SHC 58
ECES 33

Consiglio Nazionale delle Ricerche

INVESTIGATION OF THE CYCLING STABILITY OF SORBENT COMPOSITES FOR SORPTION THERMAL ENERGY STORAGE APPLICATIONS

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Introduction

Background

- Cooling/Heating **(C/H)** >**50%** primary energy consumption (fossil fuels).
- Low carbon fuels, biomass, renewables and nuclear energy only **25%** of the energy production.
- According to the International Energy Agency (**IEA**) in 2040 renewable energy sources will meet **40%** of the increase in primary energy demand.

Introduction of **Renewable Energy System**

Thermal Energy Storage (**TES**)

TES

- Sensible heat
- Latent heat
- Chemical reaction heat

  - Negligible heat losses
  - Greater energy storage density

Adsorption Thermal Energy Storage (**ATES**)

- Exotermichal adsorption (heat generation or discharge stage)
- Endothermic desorption (heat absorption or charge stage)

Adsorbate: water → non flammable
thermally stable
ecologically benign
large latent heat of evaporation

CSPMs (Composite "Salt in a Porous Matrix")

Disadvantage

- stability

Advantages

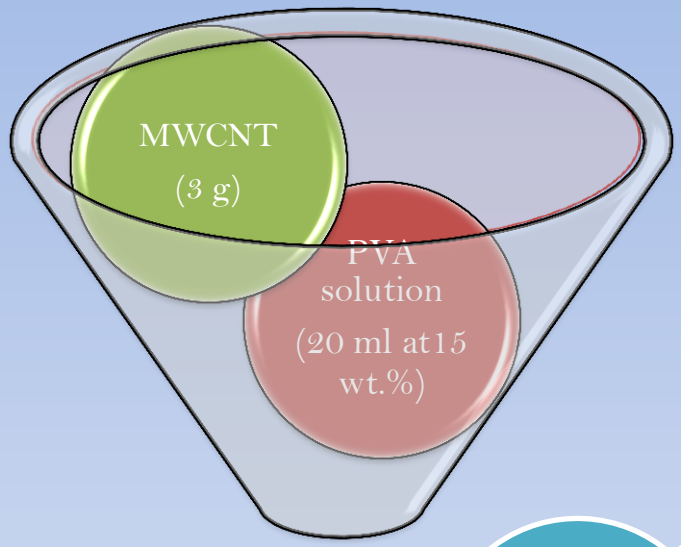
- Less adsorption/desorption hysteresis
- higher mass-transport
- high water sorption capacity (> 0.5 g/g)
- low regeneration temperature (< 95 °C)
- low cost
- simple production process

Outline

- Synthesis of a sorbent composite LiCl/MWCNT/PVA
- Investigation of water sorption capacity under typical conditions of TES daily storage cycle
- Stability characterization by temperature programmed XRD analysis and SEM analysis operating under controlled humidity and temperature conditions

Sorbent composite synthesis

Synthesis Method: dry impregnation



slurry

RT for 16h

90°C for 2h

Ar at 400°C for 4h

Grains

Impregnation

LiCl (H_2O:EtOH=1:1)

