CIC energiGUNE

MEMBER OF BASQUE RESEARCH & TECHNOLOGY ALLIANCE

ELECTRO INTRUSION

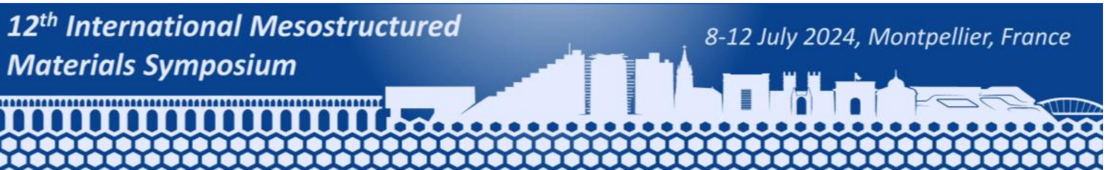
Triboelectrification during intrusion-extrusion of water in mesoporous materials

Luis Bartolomé, Josh Littlefair, Eder Amayuelas, Andrea LeDonne, Simone Meloni, Yaroslav Grosu.

12th International Mesostructured Materials Symposium

8th July 2024, *Montpellier (France)*

This project leading to this application has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101017858



Triboelectric generators

Technology for converting irregular and distributed mechanical energy into electric power by using a conjunction of triboelectrification and electrostatic induction[1].

