Large power factor improvement in a thermoelectric oxide using liquid electrolytes

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Outline

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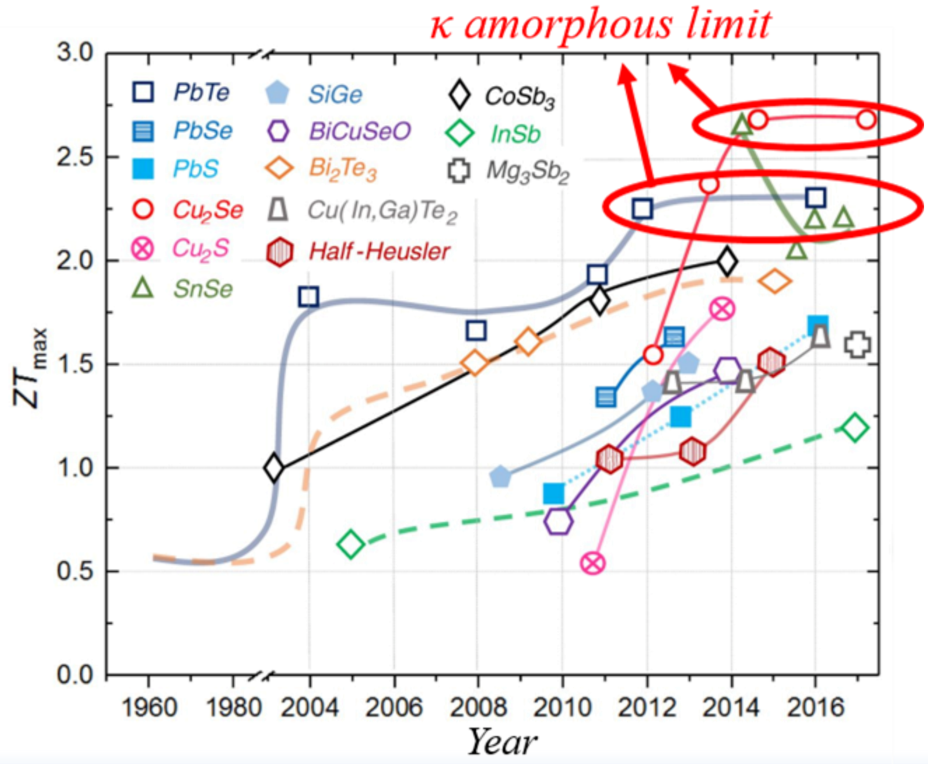
1. Introduction

Problems for widespread application

Thermoelectrics are not widely implemented due to:

- Toxicity of common materials, e.g. Bi_2Te_3, PbTe
- High cost and scarcity
- **Low efficiency** (4 – 6%)



*J. He, T.M. Tritt, **Science** 357, eaak9997 (2017)*

In the last years efficiency (ZT) has been improved, mainly by **decreasing λ** by **nanostructuring**.

But **λ** is already reaching its lowest possible values (**amorphous limit**).

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

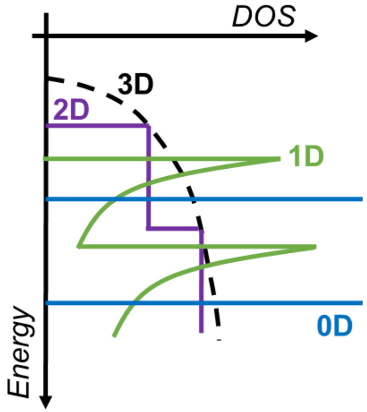
Improvements in the power factor (*PF=*$S^2\sigma$) are required.

1. Introduction

Current strategies: Seebeck coefficient enhancement

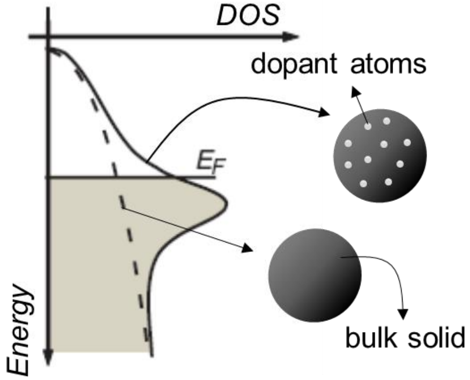
The Seebeck coefficient can be improved by introducing **sharp features** in the **density of states** (DOS) of the semiconductor

a) Quantum confinement: Sharp features in the DOS can be reached in **low-dimensional materials** such as quantum well superlattices (2D), nanowires or nanotubes (1D), and quantum dots (0D).



b) Resonant levels: Introducing **resonant states** in the conduction or valence band **by doping** a material **with certain atoms** can also create sharp features in the DOS.

ZT of p-type PbTe was doubled (from 0.71 to 1.5) by doping with Tl using this strategy.



a) Hicks, LD; Dresselhaus, MS. Effect of Quantum-Well Structures on the Thermoelectric… **Phys. Rev. B** 1993, 47 (19), 12727

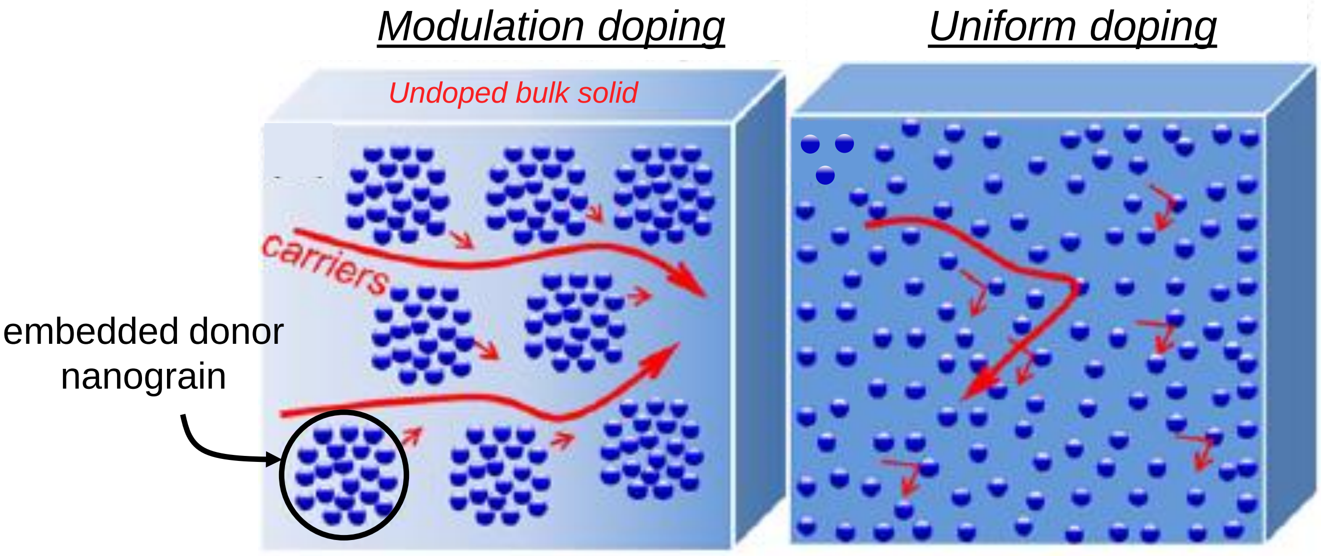
b) Heremans, JP; Jovovic, V; Toberer, ES; Saramat, A; Kurosaki, K; Charoenphakdee, A; Yamanaka, S; Snyder, GJ. Enhancement of Thermoelectric Efficiency in PbTe by Distortion of the Electronic DOS. **Science** 2008, 321, 554–557.