χ_s= 55 wt.%

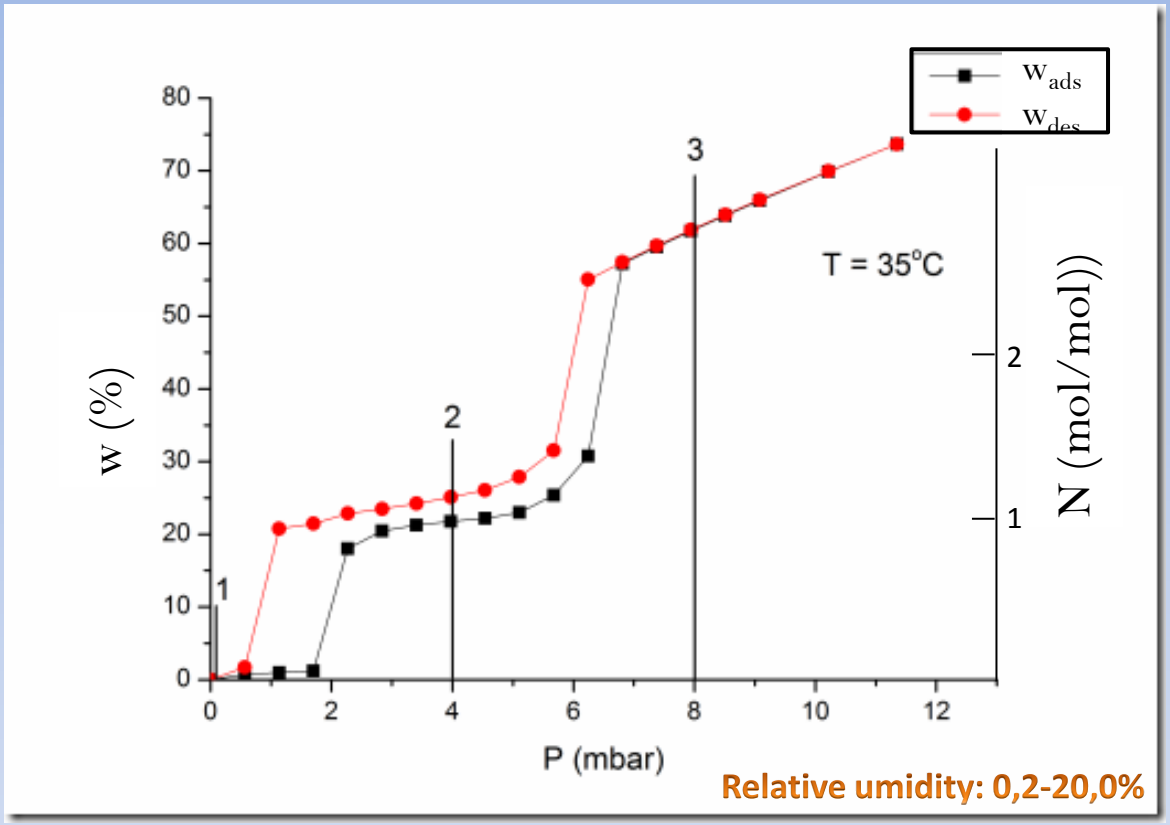
Drying

At 160°C

16 h

Sample	LiCl wt.%	V_m cm^3/g	S_{sp} m^2/g
MWCNT/PVA	-	1.30	220
LiCl/MWCNT/PVA	55	0.24	80

Water sorption test (DVS Vacuum, Surface Measurement Systems Ltd)



