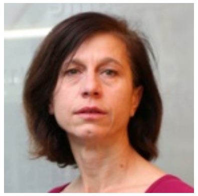
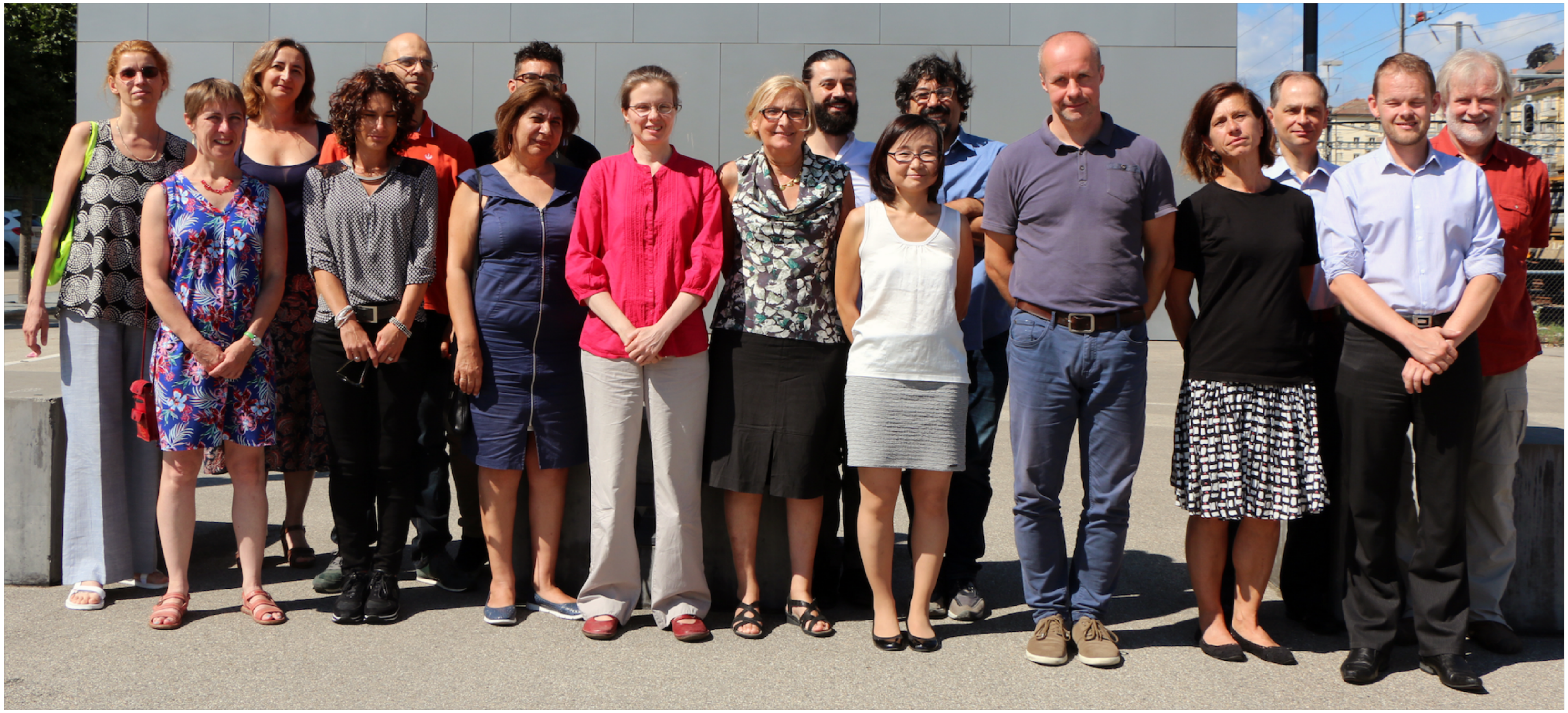
Lead Dr. S. Nakamae CEA

Surprising thermoelectric effects in Ionic Liquid /redox-couple mixtures



Edith Laux, Laure Jeandupeux, Alexandra Kaempfer-Homsy
and Herbert Keppner

Magenta consortium



Outline:

- General aspects of generators, examples
- Liquid / solid interfaces
- Thermoelectric generators based on ionic liquids
- Experimental
- Attachment model considerations
- Normal and abnormal behaviour of TEGs based on ILs
- Conclusions
- Acknowledgements

What is a generator?

A generator is a converter form one form of energy into another one.
In general electricity is preferred as the final form.

For an electric generator three requirements are mandatory:

1. **creation of free charge.**
2. **Separation of the charge**
3. **Collecting the charge by a contact to bring it to an external user.**

Note: an electric generator is best adapted to a load if its internal electrical resistivity equals to the resistivity of the external consumer

Examples:

Solar cell:

1. The free carriers are created due to absorption of photons by a semiconductor and store the photonic energy from excitation as electron – hole pair (exciton) in the semiconductor.

2. The internal electric field created due to equilibration of the Fermi levels at contact creation between two semiconductors in a e.g. p-n junction, separates the carriers.

3. The separated carriers are collected by ohmic contacts that are put on the semiconductor.

Thermoelectric generators (TEG)

1. The free carries are already present in a metal or doped semiconductor.

2. In a thermal gradient the energy flow will separate the carriers in parallel of the heat flow.

3. The collection of the carriers is carried out by ohmic contacts.

The particular case of MAGENTA:

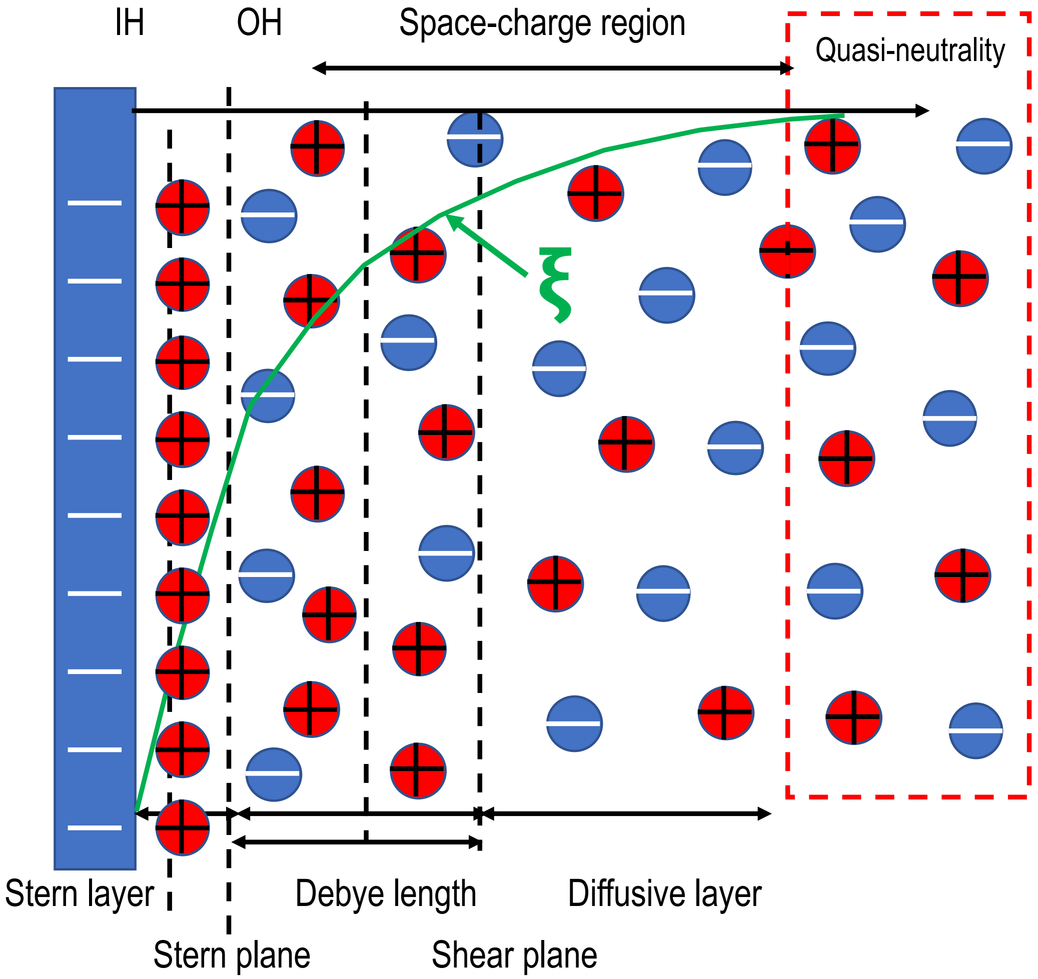
A closer look at the figure of Merit $Z \cdot T = \alpha^2 \cdot \frac{\sigma}{\lambda} \cdot T$ for TEGs

Needs to find a *harsh* compromise between highest α high σ and lowest λ.
Solid-state materials that are available are ***to good thermal conductors***.
Hence some tenth of elements (Bi, Cd, Te, Si, Ge, Pb, Hg, Sb) and their compounds together with nano-wire or multilayers approaches are used for reducing heat-conductivity. Hence a ***material problem*** is there.

The use of ***liquids*** first increases the “play ground” of possible solutions to more 15 000 ionic liquids (ILs) containing the chance of escaping from toxic and problematic further load of the biosphere. Second, λ can be drastically reduced from λ>10 $W \cdot m^{-2}K^{-1}$ for Solid-state down to λ< 0.2 $W \cdot m^{-2}K^{-1}$ for liquids.

MAGENTA has the vision of the promising implementation of Ferrofluidics combined with their magnetic properties for improving the TEGs.

If an ionic liquid touches a surface (half cell):



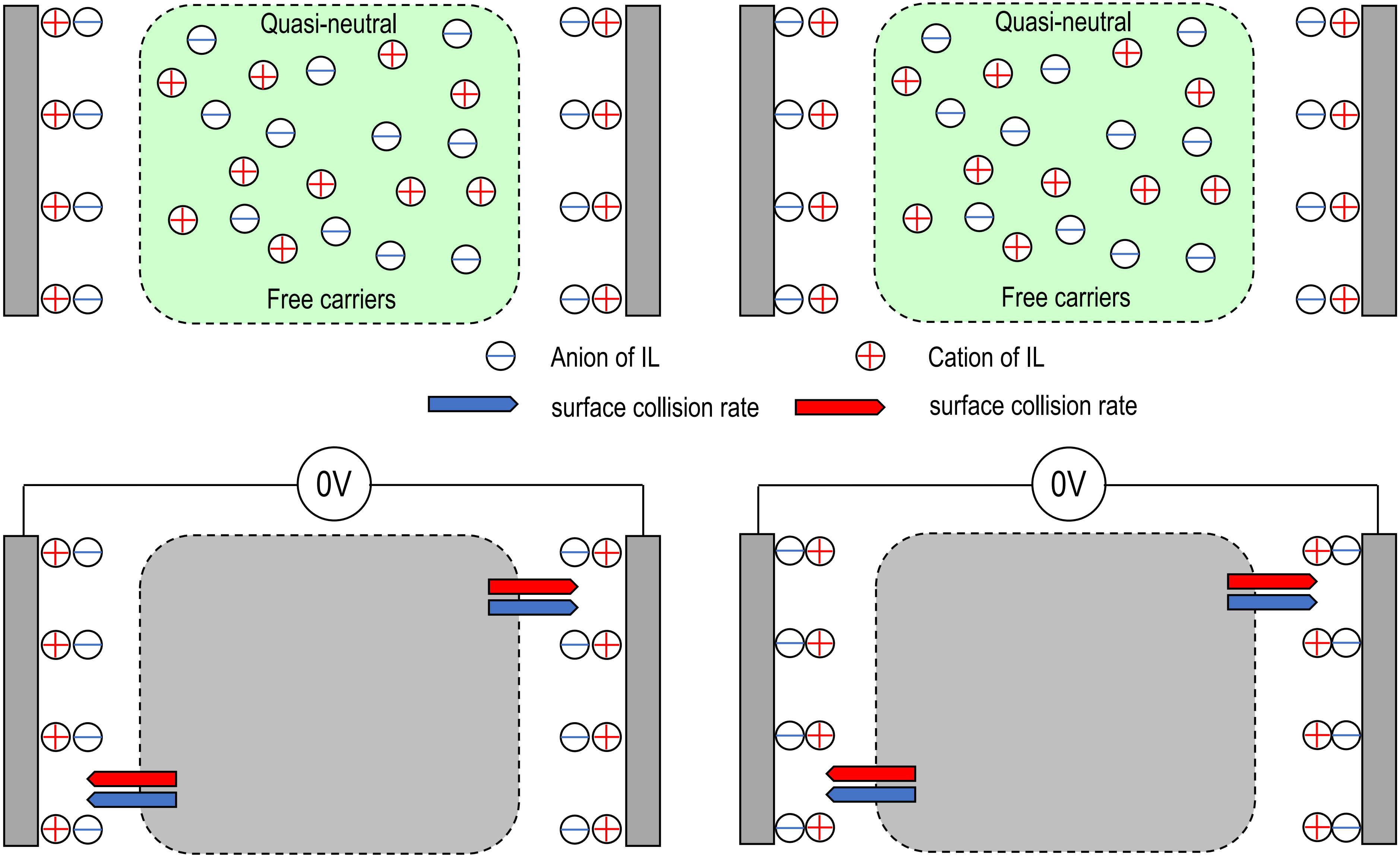
As response of the perturbation of the liquid e.g. a contact:

An electric ***double-layer*** is created, an
Inner Helmholtz plane IH
Outer Helmholtz plane OH
Slipping plane S

The ***space-charge region*** balances the charge that is attached at IH in order to arrange charge neutrality.

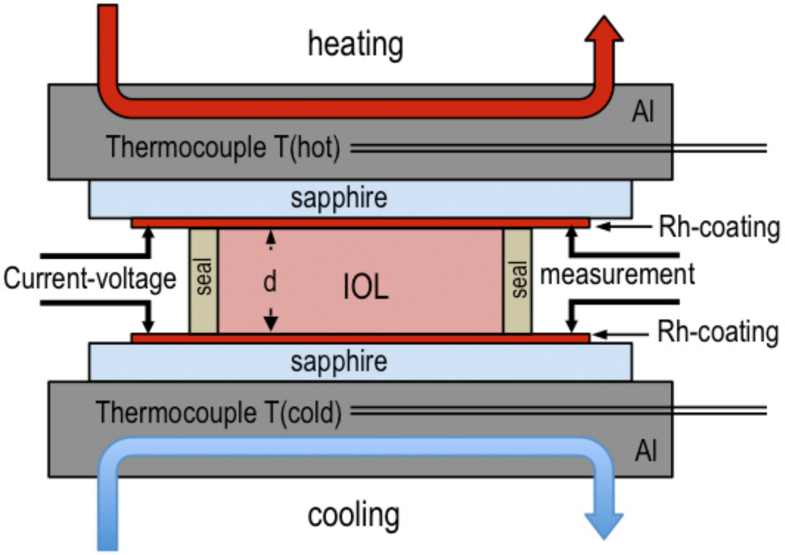
The charge is characterized by the ξ ***– potential*** that comes to zero after some distance from the electrode.

Half cell to TEG as full cell; the ionic liquid (IL) consists of anions and cations, ***no solvent***). Without heating, two cases can occur that depend on the choice of IL:



Thermoelectric generators based on ionic liquids

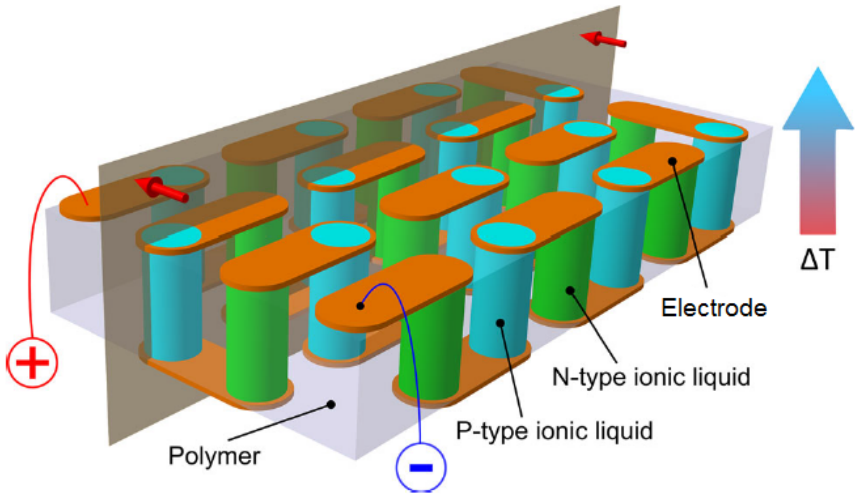
Single-junction generator for research



Similar to Mrs Bhattacharya' talk

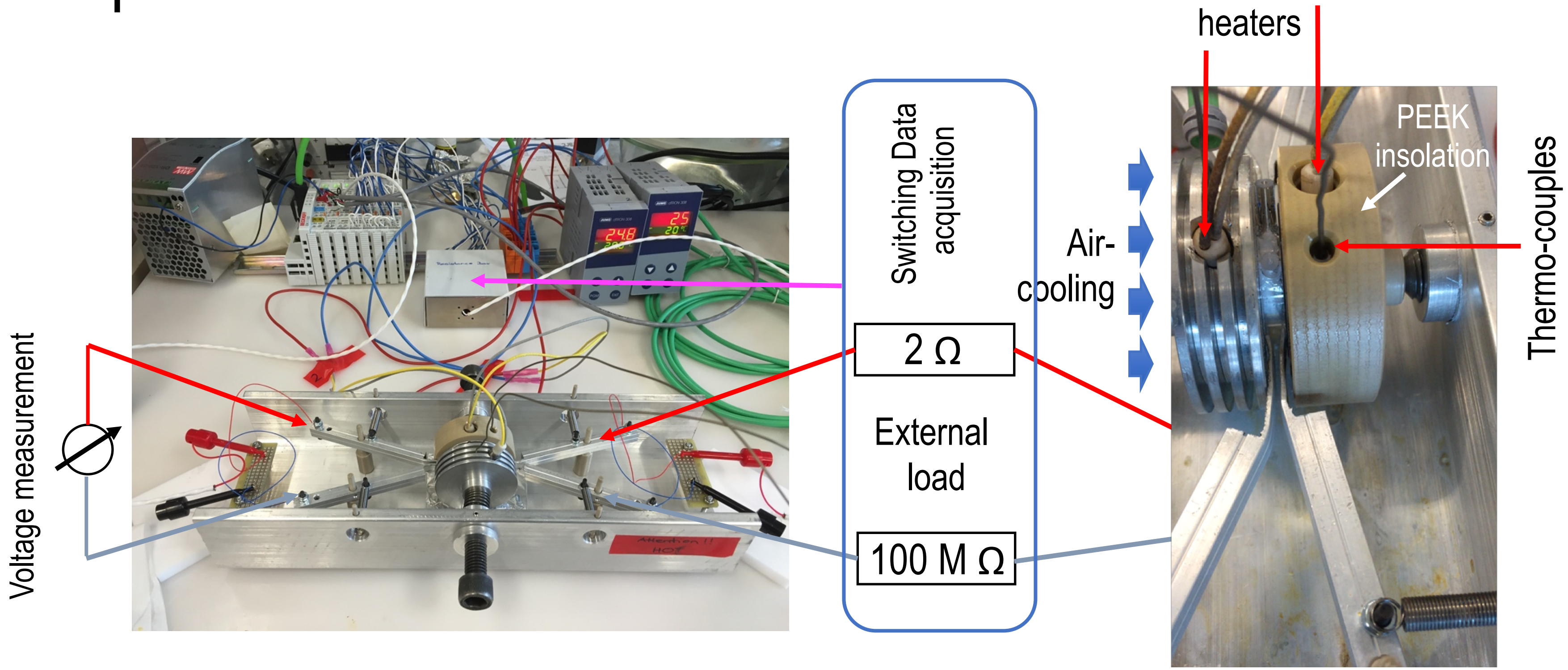
- Rhodium on sapphire contact
- filled with n-type or p-type Ionic liquid
- redox-couple for current-extraction