1. Introduction

Current strategies: Electrical conductivity enhancement

c) Modulation doping: high carrier concentration (10^{18}-10^{21} cm^{-3}) is usually achieved by **conventional doping** (uniformly distributed dopant atoms), but this can **reduce** the carrier **mobility** due to the **scattering with the dopants**.
By doping the material with **embedded nanograins** (3D modulation doping) the **scattering** can be **reduced**.

*In p-type SiGe 3D modulation doping led to around **40% PF enhancement** (*Zebarjadi, M et al. ***Nano Lett.*** 2011, *11*, 2225***)**.*



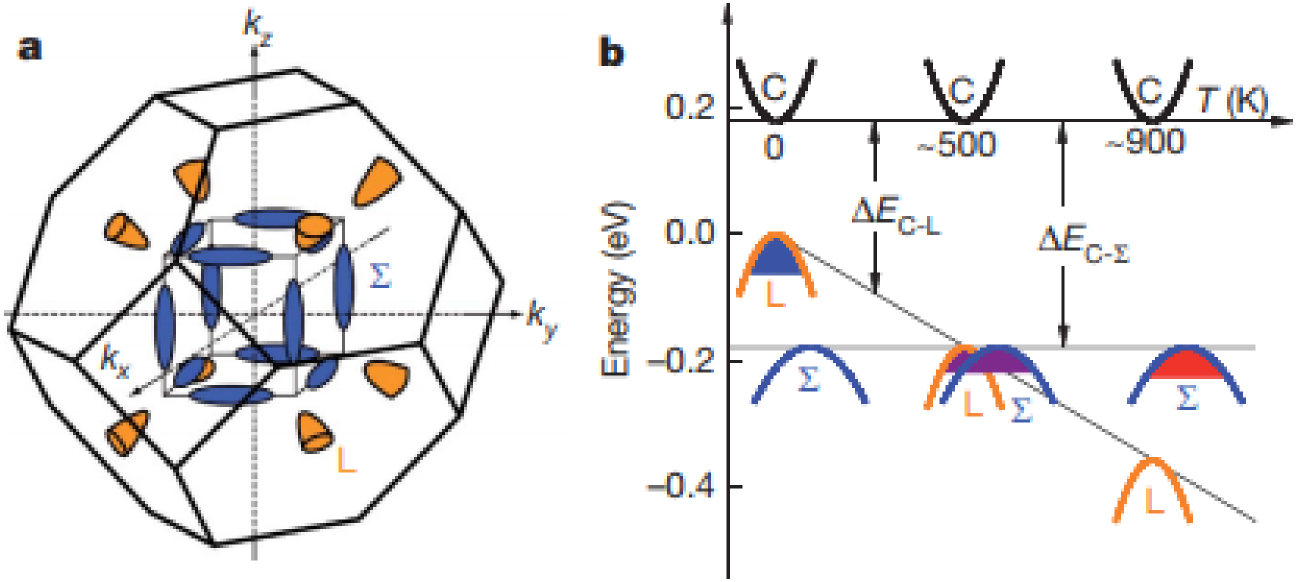
Pei, Y. L.; Wu, H.; Wu, D.; Zheng, F.; He, J. High Thermoelectric Performance Realized in a BiCuSeO System by Improving Carrier Mobility through 3D Modulation Doping. **J. Am. Chem. Soc.** 2014, 136 (39), 13902

1. Introduction

Current strategies: Electrical conductivity and Seebeck enhancement

d) Band convergence: By **doping or changing the composition** certain materials allow having a large number of energy bands in a close energy range (**band degeneracy**), which can simultaneously increase σ and S.

In PbTe doped with Sn, allowed obtaining a ***ZT=1.8***.

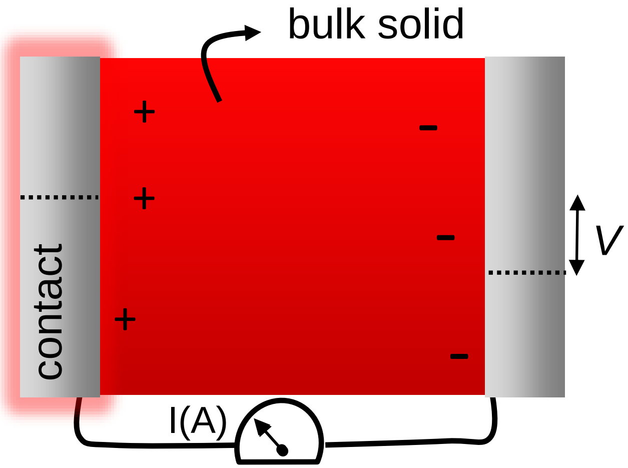


Pei Y1, Shi X, LaLonde A, Wang H, Chen L, Snyder GJ. Convergence of electronic bands for high performance bulk thermoelectrics. **Nature** 2011, 473, 66.

2. The solid-liquid hybrid system

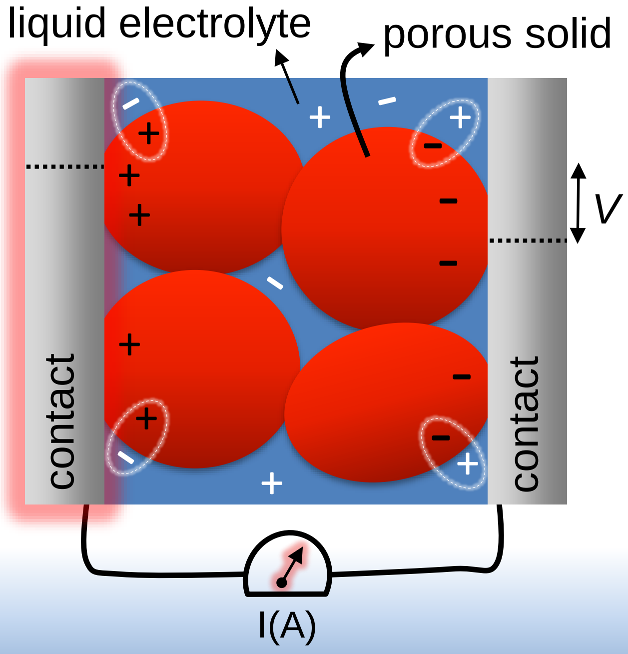
Current strategies

They have **not** produced ***very large increments*** in the *PF* and are usually **difficult to implement** and restricted to **only certain materials**.