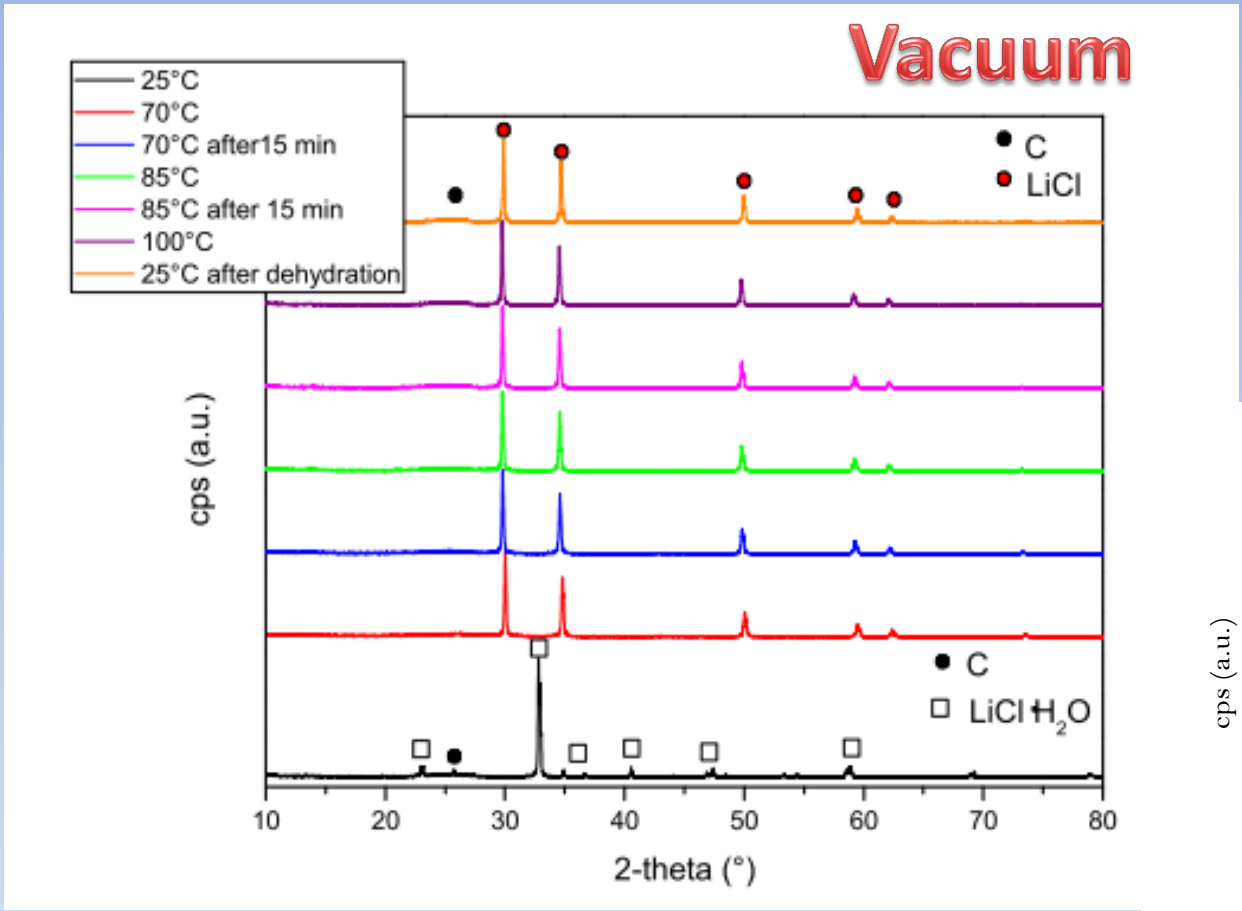
$w = [m(P_{H2O}, T)/m_0] * 100$

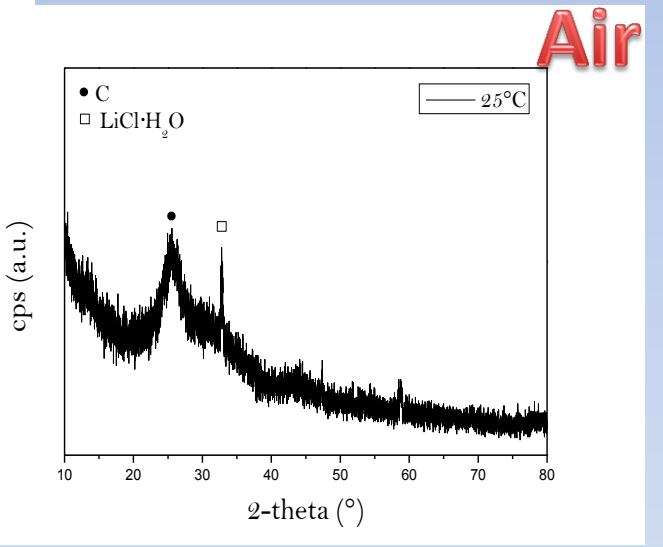
$m(P_{H2O}, T)$ and m_0 are the adsorbed water weight at equilibrium and dry weight of the sample, respectively

$N = mol_{H2O}/mol_{LiCl}$

- Initially, the sample was slowly heated up to 150°C under vacuum for 5 h (vacuum level: 0.1 Pa), in order to degas the sample and determine its dry weight.
- During water sorption, two steps are depicted, attributed to the formation of a mono-hydrate LiCl·H2O and di-hydrate LiCl·2H2O.
- An hysteresis is observed at N<2. At N>2 the isotherms are smooth curves, confirming the formation of acqueous LiCl solution.

Structural characterization (XRD, Bruker D8 Advance, Bruker, Billerica, MA, USA)





- In air the intensity of main intense peak LiCl·H2O appears low and broad, due to the hygroscopic behavior of the salt.
- In vacuum peaks appear sharp and narrow because of high degree of crystallization of the tetragonal $LiCl \cdot H_2O$. Increasing the temperature up to 70 °C the peaks of anhydrous cubic LiCl appear.
- The structure remains stable up to 150°C, remaining unchanged until room temperature.