2012 Prof. WANG Zhong Lin

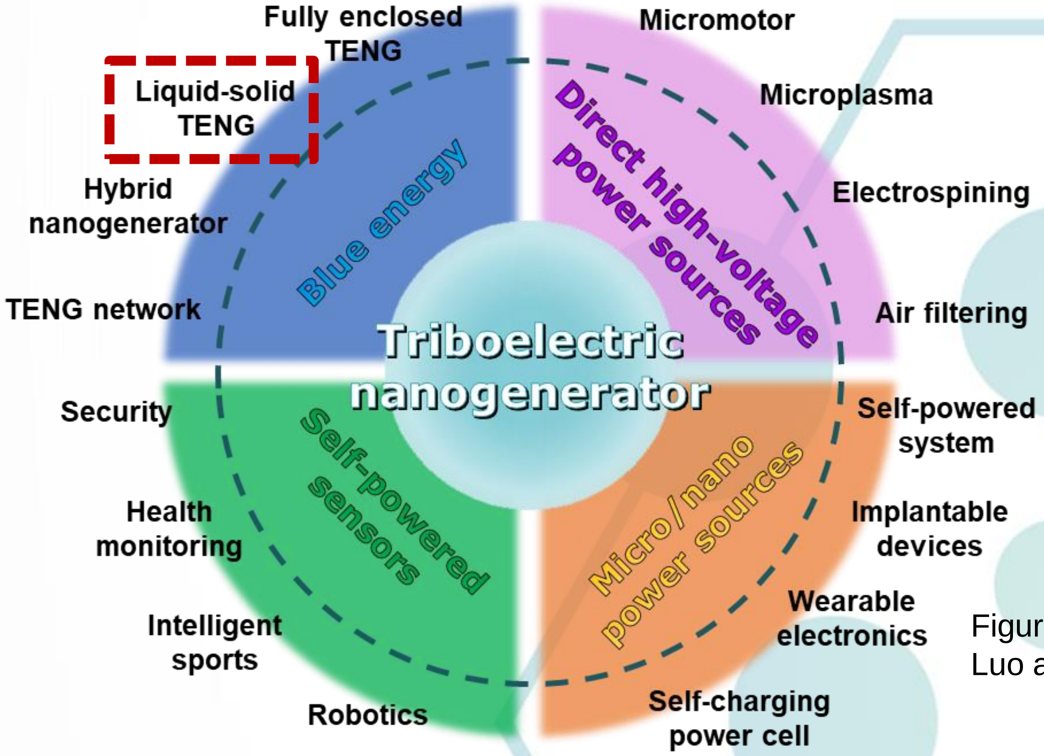
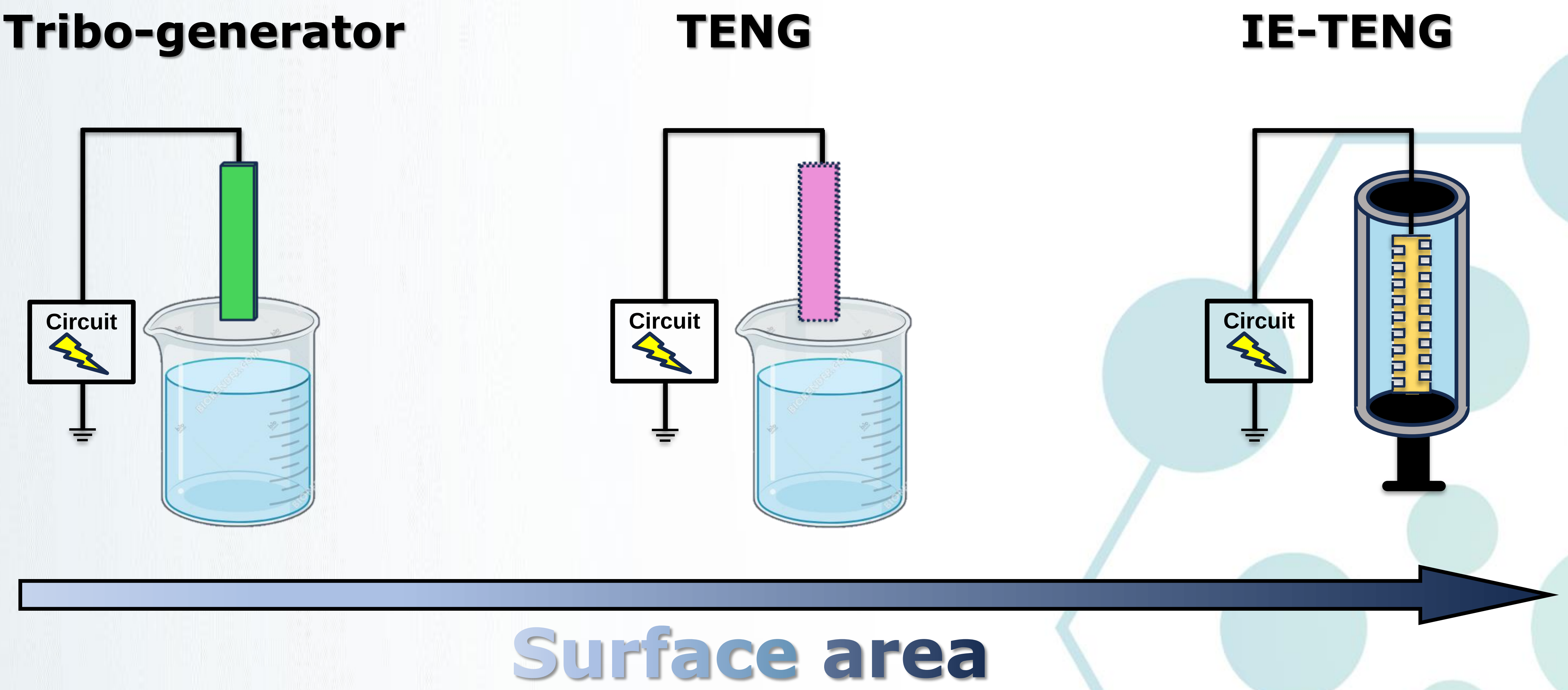


Figure adapted from Luo and Wang, 2020[2]

[1] Wang, Z.L., 2021. From contact electrification to triboelectric nanogenerators. *Reports on Progress in Physics*, *84*, p.096502.
[2] Luo, J., Wang, Z.L., 2020. Recent progress of triboelectric nanogenerators: From fundamental theory to practical applications. *EcoMat*, 2(4).