Multi-junction generator as product



- serial connected reservoirs
- filled with n-type and p-type Ionic liquid
- redox-couple for current-extraction

Experimental



Voltage measurement

Switching Data acquisition

2 Ω

External load

100 M Ω

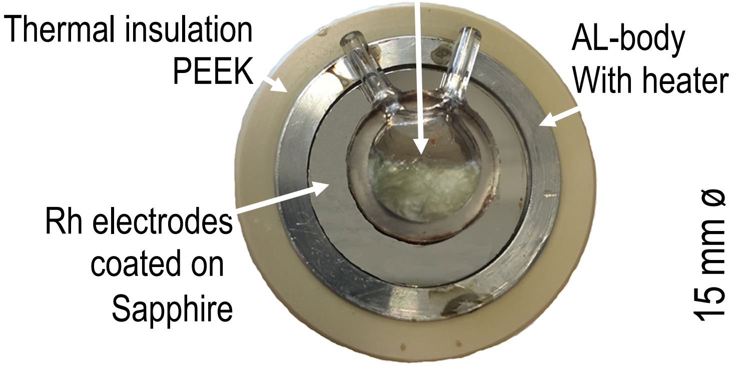
Air-cooling

heaters

PEEK insolation

Thermo-couples

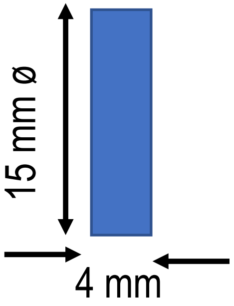
Opened cell containing IL (glass)



Thermal insulation PEEK

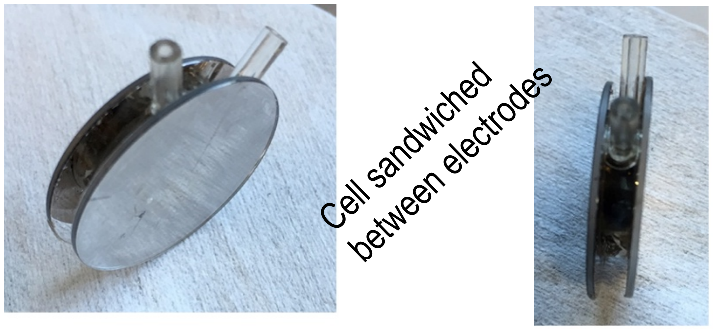
AL-body With heater

Rh electrodes coated on Sapphire



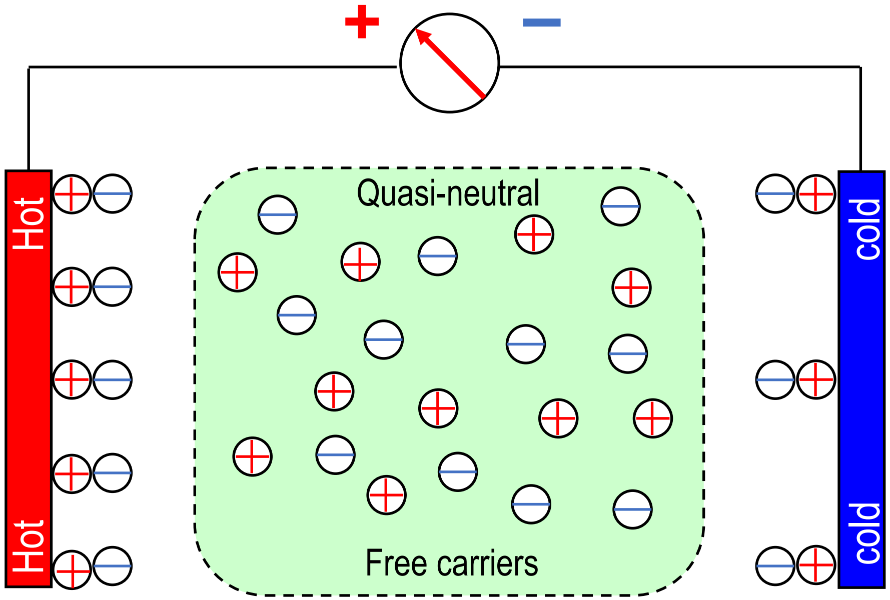
15 mm ø

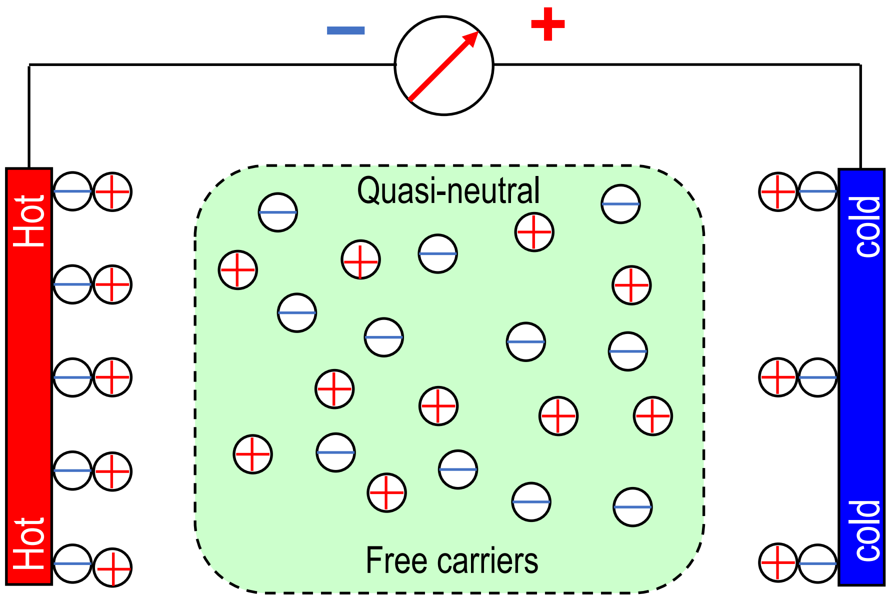
4 mm



Cell sandwiched between electrodes

The application of a temperature difference between the contact polarizes the contacts in function of the choice of the IL, an asymmetry is created.



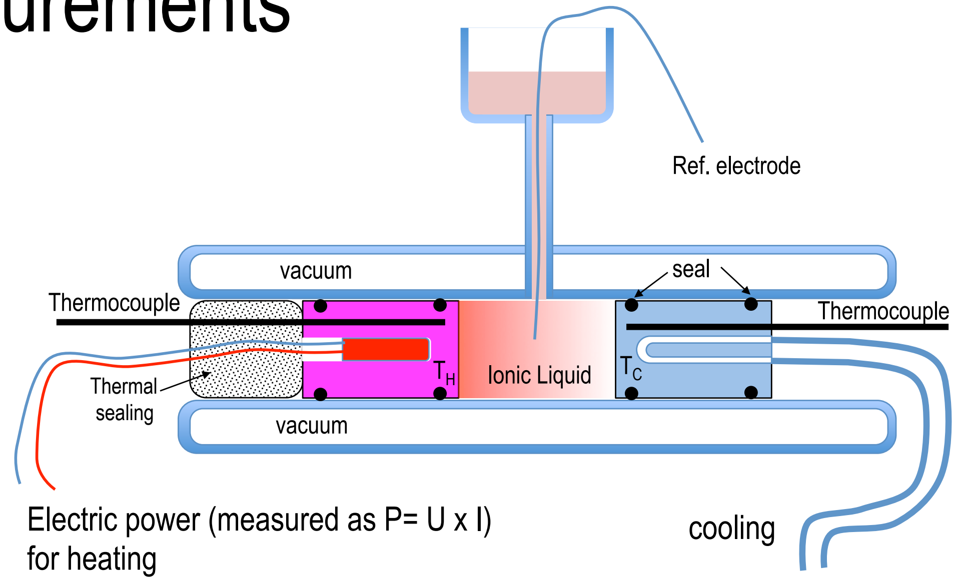


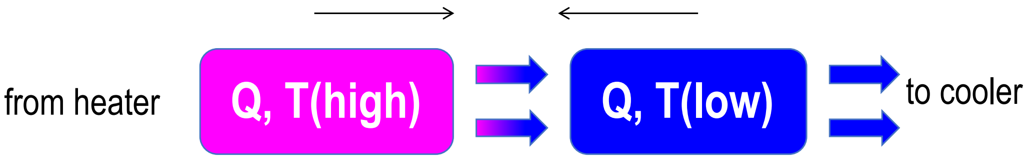
For pure 1-Butyl-3-methylimidazolium tetrafluoroborate BMIM BF4 a Seebeck coefficient of *SE = 0.851 mV/K* is measured

For pure 1-Hexyl-3-methylimidazolium iodide HMIM I2 a Seebeck coefficient of *SE= - 0,163 mV/K* is measured.

Heat- conductivity measurements

$$Z \cdot T = \alpha^2 \cdot \frac{\sigma}{\lambda} \cdot T$$



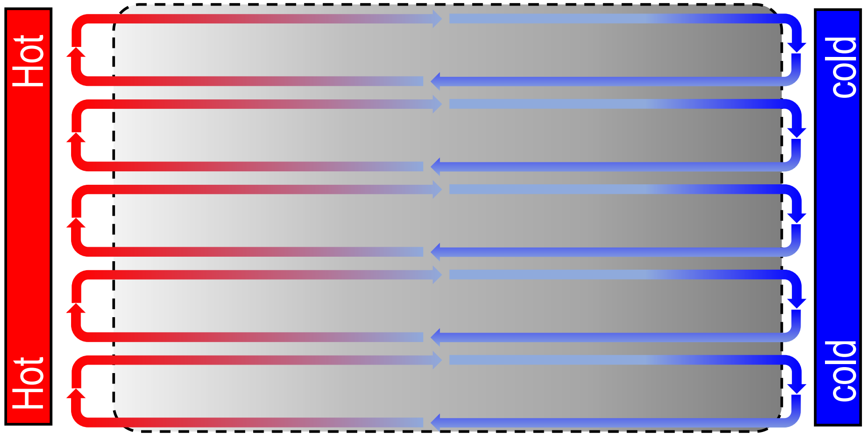


Values for λ obtained by measurement; literature value for BMIM is λ = 0.184 $W/m^2/K$

Space \ IOL	Pure	0.01 Mol redox
10 mm	0.754	0.926
5 mm	0.485	0.487
1 mm	0.26	0.360
0.1 mm	0.076	0.045

The values depend on the thickness of the TEG.
The values differ strongly from literature.
Conclusion: transport is convective

A closer look, ***asymmetry-scenarios*** when heating and cooling



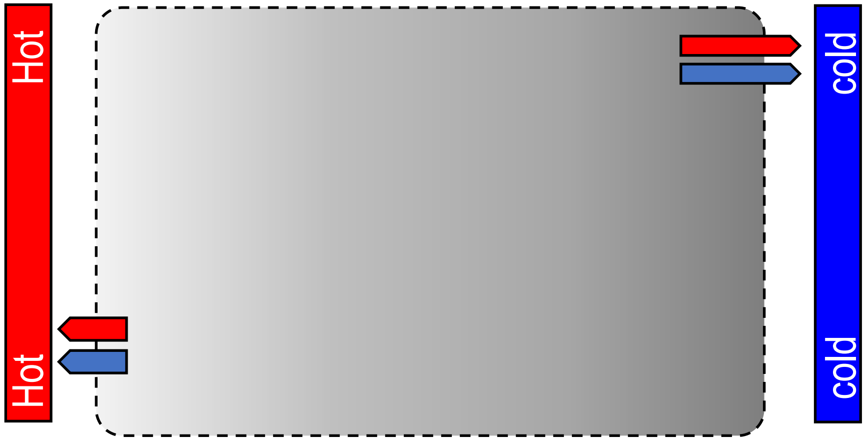
Due to the *closed system*, a *convective flow* of the liquid via so-called convection cells is occurring.
The diffuse layer will larger on the hot side.
The density of the liquid is higher at the cold side.
This convective flow is stirring the liquid and even if

Ø (cation) << Ø(anion) or inverse

[cation] = [anion] is the same in any volume element.

1. Perfect stirring of the liquid,

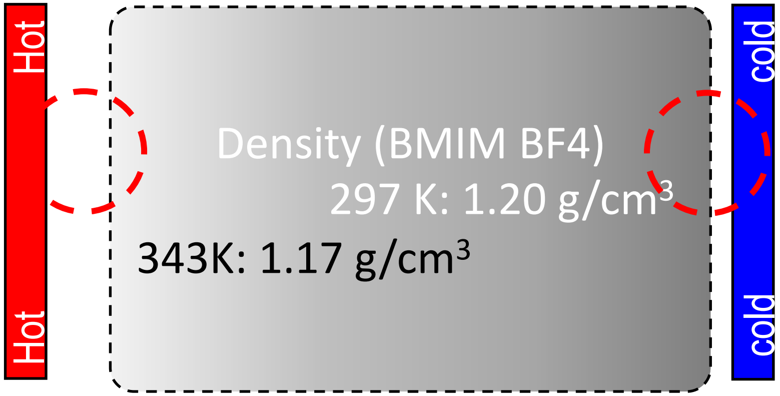
2. material flow is always coupled with the charge flow

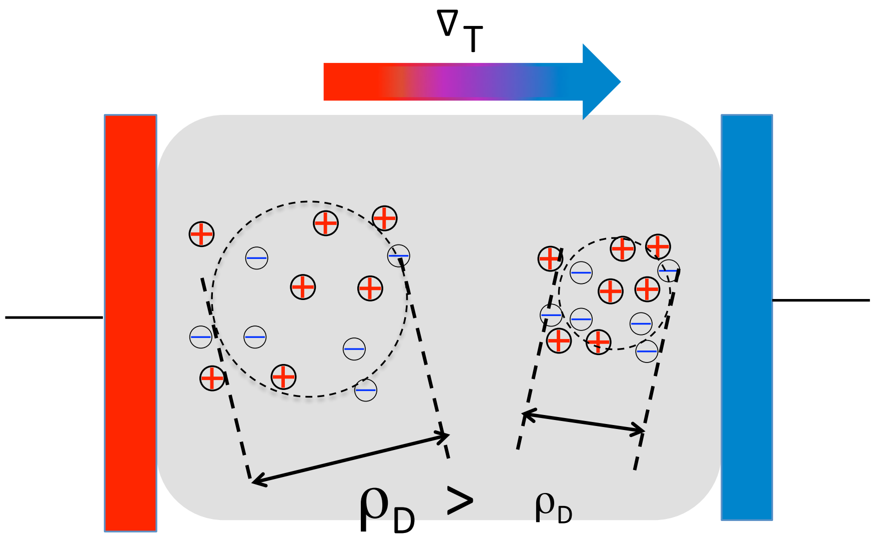


For both, the surface collision rate at the contacts for anions and cations is different at the hot and the cold side however the same for both ions.

These effects cannot explain the appearing potential difference.