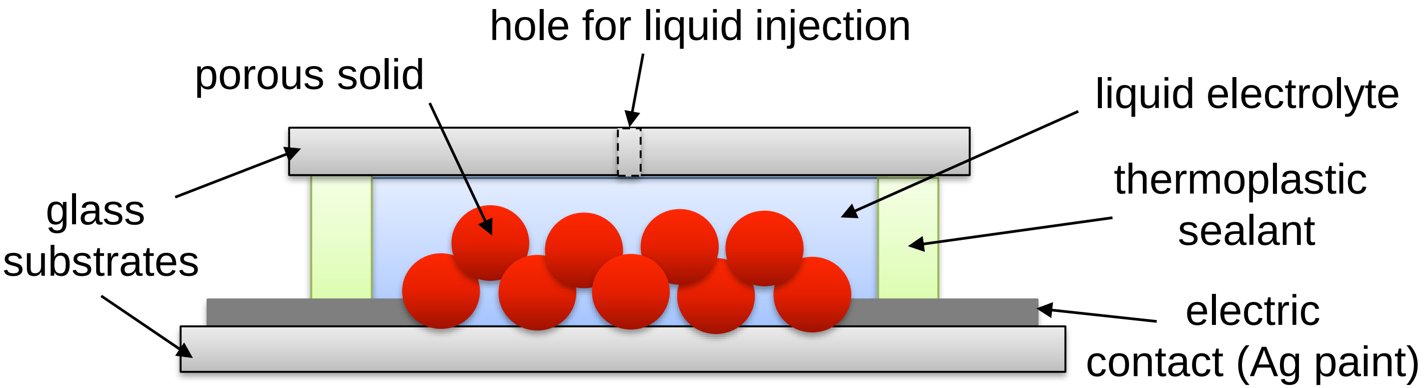
Our approach

Use of a **porous material** and **modify** its **thermoelectric properties** with a **liquid electrolyte** (dissolved ions).
Can be extended to a wide range of materials and be more **generally applied.**

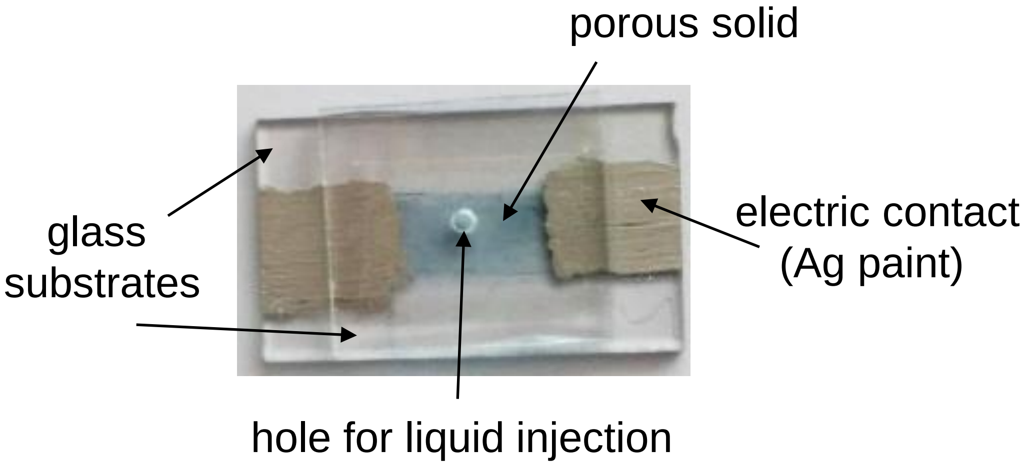


2. The solid-liquid hybrid system

The solid-liquid hybrid device



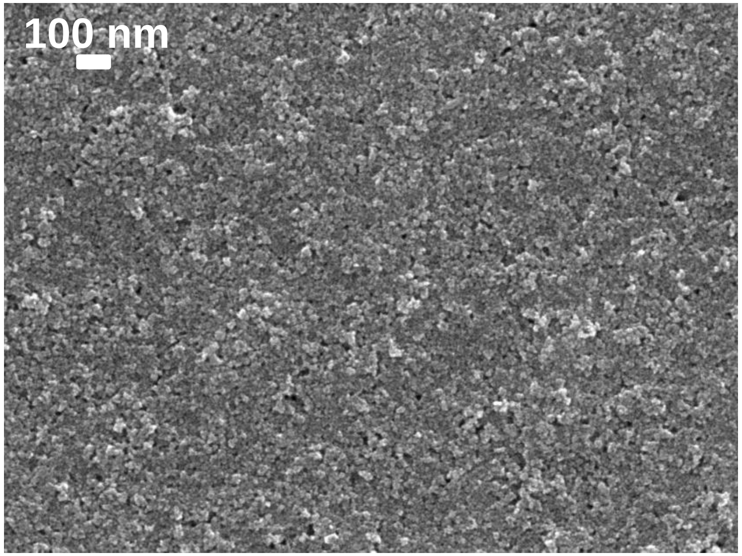
Photograph of sealed device



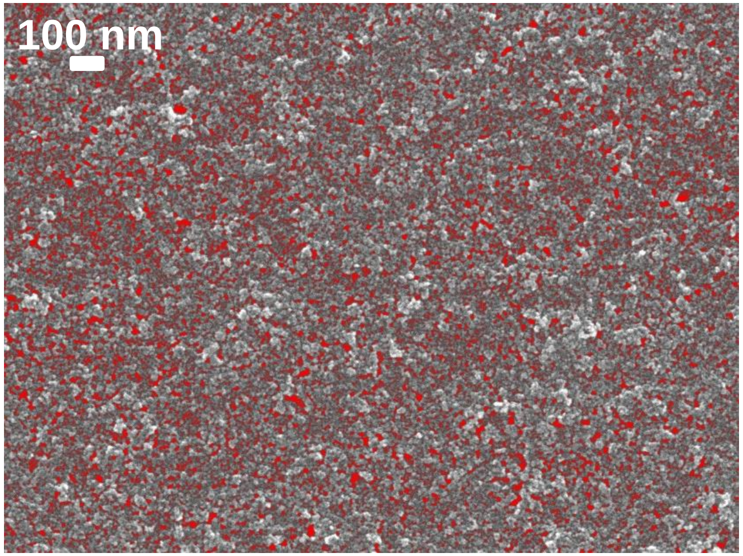
2. The solid-liquid hybrid system

The porous solid: mesoporous Sb:SnO$_2$

Prepared from commercial **colloidal water dispersion** (Keeling and Walker Ltd., UK) mixed with 60% v/v **ethanol**. Deposited by **spin coating** (several layers) and **annealed at 550 ºC** for 45 min.



(SEM image)



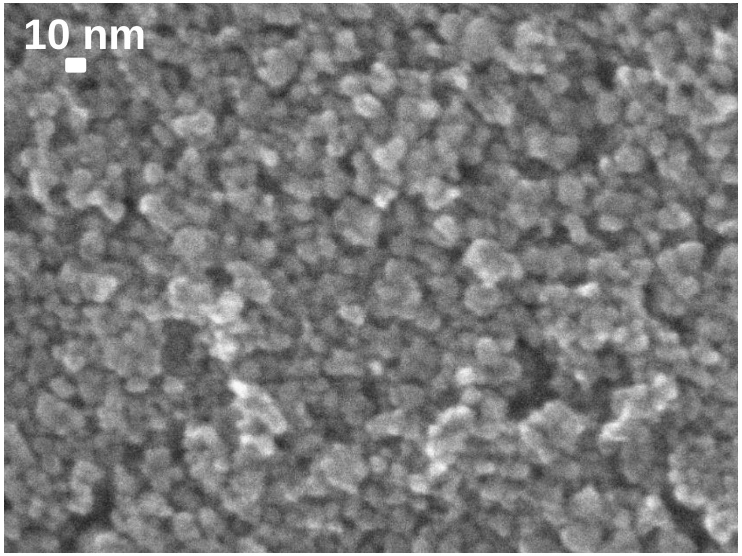
(Same SEM image with pores indicated in red)

Pores in the **2-50 nm range** (mesoporous) are present.
Image analysis provides **9.9% porosity**.