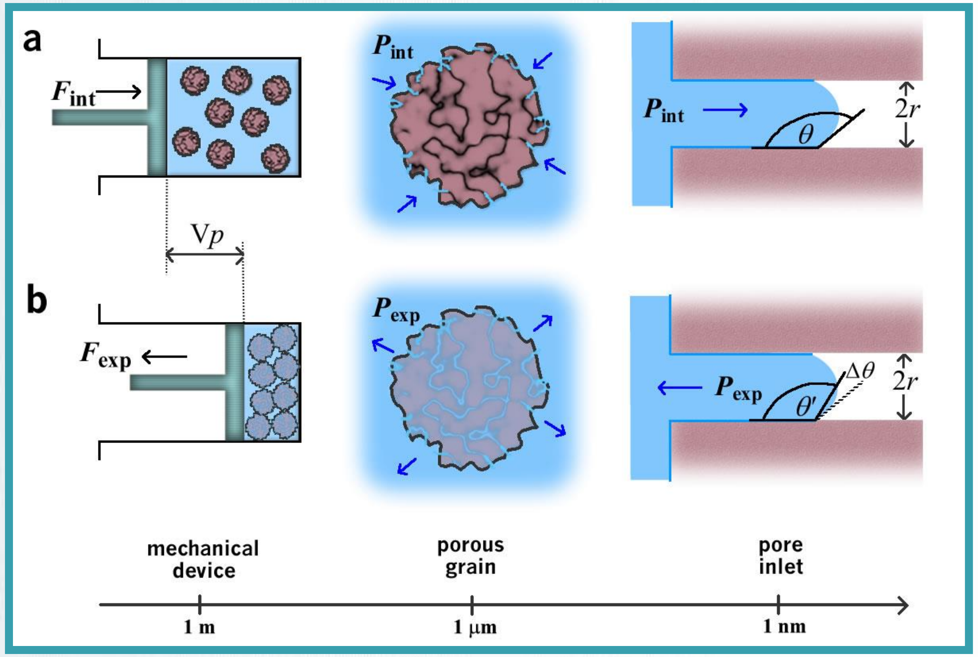
1. Introduction

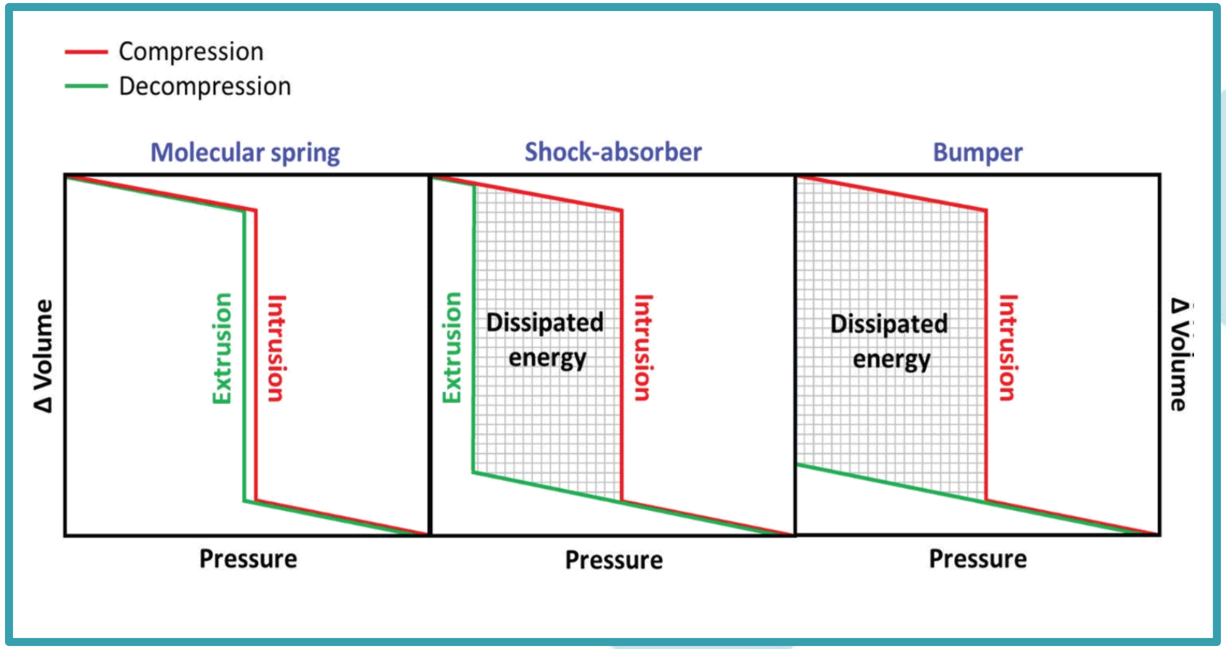
Strategy



1. Introduction

Intrusion–extrusion process

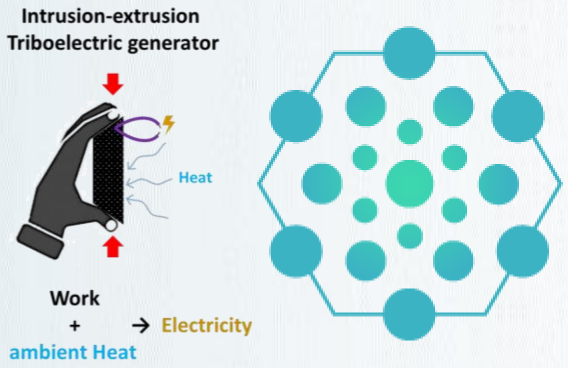




- (Super)hydrophobic materials: Contact angle >>>90º to enhance the int-ext pressure
- Mesoporous materials: Accessible pores for water intrusion and high surface areas to enhance the surface on int-ext takes place.
- High intrusion-extrusion hysteresis for a higher energy dissipation

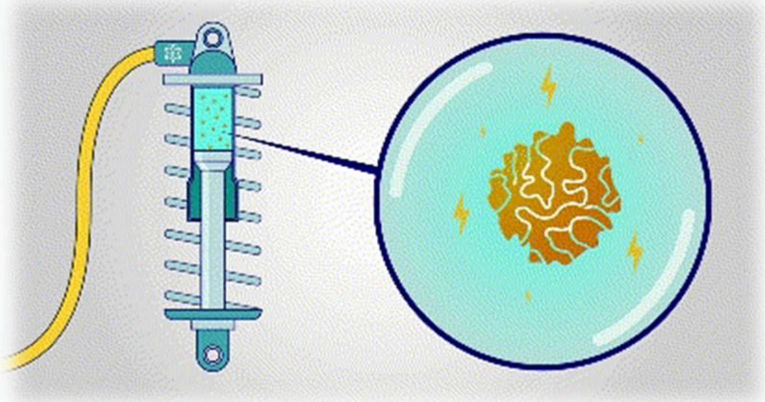
2. Electro-Intrusion project

CIC energiGUNE · University of Silesia in Katowice · Università degli Studi di Ferrara · University of Birmingham · Київський політехнічний інститут 1898 · TENNECO



Electro-Intrusion: converting vibrations into electricity.

- A new method for thermomechanical-to-electrical energy conversion
- A new type of regenerative shock-absorbers



Building triboelectric nanogenerators

- **Hydrophobic nanoporous materials with highly hysteretic H_2O int-ext performance**
  - Amorphous mesoporous SiO_2 (Φ=15nm)
  - Fluorination of SiO_2 for hydrophobization and improved electrification