The temperature-dependent asymmetry is due to:



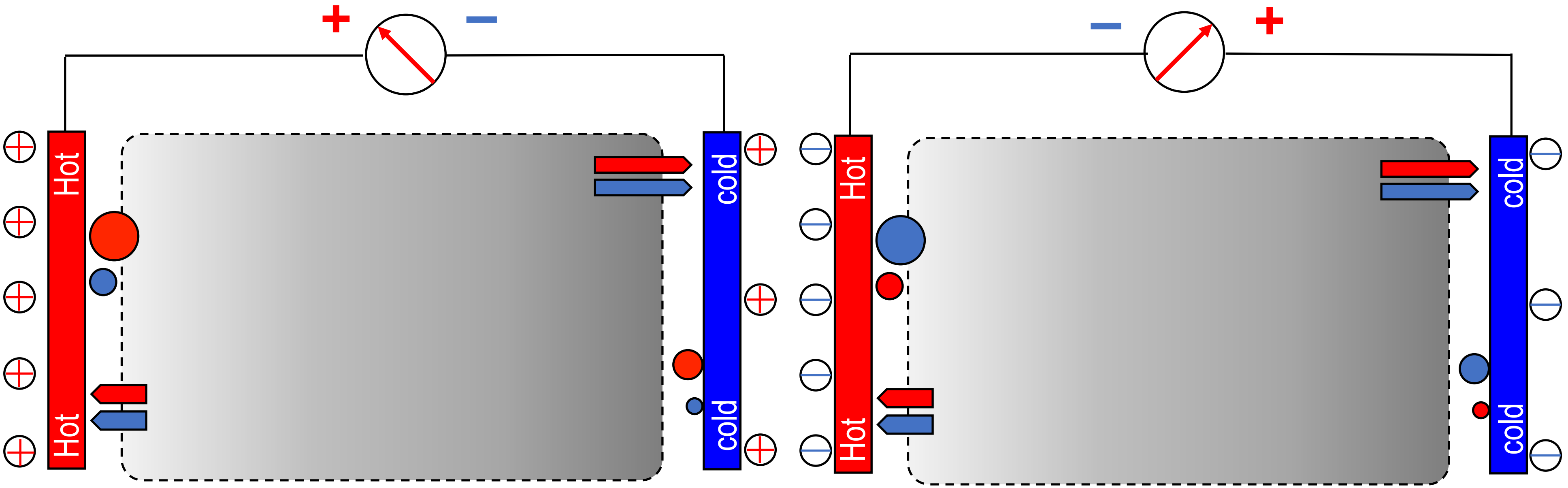


Local temperature-dependencies:

The density of the IL
The surface collision-rate of all ions with the contact.
The sticking coefficient of carriers at the electrodes.
The Debye length.
The heat-transfer from IL to electrode and electrode IL.
The diffusion-layer thickness.
The surface-charge density at IH
The gradient of carrier concentration in the bulk liquid

The sum of total surface charge of the hot half-cell and the cold half-cell gives rise of the Seebeck-voltage that can be measured externally.

A more closer look, introducing the surface sticking coefficient



⊖ Anion of IL

⊕ Cation of IL

🟦 surface collision rate

🟥 surface collision rate

🔵 sticking coefficient of Anion

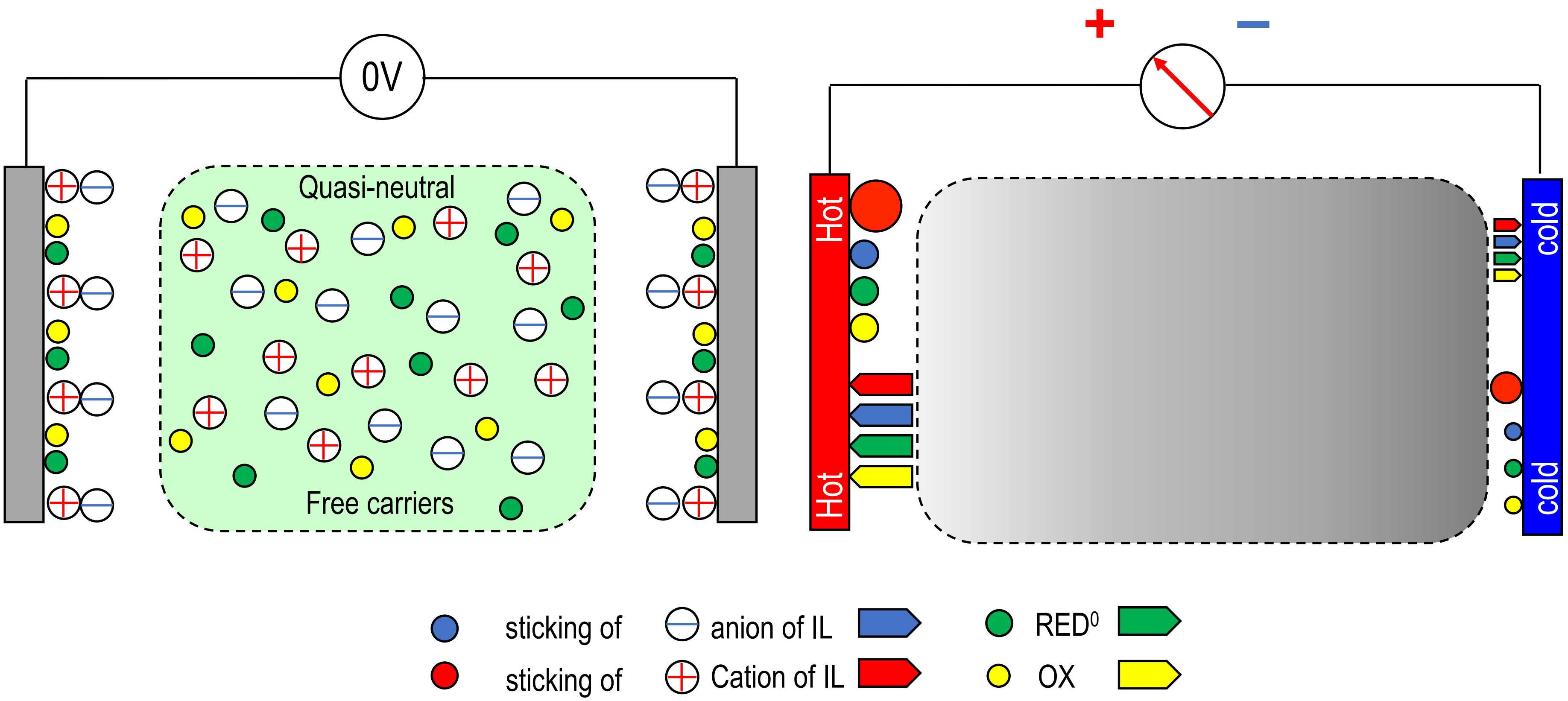
🔴 sticking coefficient of cation

The temperature-dependent sticking coefficient of the anions and cations could explain the appearance of a potential-difference between the contacts.

Note, the sticking-coefficient is the Steady-state net ratio of residence-time of a charge at a surface between attachment and release.

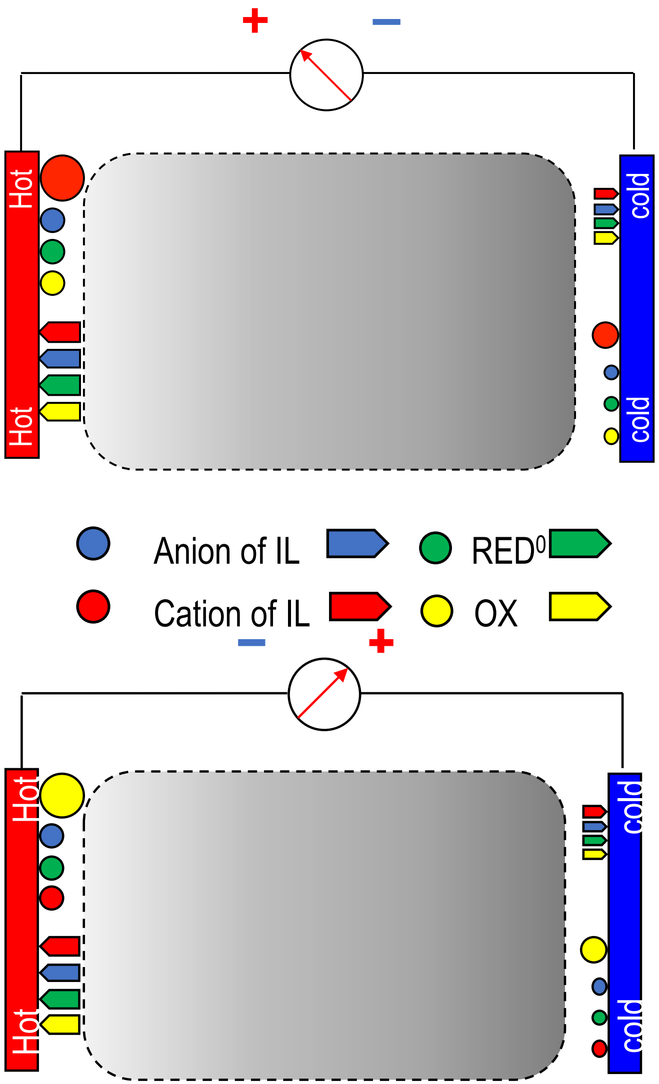
More complex case: In a IL- based TEG, the extracted current is due to redox couples that are added.

(note ***MAGENTA*** explores adding Ferrofluidic nanoparticles, additionally)

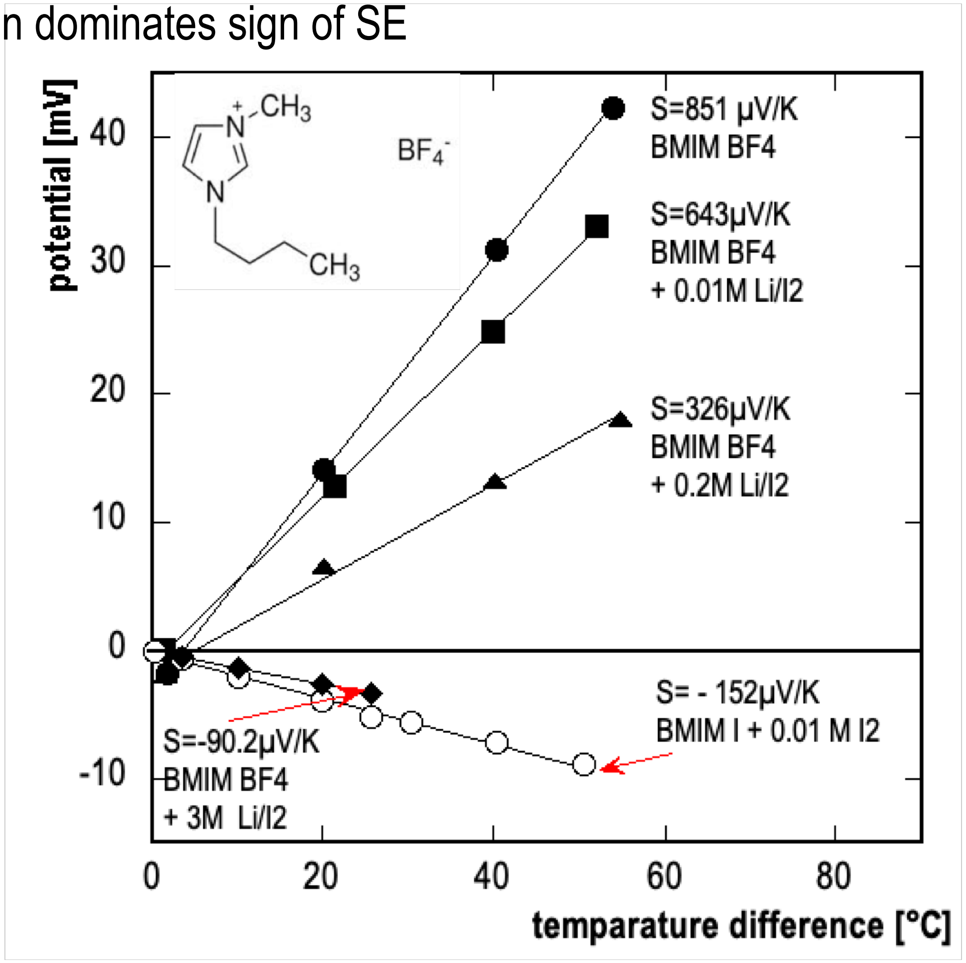


Exciting observation: for the polarization of the TEG, RED or OX must be considered to be equivalent as ions competing with the IL for sticking that can determine the value of the Seebeck coefficient even at extremely low [concentration] as compared to [anion] [cation]:

The example of BMIM BF4:



BMIM cation dominates sign of SE

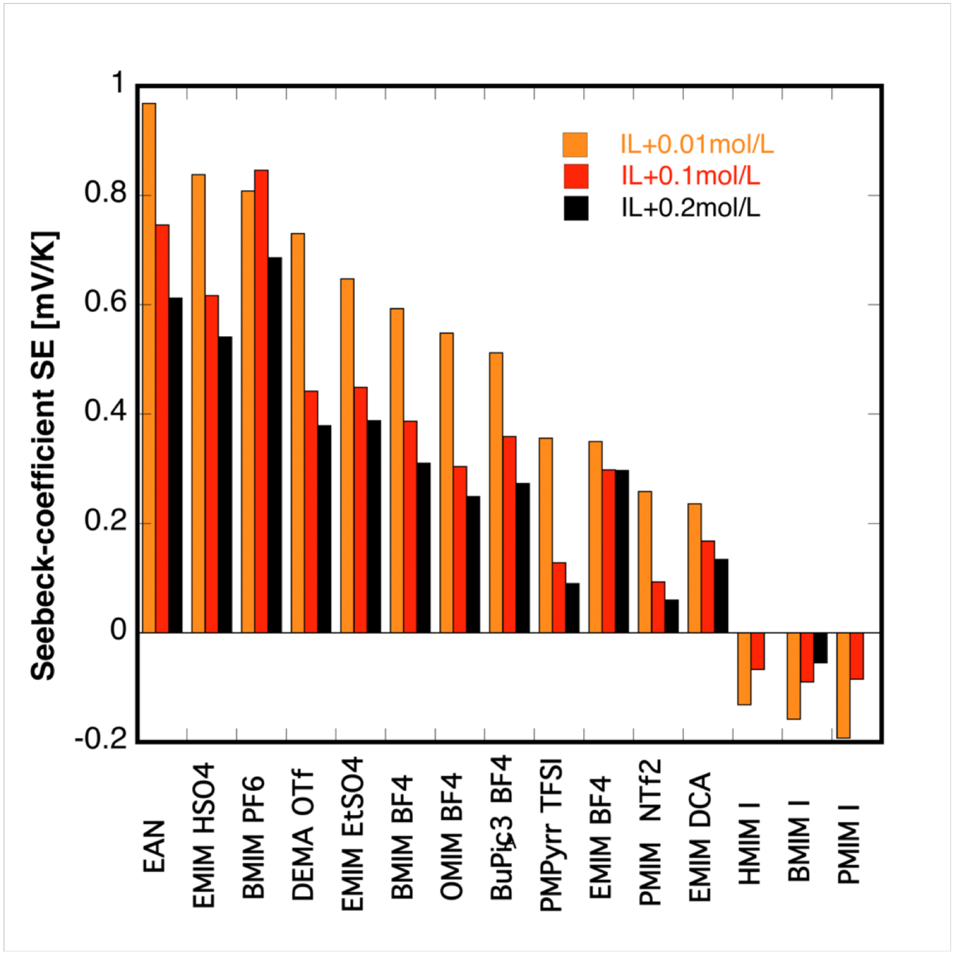


I- cation and Li/I2 redox / and Li/I2 dominate sign of SE

Conclusion: the SE can be inversed via the concentration of REDOX

Background

Ionic Liquids for Thermoelectric generators



Ionic liquids (ILs) are low melting salts (anions and cations, no solvent).
They show low thermal conductivity.
Additional redox couples are needed for TEG current extraction.

