Consiglio Nazionale delle Ricerche - CNR

ISTITUTO DI CHIMICA DELLA MATERIA CONDENSATA E TECNOLOGIE PER L'ENERGIA (ICMATE)

# Sostenibilità e materiali inorganici per l'energia

**Simona Barison**

**PADOVA**

# CHI SIAMO



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# Sostenibilità - Normativa Italiana



Il concetto di sviluppo sostenibile in Italia (D.Lgs. 3 aprile 2006, n. 152 e D.lgs 16 gennaio 2008, n. 4[6], è così definito:

- Art. 3-quater (Principio dello sviluppo sostenibile) Ogni attività umana [...] deve conformarsi al principio dello sviluppo sostenibile [....] il principio dello sviluppo sostenibile deve consentire di individuare un equilibrato rapporto, nell'ambito delle risorse ereditate, tra quelle da risparmiare e quelle da trasmettere, [...]

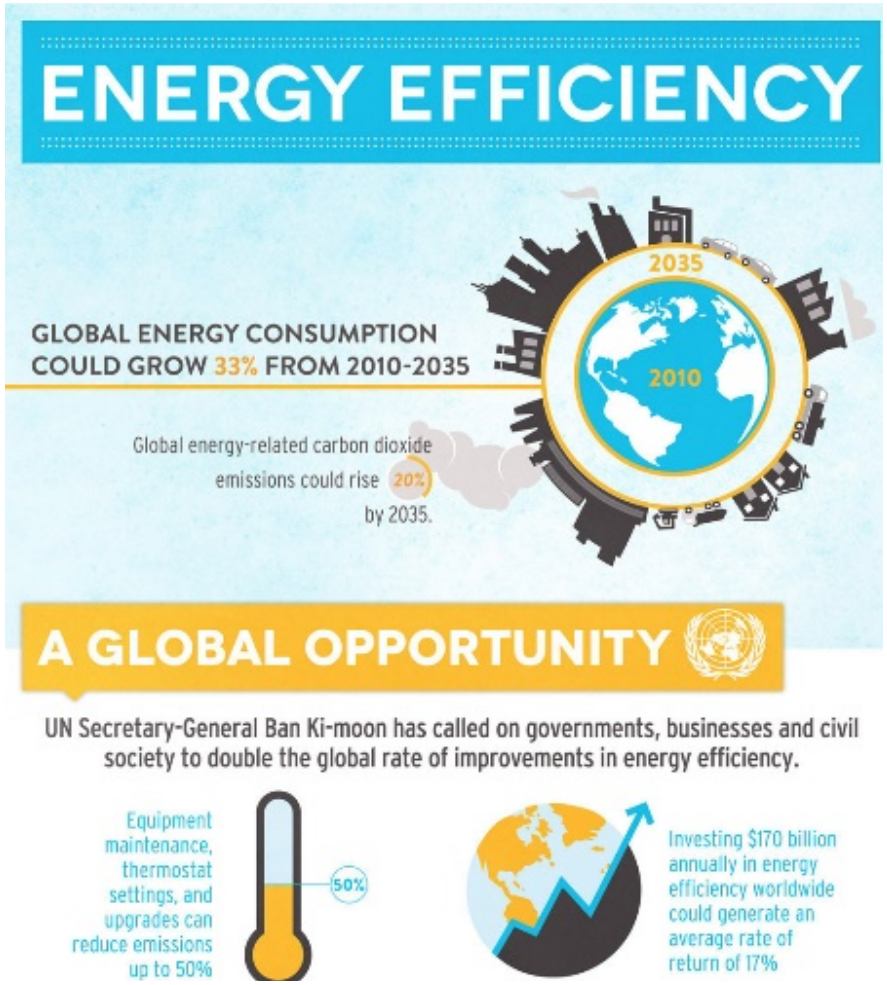
In Italia il "Piano d'azione per la sostenibilità ambientale dei consumi della pubblica amministrazione" (PAN GPP) (legge 296 del 2006 e decreto interministeriale 11 aprile 2008), ha definito **gli obiettivi ambientali strategici in Italia**:

- **efficienza e risparmio nell'uso delle risorse, in particolare dell'energia e conseguente riduzione delle emissioni di $CO_2$**
- **riduzione dell'uso di sostanze pericolose**
- **riduzione quantitativa dei rifiuti prodotti.**

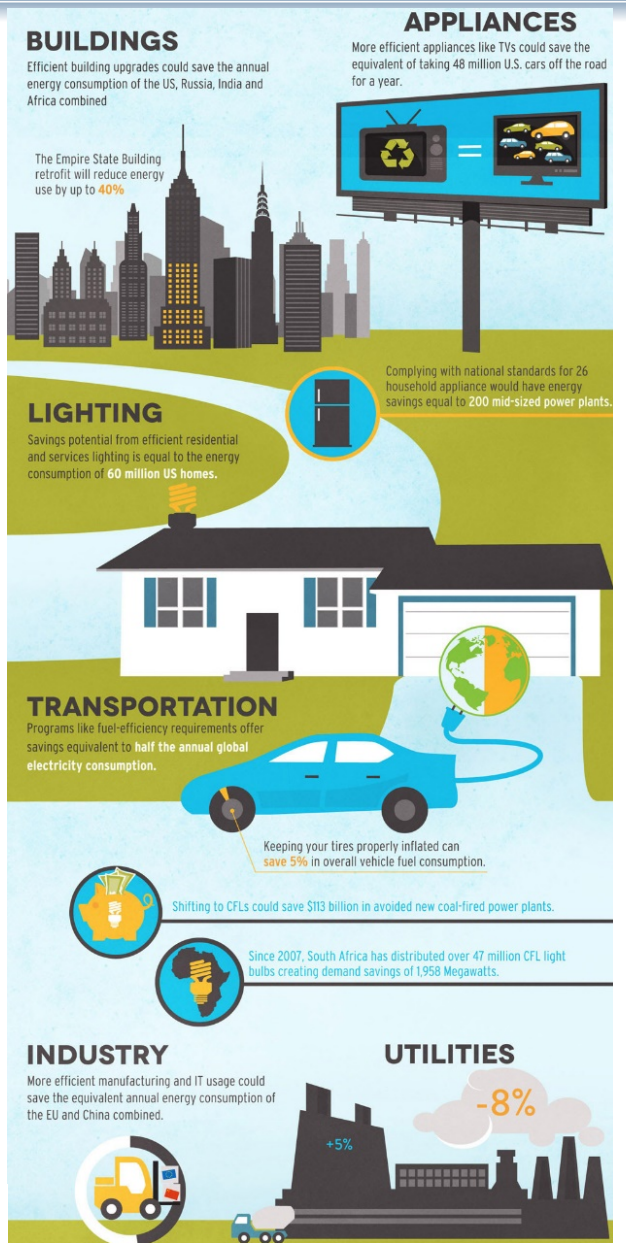
# Sostenibilità Energetica



Efficienza energetica ed energie rinnovabili sono state definite dalle Nazioni Unite come i PILASTRI GEMELLI di una energia sostenibile.




http://www.se4all.org/our-vision/our-objectives/energy-efficiency/



# ATTIVITA' DEL GRUPPO

## Efficienza energetica

**Termoelettrici per il recupero energetico di calori dispersi (studio di materiali non tossici né rari)**

**Nanolubrificanti e rivestimenti duri per il miglioramento dell'efficienza energetica di dispositivi e l'aumento del loro tempo di vita mediante riduzione di attrito e usura**

