# Thermoelectric Micro- / Nano - Cementitious Composites For Potential Thermal Energy Harvesting

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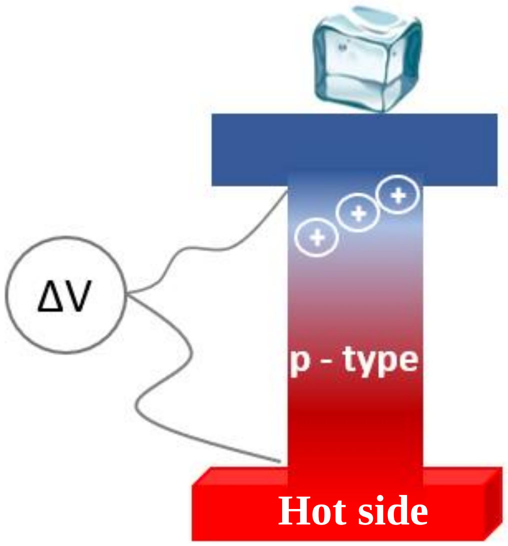
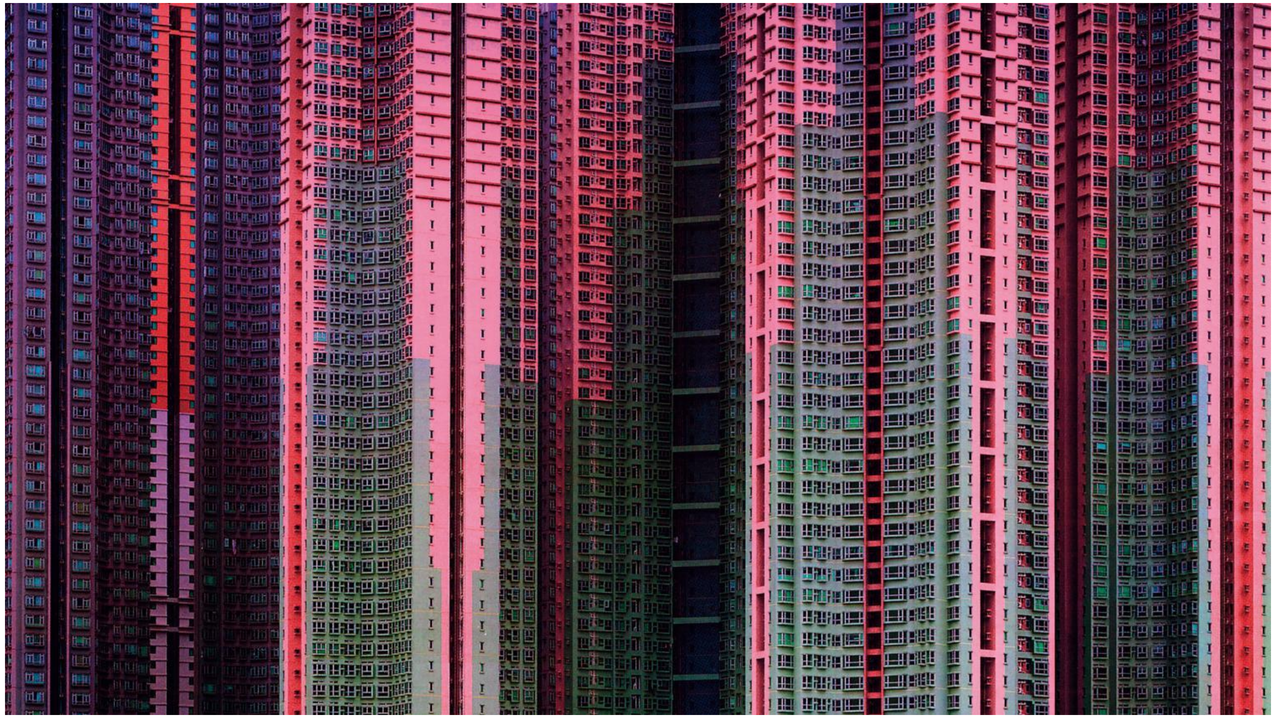


# Motivation

## Urban Environment



## Infrastructure

- Cost-effective
- Versatile
- Durable
- Constructable
- Available

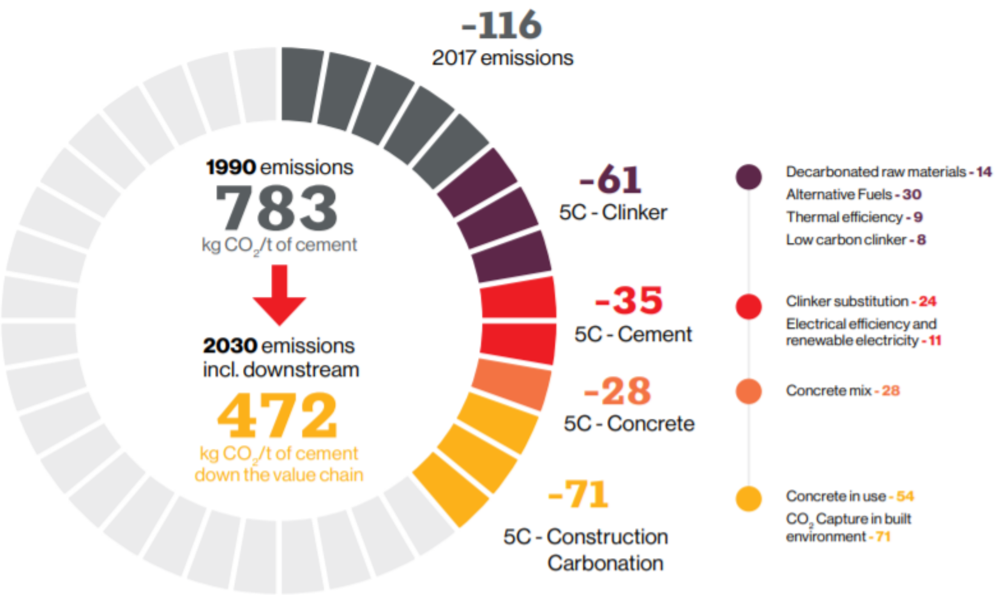
# Motivation


"Infrastructure either directly or indirectly influence all 17 of the SDGs, including 121 of the 169 targets (72%)."