Morphological analysis

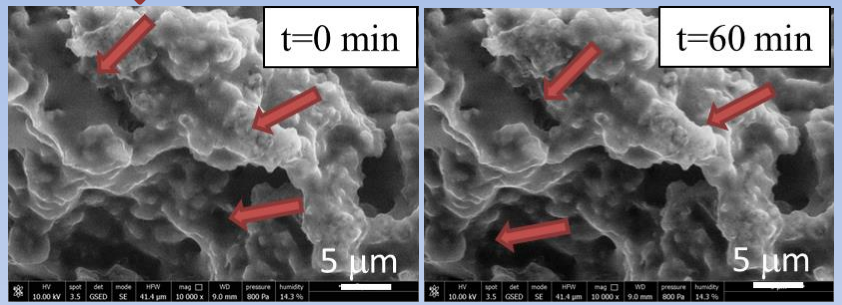
ESEM, Quanta 450, FEI, Hillsboro, OR, USA

10 kV at 35°C in controlled water vapor atmosphere, from 0,1 mbar to 8 mbar (0.1% to 14.3% of relative humidity)

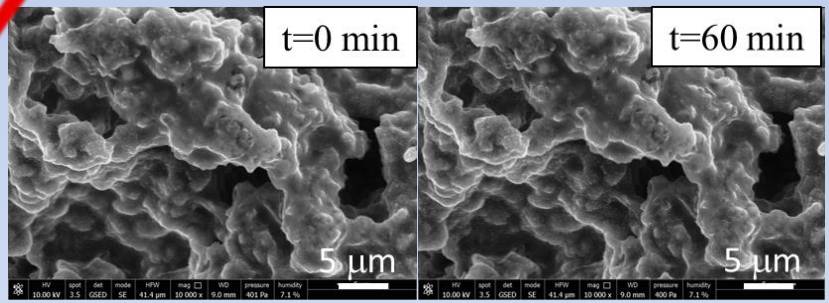
Deliquescence occurs

Hydration

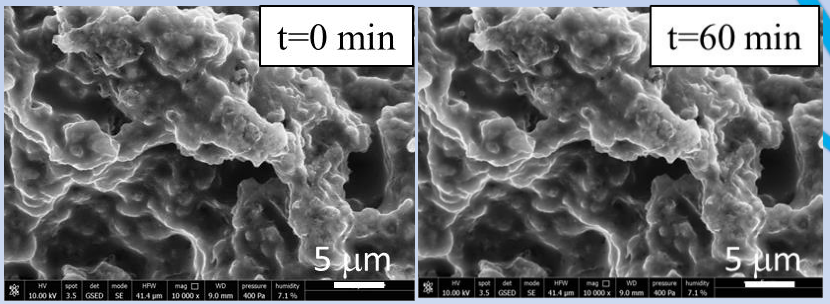
Dehydration



P= 8 mbar



P= 4 mbar



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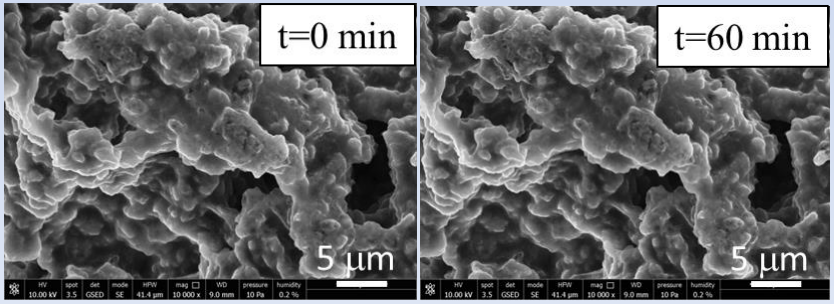
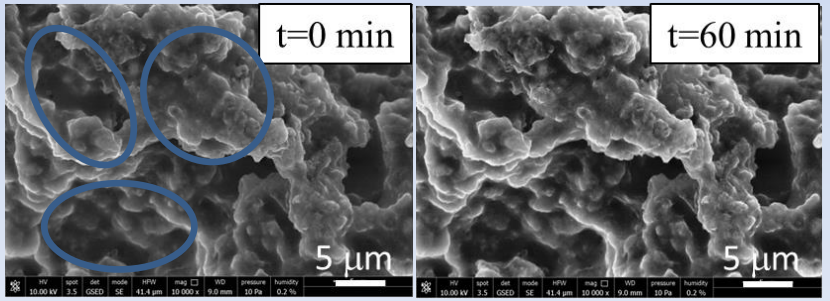
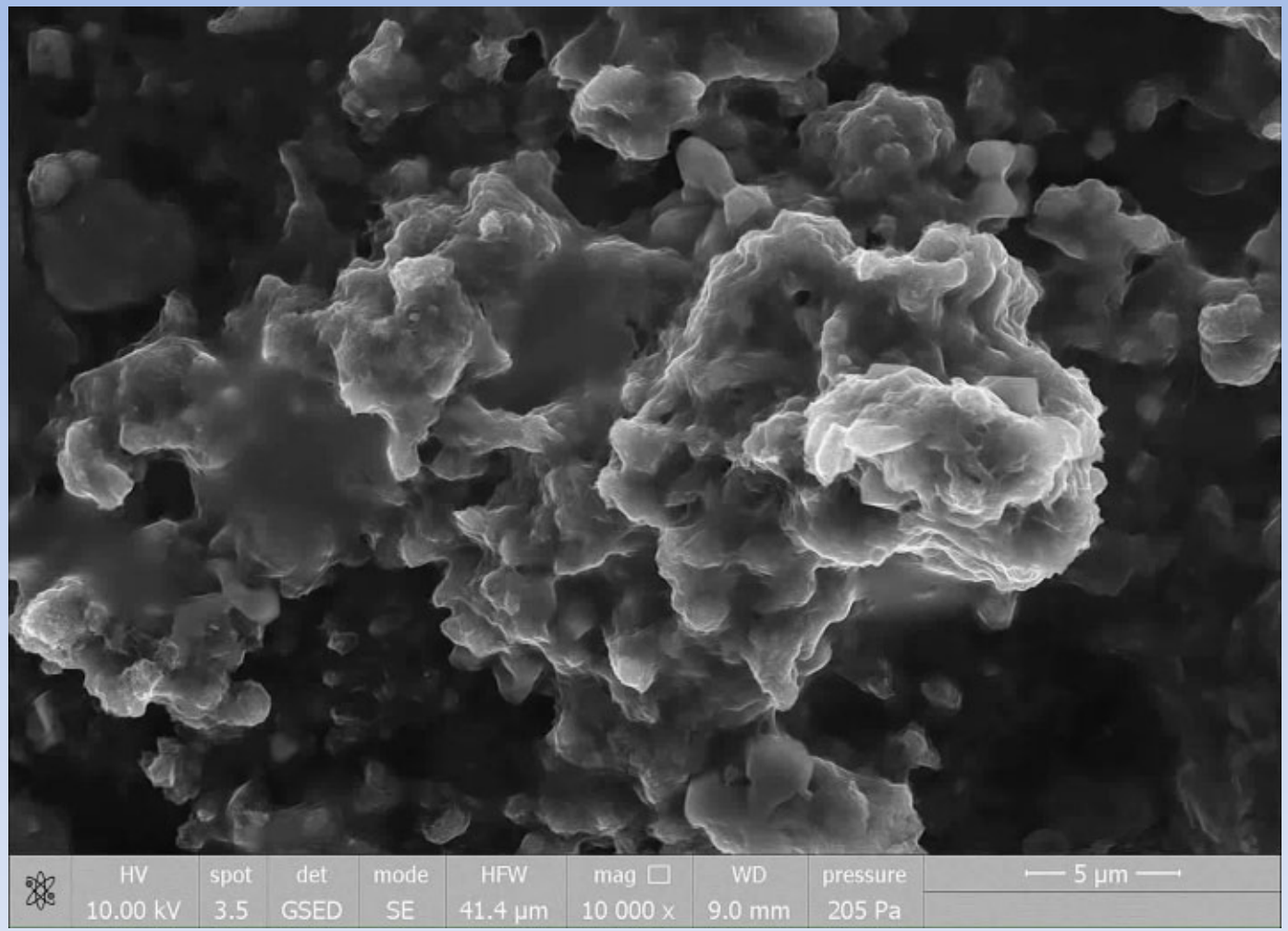


P= 0,1 mbar



P= 0,1 mbar

Morphological analysis



Conclusion

- A new sorbent composite based on LiCl supported on MWCNT was synthesized.
- Its water sorption capacity was investigated.
- During water sorption, two steps are depicted, attributed to the formation of a mono-hydrate $LiCl{\cdot}H_2O$ and di-hydrate $LiCl{\cdot}2H_2O$.
- An hysteresis is observed at $N<2$. At $N>2$ the isotherms are smooth curves, confirming the formation of acqueous LiCl solution.
- Before deliquescence occurs the material can reach 40 wt.% of water sorption capacity.
- The morphological stability of LiCl/MWCNT/PVA composite was studied.
- The crystalline hydrate $LiCl{\cdot}H_2O$ formation is likely to be a reason of the water adsorption/desorption hysteresis observed for the LiCl/MWCNT/PVA composite
- The sorbent composite can be a suitable material for TES applications and further investigation, increasing the number of ad/desorption cycles, are needed.

Thanks to

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and you for your kind attention….