**Rivestimenti per miglioramento di resistenza ad ossidazione a caldo e di prestazioni di turbine a gas**

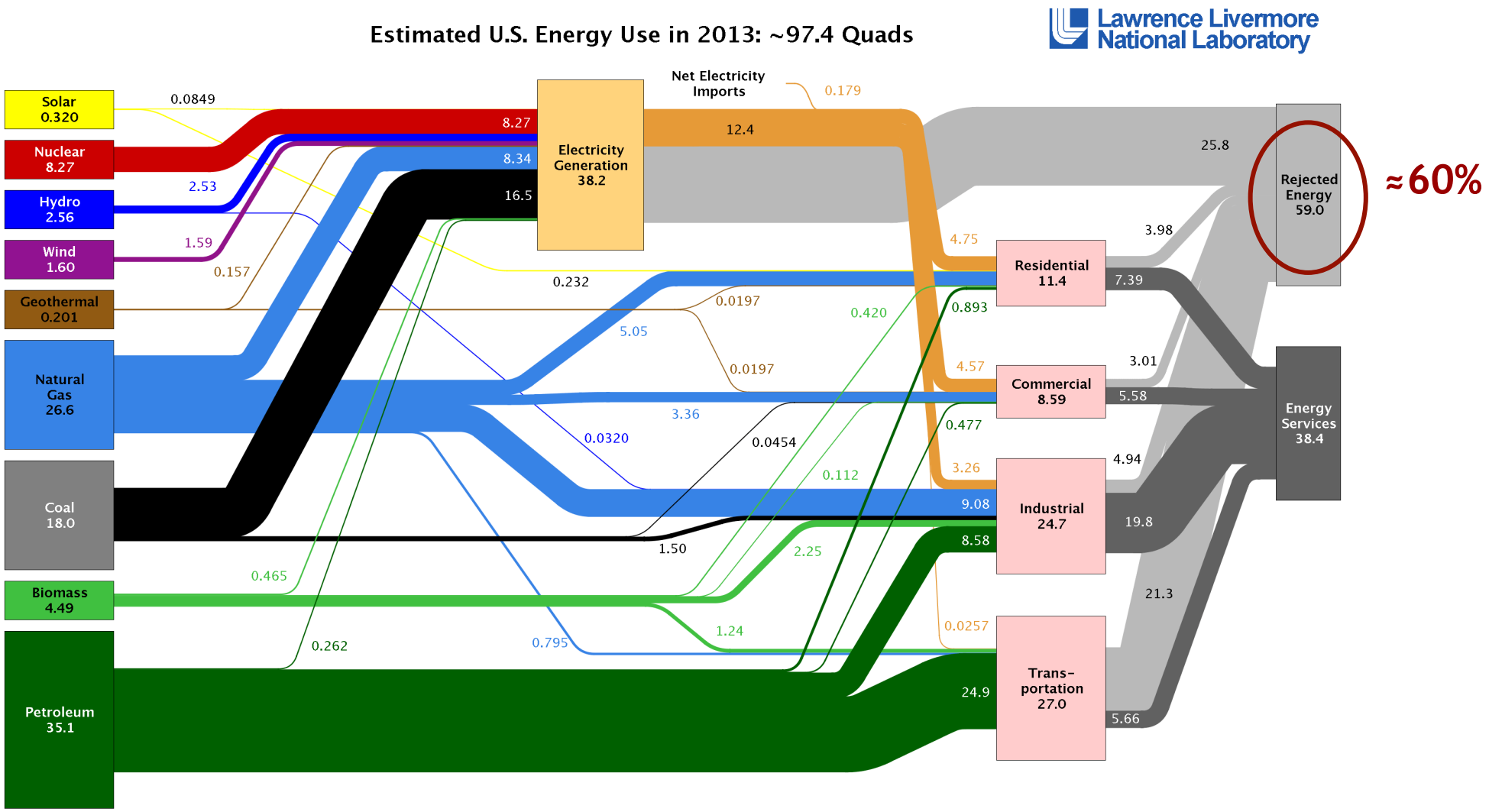
## Energie rinnovabili e economia dell'idrogeno

**Membrane per la purificazione/separazione di idrogeno prive di metalli nobili o con film sottili contenenti metalli nobili**

**Nanofluidi neri per l'assorbimento solare.**

# Generatori termoelettrici

Istituto per l'Energetica e le Interfasi — Padova

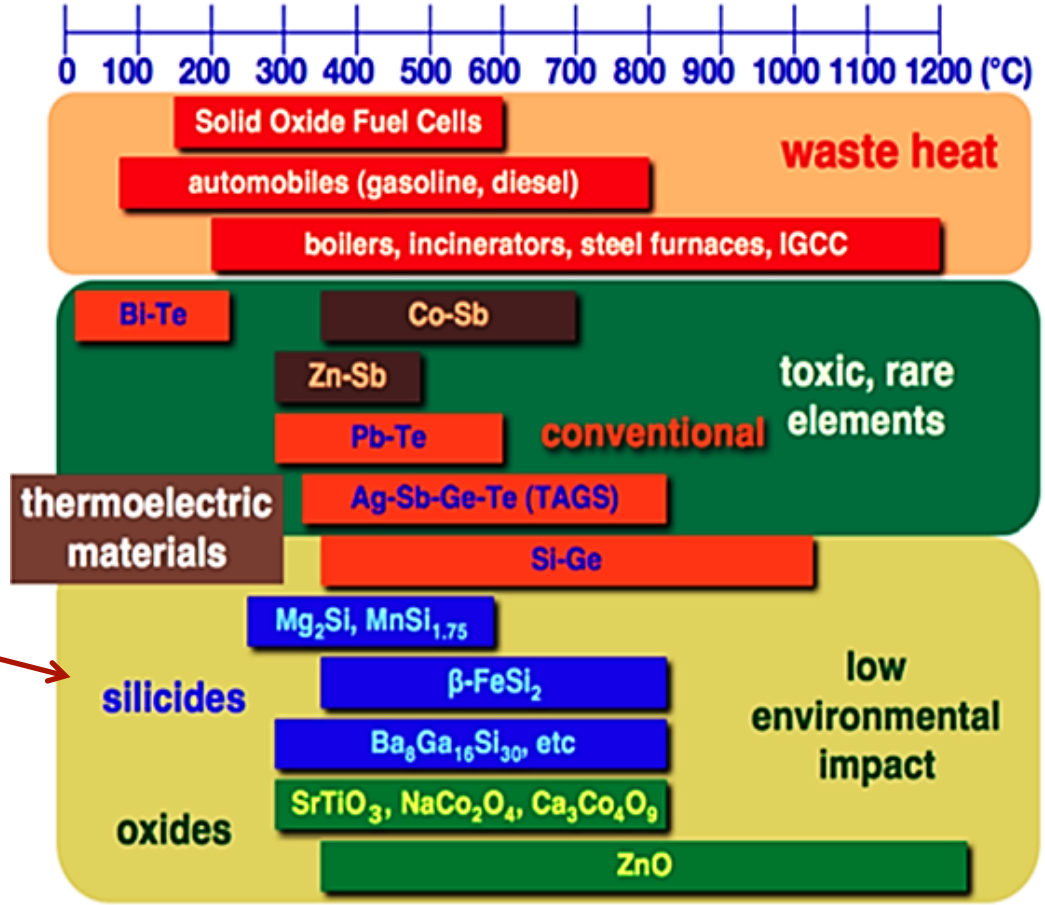



Data based on DOE/EIA-0035(2014-03), Marzo 2014

Sviluppo di materiali e dispositivi termoelettrici per il recupero di energia da cascami termici a medio-alte temperature (fino a 600°C): **Siliciuri di tipo n e p e tetraedriti.**

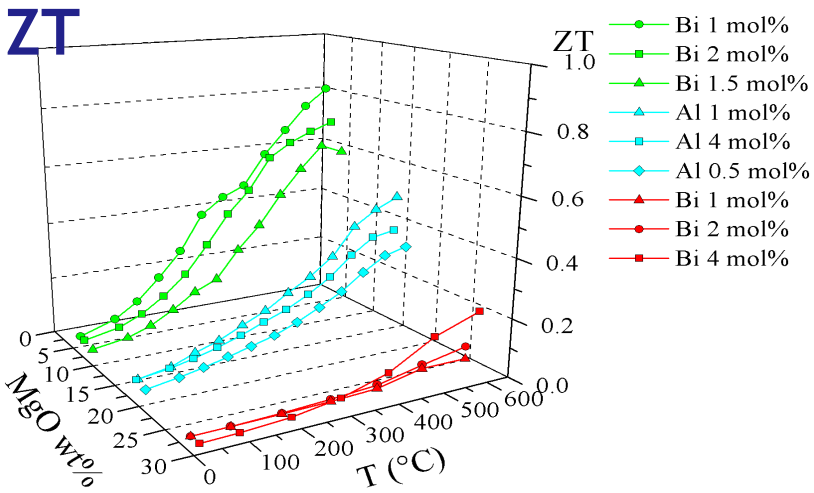
**$Mg_2Si$ e Higher manganese silicides**
**Impiego a temperature intermedie (fino a 600 °C )**
**green (basso costo, abbondanti, bassi costi di smaltimento)**
**Bassa densità**

**Tetraedriti ($Cu_{12}Sb_4S_{13}$)**
**Per temperature fino a circa 450°C**



# Siliciuri -Mg (n), Mn (p)

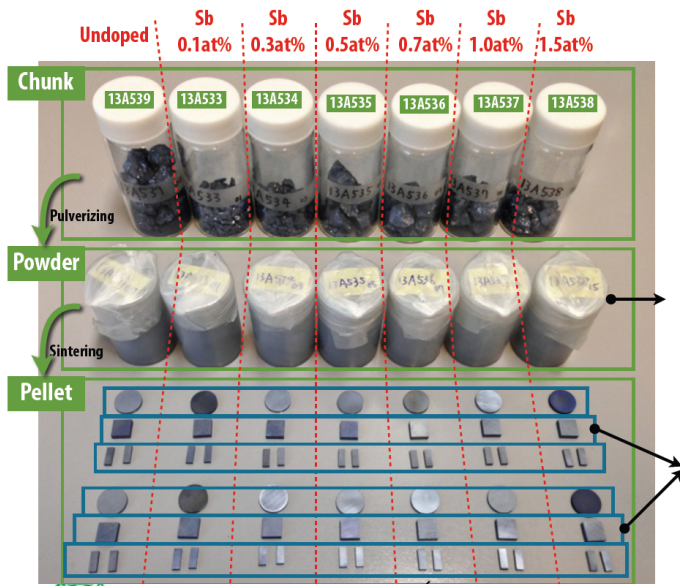





**L'elemento drogante influenza sia le proprietà termoelettriche (ZT) che la stabilità all'ossidazione**

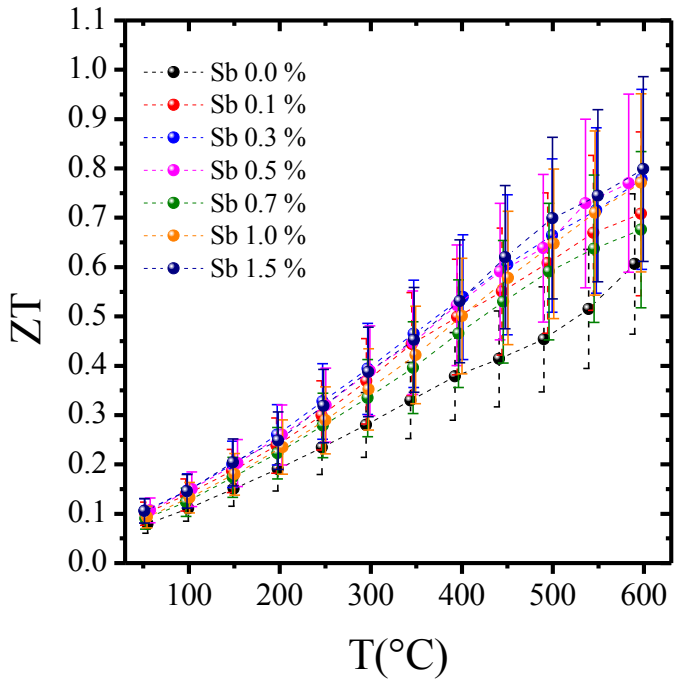
**La quantità di MgO ha un ruolo determinante nell'abbassamento dello ZT**