Thacker et al, Nature Sustainability, 2019

Cement industry

(8-10 % of global $CO_2$ emission)




2020 Global status report for buildings and construction, UN Environment programme, Global Aliance for Buildings and Construction.

**Can cement become sustainable by adding new functionalities?**

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# Smart and multi-functional cement

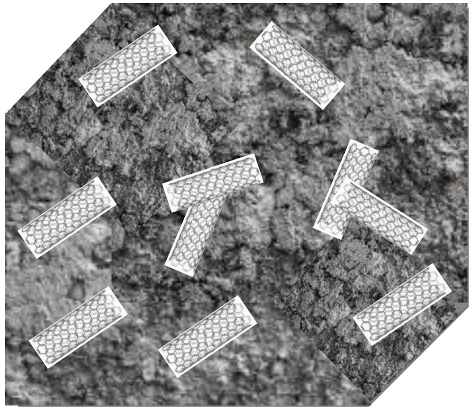
**Smart materials**: Designed with properties that can be significantly changed in a controlled fashion by external stimuli such as stress, moisture, electric field or magnetic fields.

External Stimuli

**Conventional Concrete**

No response

External Stimuli

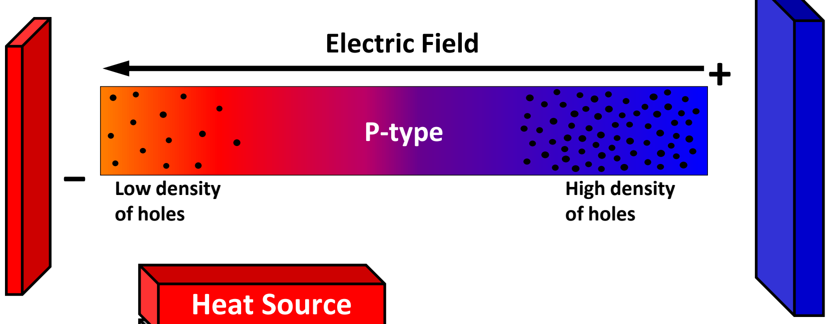


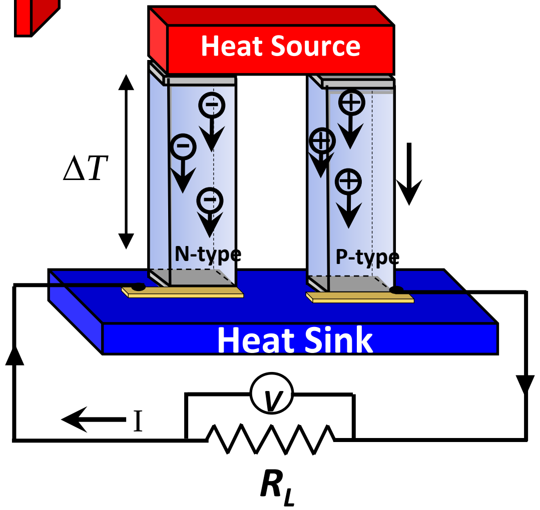
**Smart & Multifunctional Concrete**

- ✓ **Self-sensing**
- ✓ **Self-curing**
- ✓ **Enhancement in mechanical performance**
- ✓ **Electrically conductive for monitoring purposes**
- ✓ **Thermoelectrically conductive for energy harvesting**