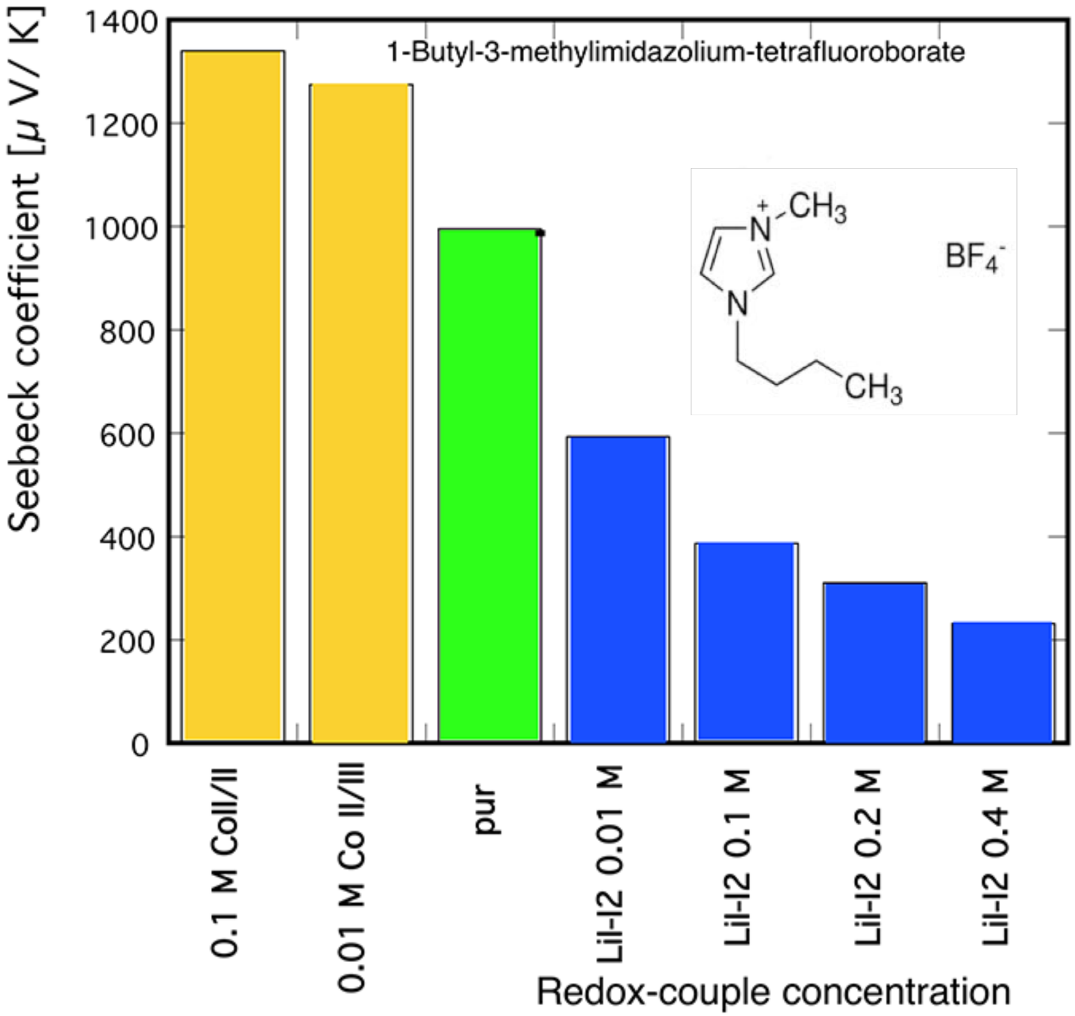
Redox concentration ⬆

Seebeck coefficient ⬇

1. E. Laux et al., Journal of Electronic Materials, 2016, DOI: 10.1007/s11664-016-4526-1

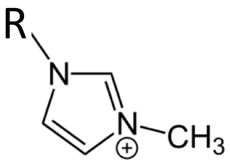
Conclusion:
High Seebeck coefficients together with a low thermal conductivity allow obtaining high generator voltages at reduced heat-flows

Choice of Redox reduces / supports SE even at low concentration



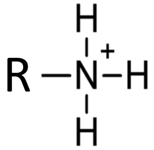
Effect of cation, cation- side-chain length, and REDOX on SE, and sign of SE

imidazole



No remarkable effect of length alkyl side-chain
SE positive, except with Iodide (all negative)
Conclusion: anion has high effect on SE

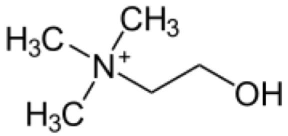
amine



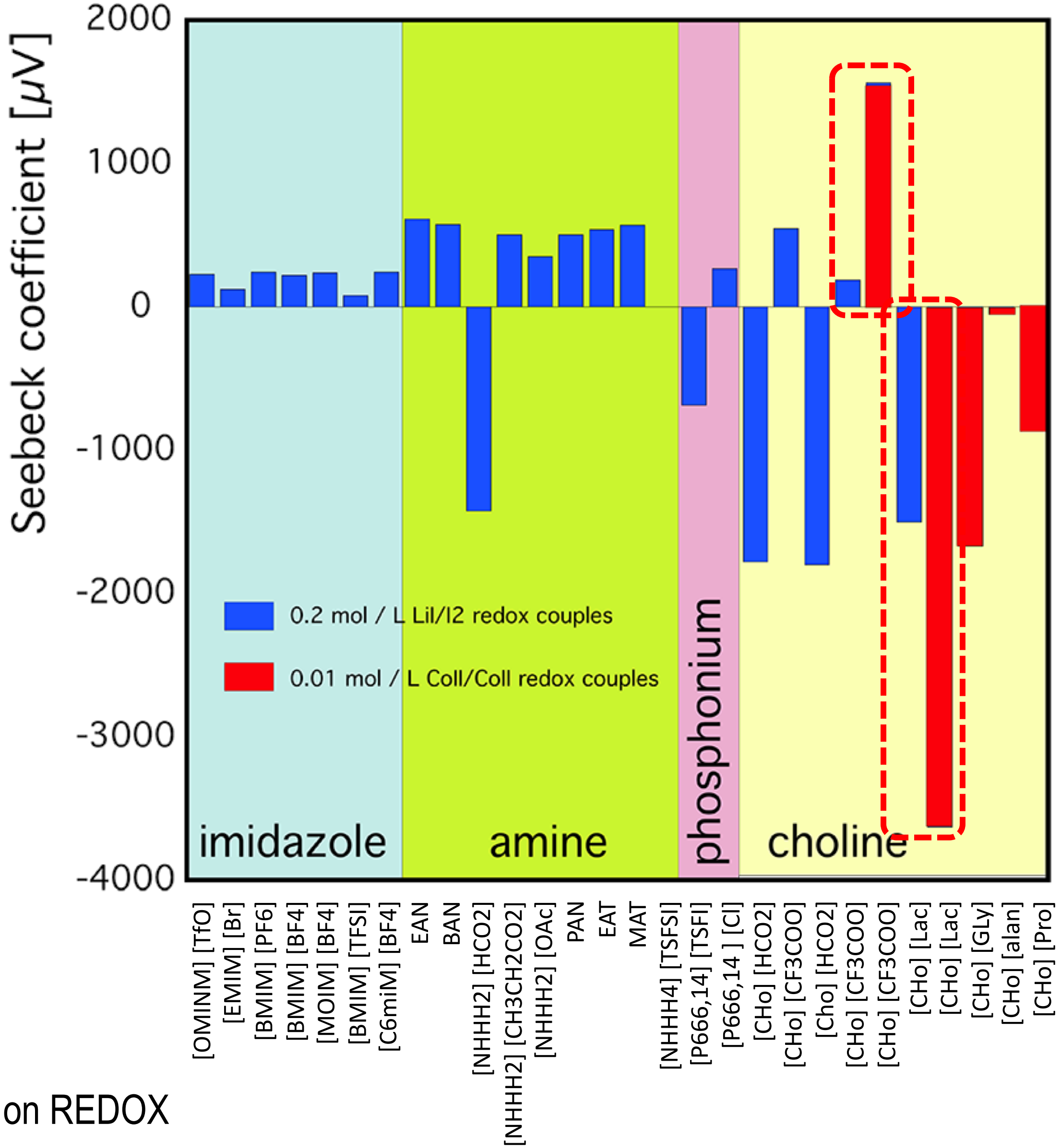
$R-\overset{H}{\underset{H}{\overset{+}{N}}}-H$

SE high to very high
SE positive and negative for format-anion
Conclusion: polarity of SE depends on anion

Choline:



SE low - very high
SE positive and negative depending on anion
Conclusion: polarity of SE depends on anion, its value on REDOX



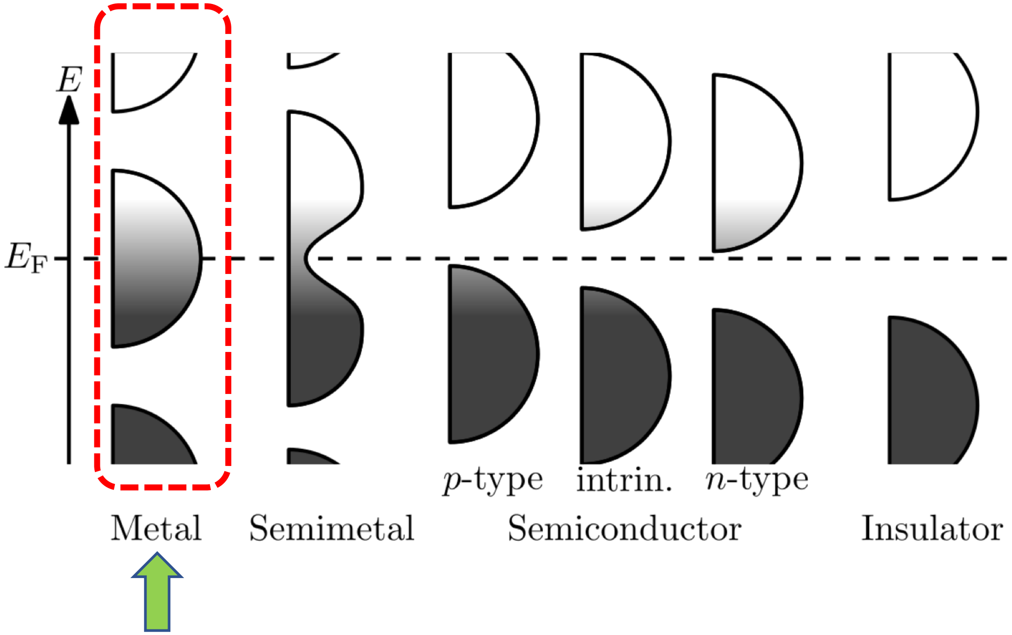
Which temperature-dependance controls the Seebeck coefficient?

Our suggestion from the previous choice:

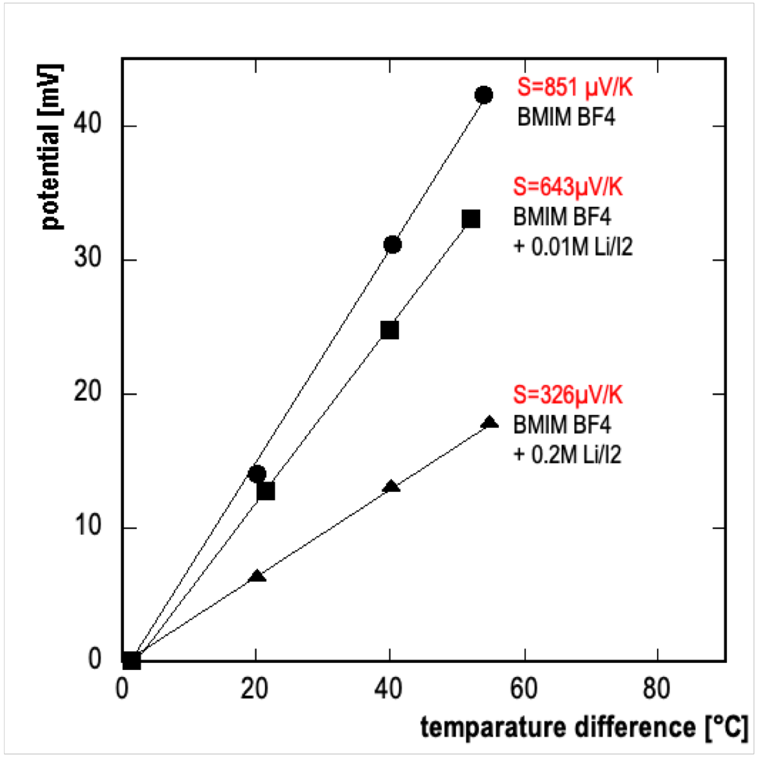
Local temperature-dependencies:

The density of the IL
The surface collision-rate of all ions with the contact.
→ The sticking coefficient of carriers at the electrodes. ←
The Debye length.
The heat-transfer from IL to electrode and electrode IL.
The diffusion-layer thickness.
The surface-charge density at IH
The gradient of carrier concentration in the bulk liquid

How can we understand sticking?



For Rhodium electrodes



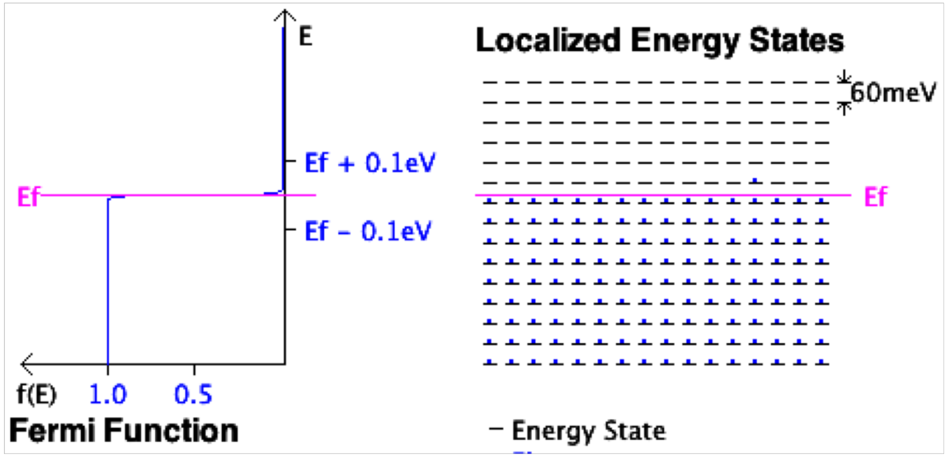
The observed Sticking is *no bonding*; it appears to be balanced by thermally induced release, because no charge storage is observed going to lower temperature.

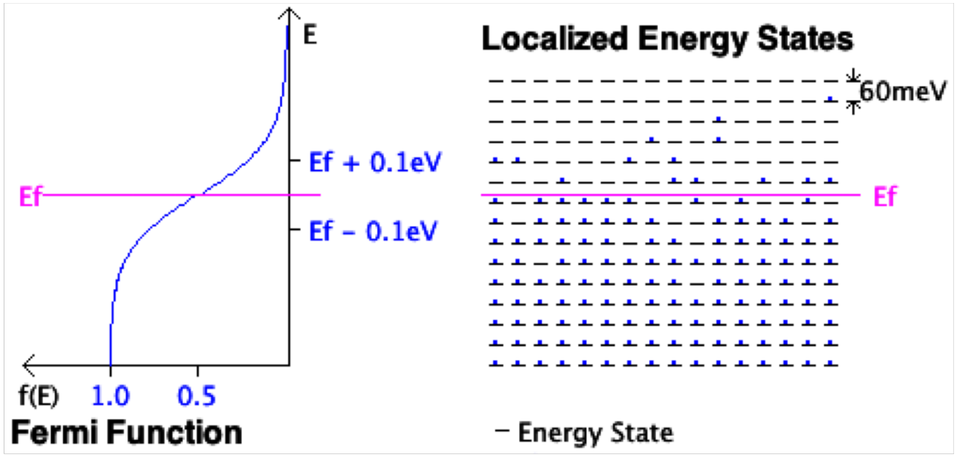
Kittel's *Introduction to Solid State Physics* 7th Edition, chapter 7.

Looking at Rh-electrode properties, we know from metal physics: what makes the difference between a warm metal and a hot metal?

$$f(E) = \left(1 + \exp\frac{E - E_F}{kT}\right)^{-1}$$

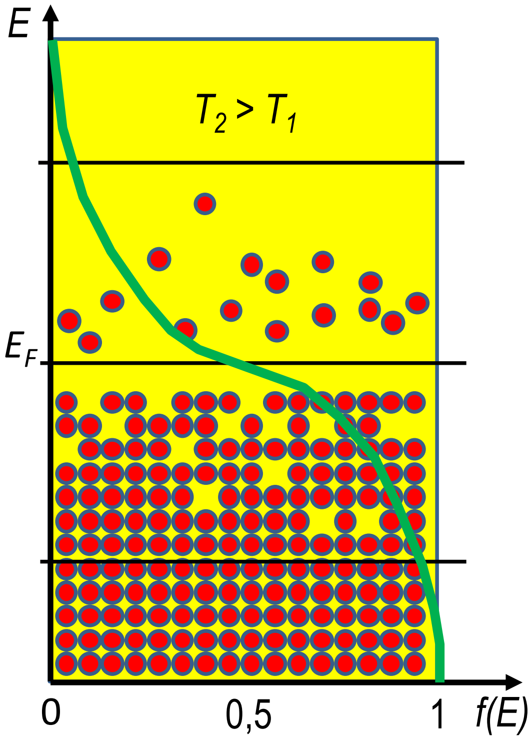
f(E) Fermi distribution function; E_F: Fermi energy
k_B: Boltzmann constant; k_B=8.63 10^{-5} eV/K



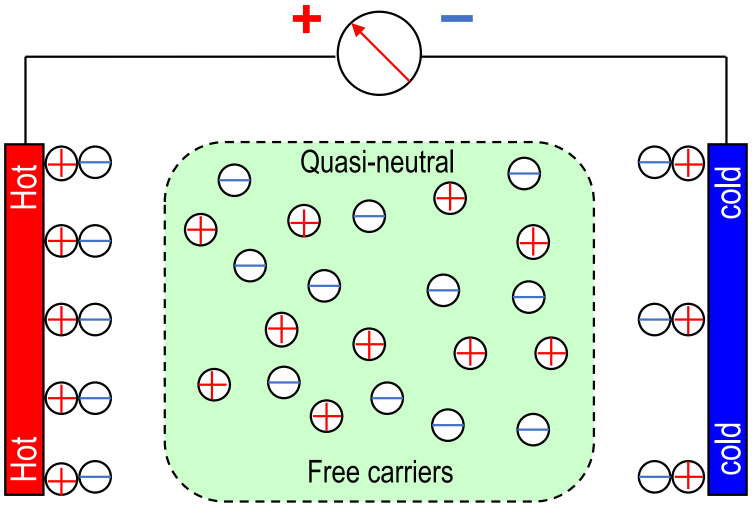


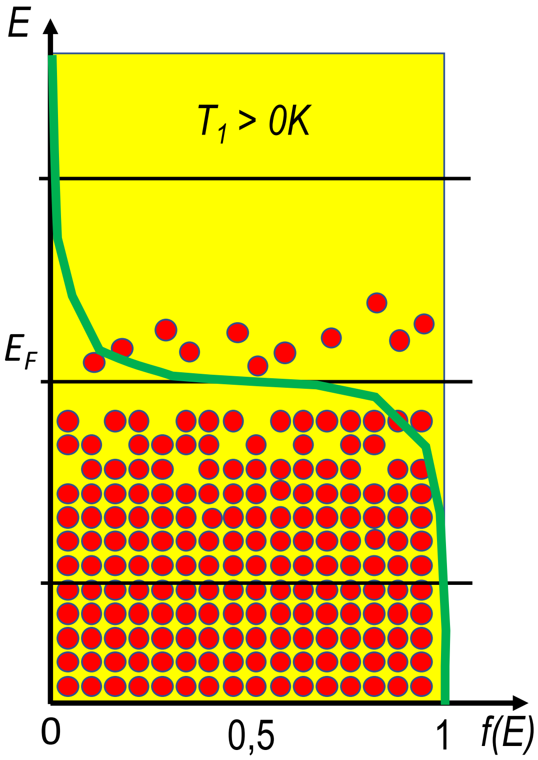
http://jas2.eng.buffalo.edu/

Asymmetry giving rise of Seebeck potential creation as soon as the electrodes are at different temperature