$$ZT = \frac{S^2\sigma}{\kappa}T$$



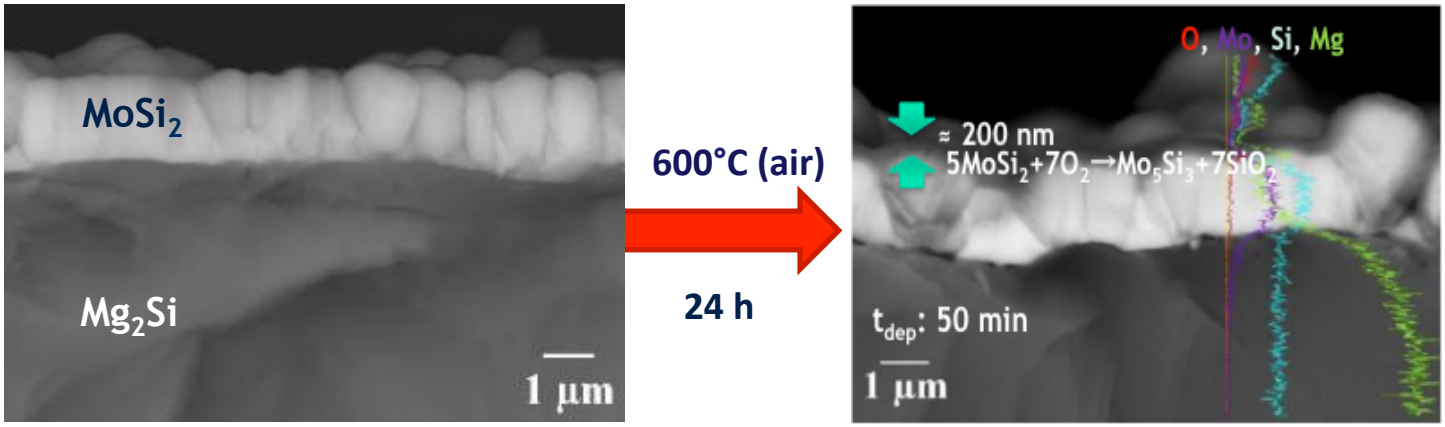

**Ball milling**

**SPS**



# Siliciuri -Mg (n), Mn (p)





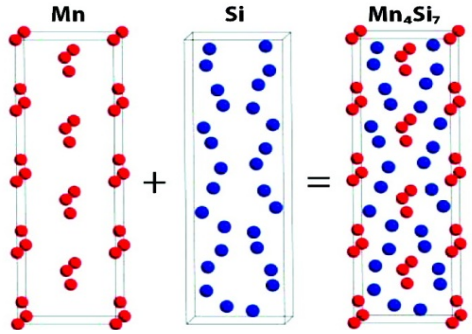

**Rivestimenti $MoSi_2$ via RF-magnetron sputtering come barriera all'ossidazione:**

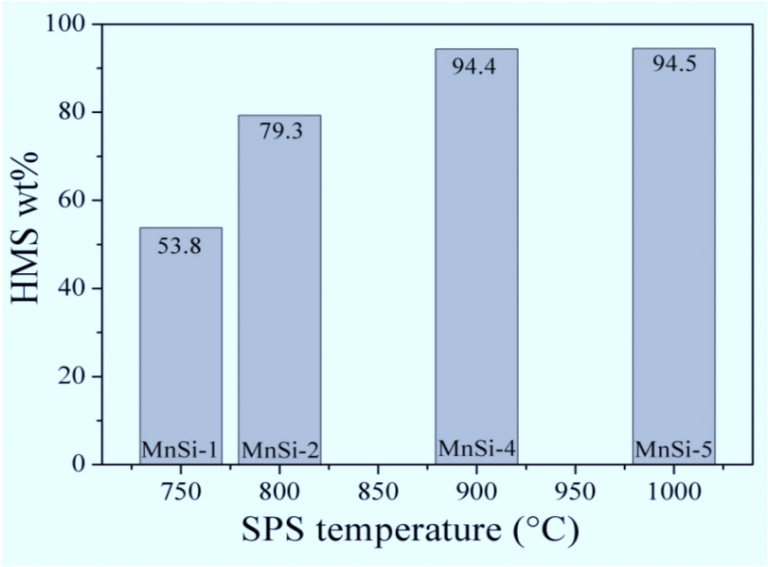
- **Alta T fusione (2030 °C);**
- **Formazione strato sottile silice;**
- **Basso costo e abbondanti.**

## Higher Manganese Silicides (HMS)

**Sintesi e sinterizzazione in un singolo step via SPS a 90 MPa e 1000°C**

**$ZT_{HMS\ 95\%}$= 0.34 @ 600 °C**

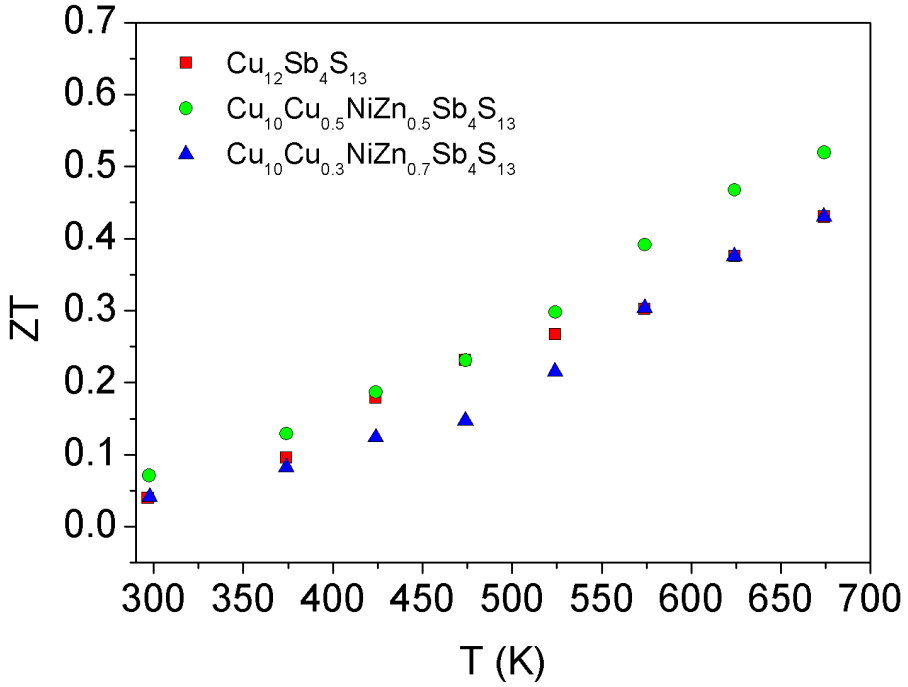


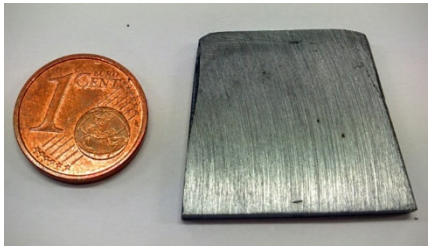
# Tetrahedrite, a possible sustainable thermoelectric material for middle temperatures (350-450 °C)

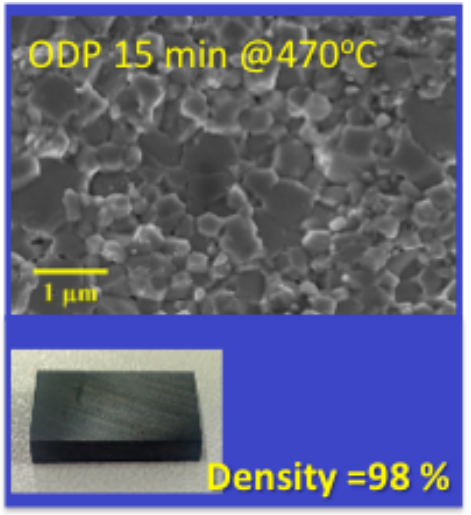
$Cu_{10}Zn_{2-x}Ni_xSb_4S_{13}$

- Ball Milling
- Solvothermal Synthesis




Consolidation Process: Open Die Pressing @ Lecco






***Poster P2:*** ***S. Battiston et al. "Simultaneous synthesis and sintering of tetrahedrite based thermoelectric materials"***