# Basics of Thermoelectricity - State-of-the-Art

## The Seebeck Effect ($S$)




Thermoelectric Power Generation

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

$$PF = S^2\sigma \ (\mu W \ m^{-1} \ K^{-2})$$

$$S = {}^{\Delta V}/_{\Delta T} \ (\mu V/K)$$

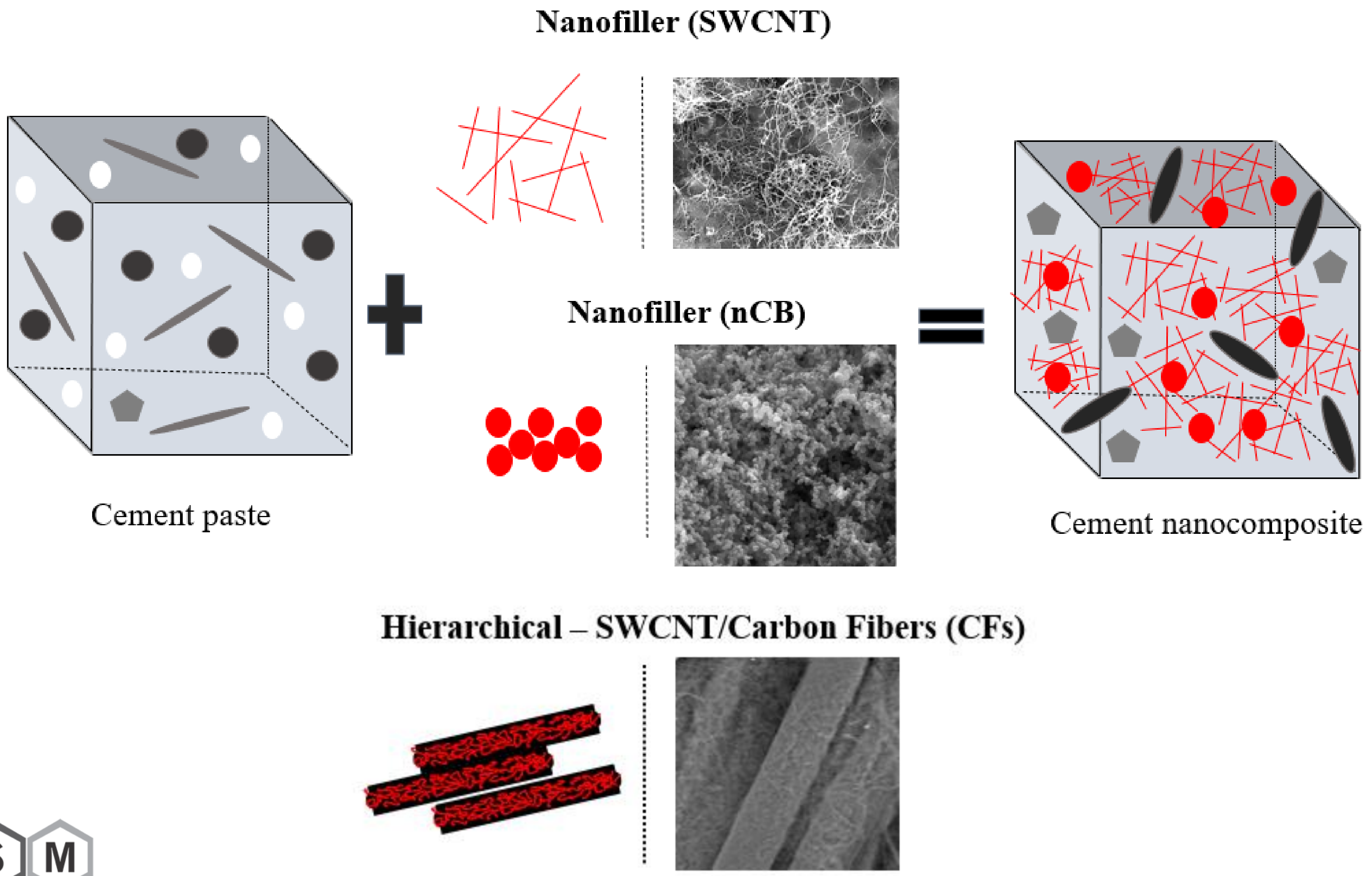
## Ideal Thermoelectric Material

Higher Seebeck coefficient ($S$)
Higher electrical conductivity ($\sigma$)
Lower thermal conductivity ($\kappa$)

- Thermoelectric properties for ***p***-type **cement-based** composites with carbon inclusions as found in the literature.

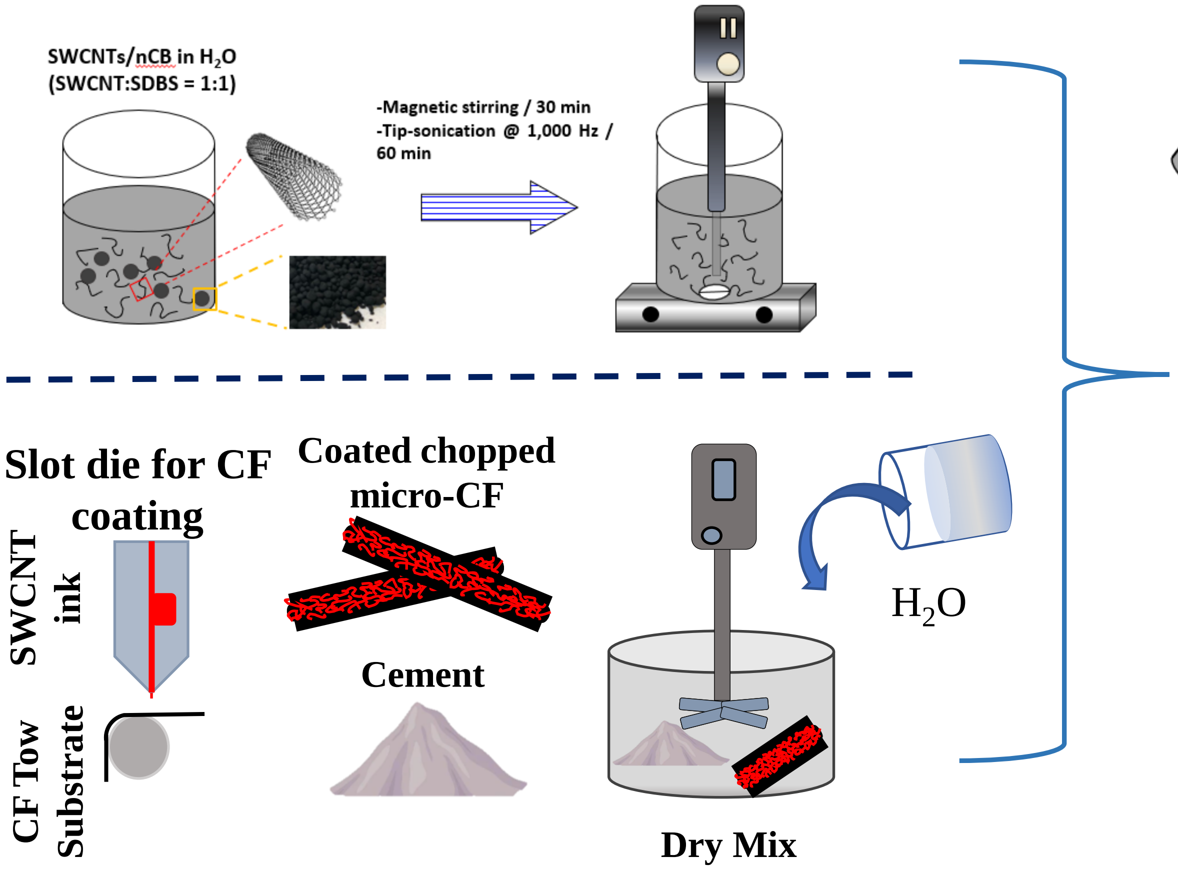
| Materials | Concentration (wt.%) | $S$ (μV/K) | Ref |
|---|---|---|---|
| Carbon Fibers + MWCNT | 0.4 + 0.5 | 21.7 | Zuo et al. 2018 |
| Graphene Nanoplatelets | 15.0 | 340 | Ghosh et al. 2019 |
| SWCNT | 0.5 | 1348.8 | Vareli et al. 2021 |
| Reduced Graphene Oxide | 0.15 | 159.7 | Cui et al. 2022 |
| TZ +nano $Fe_2O_3$ + CF | 0.6 + 0.5+0.5 | 1123.4 | Wan et al. 2023 |