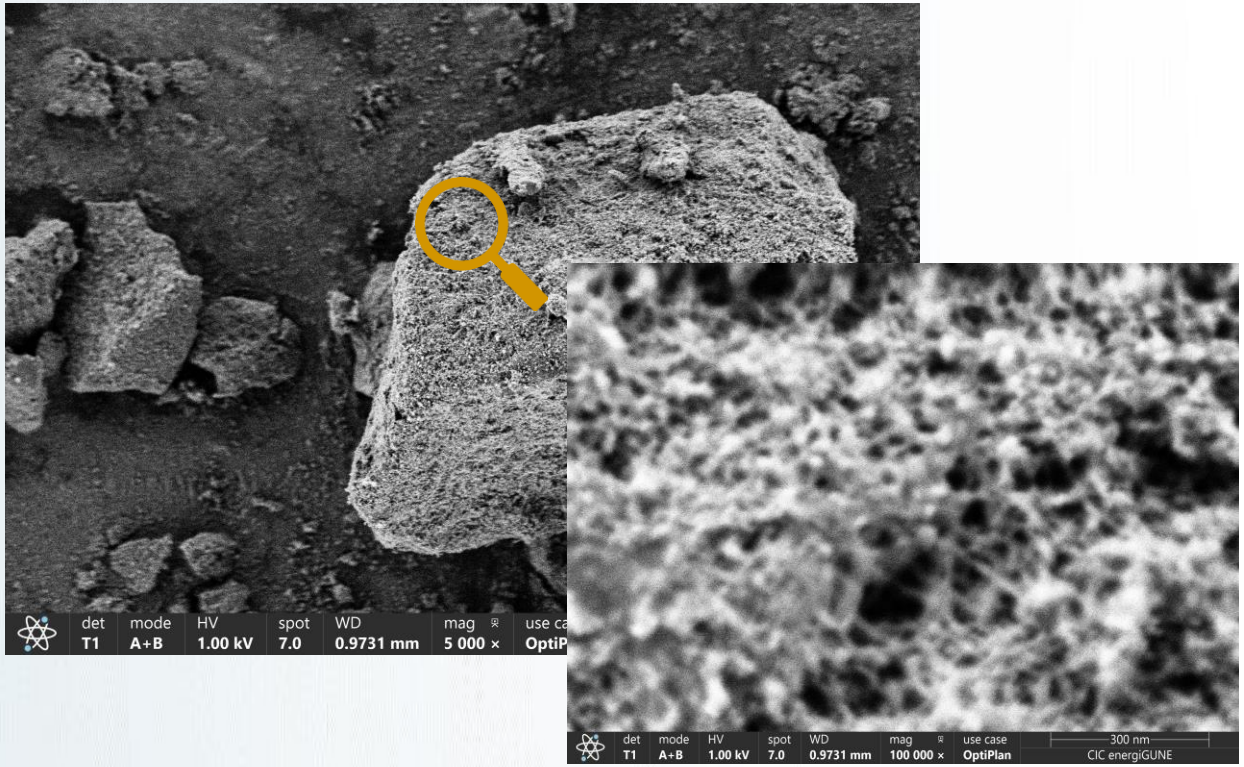
For regenerative shock-absorbers

- **Reliable materials under operation conditions**
  - Stable after thousands of int-ext cycles
  - Complete extrusion under high frequencies (real operation cond.)

3. Materials – porous silicas

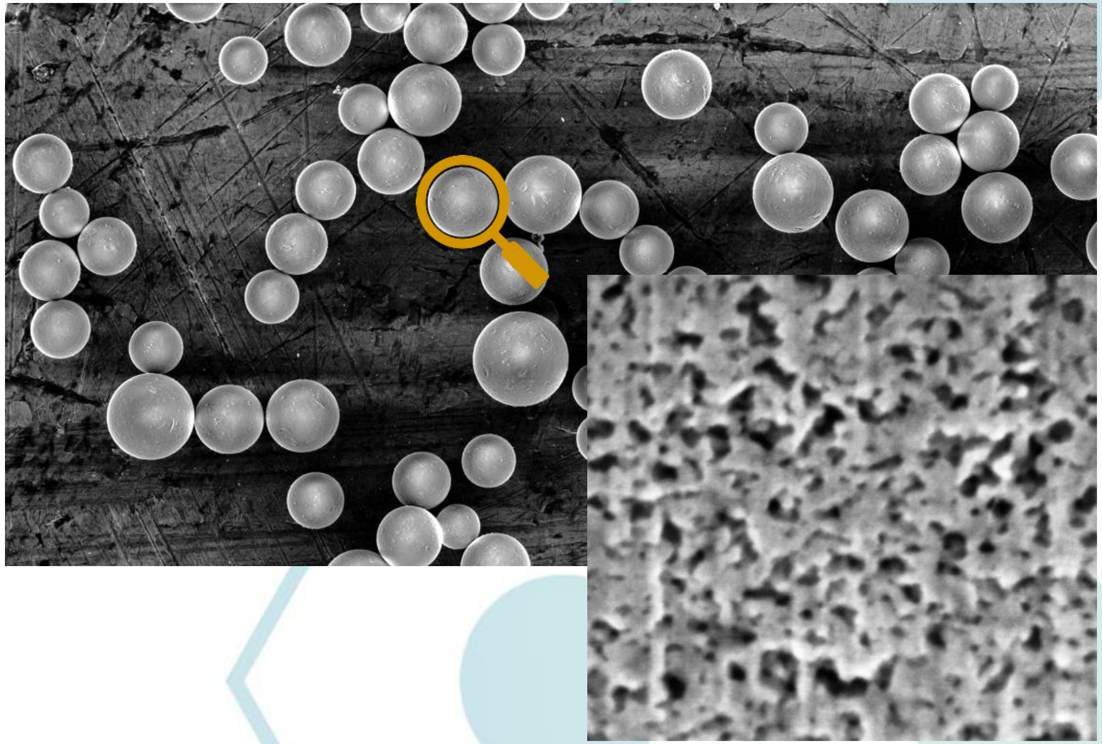
Grafted Grace 150 – **C8-CF_3**

- Amorphous SiO2
- Pore size 15 nm
- Hydrophobized with C_8 fluoroalkyl silanes



Commercial WC8 – **C8-CH_3**

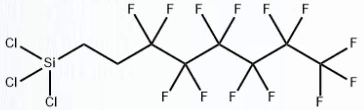
- Amorphous SiO2
- Pore size 10 nm
- Hydrophobized with C_8 alkyl silanes



