Session Organizer(s):



Yongliang Li (University of Birmingham, UK)



Vincenza Brancato (ITAE-CNR, Italy)

Session Contents:

- Topic 1: DEVELOPMENT AND CHARACTERIZATIONS OF SALT HYDRATES BASED COMPOSITES FOR ADSORPTION COOLING
- Topic 2: FORMSTABLE PHASE CHANGE MATERIALS BASED ON HYBRID SALT HYDRATES FOR COLD STORAGE
- Topic 3: INNOVATIVE STRATEGIES FOR MATERIALS DEVELOPMENT FOR LOW-TEMPERATURE THERMOCHEMICAL ENERGY STORAGE
- Topic 4: AGING ISSUES ON NOVEL COMPOSITE MATERIALS FOR LOW TEMPERATURE THERMOCHEMICAL ENERGY STORAGE APPLICATIONS
- Topic 5: NANOCONFINED SALT IN ANISTROPIC GRAPHENE AEROGEL MATRIX FOR THERMOCHEICAL ENERGY STORAGE
- Topic 6: DYNAMICS OF WATER VAPOUR ADSORPTION FOR HEAT CONVERSION SYSTEMS: COMPARATIVE STUDY OF LOOSE ADSORBENTS GRAINS AND CONSOLIDATED LAYERS

Topic 1: DEVELOPMENT AND CHARACTERIZATIONS OF SALT HYDRATES BASED COMPOSITES FOR ADSORPTION COOLING

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Abstract: In this study, various types of composites were synthesized and studied for the selection the best candidate for cooling applications. Mesoporous silica gel (SG) and macroporous vermiculite (VERM) were chosen as the matrices, while LiCl, CaCl₂, K₂CO₃ were used as the enclosed salts. Dry impregnation method was employed to develop the composites. The developed composites include SG-25%CaCl₂, SG-30%CaCl₂, VERM-45%LiCl, SG-30%LiCl, VERM-35%K₂CO₃.

Isotherm adsorption at 30, 40 and 50°C and isobaric adsorption at 1.71 kPa and 2.34 kPa were measured using DVS instrument. It was found that almost all the composites experience three adsorption stages- physisorption, chemisorption and liquid absorption, which can be reflected by the platforms on the adsorption isotherms and isobars. Generally, the water uptake amount increases with increasing vapor pressure and salt content and decreasing the temperature. The obtained results were further used to obtain the parameters for the D-A (Dubinin – Astakhov) equation which can describe a temperature independent characteristic curve both for adsorption and for desorption.

To have a thorough investigation of the adsorbent material behavior and to evaluate the adsorption heat in various operating conditions, several experiments were carried out by a thermogravimetricdifferential scanning calorimetry, modified to be operated under pure water vapor atmosphere and equipped with a water vapor generator. Each test shows two or three exothermic peaks on the heat flow lines, due to the multistage adsorption processes. The adsorption enthalpy increased increasing the desorption temperature evaporation temperature.

Keywords: Adsorption cooling, Composite, Silica gel, Vermiculite, Salt hydrates.

Acknowledgments: This work has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement CO-COOL (101007976).

Short Bio:



Dr. Yannan Zhang graduated in Energy & environmental systems engineering at Zhejiang University, China, in 2014 and completed her Ph.D. in Power Engineering and Engineering Thermophysics at Shanghai Jiao Tong University in 2019. She currently works as a postdoc researcher in CNR-ITAE since 2020. Her research activity mainly focus on the development and characterizations of high-performance adsorption materials and the development and modification of adsorption-based thermal energy storage systems and desalination systems. She has published 12 papers on international Journals.