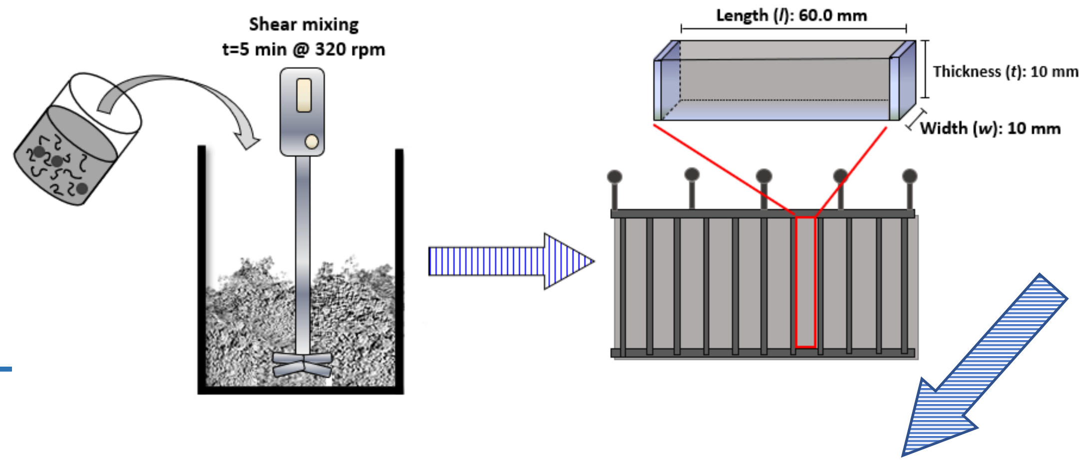
# Micro- and nano- conductive cement-based nanocomposites

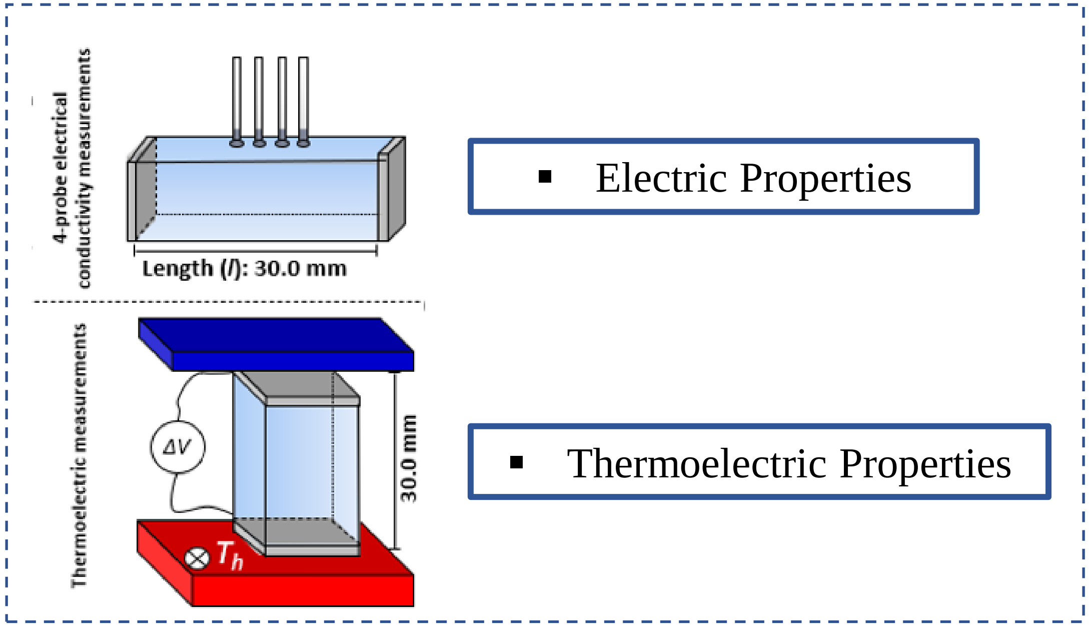



- Electrically and Thermoelectrically conductive
- Energy Storage
- Energy Harvesting

# Micro- and nano- composites fabrication &characterisation




"Monitoring the properties of cementitious composite materials with advanced functionalities", **A. Gkaravela**, I.Vareli, N.-M.Barkoula and A.S. Paipetis