State of Hot electrode
facing the Inner Helmholtz layer

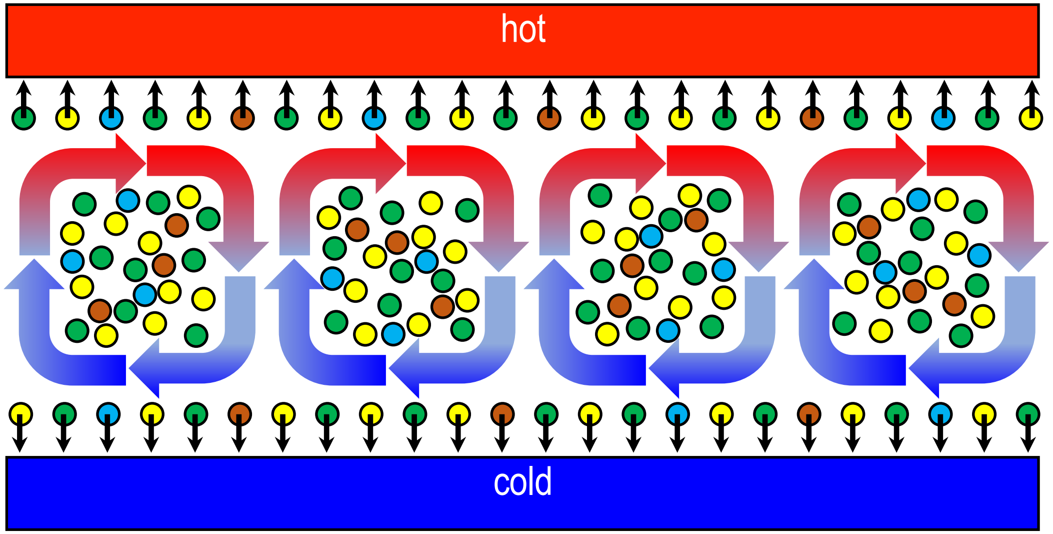


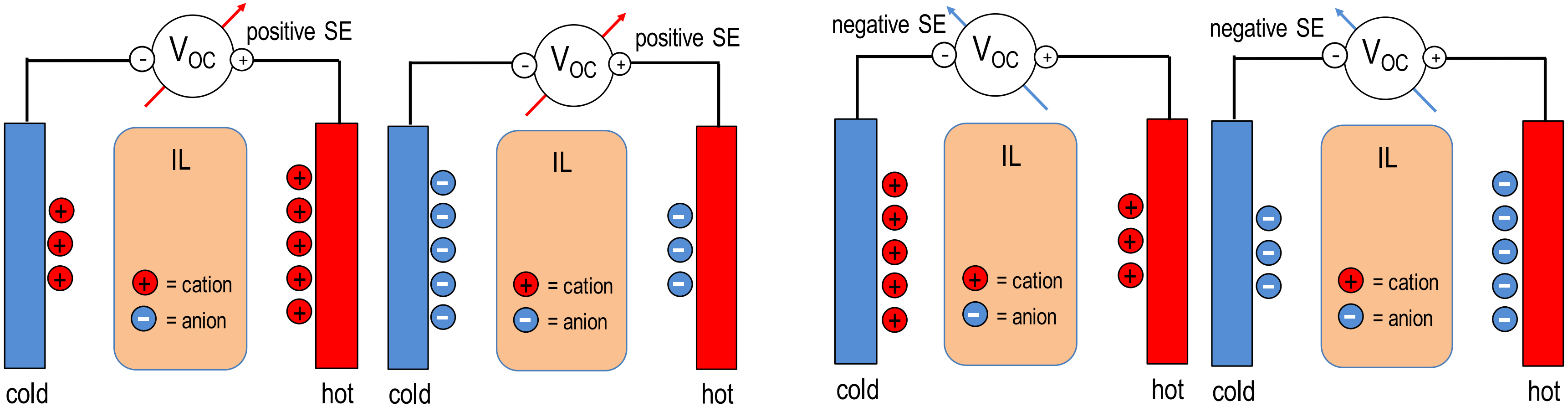


State of cold electrode
facing the Inner Helmholtz layer

Note Rhodium is a perfect metal, chosen due it chemical inertia.
What other effect could justify the asymmetry.

Further work needed: what are the true rules of sticking?





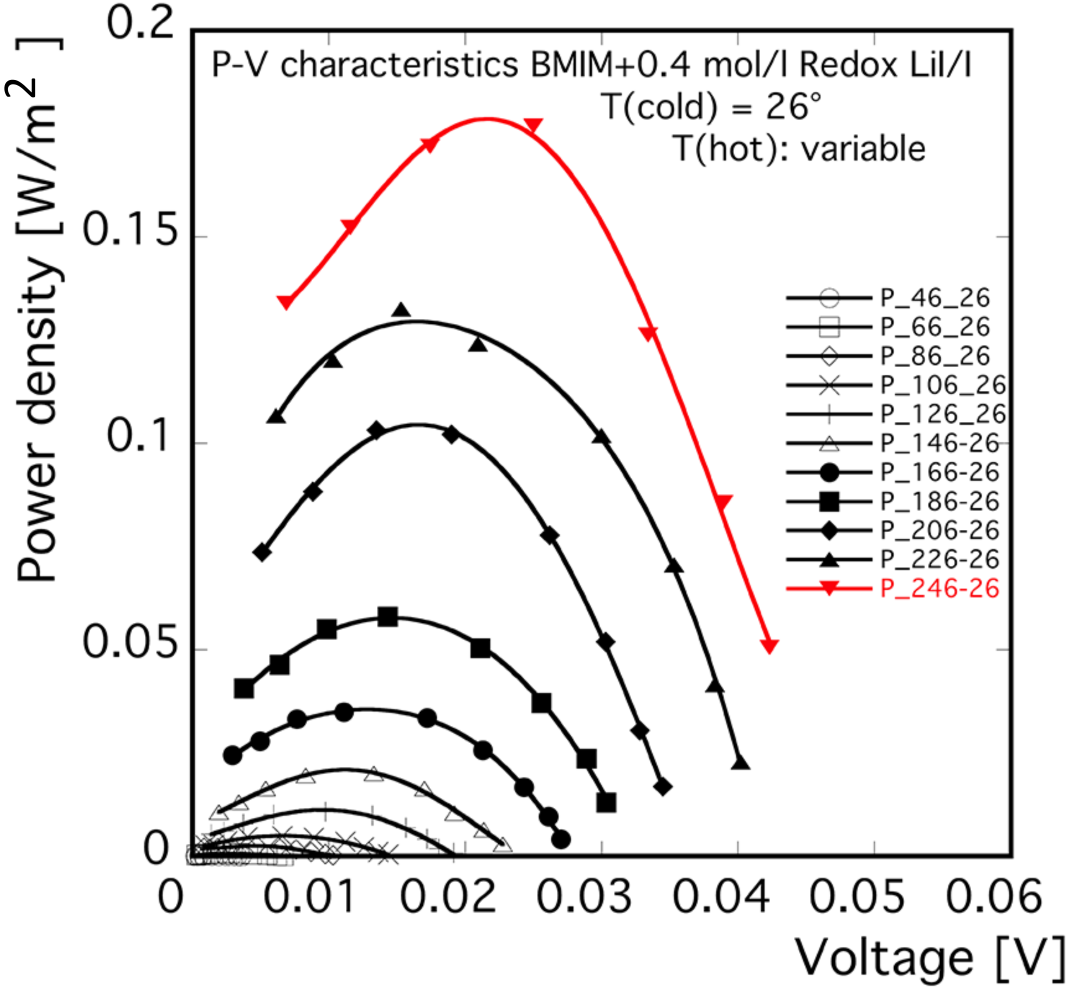
« Normal » and « abnormal » behaviour of TEGs based on ILS

Normal means

- The Seebeck coefficient is constant throughout the entire temperature regime (within the stability limit of the IL) and is independent of ΔT
- The current depends only on ΔT

Abnormal means: see examples 1-6.

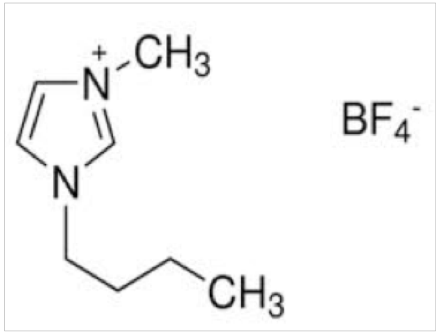
Example of « Normal » behaviour of ILS



BMIM

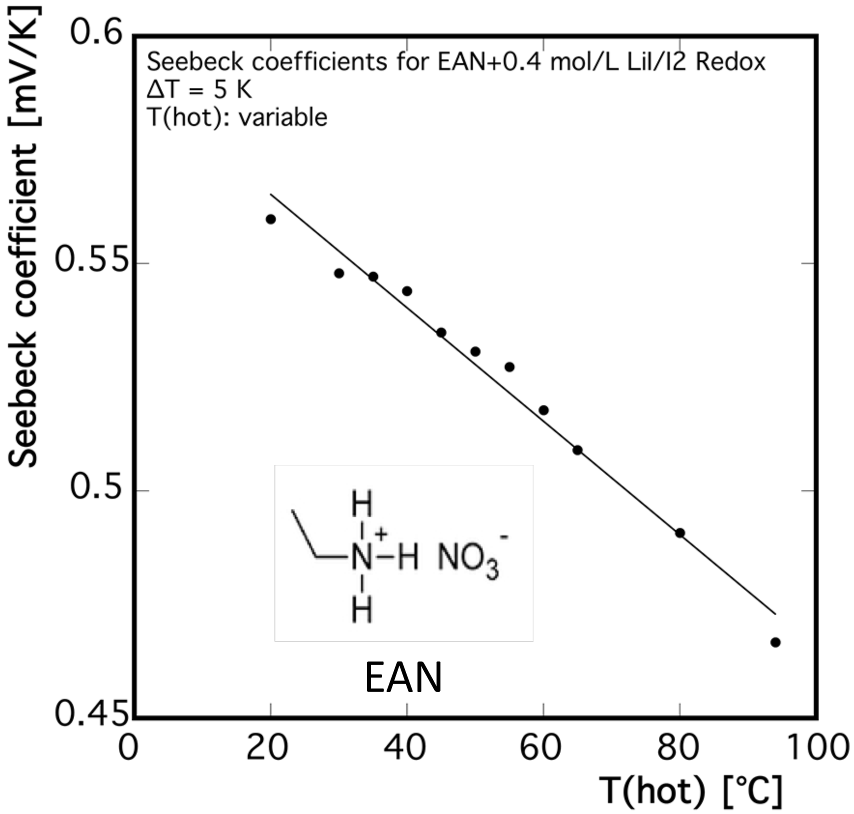
1-Butyl-3- Methylimidazolium

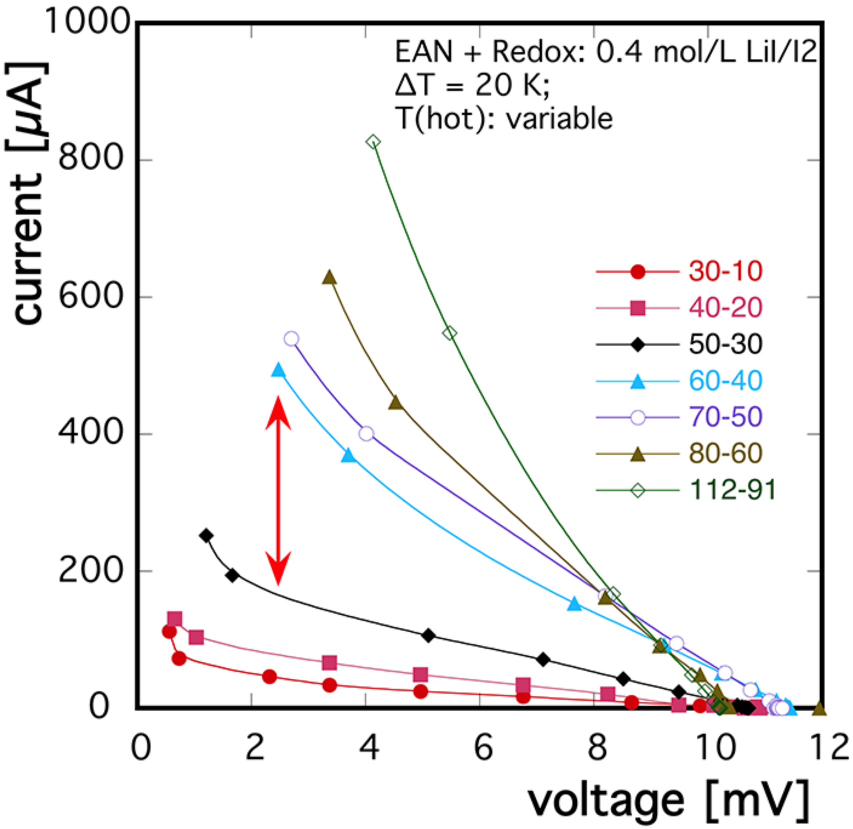
-tetrafluoroborate + LiI/I_2



E. Laux et al. *Journal of ELECTRONIC MATERIALS, Vol. 45, No. 7; DOI: 10.1007/s11664-016-4526-1; (2016).*

Abnormal 1: EAN+Li/I2 (Ethyl-ammonium-nitrate)





Observation 1:
For ΔT= const. SE decays for increasing T(hot)

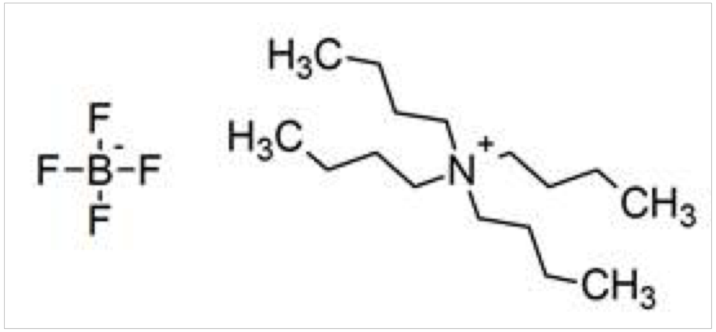
Observation 2:
For ΔT= const. the current increases for T(cold) > 30°C significantly

Model: Attachment is stronger competed by thermal release

Model: the re-injection of electrons at the cold electrode is thermally activated.

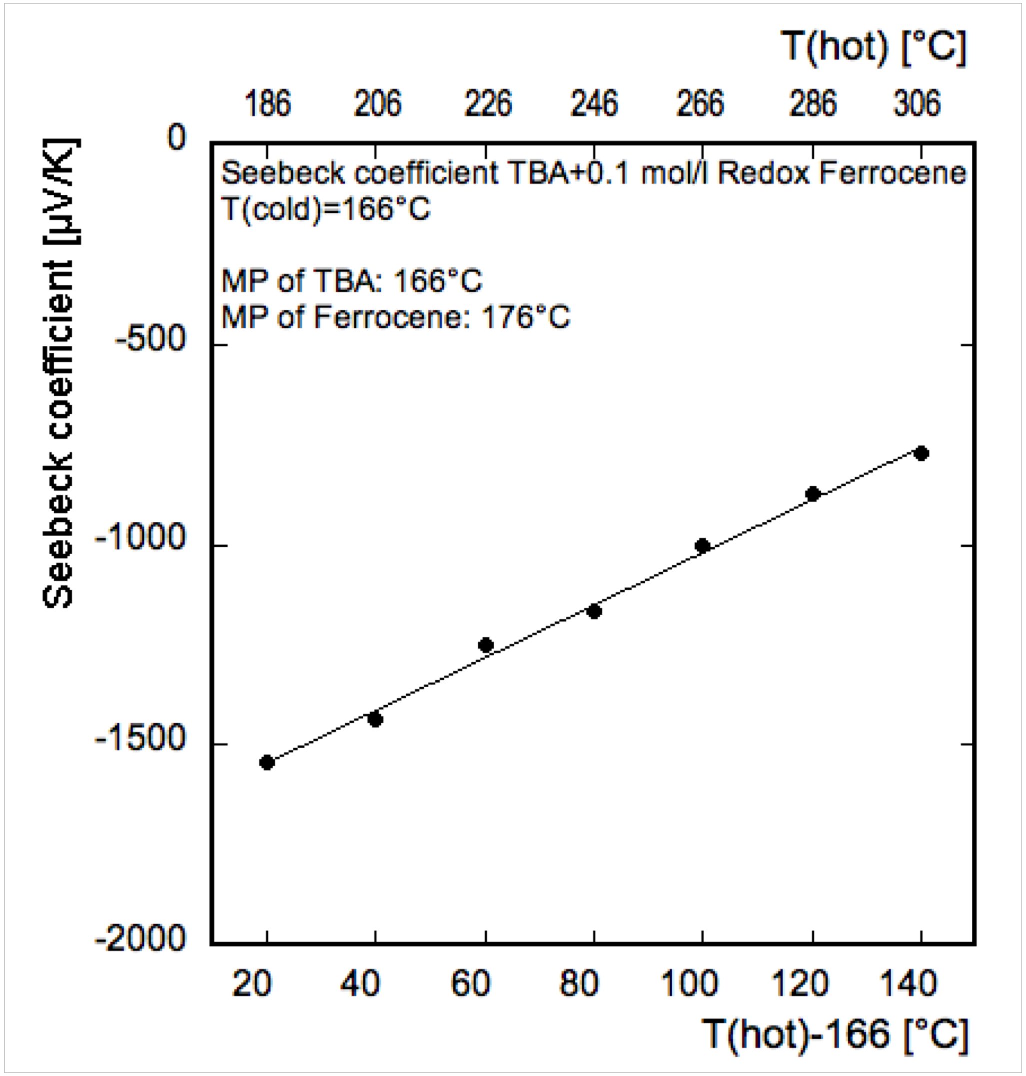
Abnormal 2: decreasing Seebeck coefficient at higher T(hot)