# Caratterizzazione funzionale

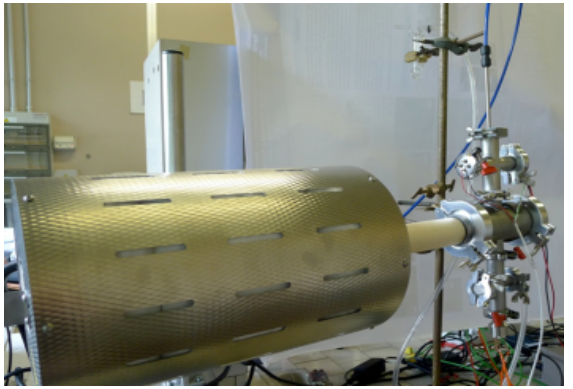


**Simultaneous Seebeck coefficient and electrical conductivity measurement**

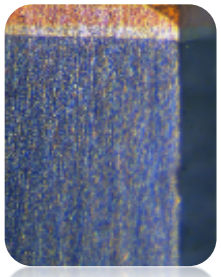
**2 configurations: RT – 1000K and RT-1500K temperature ranges**

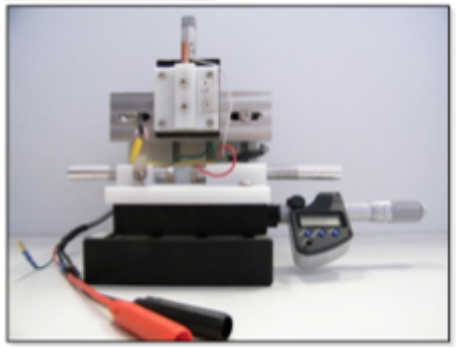
**LabView automated procedure**

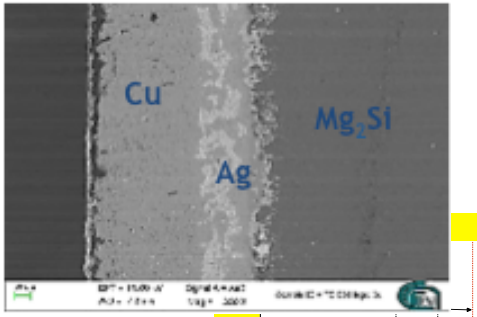
**Laser Flash Thermal Diffusivity**

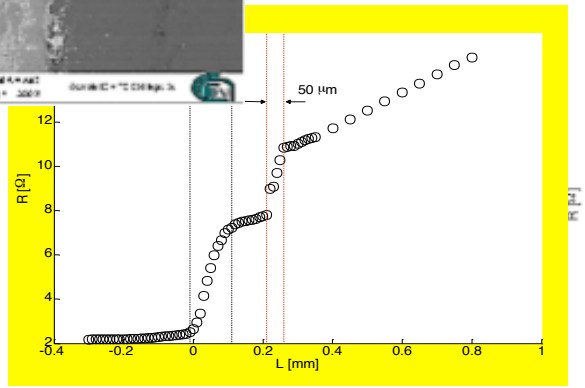


## Misura di resistenza di contatto

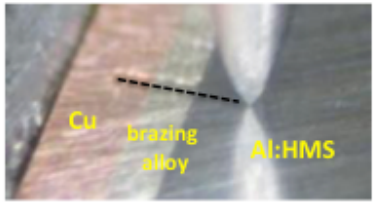


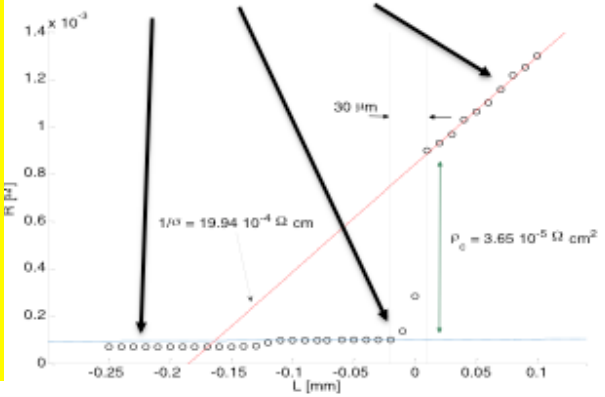





## Esempio di HMS/$Ag_{alloy}$/Cu



# Multiphysics modeling of thermoelectric generator

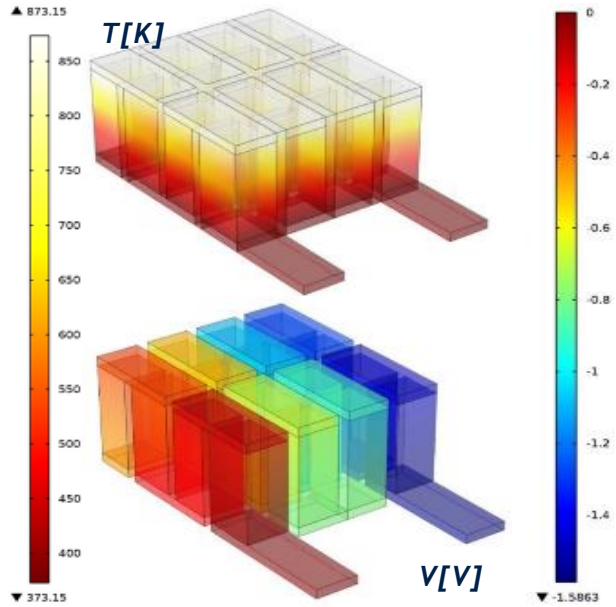
Istituto per l'Energetica e le Interfasi

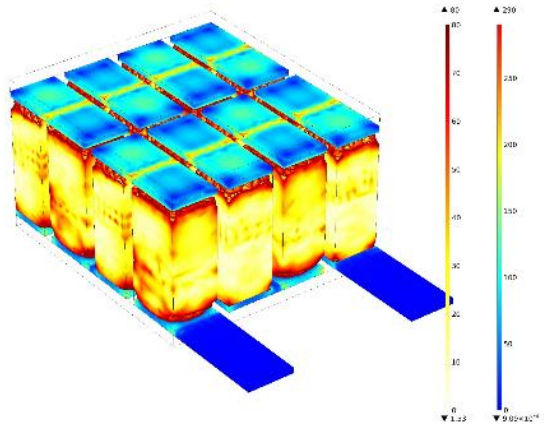
Padova

*Numerical calculation of temperature and voltage distributions for different values of (Ap/An) ratio*

**Evaluation of heat flux and output power**

***Evaluation of maximum efficiency***

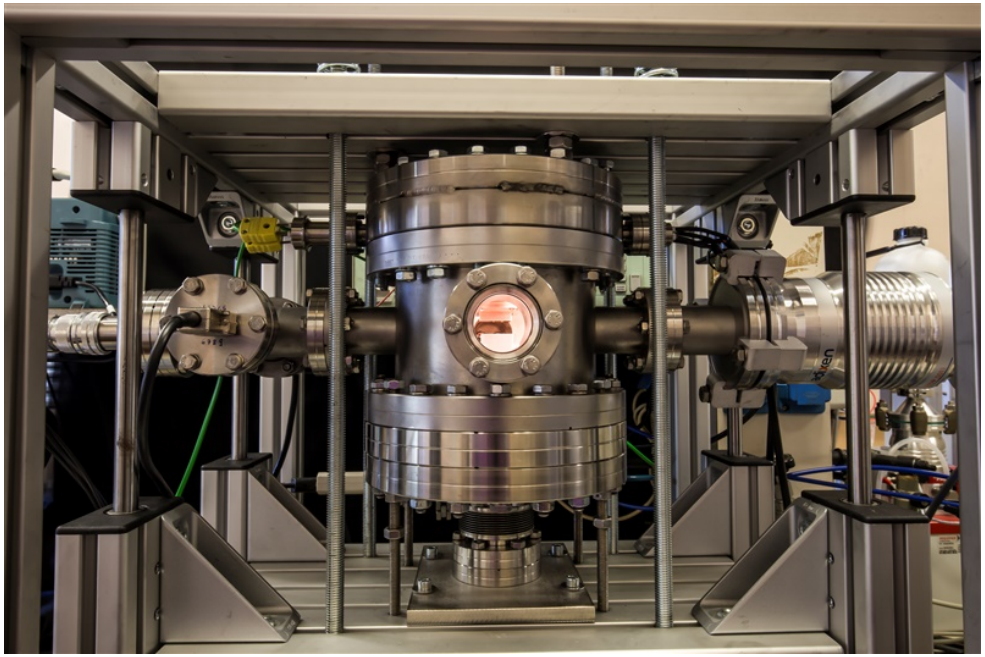


***Evaluation of mechanical strength of the modules***

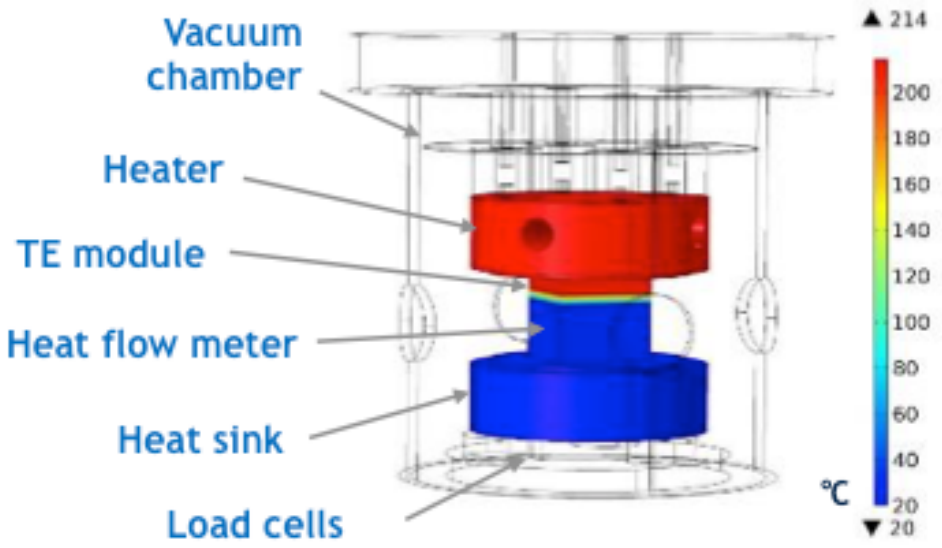
***Poster P5:*** *A. Miozzo et al. "Analisi agli elementi finiti per applicazioni in campo energetico"*