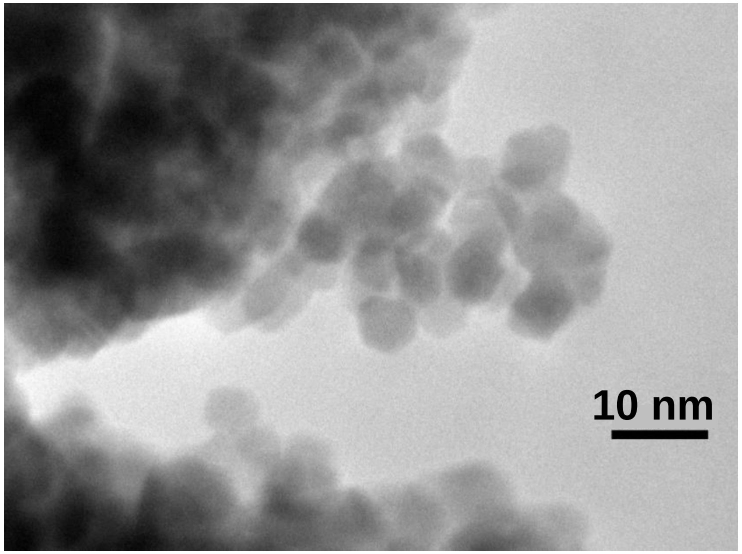
2. The solid-liquid hybrid system

The porous solid: nanostructured and mesoporous Sb:SnO$_2$

Film is formed by interconnected **nanoparticles** of around **4 to 10 nm** diameter.
The film thickness varied from 0.5 to 1.0 µm (Dektack 6, Veeco).



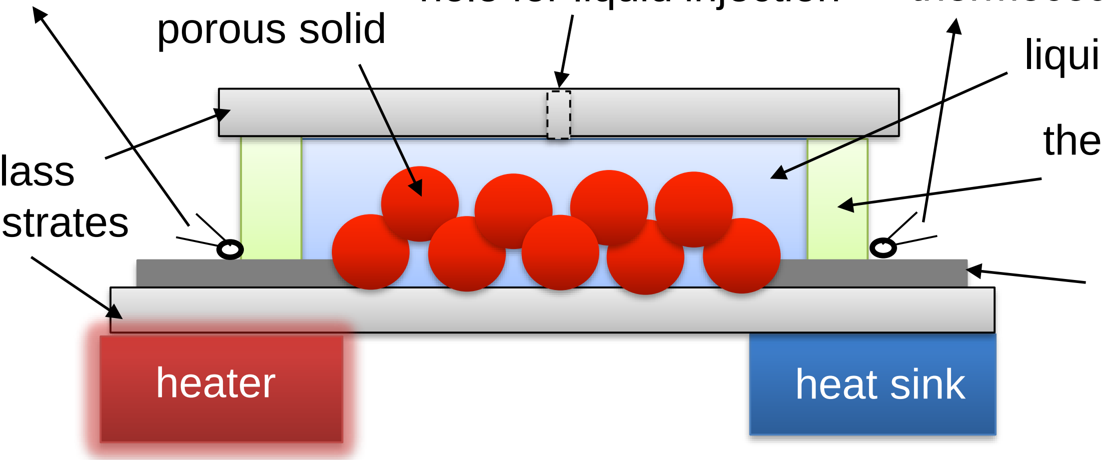
(SEM image)



(TEM image)