TBA
Tetrabutylammonium
Tetrafluoroborate
MP 166° C
0.1 Mol FeII/III [CN_6] as redox



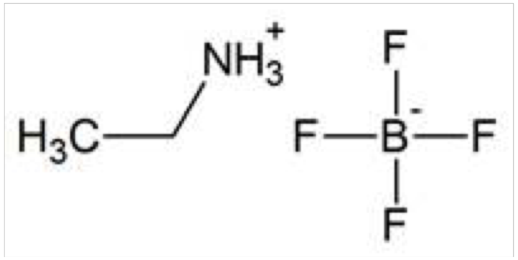
Observation 3:
For constant T(cold) = 166°C
The high negative SE decreases at increased T(hot)

Model: Attachment is stronger competed by thermal release



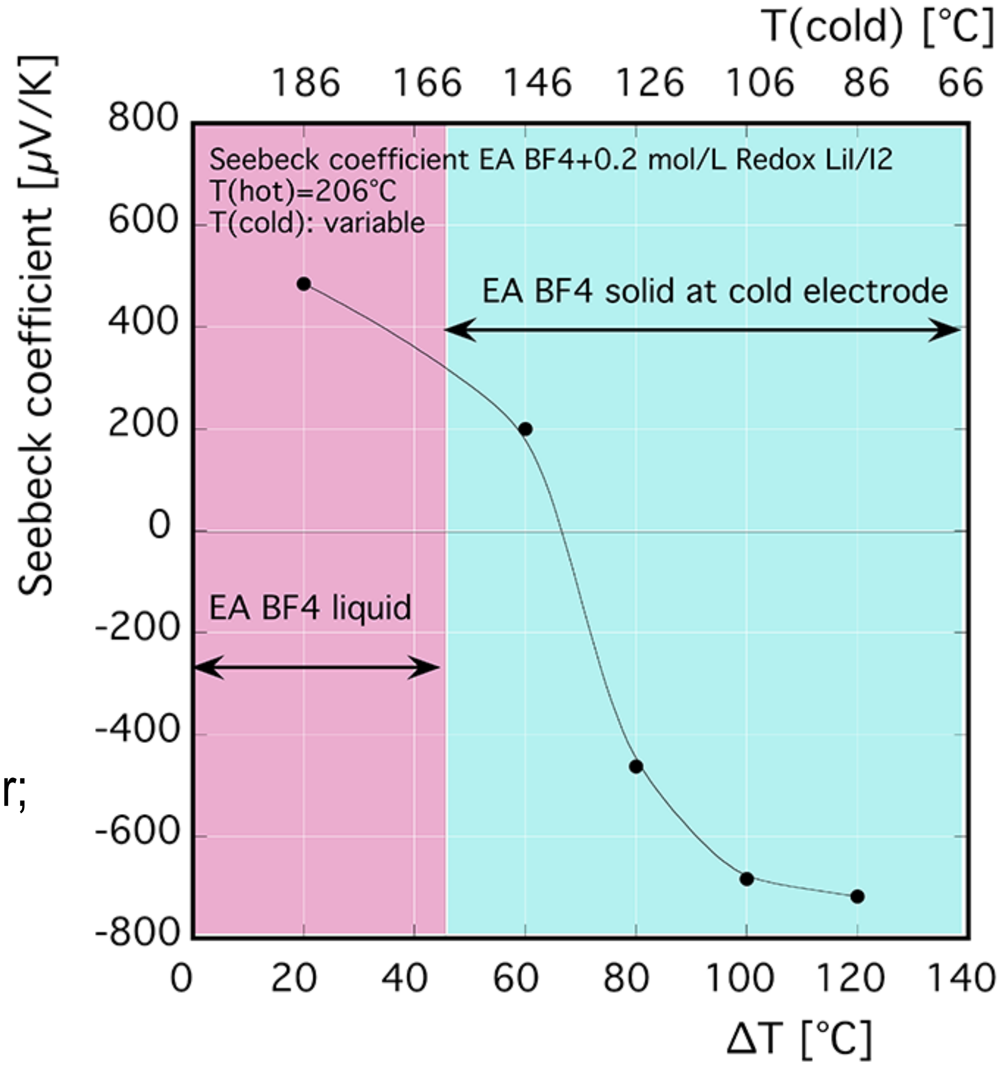
Abnormal 3: SE is inversed across phase-transition

EATB
Ethylammonium Tetrafluoroborate
+ LiI/I_2
Melting Point EATB 167°C

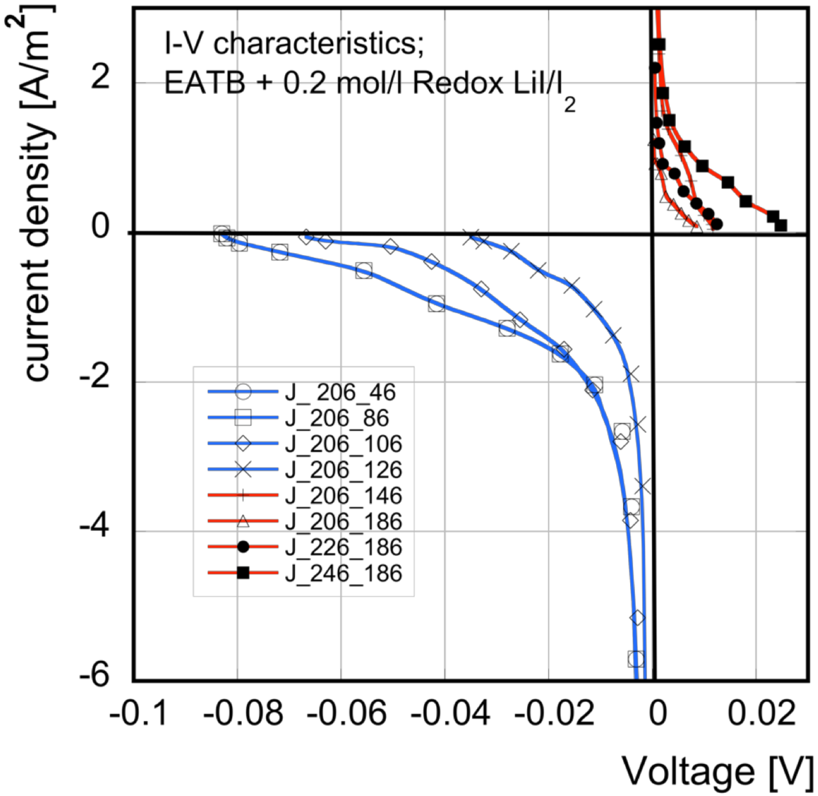


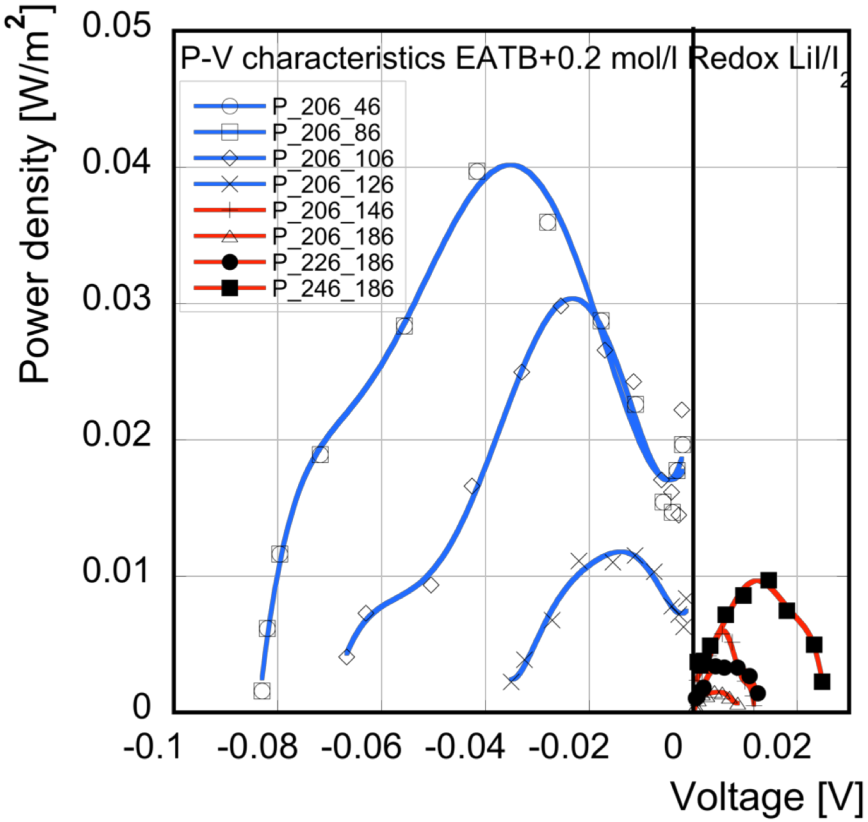
Observation 4:
Below phase transition at cold electrode
SE negative,
Rh electrode is replaced by solid ad-layer;

All EATB liquid: SE positive.



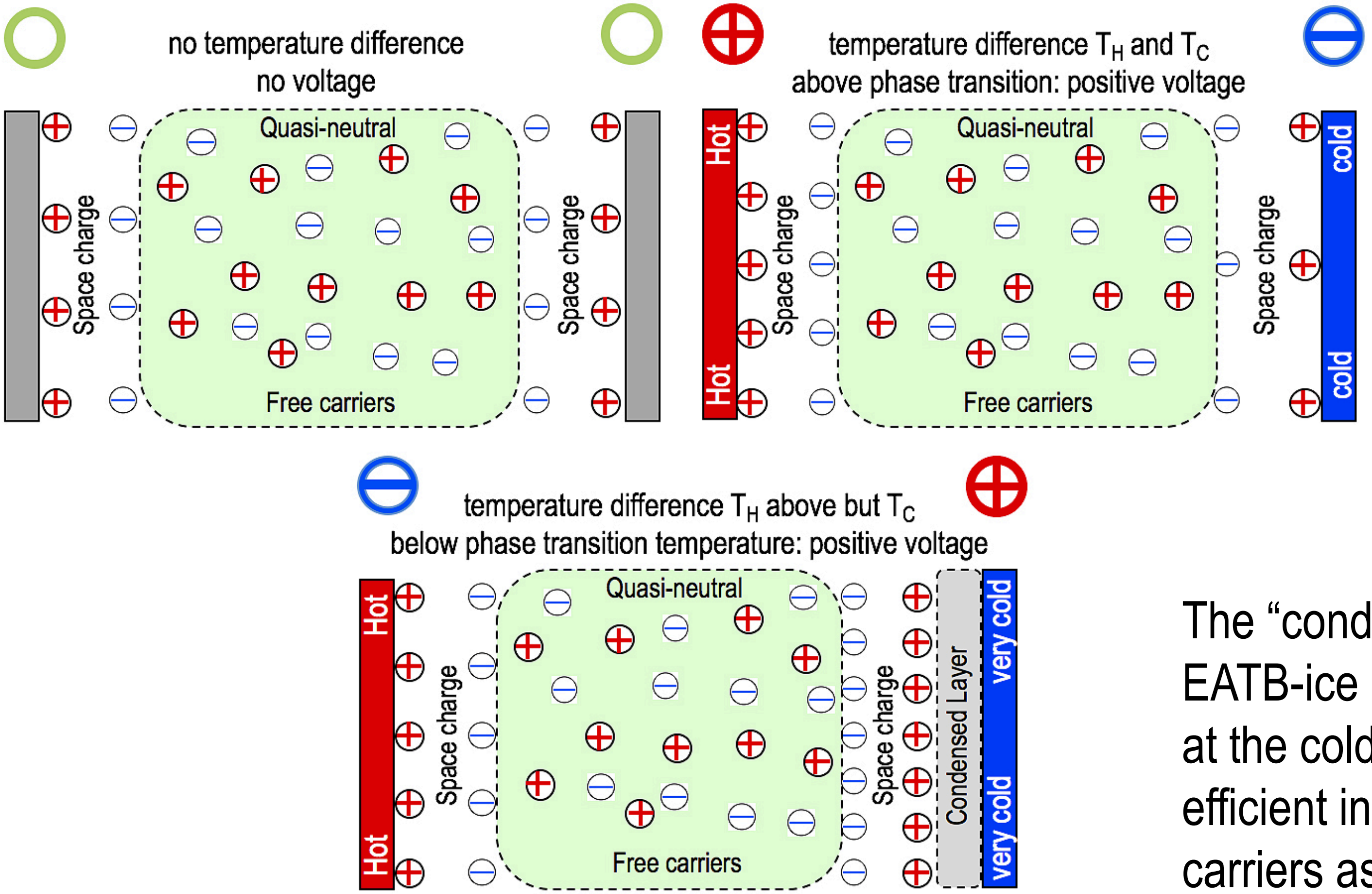
High temperature Experiments with aprotic RT solid ILs





Observation: the Seebeck coefficient change its sign as soon as the Temperature of the cold electrode in below the melting point of the EATB Temperature limitation: 246°C

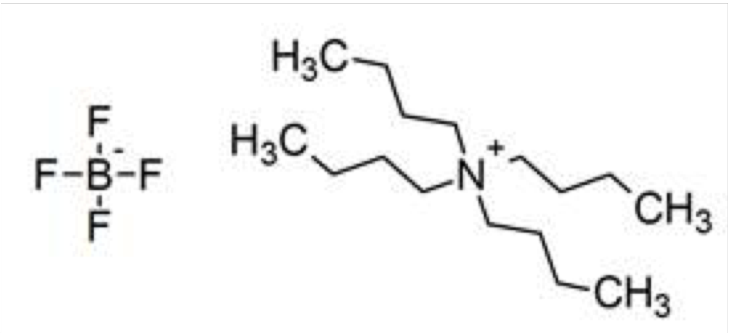
Simple model explaining the EATB phenomenon



The “condensed layer”
EATB-ice
at the cold electrode is more efficient in attaching positive carriers as compared to the real RH electrodes.

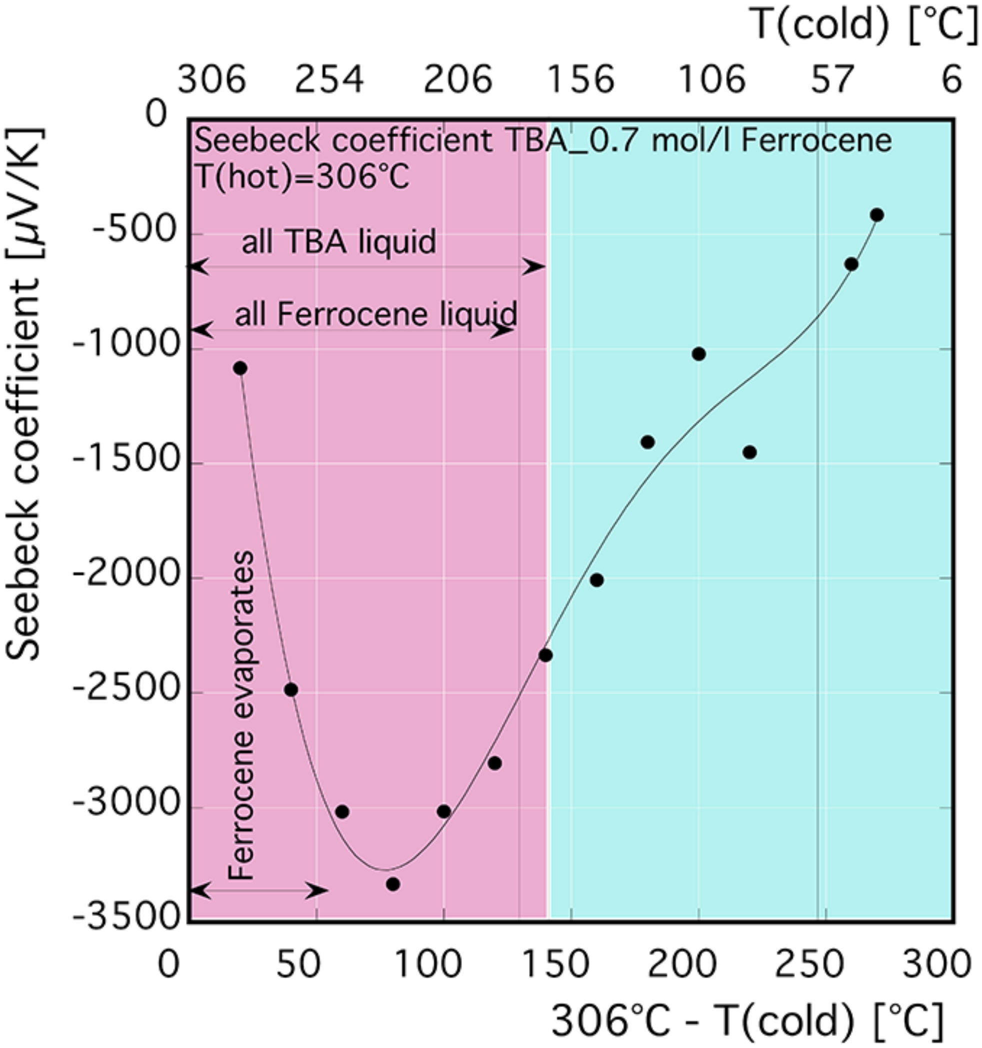
Abnormal 4: SE Temperature-regime dependence of SE if REDOX is not dissolved.