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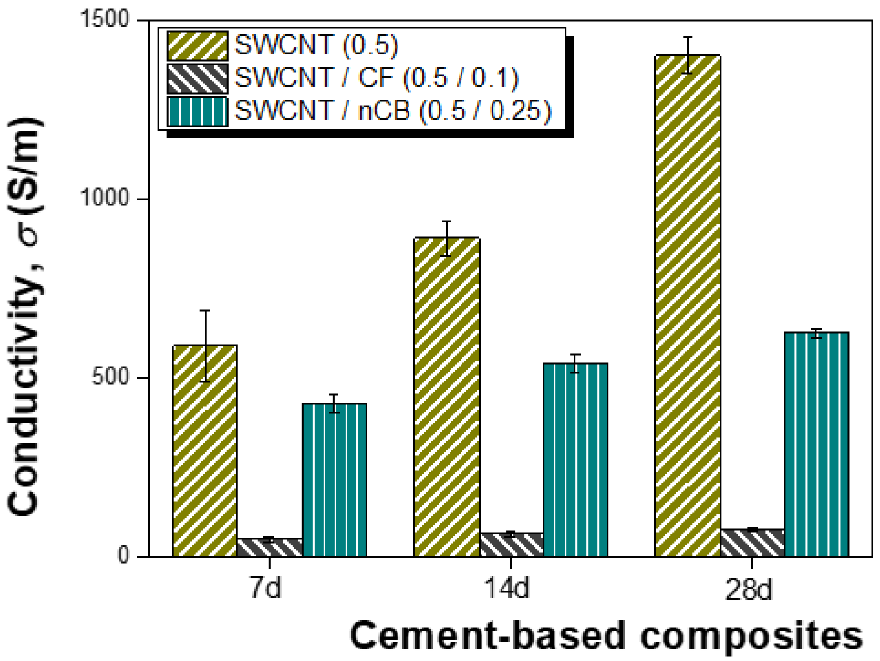
# Electrical conductivity of cement-based micro- and nanocomposites

<u>Cement/micro- and nano-composites</u>

- Examined at: 7, 14 and days

- Higher electrical conductivity ($\sigma$ **= 1.41 × 10$^3$ S/m**) corresponds to the cement/SWCNT enhanced with 0.5 wt.% SWCNT

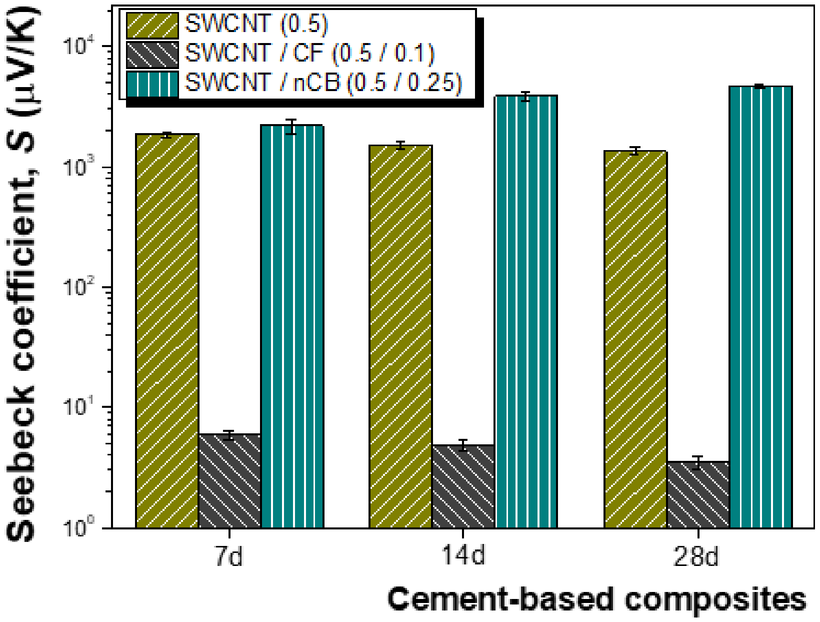
- High value compared to the SWCNT inherent electrical conductivity ($\sigma$ **= 10$^4$ S/m**)

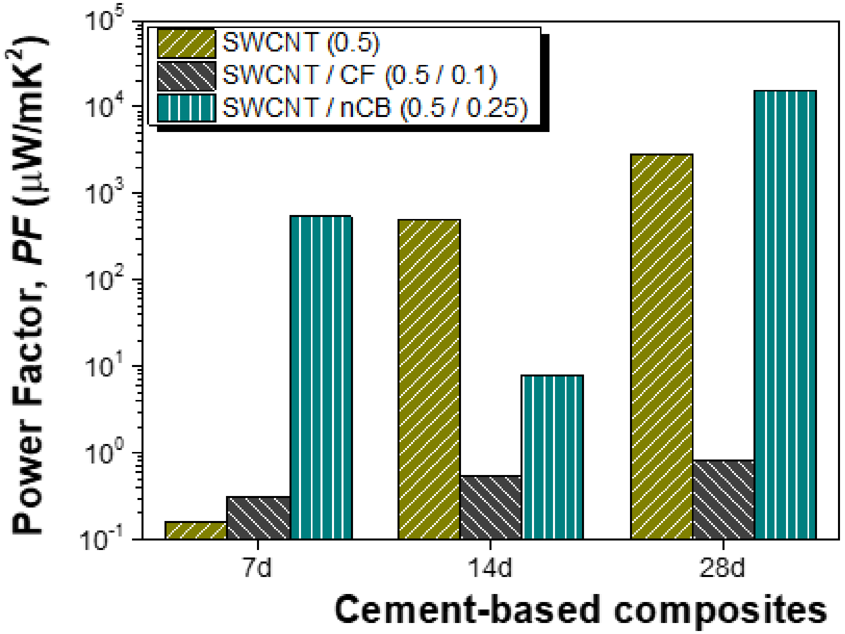



# Thermoelectric properties (*S*, *PF*) of cement/SWCNT-nCB nanocomposites

Cement/micro- and nano-composites

- Seebeck coefficients (***S***) at 7, 14, 28 days, at the steady state.
- $S = S_{el} + S_{ionic}$
- Highest measured ***S*** value for cement/SWCNT-nCB (0.5-0.25) = 4644.2 μV/K at Δ*T* = 25 K.
- Energy filtering at the interface of SWCNT-nCB greatly enhance *S*.
- Intentionally chosen **low thermal gradients** keeping in mind the potential TE applications.
- The *σ*, *S* and *PF* = $1.51\times10^4$ μW $m^{-1}$ $K^{-2}$, values reported here are the highest among carbonaceous cement-based composites.



# Cement/SWCNT TEG device performance and power output characteristics

Cement/SWCNT TEG device

- **10** cement/ SWCNT (0.5) p-type thermoelements serially interconnected at $\Delta T$ = 25 K.