2. The solid-liquid hybrid system

Thermoelectric characterisation



thermocouple

porous solid

hole for liquid injection

thermocouple

liquid electrolyte

glass
substrates

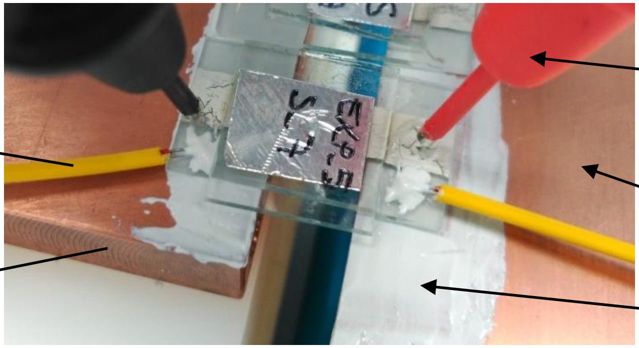
thermoplastic
sealant

electric
contact

heater

heat sink

Photograph



thermocouple

electric
contact probe

heat sink Cu block

heater block

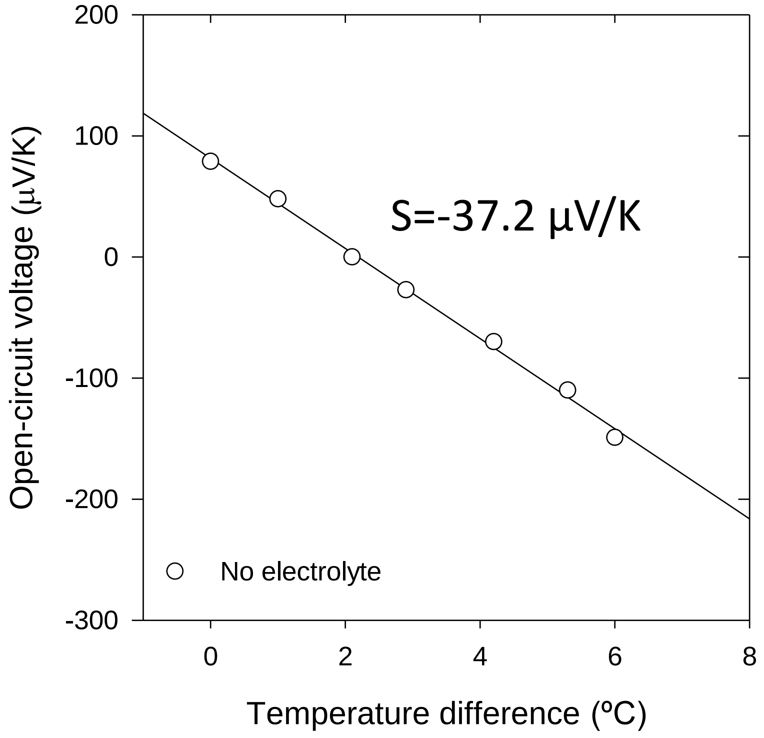
thermal grease

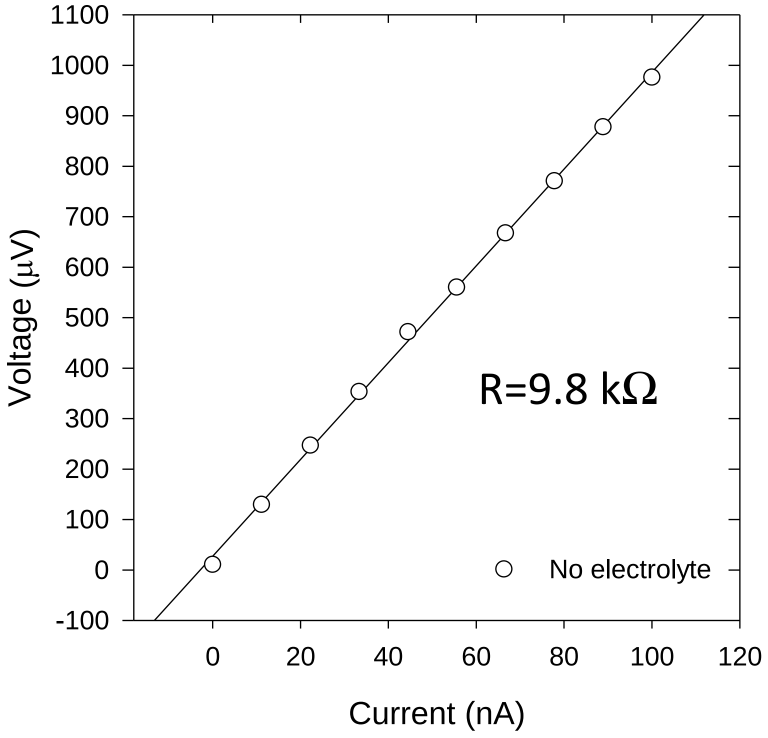
(Device with liquid being measured)

2. The solid-liquid hybrid system

Thermoelectric measurements: No electrolyte

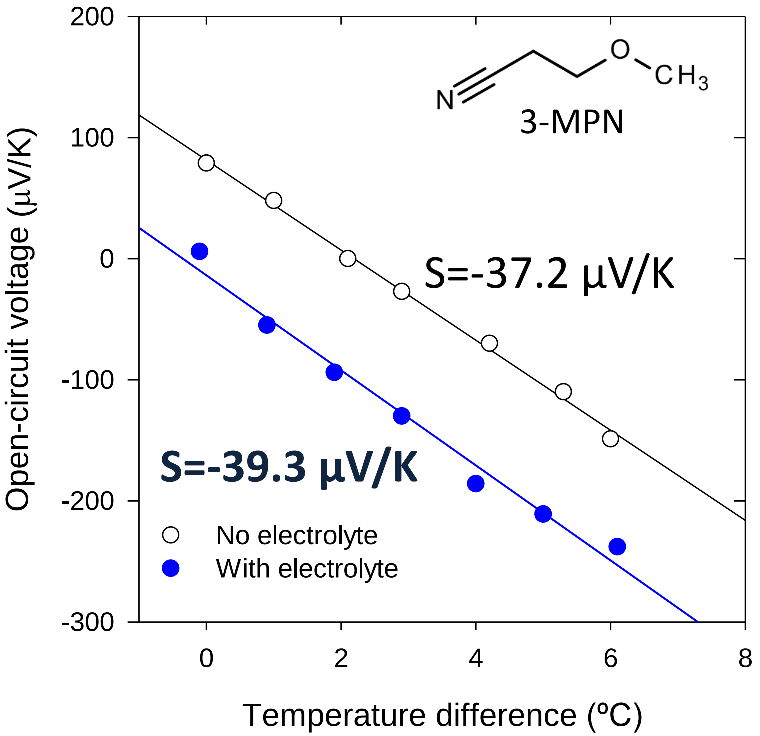
Seebeck coefficient: Extracted from the slope of the V_{oc} – ΔT plot.
Device electrical resistance: Extacted from the slope of the V – I curve under no T difference.

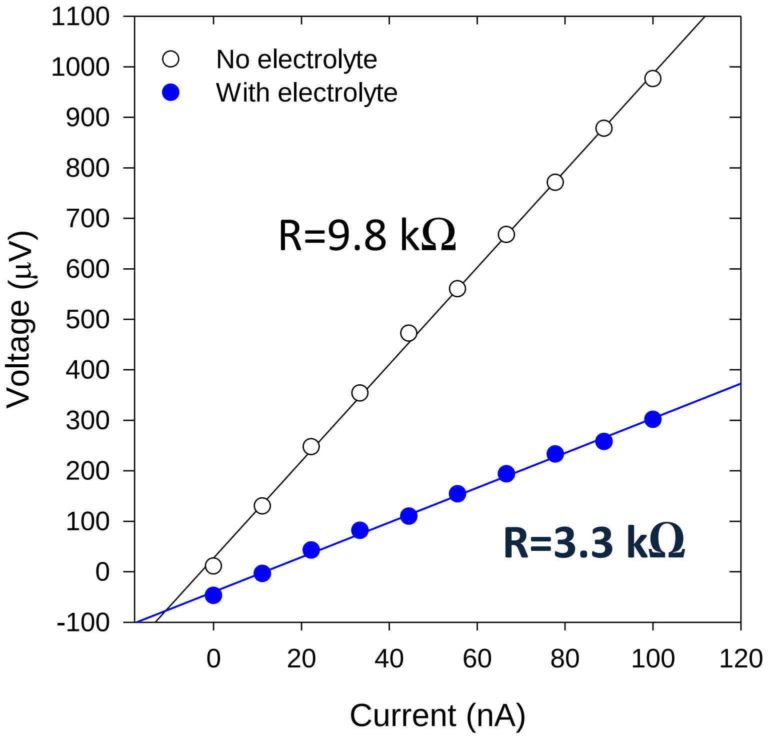




2. The solid-liquid hybrid system

Device permeated with LiBF$_4$ 1 M in 3-metoxipropionitrile (3-MPN)





A **66 % reduction of the electric resistance** is achieved **without a change in the Seebeck coefficient**.

This leads to **3.3 improvement** in the **power factor** by the addition of the electrolyte.