# *TE module measurement apparatus*



**We developed a testing device oriented to the maximum flexibility, based on the heat flow meter method at the cold side of the module**

***Operating in vacuum (from RT up to 900 K) or inert atmosphere***




***Presentazione Martedì 1 ore 12.15:* A. Ferrario "Termoelettrici per temperature intermedie: sviluppo e caratterizzazione di moduli"**

## Efficienza energetica e sostenibilità ambientale

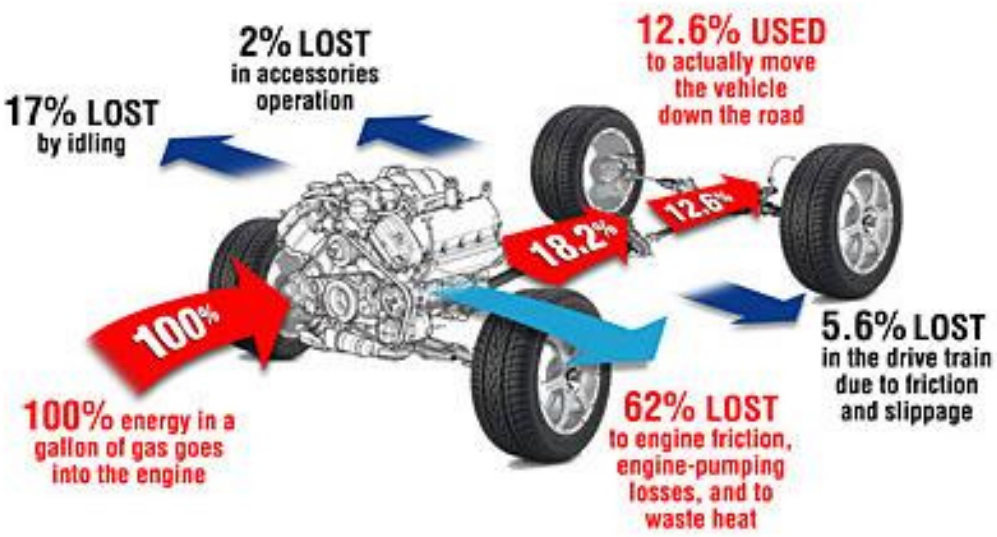
**Nanolubrificanti e rivestimenti duri per il miglioramento dell'efficienza energetica di dispositivi e l'aumento del loro tempo di vita mediante riduzione di attrito e usura**

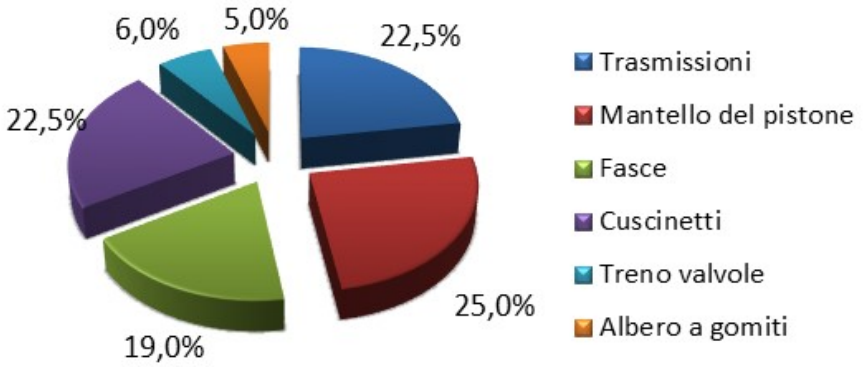
# Efficienza energetica – riduzione di attrito e usura

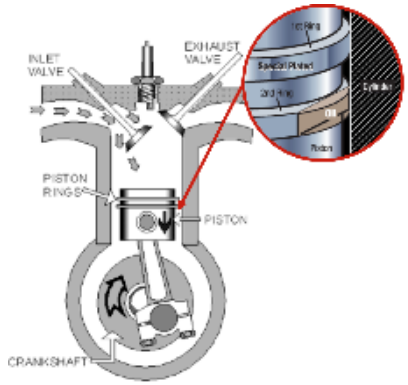


**Development of new lubricants containing nanoparticles able to warrant better performances than commercial oils (durability, wear resistance, friction and heat transfer).**

**In combustion engines an important part of energy output is lost due to friction.**

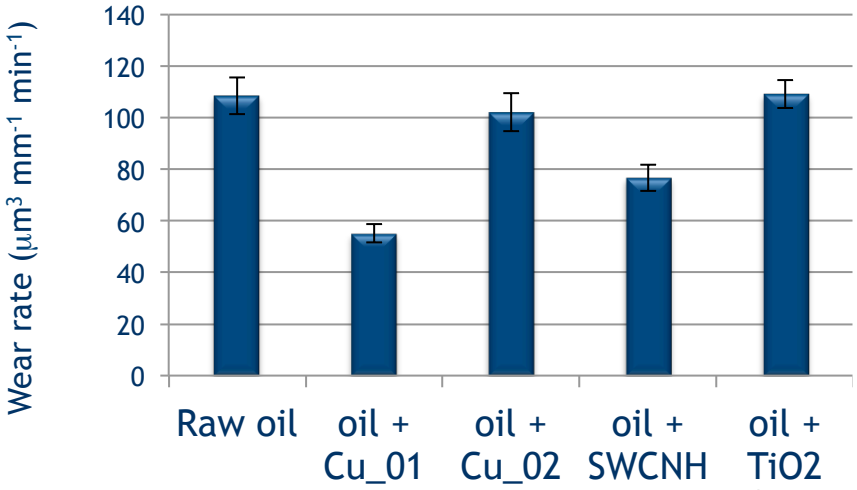


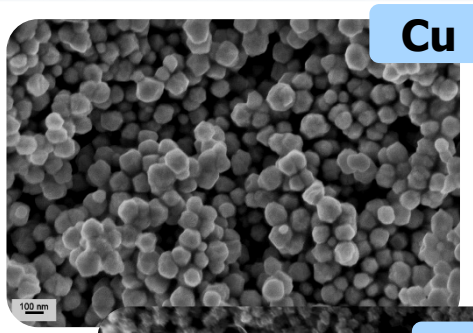



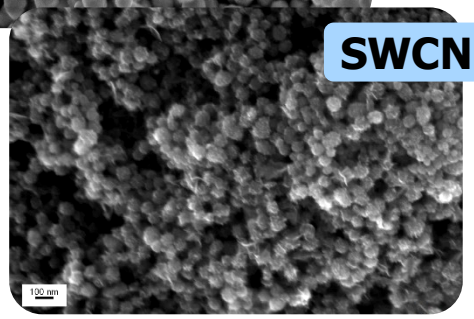



# Sinergia rivestimenti + nanolubrificanti

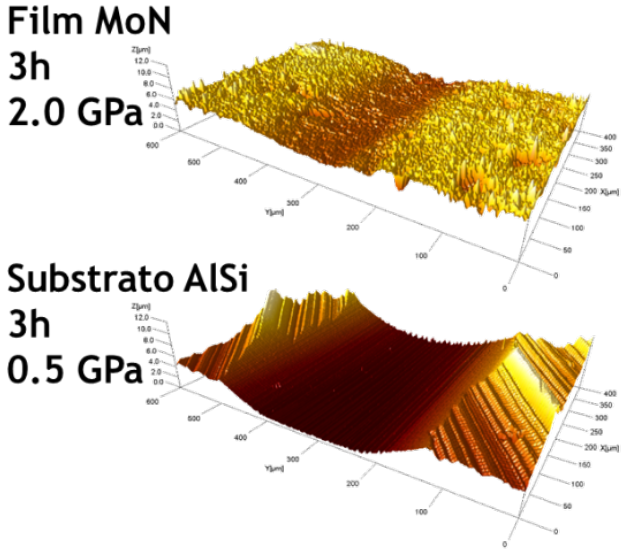










***Presentazione Martedì 1 ore 13.00:*** ***V. Zin "Approccio tribologico nella caratterizzazione funzionale di rivestimenti e lubrificanti"***