TBA Tetrabutylammonium
Tetrafluoroborate
0.7 mol /L Ferrocene



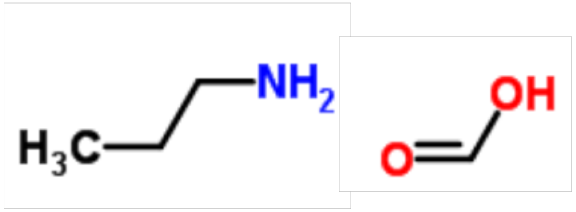
Observation 5:

1. Blue regime: below phase transition of REDOX (solid Ferrocene at cold electrode) reduced negative SE at increased ΔT
2. Red regime: All Ferrocene is liquid and loss for highest temperatures.



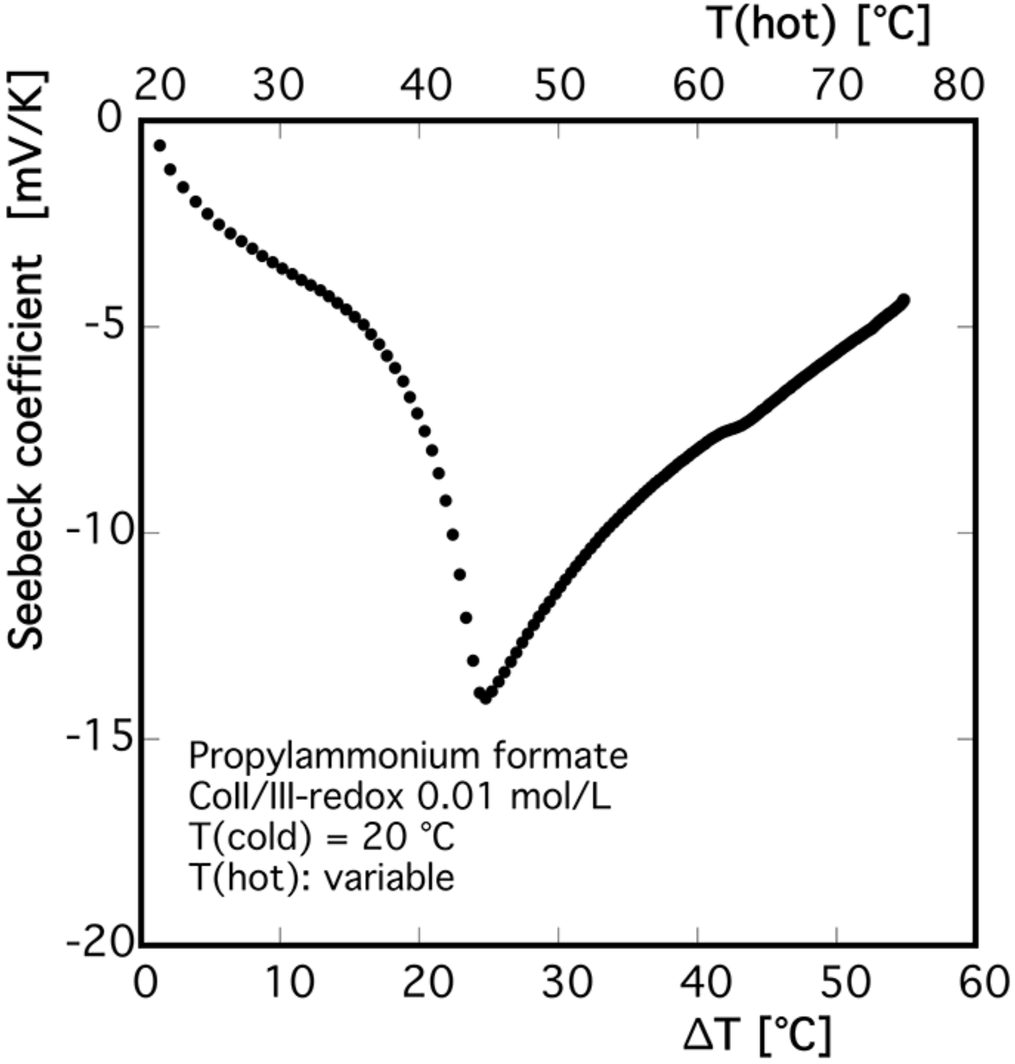
Abnormal 5: SE depends on temperature-regime.

Propylammonium formate

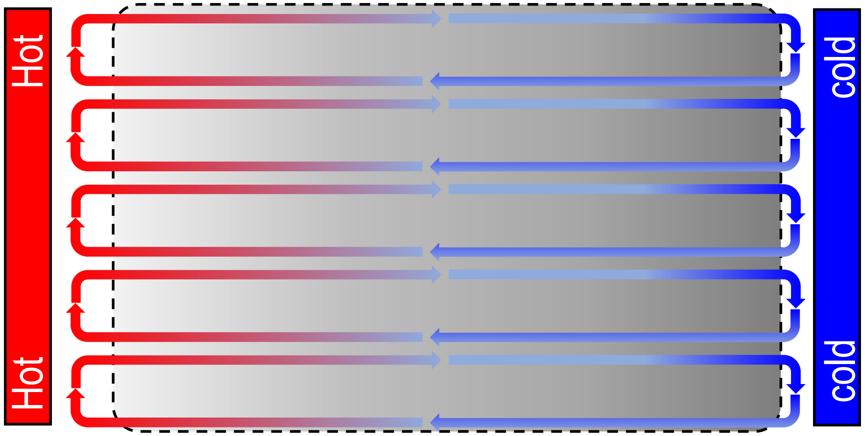


Observation 6: Temperature selective effects - SE not linear; in a strongly limited regime ΔT = 25°C, SE is very high (highest ever reported)

Model: Attachment is stronger competed by thermal release

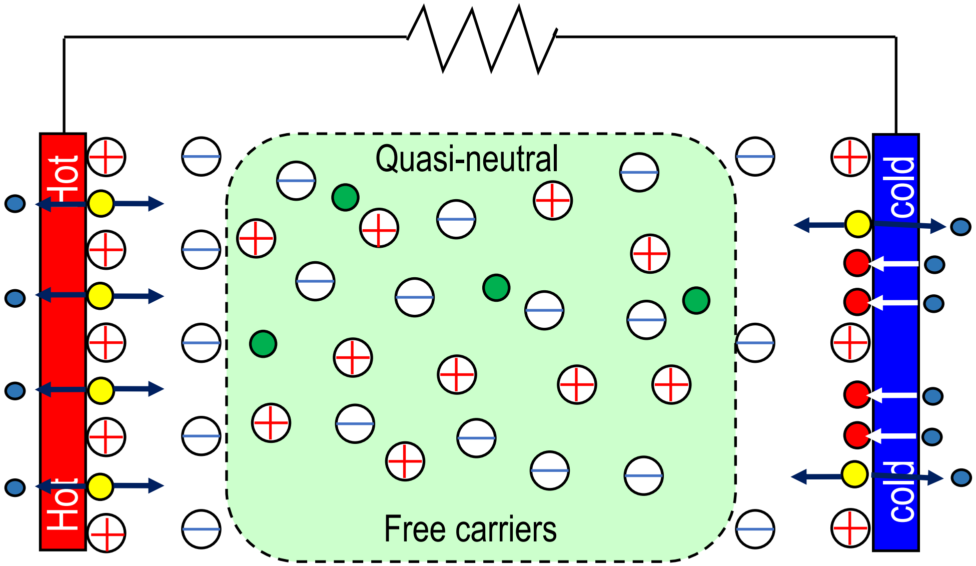


Bottlenecks to be overcome:



carrier transport = material transport

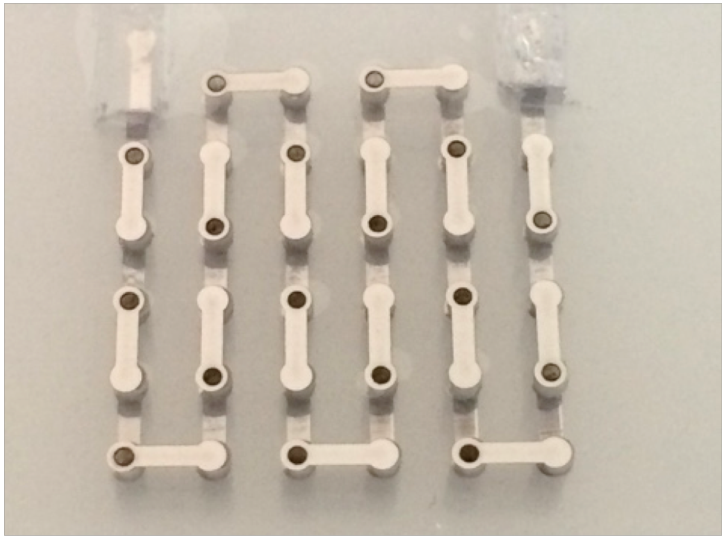
At the cold electrode the energy-flow is not transferred (convection) and the carriers are driven back to hot.

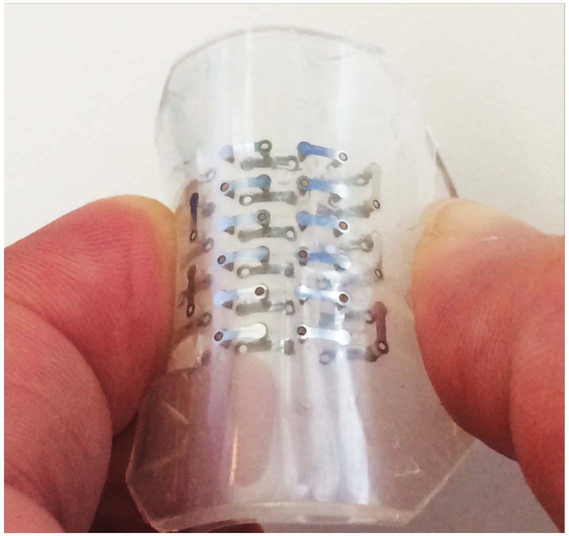


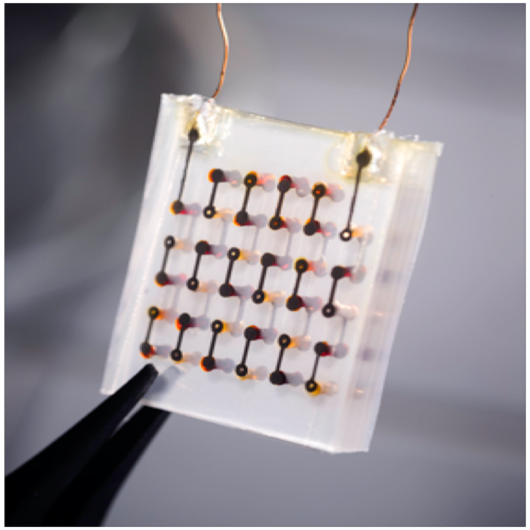
The current that is injected into an external circuit (e.g. Reduction at hot electrode) must be re-injected at the cold electrode (Oxidation). Any limitation limits the current.

Low- $\Delta T < 100°C$ T(hot)<150°C flat IL/FF/NP - filled TEGs

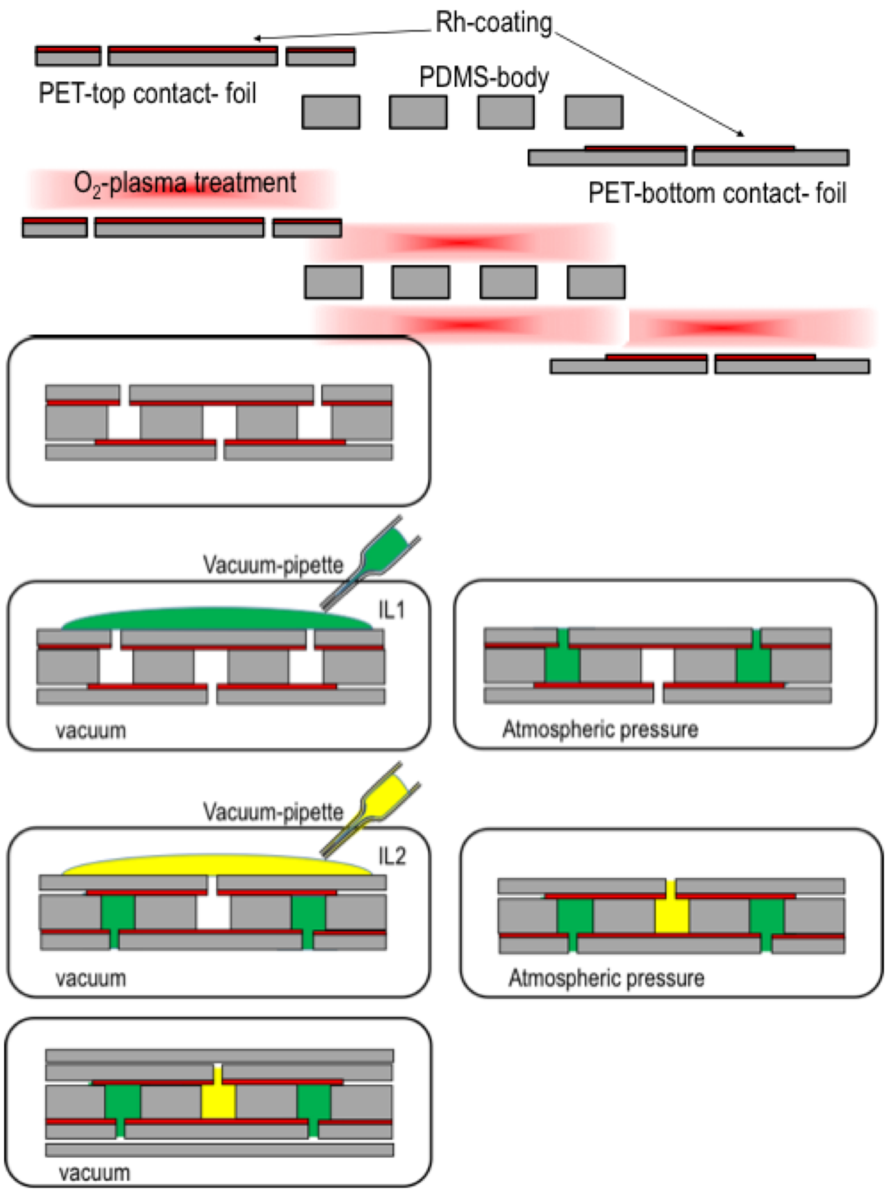
Technology developed by Stefanie Uhl and Laure Jeandupeux
may be considered as established technology







Assembling of highly integrated series connected low ΔT- TEG



Step 1: patterning and metallization

Step 2: surface conditioning

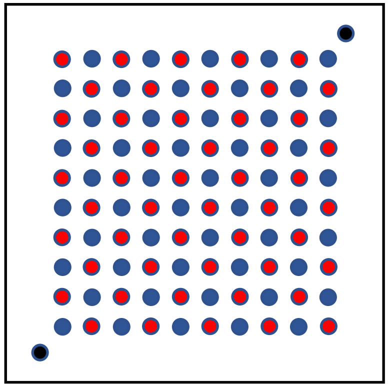
Step 3: SiO_2 on PET, O_2 for surface activation plasma and plasma induced bonding

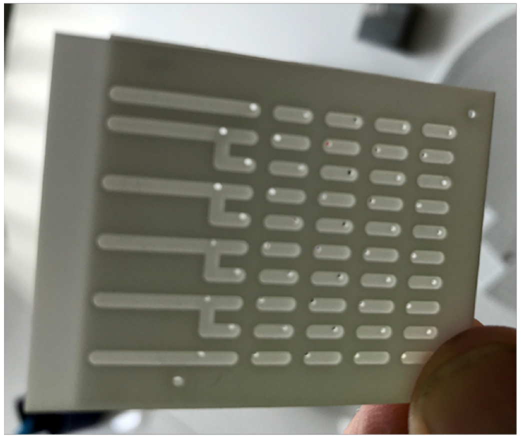
Step 4:
p-SE IL + (redox + FF) on top side
n-SE ILII + (redox + FF) on bottom side

Step 5: both sides sealing

Construction of the low ΔT generator for body-heat conversion with 100 junctions

Consists of a stack of 5 sheets:
Top cover sheet (PET)
Top contact sheet (PET)
Body sheet (PDMS)
Bottom contact plate (PET)
Bottom cover plate (PET)

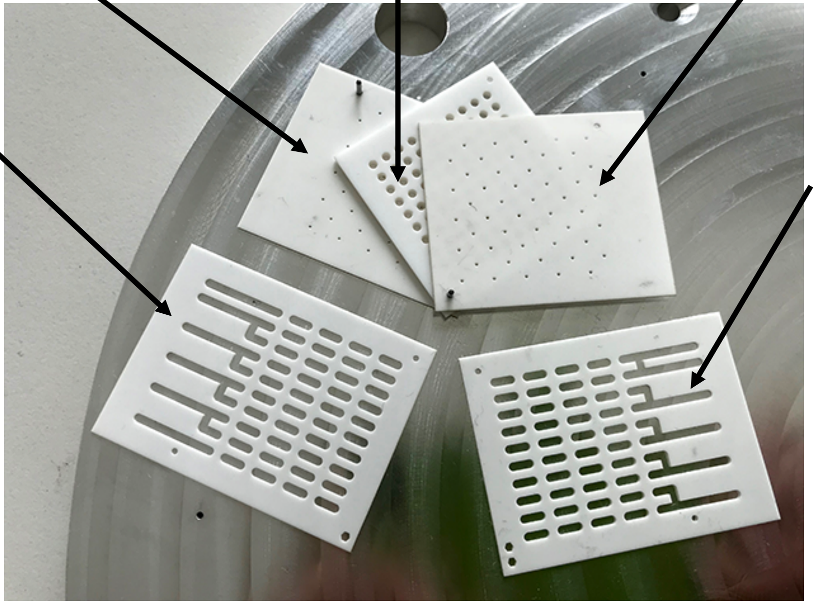




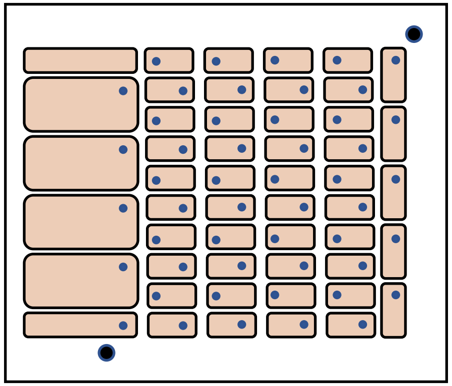
Top-contact sheet Al_2O_3 + Rh contact

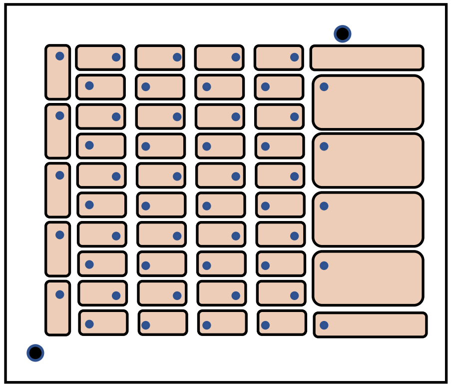
bottom-contact sheet Al_2O_3 + Rh contact