Topic 2: FORMSTABLE PHASE CHANGE MATERIALS BASED ON HYBRID SALT HYDRATES FOR COLD STORAGE

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Abstract: Thermal energy storage (TES) based on latent heat of reversible phase change materials (PCMs) is considered a capable technology to functional cold storage. Owing to their low cost, sufficient thermal conductivity and easy availability, salt hydrates have been extensively operated as a PCMs in cold storage. However, salt hydrates are suffering due to some serious challenges including phase segregation, phase separation, high supercooling and corrosion. In this study, we aim to design a hybrid salt-hydrate system by grouping organic and inorganic salt for cold storage application covering temperature range 7 to 11 °C. Numerous organic and inorganic salts have been employed to regulate the melting point of selected salt-hydrate with keeping energy density in the range of 120-180 j/g demonstrating almost ~60 % (in average) of the selected salt hydrate. Furthermore, functionalized silica nanoparticles and carbon nanotubes decorated graphene oxide substrates are employed to provide the nucleation cites as well as enhanced thermal conductivity which significantly reduced the supercooling up to ~2 degree. To prevent phase separation, the resultant hybrid salt-hydrate is encapsulated via in-situ polymerization which enable our designed PCMs system to maintain its performance even after 2000 cycles. We believe, our research findings will open some new gateways for scientific community and upcoming researchers.





Short Bio:



Muhammad Maqbool is currently research fellow in the Birmingham Centre for Energy Storage at University of Birmingham. He obtained his PhD degree in Materials Science and Engineering from Peking University in 2022. After his graduation, he joined Inha University, South Korea for a short-term Project as research fellow. He has contributed over 11 articles in peer reviewed high impact (total impact factor >110) journals and have received over 260 citations. His contributions have been awarded with Governor's Bronze Medal and Peking University Academic award. His research interests mainly focus on development

of polymer-based materials for thermal management including heat transfer and storage.

Topic 3: INNOVATIVE STRATEGIES FOR MATERIALS DEVELOPMENT FOR LOW-TEMPERATURE THERMOCHEMICAL ENERGY STORAGE

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Abstract: Low-temperature thermochemical heat storage (TCS) technology exploits a reversible dehydration/hydration reaction of salt hydrates for storing heat and releasing it on demand: $A \cdot mH_2O(s)$ \neq A·(m-n) H₂O(s) + n H₂O(g) (m \geq n). These systems suffer from several drawbacks due to their tendency to deliquesce. For overcoming these drawbacks, two strategies have been explored: (i) confinement of the salt into a porous matrix permeable to water vapor; (ii) investigation of innovative highly insoluble organic hydrated salts. For the first strategy, we proposed a composite material based on silicone vapor-permeable foam (PDMS) filled with LiCl salt hydrate, aiming at confining the salt in a matrix to prevent deliquescence-related issues but without inhibiting the vapour flow. We obtained an effective embedding of the material, limiting the salt solution release when overhydrated. The flexibility of the matrix allows for the volume shrinkage/expansion of the salt caused by the cyclic dehydration/hydration without any structural damage. For the second strategy, we explored innovative materials based on highly insoluble organic hydrated salts able to coordinate a high number of water molecules. Calcium ceftriaxone (CaCf) and calcium lactate (CaL) were selected as model compounds for investigation. In contrast to their inorganic counterparts, these organic salts are stable upon exposure at an RH of 90% at 30 °C, assuring no drawbacks related to deliquescence and, at the same time, fully rehydrating at low temperature. The materials' heat storage capacities are comparable with that of other inorganic salts, without appreciable energy efficiency losses as cycles are performed due to unconverted material.

Keywords: thermochemical storage, deliquescence, salt hydrates, foam

Acknowledgments: This research study was funded by the Italian Ministry of University and Research (MUR), program PON R&I 2014/2020—Avviso n. 1735 del 13 July 2017—PNR 2015/2020, under project "NAUSICA—NAvi efficienti tramite l'Utilizzo di Soluzioni tecnologiche Innovative e low CArbon", CUP: B45F21000680005.