# Efficienza energetica – riduzione di attrito e usura



**Only for domestic applications, *1,4 billion refrigerators and freezers* in use worldwide (EU data 2013), accounting for *almost 14% of total electricity consumption* from residential sector. Investigation on the potential advantages of nanolubricants in a compressor used in the refrigeration/air conditioning.**

**Some studies demonstrated an important reduction in energy consumption due to even small changes in lubricant properties.**

$CO_2$ advantages:

low viscosity,

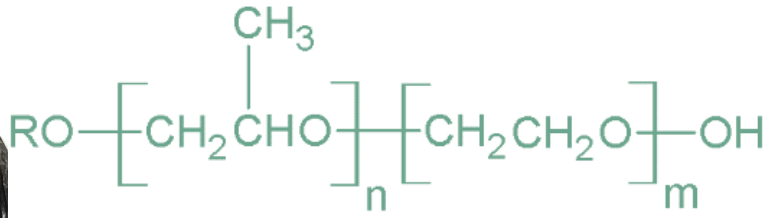
low tossicity and

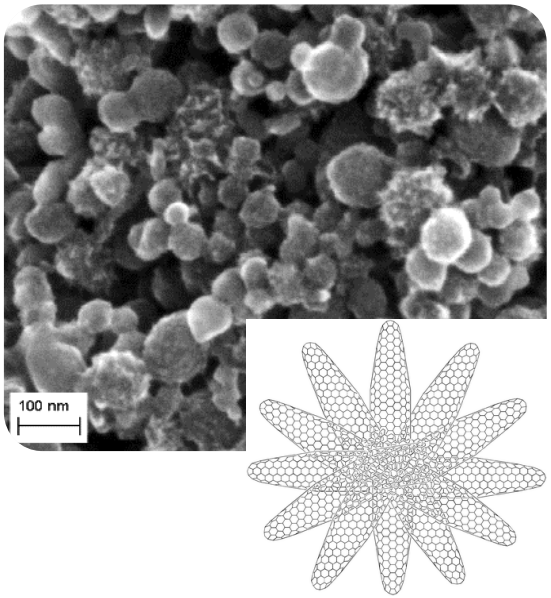
flammability,

…

**Base fluid**

**Commercial Poly-Alkylene Glycol (PAG) for $CO_2$ refrigeration**

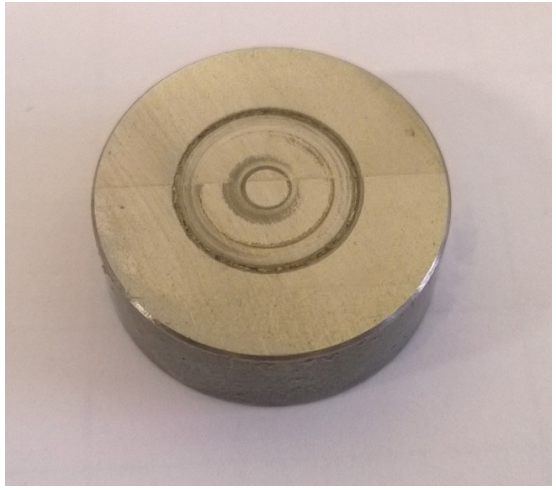


# Nanolubrificanti per refrigerazione



| | |
|---|---|
| **Config** | Pin-on-disk |
| **Lubricant** | PAG<br>PAG + 0,2%$_{wt}$ SWCNHs |
| **T and P** | Room T and P |
| **Normal Force** | 140 N |
| **Sliding speed** | 0,2 m/s |

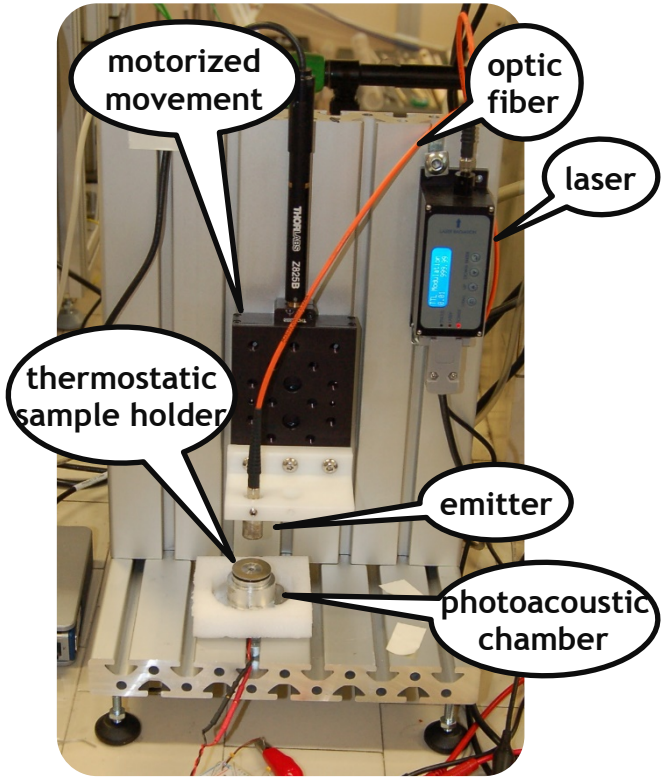


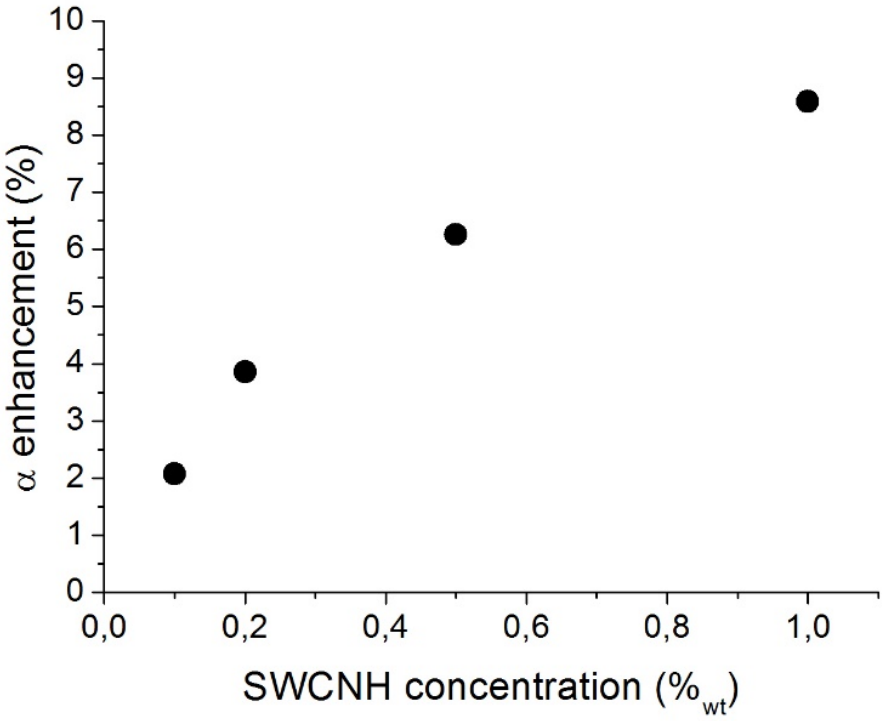
**Pin and disk from test performed with the base oil showed intense wear, and great damage, because of the achievement of the failure conditions, which brought materials to breakage.**

**Test with nanolubricant lasted for 125'000 cycles without reaching such failure conditions.**

The thermal diffusivity of raw oil and nanolubricants was evaluated in the 25°–65°C range, by **photoacoustic measurements**.

**THERMAL DIFFUSIVITY**




**A non-linear increase of average thermal diffusivity with nanoparticles % was observed.**

**Maximum increase of 9%**

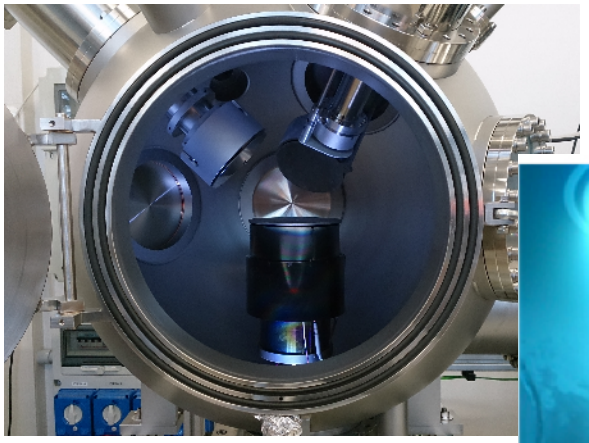
## Efficienza energetica

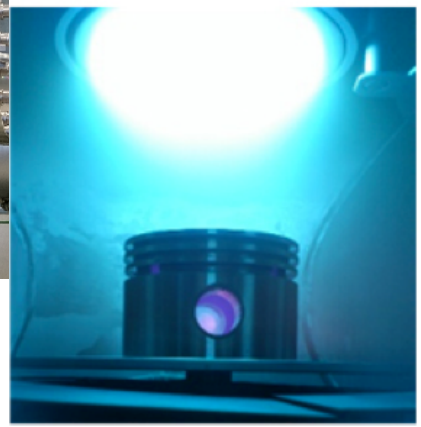
**Rivestimenti per miglioramento di resistenza ad ossidazione a caldo e di prestazioni di turbine a gas**