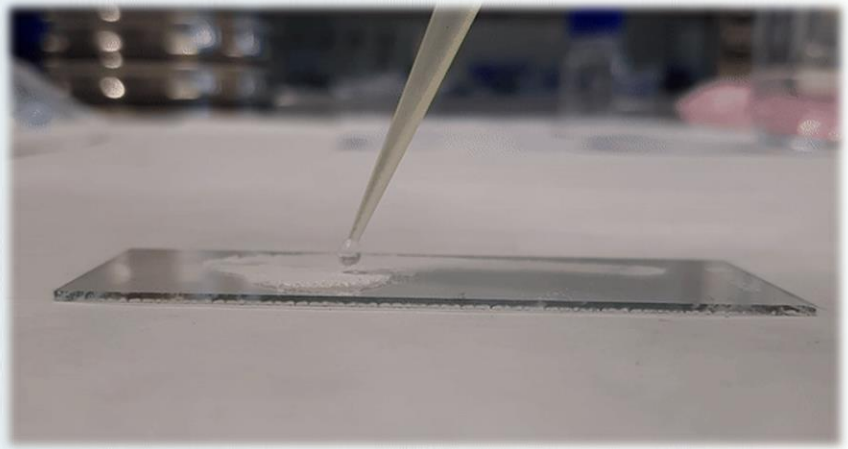
3. Materials – porous silicas

Grafting protocol

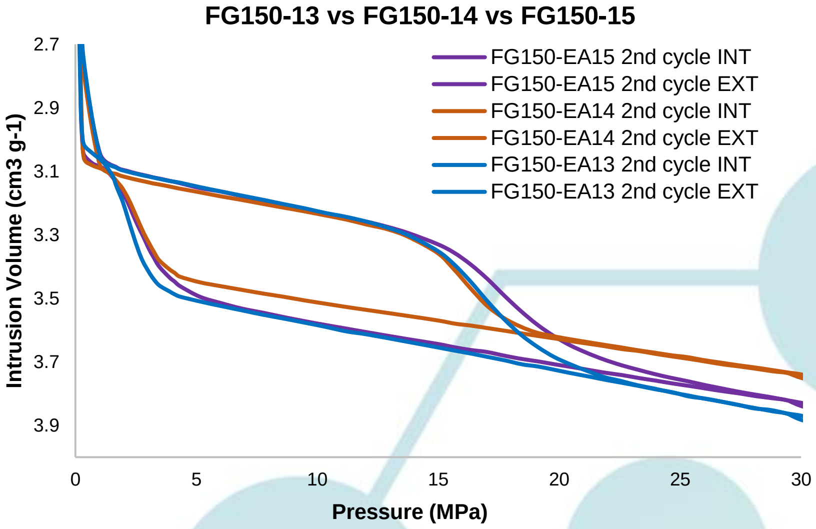
- 120 h in non-aqueous ethanolic ammonia solution // 50 ºC// CF_3 grafting density: 5 molecules/nm^2
  - **SiO_2 GRACE 150 – G150 (Φ = 15 nm)**