2. The solid-liquid hybrid system

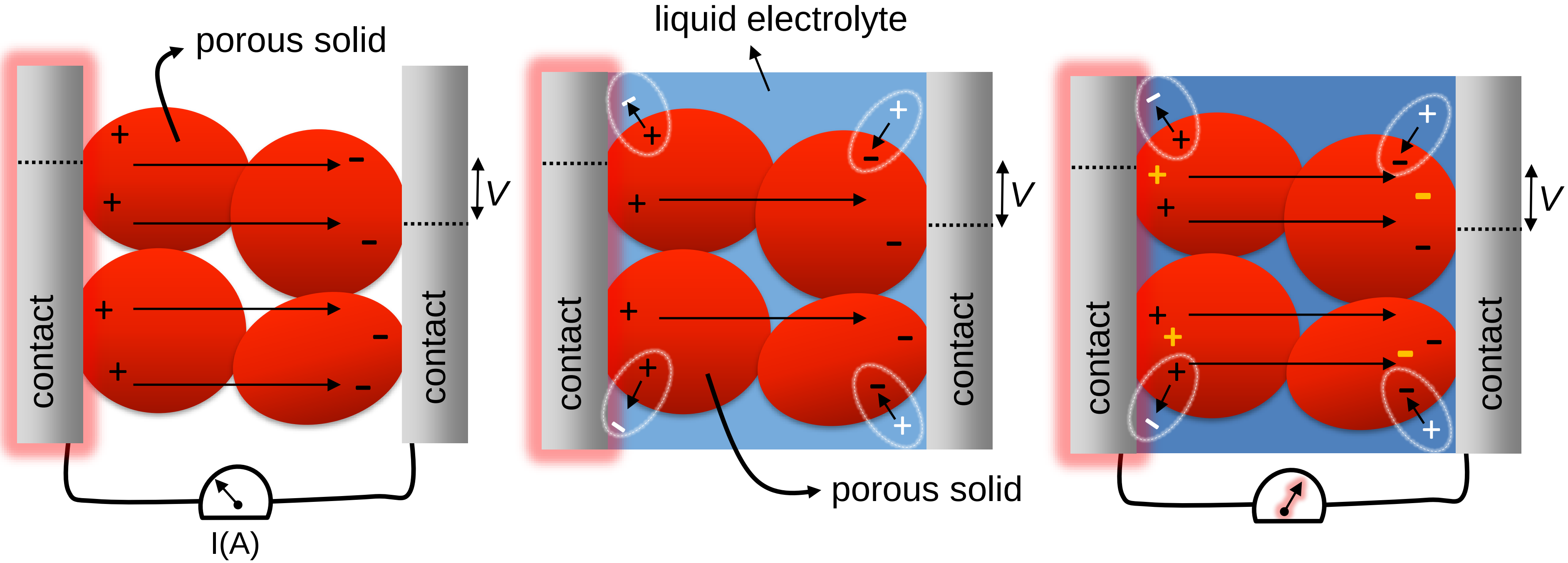
Electrolytes with 3-MPN solvent

Electrolyte	**Device**	**Seebeck coefficient (μV/K)**		**Electric resistance (kΩ)**		**$PF_{with}/PF_{without}$**
		Without electrolyte	With electrolyte	Without electrolyte	With electrolyte	
1 M $LiBF_4$	1	-37.2	-39.3	9.8	3.3	**3.3**
	2	-35.6	-37.8	11.0	3.3	**3.8**
	3	-35.8	-44.5	9.7	4.9	**3.1**
	No film	-	-759	-	147.6	**-**
1 M $NaBF_4$	1	-42.8	-47.8	6.9	13.0	**0.7**
	2	-43.5	-37.4	9.3	12.1	**0.6**
	3	-41.5	-34.4	5.1	8.7	**0.4**
	No film	-	-582.2	-	641.7	**-**
1 M KBF_4	1	-41.3	-33.9	6.1	8.6	**0.5**
	2	-39.0	-38.4	5.2	6.7	**0.7**
	3	-35.6	-41.0	4.8	10.3	**0.6**
	No film	-	N/A	-	414.6	**-**
3-MPN	-	-32.2	-32.1	4.9	6.4	**0.8**

Average **61.9 % decrease** of ***R*** and **3.4** times ***PF* improvement**. **Larger ions** than Li^+ increase the electric resistance.

2. The solid-liquid hybrid system

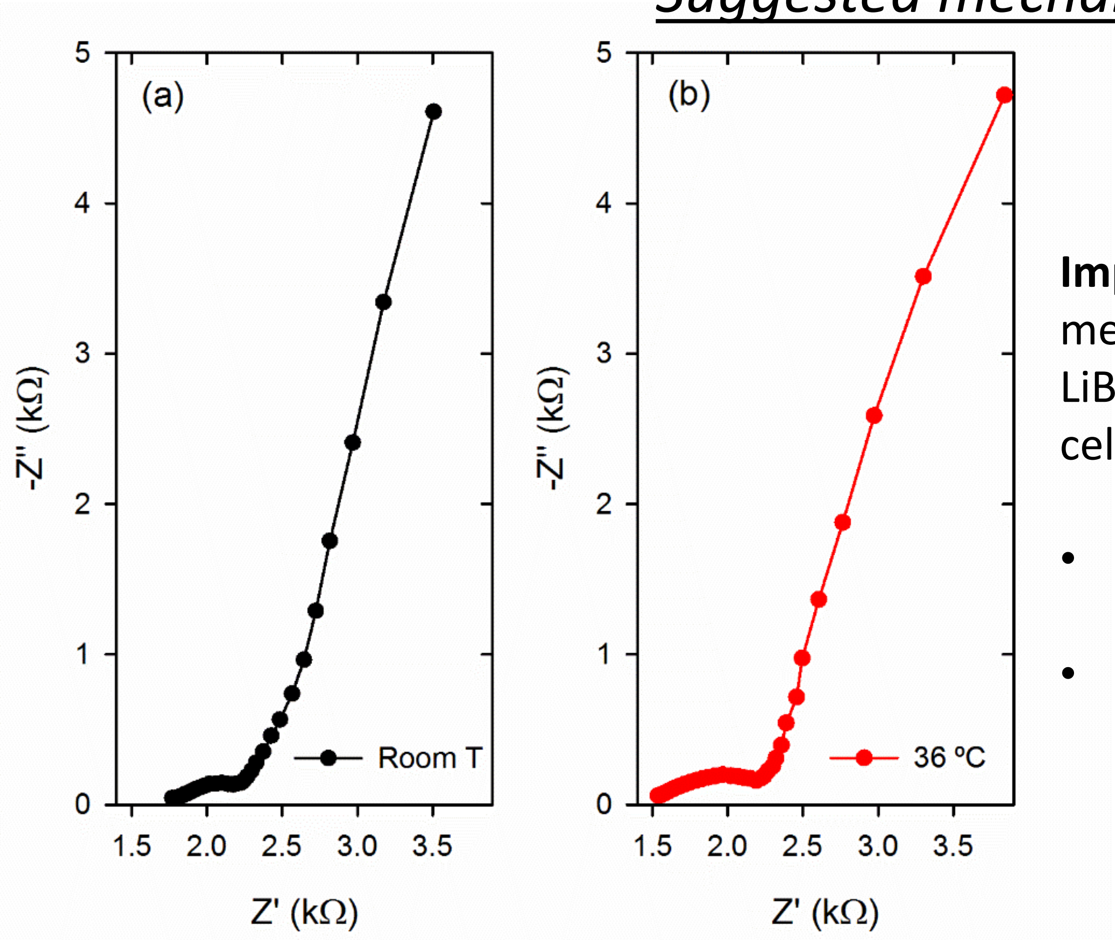
Suggested mechanism



The **ions** in the electrolyte **screen** part of the electric field and **new charges** are separated to **restore it**, leading to a **higher current output** (lower resistance).