- Experimentally measured $\boldsymbol{R_{TEG}}$ , $\boldsymbol{V_{TEG}}$ (otherwise defined as $\boldsymbol{V_{out}}$ or open circuit voltage $\boldsymbol{V_{oc}}$ of the device) and short circuit current ($\boldsymbol{I_{sc}}$).

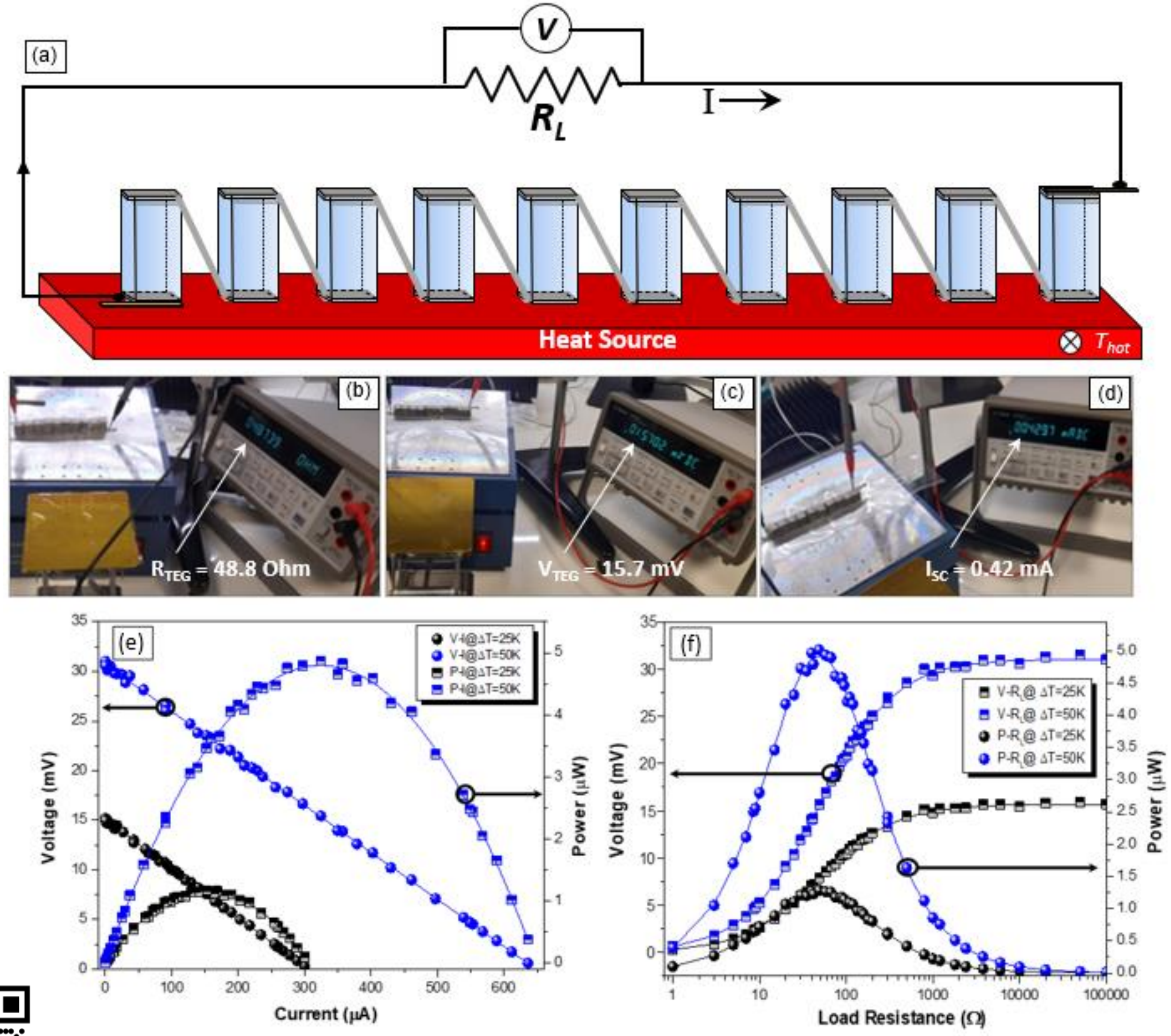
- *Experimentally measured* $\boldsymbol{V_{TEG}}$ = *15.7* mV
  ($V_{TEG} = V_1 + V_2 + ... + V_{10}$)
  Expected and theoretical $\boldsymbol{V_{TEG}} = N \times S \times \Delta T = 337$ mV

- Cement ions are not harvested to the external circuit at the TEG level; still contribute to charge-transfer doping to the SWCNTs enhancing their p-type character.

- Maximum electrical power output ($\boldsymbol{P_{max}}$)

$$P_{max} = \frac{(N\,S\,\Delta T)^2}{4R_0} = \frac{\Delta V^2}{4R_0} \quad \text{(Eq.1)}$$

- Expected $\boldsymbol{P_{max}}$ = 1.26 μW at $\Delta T$ = 25 K
  Experimentally measured $\mathbf{P_{max}}$ = 579.4 μW at $\Delta T$ = 25 K