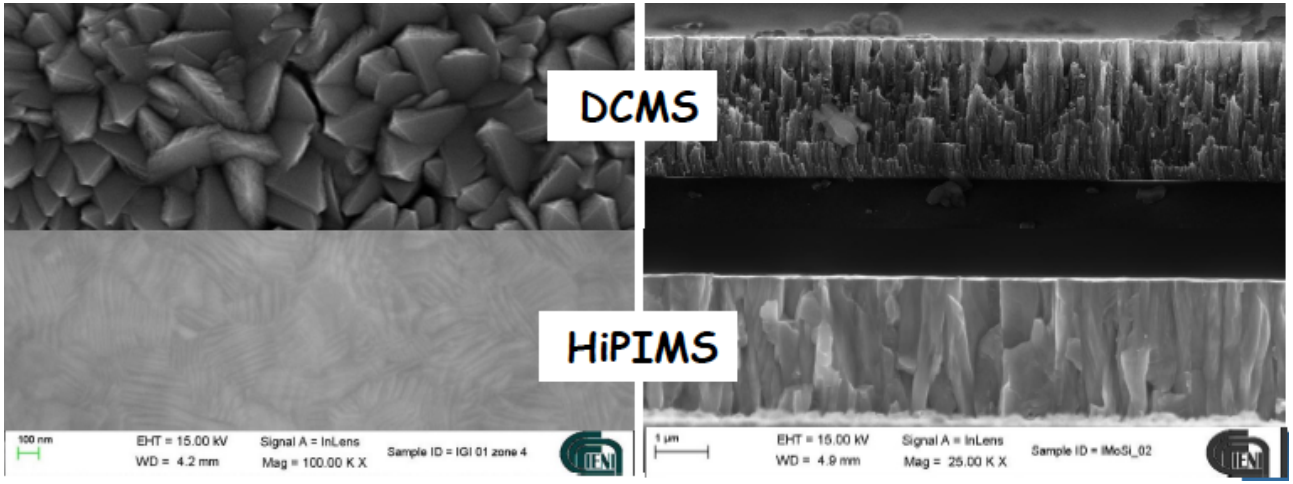
# HiPIMS – High Power Impulse Magnetron Sputtering

Istituto per l'Energetica e le Interfasi

Padova







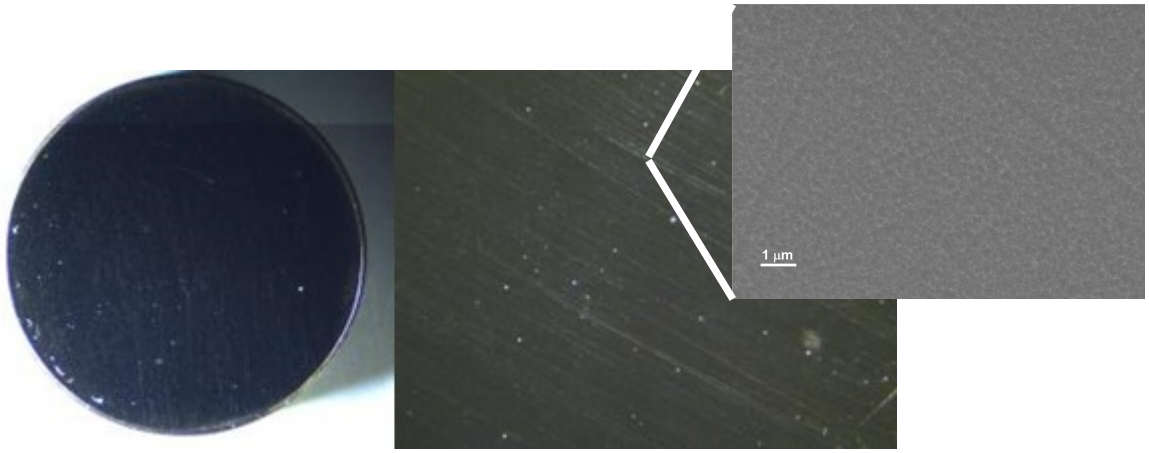
# Rivestimenti per turbine a gas



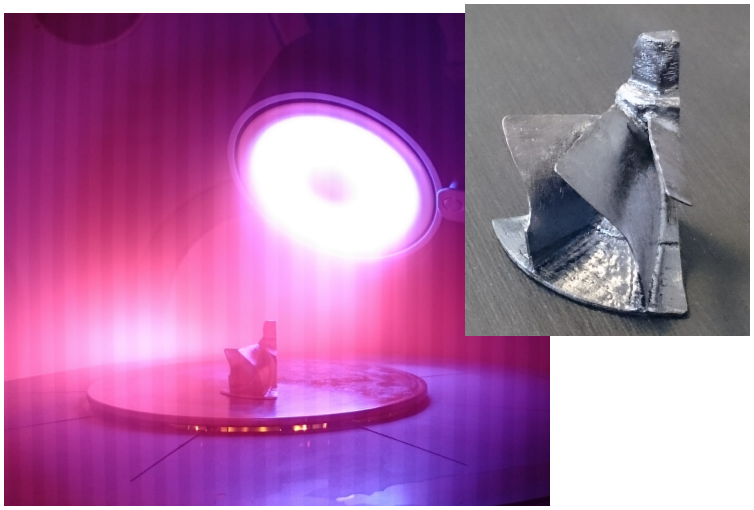
L'utilizzo di leghe TiAl in luogo di superleghe a base nichel permetterebbe una riduzione del peso di componenti strutturali delle turbine a gas del 20-30%, con miglioramento delle prestazioni della turbina e riduzione dei consumi.

È però necessario aumentarne la resistenza all'ossidazione (temperature fino a 850°C).

Il rivestimento con film a base di AlTiN via HiPIMS è mirato al miglioramento della resistenza ad ossidazione a caldo e al miglioramento della resistenza ad usura (test burner rig).




**AlTiN_001 depositato su lega a base TiAl**



***Poster P38:* E. Miorin et al. "HiPIMS films for extreme conditions"**

## Economia dell'idrogeno sostenibile

**membrane per la purificazione/separazione di idrogeno prive di metalli nobili o con film sottili contenenti metalli nobili**

# Membrane per separazione $H_2$



**Più del 90% dell'idrogeno viene da fonti fossili (US DoE)**

**Steam Methane Reforming (SMR):** $CH_4 + H_2O \leftrightarrow CO + 3H_2$

**Additional $H_2$ Water Gas Shift (WGS):** $CO + H_2O \leftrightarrow CO_2 + H_2$

**Target di costo previsti dal DoE = 1000$/m$^2$ ➡ Pd assente o spessore < 5 μm**

| **MEMBRANES TYPES** | **Dense polymer** Polyesters, urethanes | **Microporous ceramic** Silica, Alumina | **Dense metallic** Pd, V, Ta, Nb, their alloys | **Porous carbon** C | **Dense ceramic** Proton conducting ceramics |
|---|---|---|---|---|---|
| **T (°C)** | <100°C | 200-600°C | 300-600°C | 500-900°C | 600-900°C |
| **$H_2$ selectivity** | High | Moderate | Extremely high | Moderate-Low | Very High |
| **Transport mechanism** | Solution-diffusion | Molecular sieving | Solution-diffusion | Surface diffusion Molecular sieving | Solution-diffusion |
| **Advantages** | low cost, good scalability | Cost and Scalability | Selectivity | Temperature range | Selectivity |
| **Issues** | Chemical resistance Mechanical strength Swelling | Limited stability in steam Brittle | Material Cost Phase transition CO poisoning | Very brittle Oxidising Difficult processing | Stability ($CO_2$, $H_2O$) Early stage of development |

# Membrane per separazione $H_2$

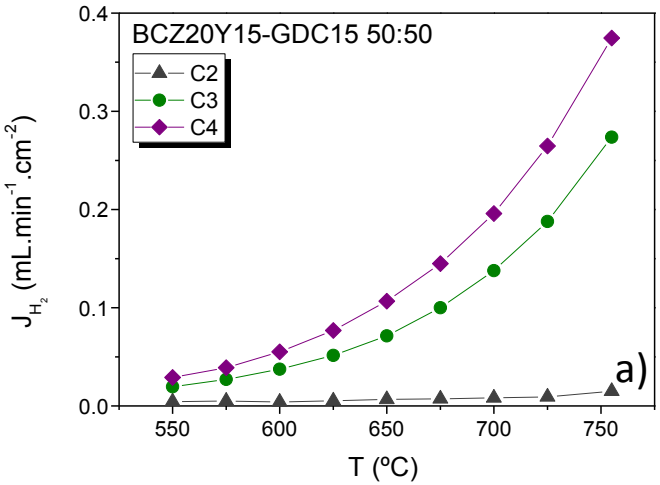
Istituto per l'Energetica e le Interfasi — Padova