Short Bio:



Emanuela Mastronardo received her PhD in Materials Engineering and Chemistry in 2016 at the Engineering Department of the University of Messina, Italy. The researcher developed part of her doctoral work at the Laboratory for Advanced Nuclear Energy of the Tokyo Institute of Technology, Japan. In 2017 she received funding from the European Union's Marie Sklodowska-Curie Individual Global Fellowhip Horizon 2020 research and innovation program N ° 74616. EM was a Post-doctoral Researcher at the Materials Science and Engineering Department of Northwestern University, US, (2017-2019) and at the Institute of Catalysis and

Petrochemistry of CSIC, Spain (2019-2020). Currently, she is "Senior" Researcher at the Engineering Department of the University of Messina and lecturer in the course of Materials Science and Technology. The researcher is the author of 33 publications (h-index 13), she participated to several international and national conferences, also as Keynote Speaker and member of the scientific committee. She received the "Seal of Excellence" award issued by the European Commission, and the "AICIng for young researchers" award. The researcher is also a member of AIMAT - the Italian Association of Materials Engineering, of the joint program International Energy Agency Solar Heating and Cooling (IEA / SHC) / Energy Conservation and Energy Storage (ECES), and of SolarPACES Task III.

Topic 4: AGING ISSUES ON NOVEL COMPOSITE MATERIALS FOR LOW TEMPERATURE THERMOCHEMICAL ENERGY STORAGE APPLICATIONS

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Abstract: Thermal energy storage (TES) technologies are classified into three categories: sensible, latent and thermochemical. Thermochemical ones are a promising solution, able to reach high energy density and to store it indefinitely as long as the components that take part in the reaction remain separate. However, some drawbacks of this class of materials, such as deliquescence, chemical instability, limited mass transfer and corrosion issues, have significantly hindered his extension in application fields. In such a context, new research frontiers oriented toward the development of innovative micro- and nano- structured composite sorbents for TCS applications are growing the interest in this research topic. This has opened a demand about the stability and durability of these materials in the critical environmental conditions in which they operate.

The purpose of this talk is to introduce a short insight on different characterization techniques able to evaluate the durability and degradation of novel composite materials and coatings developed for thermochemical energy storage applications. The topic is addressed toward different aging conditions: e.g. wet/dry cycles, accelerated ad/desorption test, immersion test at controlled temperature, salt-spray test by means of a salt-fog chamber. Furthermore, in order to verify the stability and durability of the composite material, different approaches, ranging from mechanical, morphological and chemophysical modification, will be assessed.

Keywords: thermochemical energy storage, composites, coatings, materials durability, aging

Short Bio:



Prof. Luigi Calabrese (M) graduated from Material Engineering in 1998 and obtained his Ph.D. in Materials Chemistry and Engineering at University of Messina, in 2002. Currently, he is Associate Professor in the field of Material Science and Technology at the Department of Engineering of the University of Messina. His main research activities are focused on: - Synthesis and characterization of adsorbent materials for sustainable energy technologies; - Advanced composites and functional materials for industrial applications; Materials durability and degradation. Up to date, he has published over 180 articles in indexed international journals. 5 Chapters on scientific books. 1

Book on Springer Scientific series and 7 patents. His publications gained 3355 citations and are ranked with an h-index of 34.

Topic 5: NANOCONFINED SALT IN ANISTROPIC GRAPHENE AEROGEL MATRIX FOR THERMOCHEICAL ENERGY STORAGE

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Abstract: Sorption thermochemical energy storage (STES) based on reversible reaction between sorbent and sorbate working pair is considered a promising technology to realize near-zero-carbon heating and cooling. Salt hydrates have been widely employed as sorbent materials in STES due to their low cost, high hydration/solvation enthalpy, and high sorption capacity through chemisorption process. However, almost all known salts suffer from powder agglomeration and deliquescence phenomenon at required level of relative humidity which led to the deteriorating performance in multicycles. Recent advancement in confinement of hygroscopic salts inside porous matrices have shown promising solution to solve above mentioned problems. Several porous matrices such as nanostructured carbons, polymers, and metal-organic frameworks have been explored to confine salt inside porous cavities for STES. All these innovative sorbents possess both advantages and drawbacks and there has been no "ideal" sorbent developed so far. This work aims to confine salt hydrates into anisotropic graphene aerogel matrix to overcome agglomeration and deliquescence problems as well as realize fast reaction kinetics. Anisotropic graphene aerogel is fabricated by hydrothermal assembly of graphene oxide sheets to graphene hydrogel followed by directional freeze-drying. Directional

growth of ice crystals during hydrogel freezing and subsequent drying results in aligned nanopores (>100 nm in size) and interconnected mesopore (2-50 nm in size) in graphene aerogel. The aligned nanopores benefit fast sorption/desorption kinetics and interconnected mesopores benefit encapsulation to avoid agglomeration and leakage. In addition to fast reaction kinetics and limited agglomeration, the developed microstructure is also beneficial to fast thermal transport in desired direction due to alignment of graphene sheets.