# Cement/SWCNT-nCB TEG device performance and power output characteristics

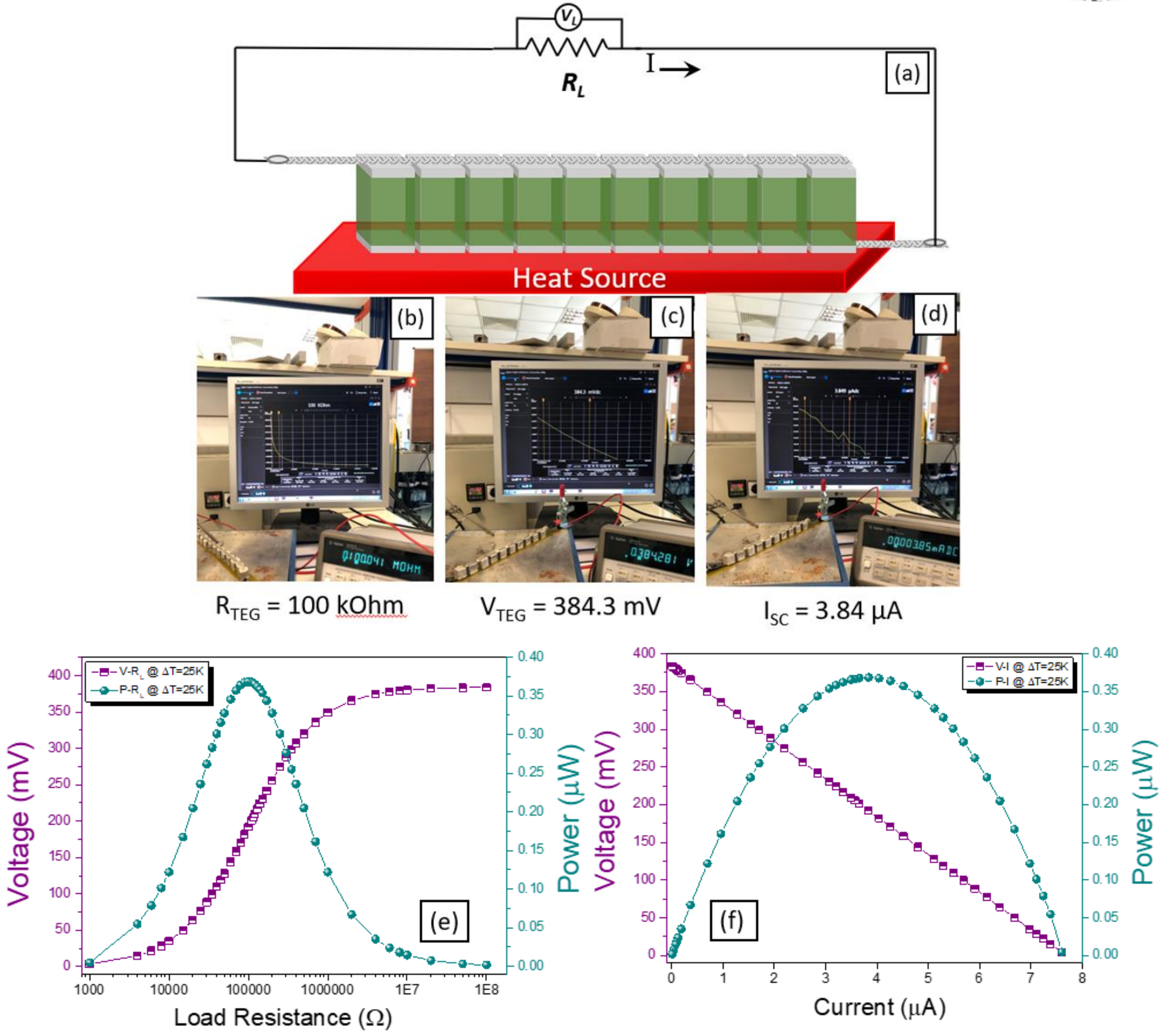
Cement/SWCNT-nCB TEG device

- **10** cement/ SWCNT-nCB (0.5-0.25) p-type thermoelements interconnected in parallel at $\Delta T$ = 25 K.

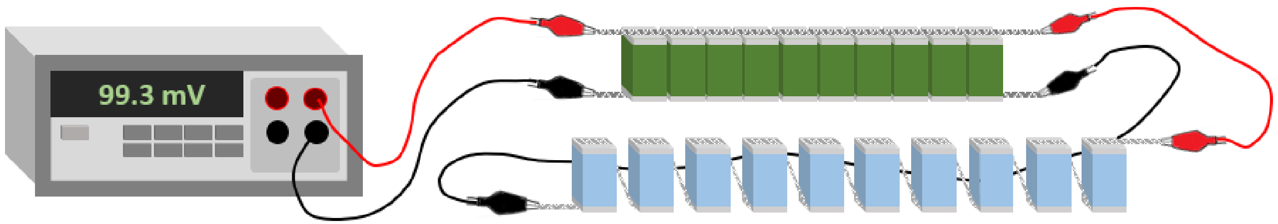
- *Experimentally measured* $\boldsymbol{V_{TEG}}$ = *384.3* mV
($V_{TEG} = V_1 + V_2 + ... + V_{10}$)
Expected and theoretical $\boldsymbol{V_{TEG}} = N \times S \times \Delta T$ = 1.85 V

- Cement ions are not harvested to the external circuit at the TEG level; still contribute to charge-transfer doping to the SWCNTs enhancing their p-type character.

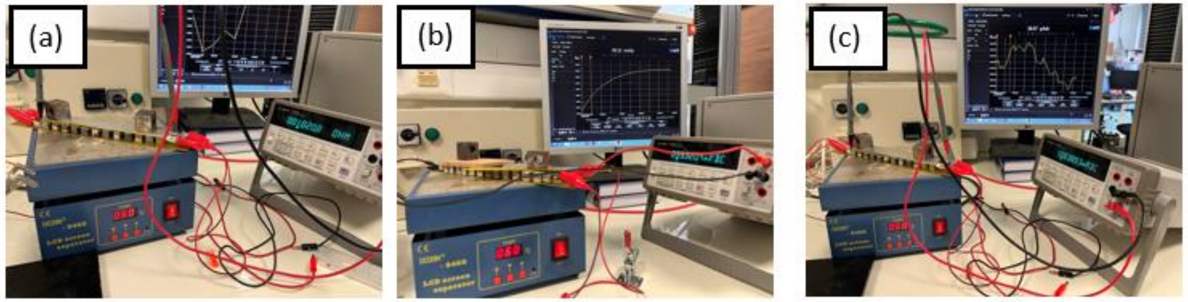
- Expected $\boldsymbol{P_{max}}$ = 3.55 μW at $\Delta T$ = 25 K
Experimentally measured $\mathbf{P_{max}}$ = 0.369 μW at $\Delta T$ = 25 K