Al_2O_3 shadow mask for Rh contact deposition



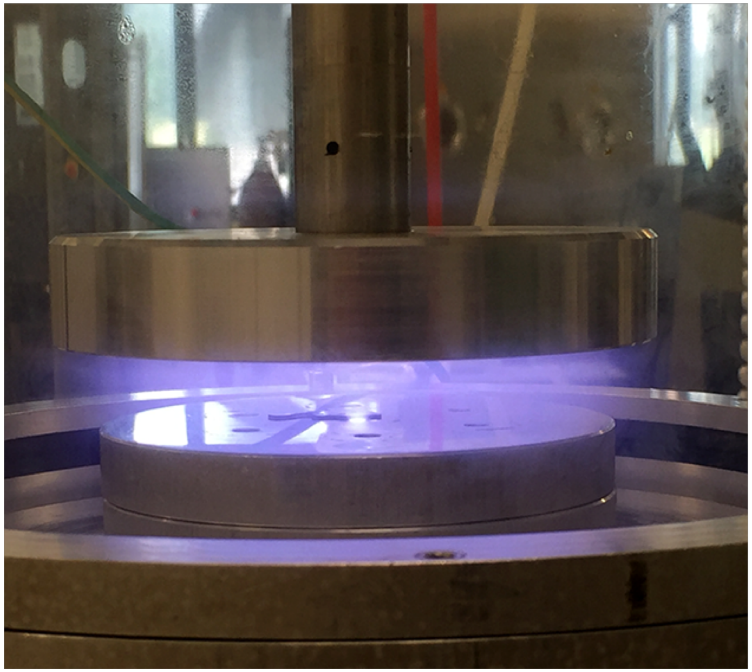
Al_2O_3 shadow mask for Rh contact deposition

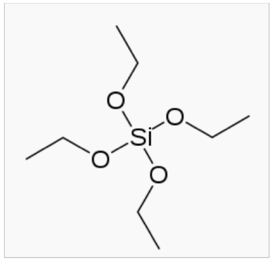




Assembling how?

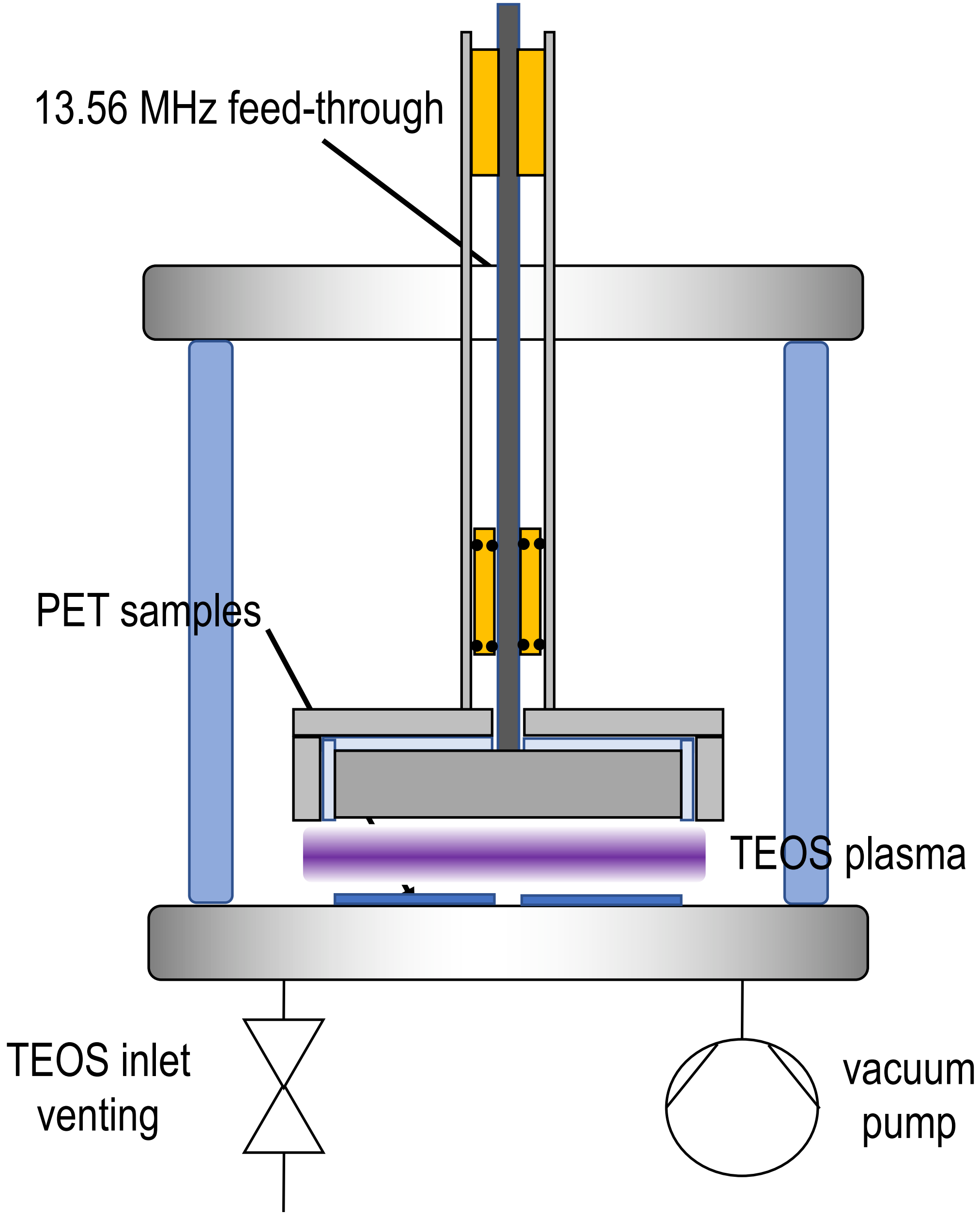
First: PET substrates must be SiO_x –coated
Using PECVD with TEOS





TEOS: Tetra ethyl ortho-silicate

$Si(OC_2H_5)_4$



13.56 MHz feed-through

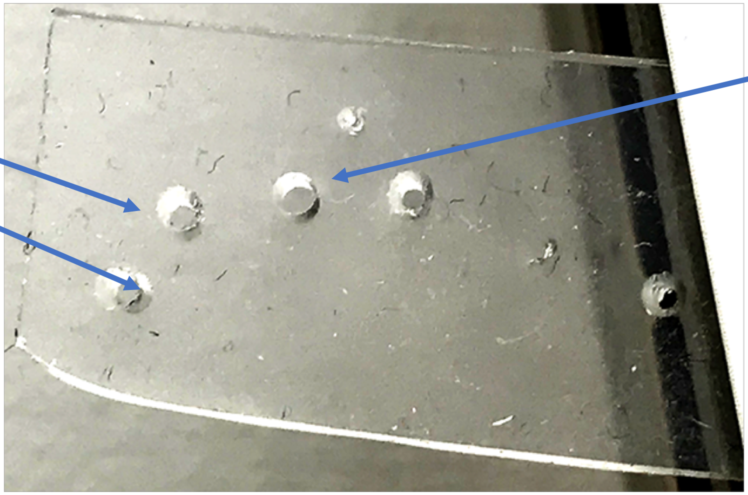
PET samples

TEOS plasma

TEOS inlet
venting

vacuum
pump

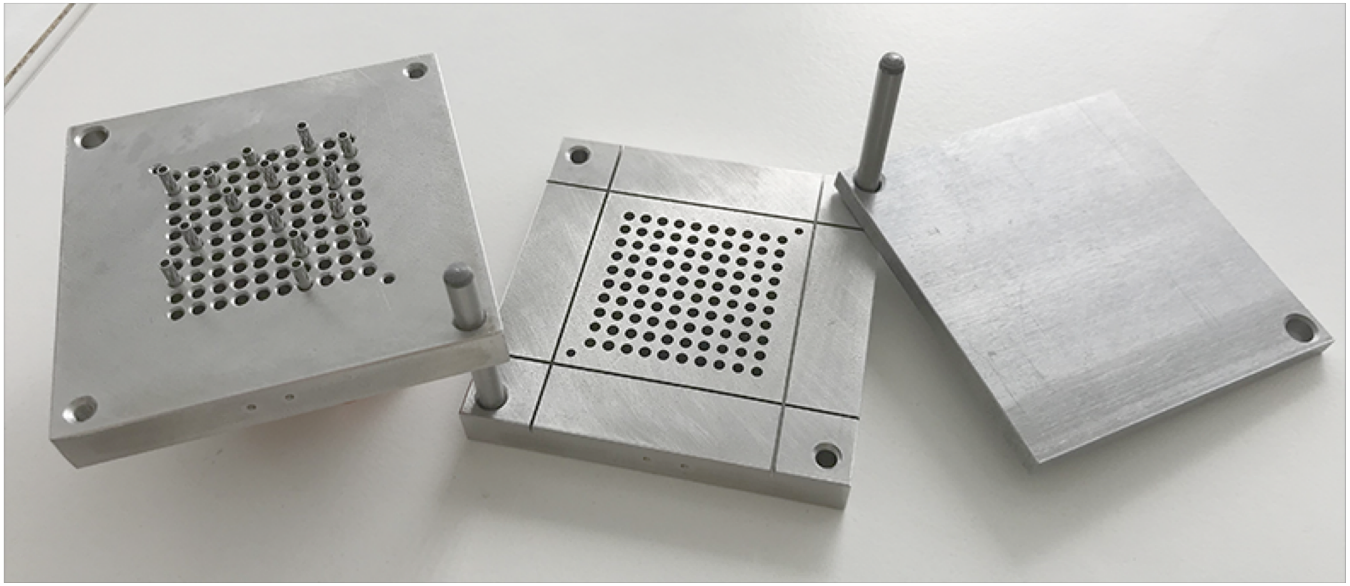
“drilling” of 100 openings for p-SE (+) and n-SE (+) into 1.6 mm thick PDMS



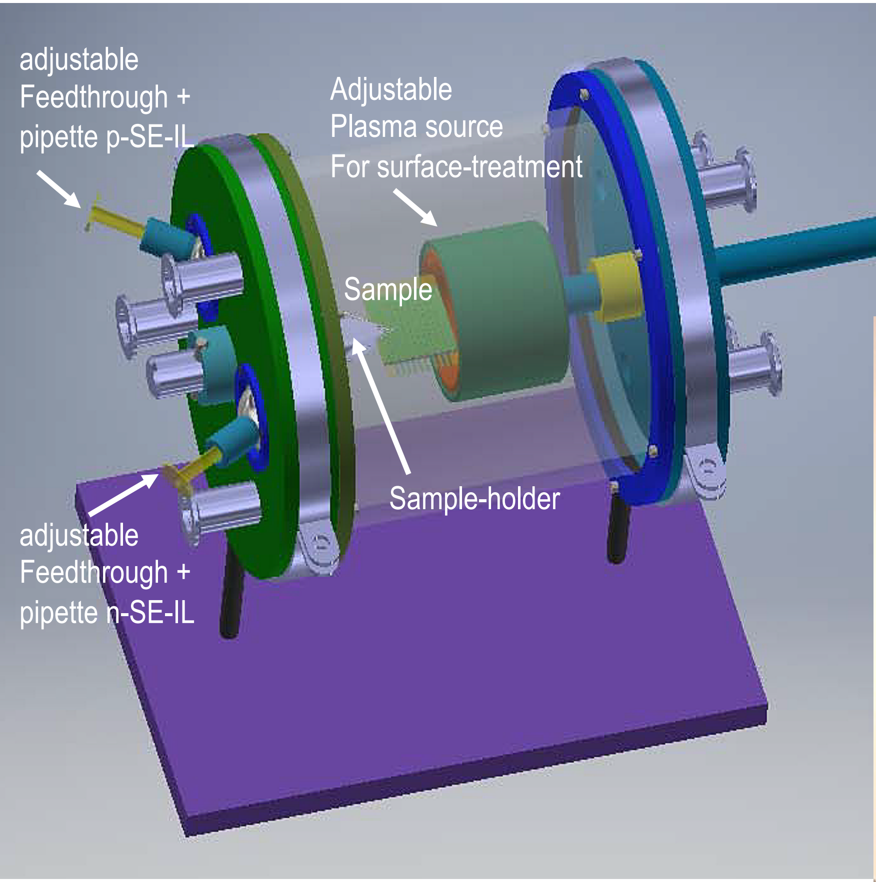
330nm UV Fs laser:
poor quality

Stamping:
better quality

100 holes stamp tool:



Vacuum system for IL insertion and hermetic sealing



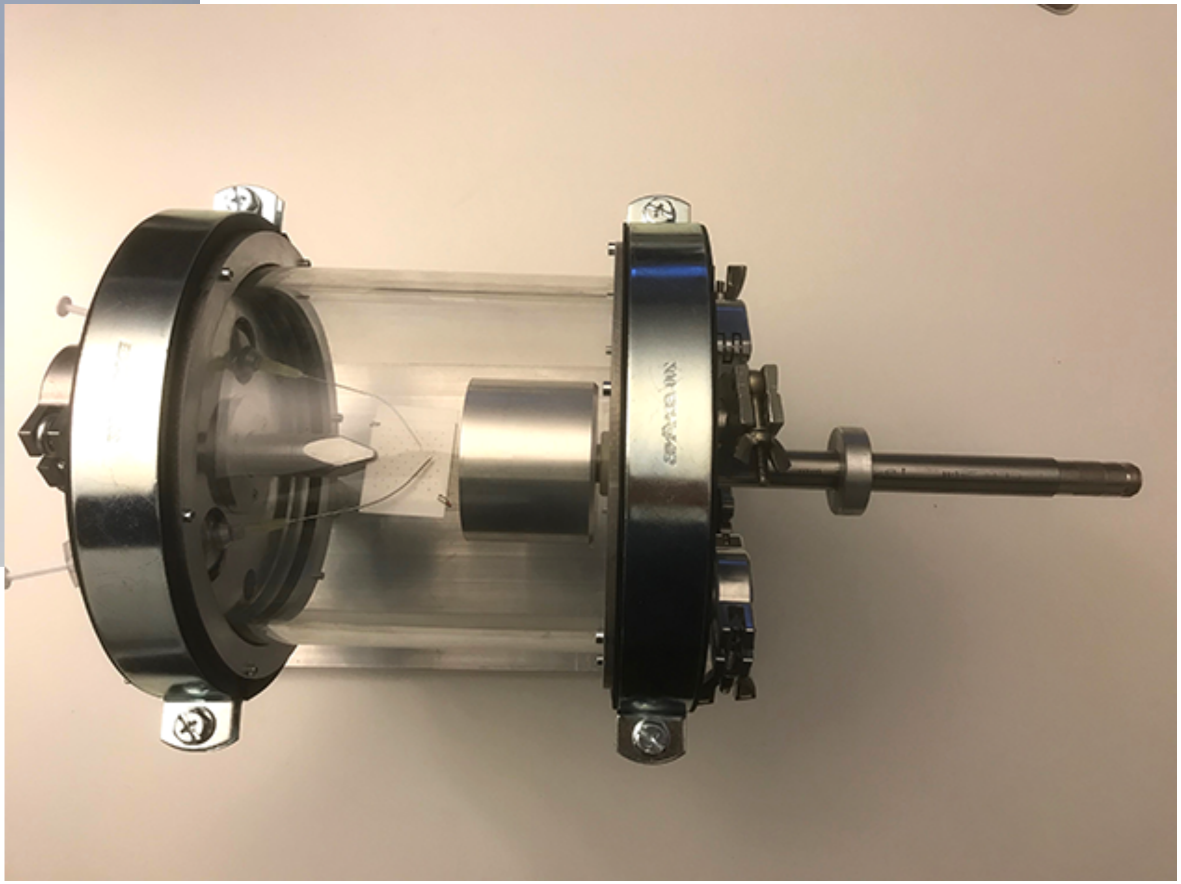
adjustable
Feedthrough +
pipette p-SE-IL

Adjustable
Plasma source
For surface-treatment

Sample

Sample-holder

adjustable
Feedthrough +
pipette n-SE-IL



Conclusions

The factor that determines the value of the Seebeck effect in Metal / IL /metal TEGs was assumed to be due the temperature-dependent dynamic sticking coefficient ratio between hot and cold electrode.

The value is assumed to be a function of the temperatures T(hot) and T(cold); both temperatures are the result of the heat transport through the device for a given heat-flow. Here the total heat conductivity comes in

The transport of carriers in the cell is connected to the transport of matter.

The realization of sealed 100 junction cell on flexible carrier is on the way

The systems are waiting for complete filling containing: IL, redox couples and FF nanoparticles.

Acknowledgements

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Thank you

for your attention !