Keywords: Anisotropic graphene aerogel, hygroscopic salt, nanoconfinement, fast kinetics, thermochemical storage.

Short Bio:



Dr. Waseem Aftab is currently a research fellow in the Birmingham Centre for Energy Storage at University of Birmingham. He obtained his PhD degree in Materials Science and Engineering from Peking University in 2019. He was awarded International Exchange Talent Fellowship at the same institution from 2019 to 2021 and President Fellowship at Southern University of Science and Technology from 2021 to 2022. He has contributed over 35 articles in peer reviewed high impact journals and have received over 1900 citations, with h-index of 19. His contributions have been awarded with Governor Gold

Medal, Outstanding PhD scholar award, and Peking University Academic award. His research interests mainly focus on development of novel materials for thermal energy harvesting, storage, and utilization.

Topic 6: DYNAMICS OF WATER VAPOUR ADSORPTION FOR HEAT CONVERSION SYSTEMS: COMPARATIVE STUDY OF LOOSE ADSORBENTS GRAINS AND CONSOLIDATED LAYERS

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Abstract: Adsorption heat conversion (AHC) is an energy and environment saving technology for cooling and heating. Owing to the utilization of low-grade thermal energy and environmentally benign working fluids (water, methanol, ammonia) it is considered a promising alternative to compression chillers. An increase in the Specific Power (SP) of AHC devices is needed to improve their competitiveness and promote wider dissemination. The SP of AHC units mainly depends on the Adsorber - Heat Exchanger (Ad-HEx) configuration and is governed by the coupled heat and mass transfer. Accordingly, optimization of the Ad-HEx configuration is a key-factor to improve SP of AHC. Here we present the results of studying the dynamics of water vapor adsorption on a composite LiCl/silica, silicoaluminophosphate FAM-Z02, and metal-organic framework MOF-801, being promising for AHC. Two common Ad-HEx configurations (the loose adsorbent grains located on a metal support and thin adsorbent coatings on the support), and one innovative configuration (the grains "glued" to the support surface with a binder) are compared. Both inorganic and organic substances are used as binders. The morphology and porous structure of the consolidated layers are characterized, and the water vapour adsorption dynamics is studied under conditions of a typical adsorption cooling cycle by Large Temperature Jump method. The effective heat transfer coefficients were measured in air and calculated from the initial parts of the kinetic curves. Based on the obtained results, recommendations are formulated for optimizing the Ad-HEx configuration for the studied adsorbents, which will promote the further dissemination of AHC technology.

Keywords: adsorption heat conversion, water vapor, adsorption dynamics, consolidated adsorbent beds.



Short Bio:

Larisa G. Gordeeva is a Leading Researcher at Boreskov Institute of Catalysis (BIC), Novosibirsk, Russia (the <u>Department of Unconventional Catalytic Processes</u>, the Group of Energy Accumulating Materials and Processes).

She received her Ph.D. in Chemical Kinetics and Catalysis at BIC in 1998, and Dr. Sci. degree (Dr. Hab.) in Physical Chemistry at the same Institute in 2013. Her research interests are in the field of Material chemistry, Nanocomposites salt/matrix, Metal-Organic Frameworks, Adsorption, Adsorptive heat transformation and storage, Rational design of adsorbents for various applications. She has about 100 relevant publications in

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Larisa Gordeeva is deeply involved in joint international projects. She was a Visiting Researcher/Professor at Institute of Advanced Energy Technologies (Italy), Institute of Chemical Engineering (Poland), University of Warwick (UK). L. Gordeeva is a member of the Organizing/Advisory Committees of the International Conferences: Heat Powered Cycles (HPC), Enerstock, Actual Problems of Adsorption and Catalysis, etc.