**Membrane ceramiche: per trasporto non galvanico di idrogeno devono trasportare $H^+$ e elettroni**

| $H^+$-conductors |
|---|
| $BaCe_{1-x}Zr_xY_{0.15}O_{3-\delta}$ |

| $e^-$-conductors |
|---|
| $Ce_{1-y}M_yO_2$ (M = Y, Gd) |

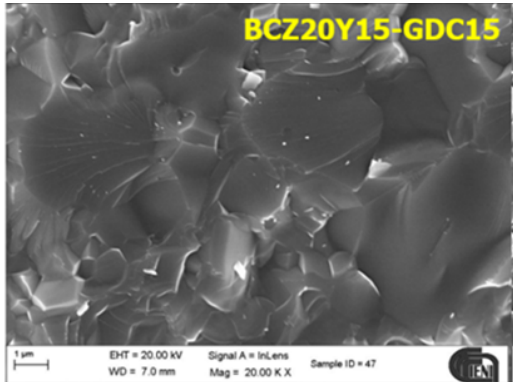
| Requisiti |
|---|
| Elevata conducibilità protonica e elettronica |
| Alti flussi $H_2$ (> 0,1 $m^3/h/m^2$) |
| Adeguata robustezza meccanica |
| Stabilità chimica alle T di esercizio (600-800°C) e in presenza di gas quali $CO_2$, CO, $CH_4$, $H_2S$, .. |
| Bassi costi di fabbricazione |




**For BCZ20Y15-GDC15 50:50 membrane, $H_2$ flow up to 0.35 mL·min$^{-1}$·cm$^{-2}$ at 755°C**

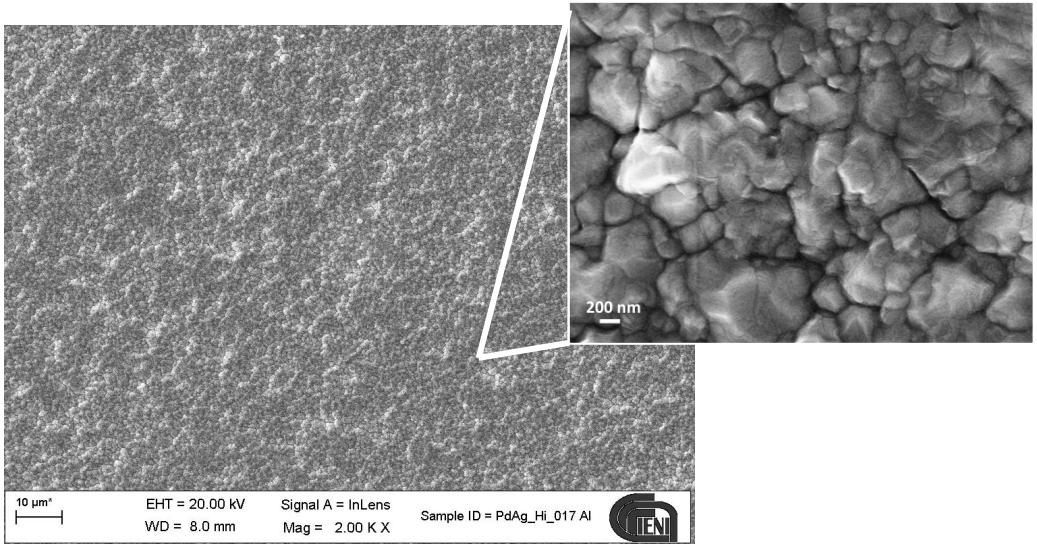
**Among the highest $H_2$ flows for bulk mixed protonic-electronic membranes**

**Stability demonstrated in $CO_2$ environment**

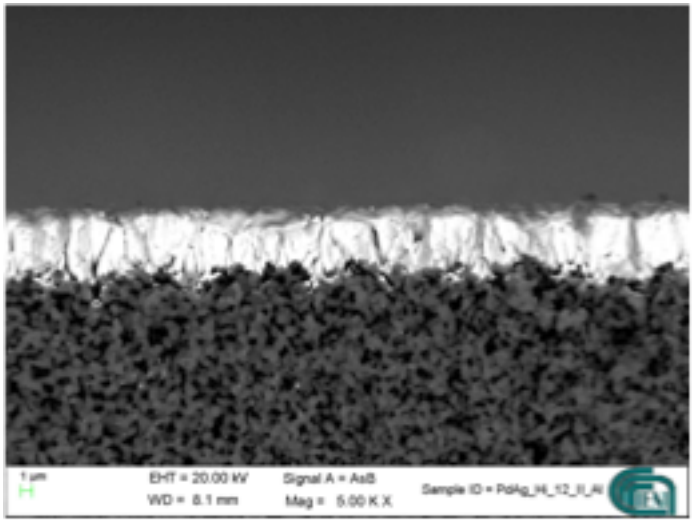



***Poster P34:*** *E. Rebollo et al. "Notable hydrogen permeation and $CO_2$-stability of ceramic-ceramic composite membranes based on $BaCe_{0.65}Zr_{0.2}Y_{0.15}O_{3-d}$ and Y- or Gd-doped $CeO_2$"*

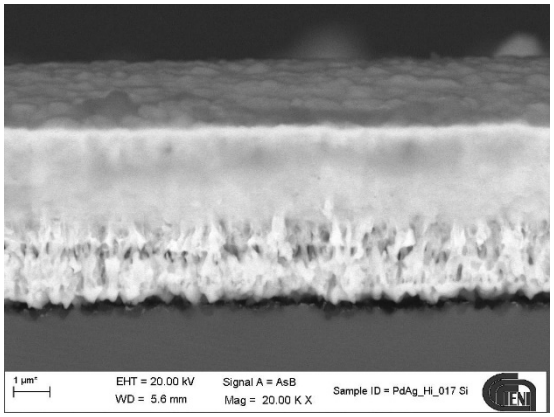
# Membrane metalliche di PdAg (Pd 77 wt% - Ag 23 wt%)




Pd-Ag su allumina porosa (superficie)




Pd-Ag su allumina porosa (sezione)




Pd-Ag su Si

**Altre leghe di Pd in fase di studio**

## Energie rinnovabili sostenibili

# Nanofluidi neri per l'assorbimento solare.

# Nanofluidi neri per l'assorbimento della radiazione solare

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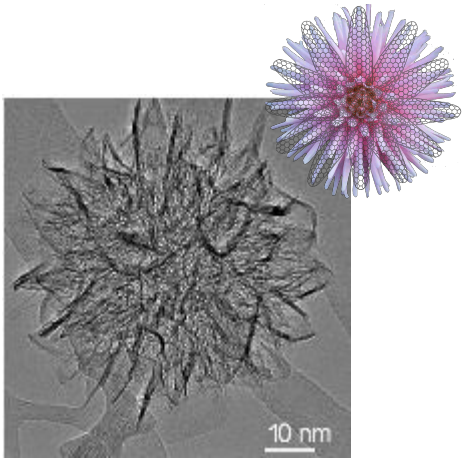
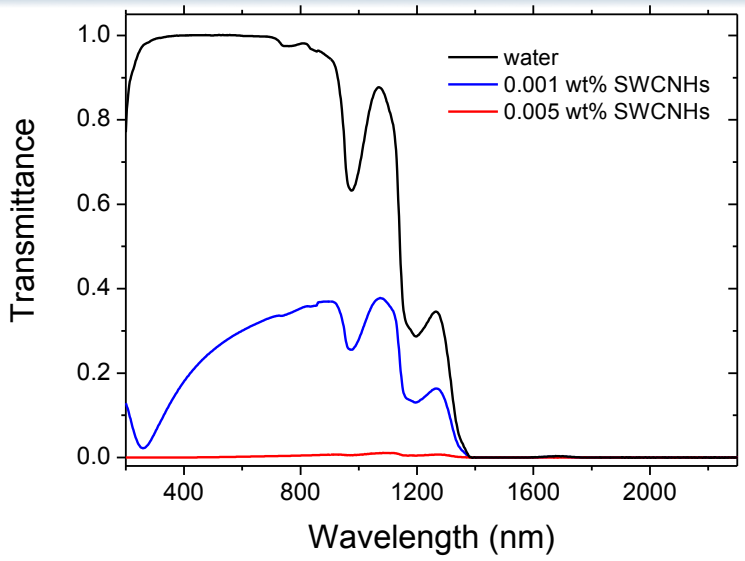
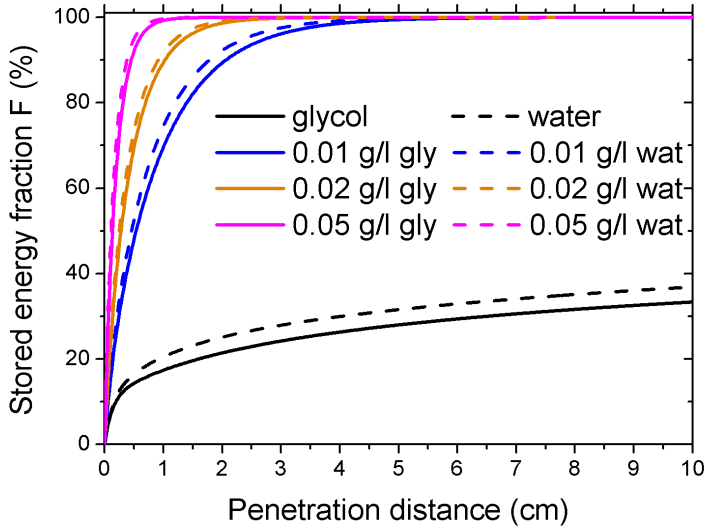
**0.005wt%** **0.001wt%**




***Presentazione Lunedì 29 ore 17.15: S. Fasolin "Metodologie di sintesi di materiali per l'energetica"***