2. The solid-liquid hybrid system

Suggested mechanism



(Open circuit potential dc voltage, 10 mV ac amplitude, 50 mHz -50 kHz frequency range)

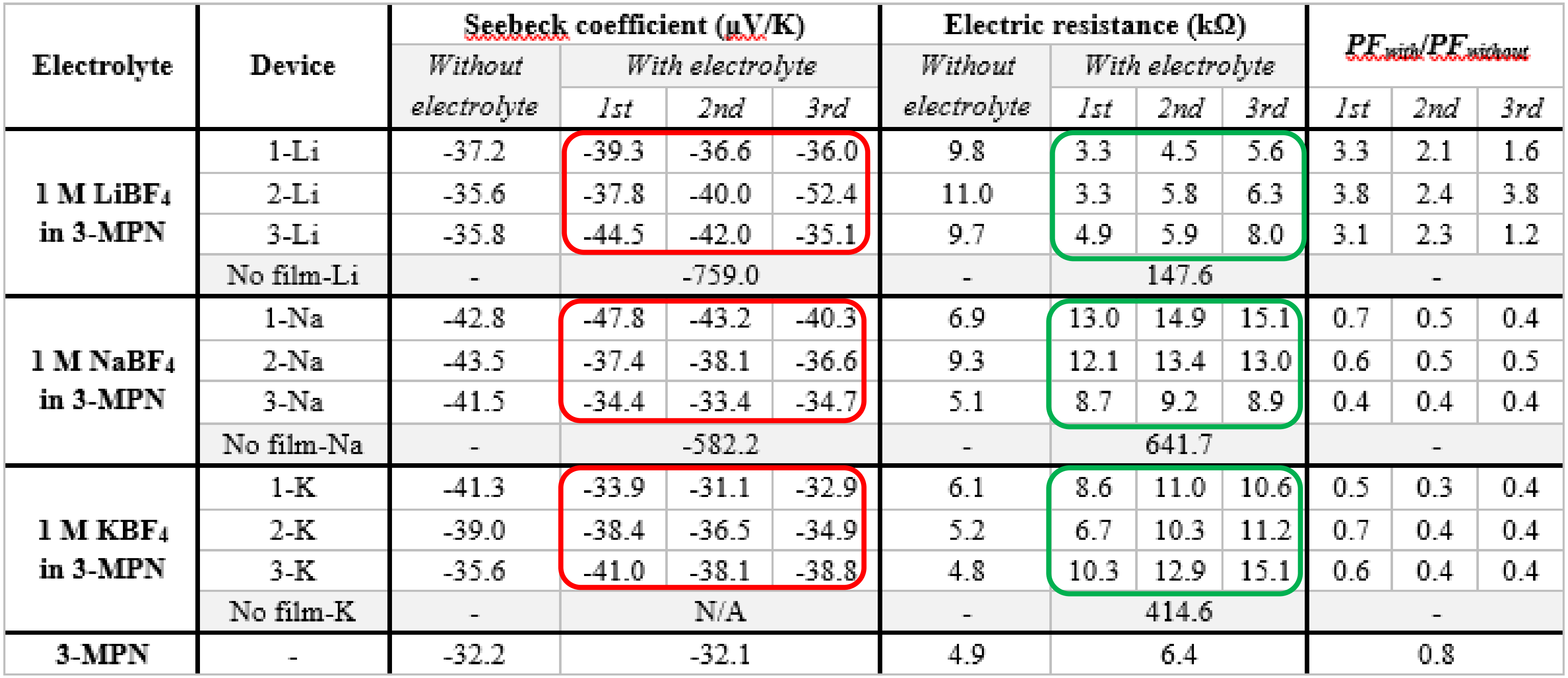
Impedance spectroscopy measurements of the film with the 1M $LiBF_4$ in 3-MPN electrolyte (3-electrode cell configuration) shows that:

- The formation of the **double layer (screening)** occurs.
- **Li^+ is intercalated** into the oxide lattice.

Fabregat-Santiago, F. et al. Dynamic Processes in the Coloration of WO3 by Lithium Insertion. *J. Electrochem. Soc.* **2001**, *148*, E302

2. The solid-liquid hybrid system

Device stability



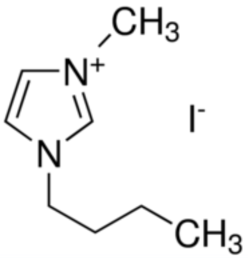
Electrolyte	Device	Seebeck coefficient (μV/K)				Electric resistance (kΩ)				$PF_{with}/PF_{without}$		
		Without electrolyte	*With electrolyte*			*Without electrolyte*	*With electrolyte*					
			1st	*2nd*	*3rd*		*1st*	*2nd*	*3rd*	*1st*	*2nd*	*3rd*
1 M $LiBF_4$ in 3-MPN	1-Li	-37.2	-39.3	-36.6	-36.0	9.8	3.3	4.5	5.6	3.3	2.1	1.6
	2-Li	-35.6	-37.8	-40.0	-52.4	11.0	3.3	5.8	6.3	3.8	2.4	3.8
	3-Li	-35.8	-44.5	-42.0	-35.1	9.7	4.9	5.9	8.0	3.1	2.3	1.2
	No film-Li	-	-759.0			-	147.6			-		
1 M $NaBF_4$ in 3-MPN	1-Na	-42.8	-47.8	-43.2	-40.3	6.9	13.0	14.9	15.1	0.7	0.5	0.4
	2-Na	-43.5	-37.4	-38.1	-36.6	9.3	12.1	13.4	13.0	0.6	0.5	0.5
	3-Na	-41.5	-34.4	-33.4	-34.7	5.1	8.7	9.2	8.9	0.4	0.4	0.4
	No film-Na	-	-582.2			-	641.7			-		
1 M KBF_4 in 3-MPN	1-K	-41.3	-33.9	-31.1	-32.9	6.1	8.6	11.0	10.6	0.5	0.3	0.4
	2-K	-39.0	-38.4	-36.5	-34.9	5.2	6.7	10.3	11.2	0.7	0.4	0.4
	3-K	-35.6	-41.0	-38.1	-38.8	4.8	10.3	12.9	15.1	0.6	0.4	0.4
	No film-K	-	N/A			-	414.6			-		
3-MPN	-	-32.2	-32.1			4.9	6.4			0.8		

The **Seebeck coefficient does not significantly change** after several cycles in most cases, but the **electric resistance** experiences an **increase for the $LiBF_4$ salt**, producing a **decrease of the *PF* enhancement**.