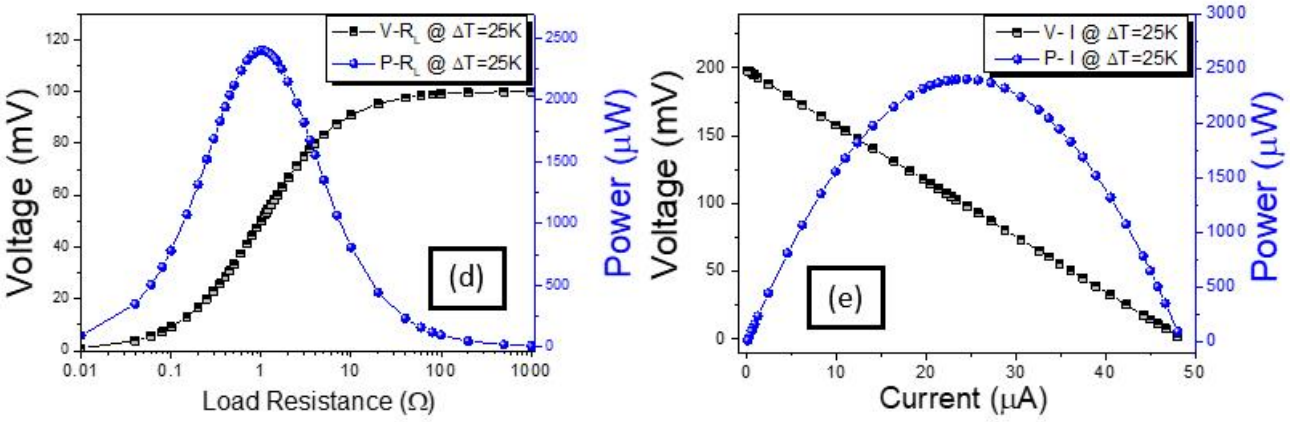
# Hybrid-TEG device performance and power output characteristics




| Number of TE | Type of TE | TE connection | TEG connection | TEG Power density @ $\Delta T$=25K |
|---|---|---|---|---|
| 10 | Cement/ SWCNT | In series | - | 1.28 $mW/m^2$ [19] |
| 10 | Cement/SWCNT-nCB | In parallel | - | **0.36 $mW/m^2$ (This work)** |
| 20 | Cement/SWCNT-nCB & Cement/ SWCNT | - | In parallel | **1.20 $W/m^2$ (This work)** |




$R_{TEG}$ = 1.02 Ohm  $V_{TEG}$ = 99.32mV  $I_{SC}$ = 38.93 μA



# Summary – Next Steps

- The **thermoelectric properties** of **cement nanocomposites** with **single-walled carbon nanotubes (SWCNT)**, **nano-Carbon Black** and **Hierarchical Carbon Fibers** at **28** days of hydration are reported.

- The as-developed thermoelements with inherent **p-type** semiconductor characteristics were introduced into the cementitious matrix as thermoelectric materials for future energy harvesting applications.

- **28** days cement/SWCNT-nCB sample with **0.5 wt.% and 0.25 wt.% loading** exhibited the highest performance in terms of $S$ (+ 4644.2 μV/K) and $PF$ ($1.51\times10^{4}$ μW $m^{-1}$ $K^{-2}$)

- **(i) Cement/SWCNT (0.5) , Cement/SWCNT-nCB(0.5 – 0.25),** and **Cement/SWCNT-CF** was used for the fabrication of a thermoelectric generator (**TEG**) device exhibiting a maximum **power output** ($P_{max}$) of 0.789 μW upon being exposed to a temperature difference ($\Delta T$) of 25 K.

- In conclusion, p-type cement/SWCNT-nCB nanocomposites act differently when incorporated into a TEG device.

○ Fabrication of $p^+/n^-$ TEG device

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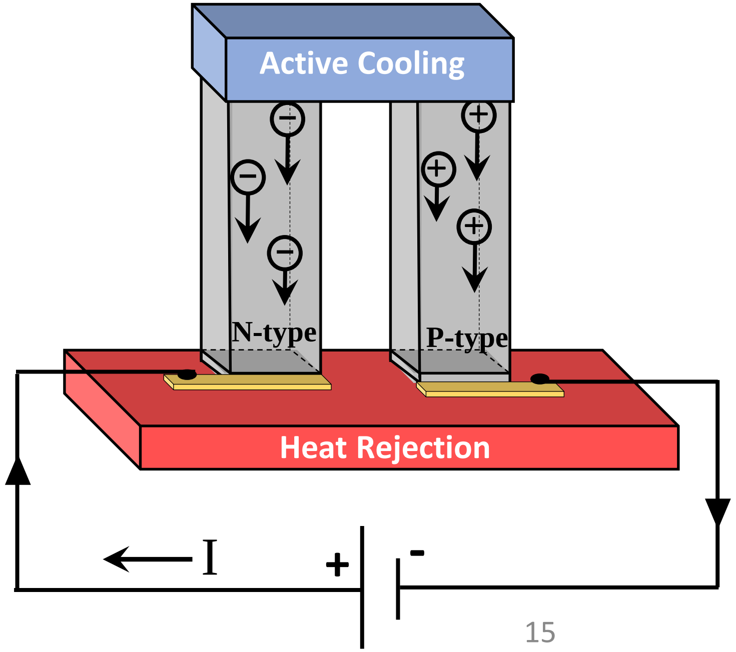
# Thank you for your attention.
# Any questions?

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