3. Ionic liquids in the hybrid system

1-Butyl-3-methylimidazolium (BMI X, X=I^-, BF4$^-$) ionic liquids

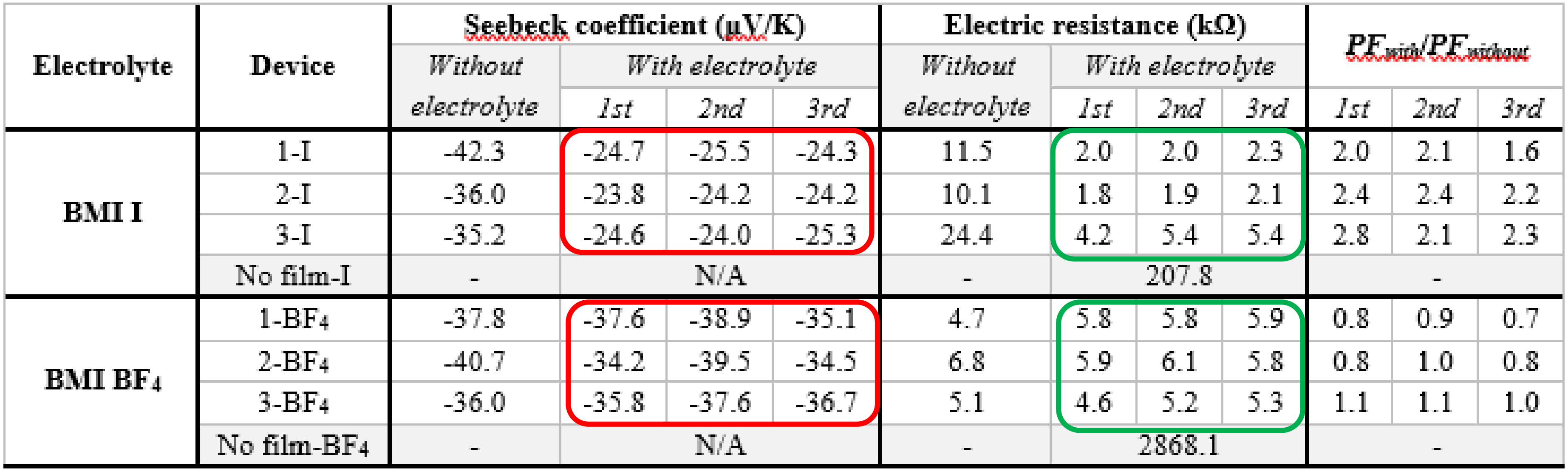
Electrolyte	**Device**	**Seebeck coefficient (μV/K)**		**Electric resistance (kΩ)**		**$PF_{with}/PF_{without}$**
		Without electrolyte	With electrolyte	Without electrolyte	With electrolyte	
BMI I	1	-42.3	-24.7	11.5	2.0	**2.0**
	2	-36.0	-23.8	10.1	1.8	**2.4**
	3	-35.2	-24.6	24.4	4.2	**2.8**
	No film	-	N/A	-	207.8	**-**
BMI BF_4	1	-37.8	-37.6	4.7	5.8	**0.8**
	2	-40.7	-34.2	6.8	5.9	**0.8**
	3	-36.0	-35.8	5.1	4.6	**1.1**
	No film	-	N/A	-	2868.1	**-**



- The **BMI I** ionic liquid produces an average **82.5 % drop in electric resistance** but **reduces the Seebeck** coefficient by **35 %**. The **power factor** improvement is **2.4**.
- The **BMI BF_4** produces no significant changes in the Seebeck coefficient, and small differences in the electric resistance, not influencing significantly **the power factor**.

3. Ionic liquids in the hybrid system

Device stability



Electrolyte	Device	Seebeck coefficient (µV/K)				Electric resistance (kΩ)				$PF_{with}/PF_{without}$		
		Without electrolyte	*With electrolyte*			*Without electrolyte*	*With electrolyte*					
			1st	*2nd*	*3rd*		*1st*	*2nd*	*3rd*	*1st*	*2nd*	*3rd*
BMI I	1-I	-42.3	-24.7	-25.5	-24.3	11.5	2.0	2.0	2.3	2.0	2.1	1.6
	2-I	-36.0	-23.8	-24.2	-24.2	10.1	1.8	1.9	2.1	2.4	2.4	2.2
	3-I	-35.2	-24.6	-24.0	-25.3	24.4	4.2	5.4	5.4	2.8	2.1	2.3
	No film-I	-	N/A			-	207.8			-		
BMI BF_4	1-BF_4	-37.8	-37.6	-38.9	-35.1	4.7	5.8	5.8	5.9	0.8	0.9	0.7
	2-BF_4	-40.7	-34.2	-39.5	-34.5	6.8	5.9	6.1	5.8	0.8	1.0	0.8
	3-BF_4	-36.0	-35.8	-37.6	-36.7	5.1	4.6	5.2	5.3	1.1	1.1	1.0
	No film-BF_4	-	N/A			-	2868.1			-		

***PF* improvements** introduced by the presence of the **BMII ionic liquid** were **predominantly maintained** along the different cycles and only slight variations (**from** an average **2.4** improvement **to 2.1**) were produced.
The **$BMIBF_4$ ionic liquid** remained also **stable**.

With ionic liquids **intercalation** is **more restricted** and the **drop in *R* also takes place**, this supports that the **screening mechanism is governing** this effect.
Intercalation could **influence the device stability**.

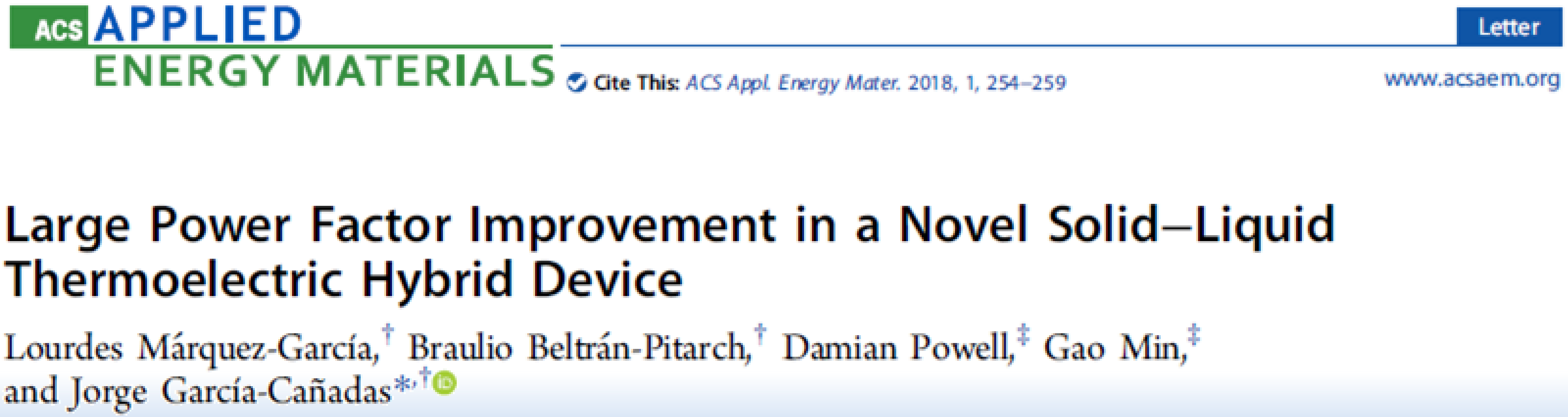
4. Summary

- A **new hybrid system** formed by a nanostructured **mesoporous solid** permeated by a **liquid** electrolyte has been conceived to **improve** the thermoelectric **power factor**.

- The concept has been **demonstrated** employing **Sb:SnO_2** and different electrolytes.

- More than **3 times improvement** in the power factor has been achieved by a **61.9 % reduction of the electric resistance** of the system **without modifying the Seebeck** coefficient using **$LiBF_4$ 1 M in 3-methoxipropionitrile**.

- An imidazolium iodide **ionic liquid** produces an **82.5 % drop in the electric resistance although** with a **reduction in the Seebeck** coefficient, leading to **2.4 times improvement** in the *PF*.



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Letter

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Large Power Factor Improvement in a Novel Solid−Liquid Thermoelectric Hybrid Device

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5. Acknowledgements

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