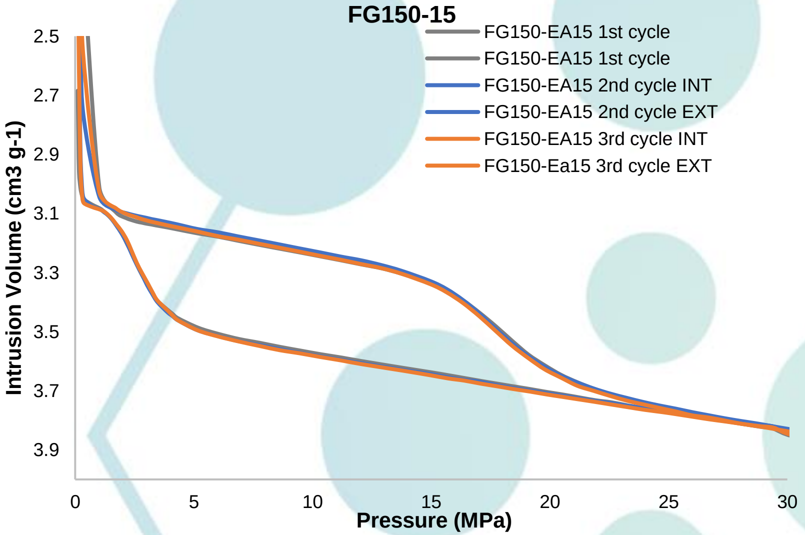


Trichloro(1H,1H,2H,2H-perfluorooctyl)silane
(PFOTCS)



Material	P_{int} (Mpa)	V_{int} (mL/g)
FG150-13	16,7	0,315
FG150-14	16,5	0,241
FG150-15	17,6	0,302

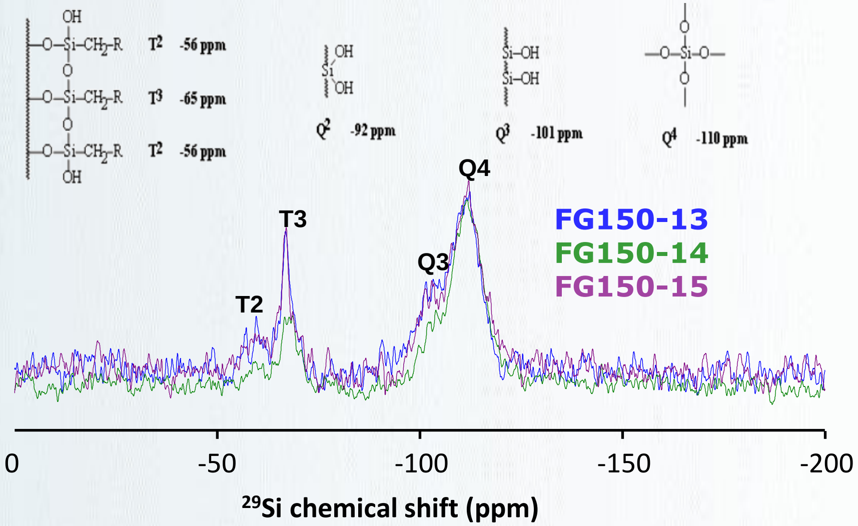




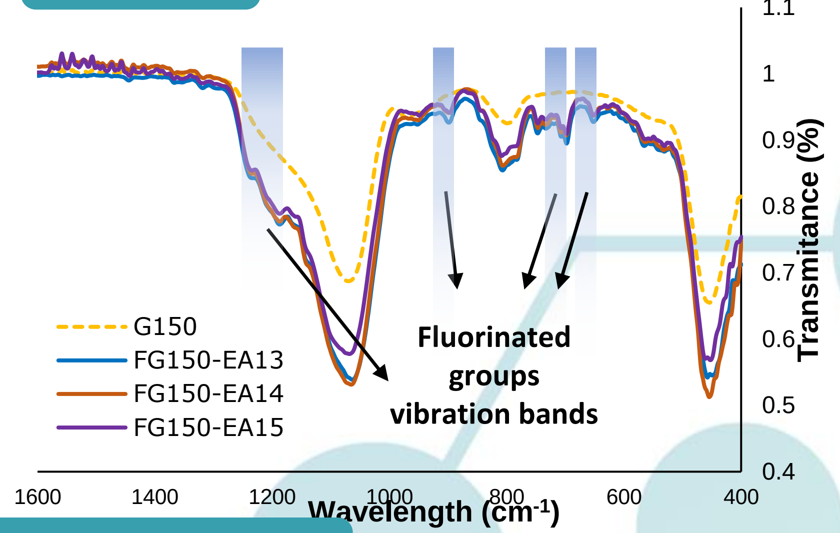
- **Reproducible grafting protocol with slight variation between batches.**
  - ¿Dependence of amorphous structure → variation of attaching points/nm^2?
- **Low energy cost synthesis: space for improvement the accuracy of grafting (avoid humidity, modify starting particle size, (meso)structures staring materials…).**

3. Materials – porous silicas

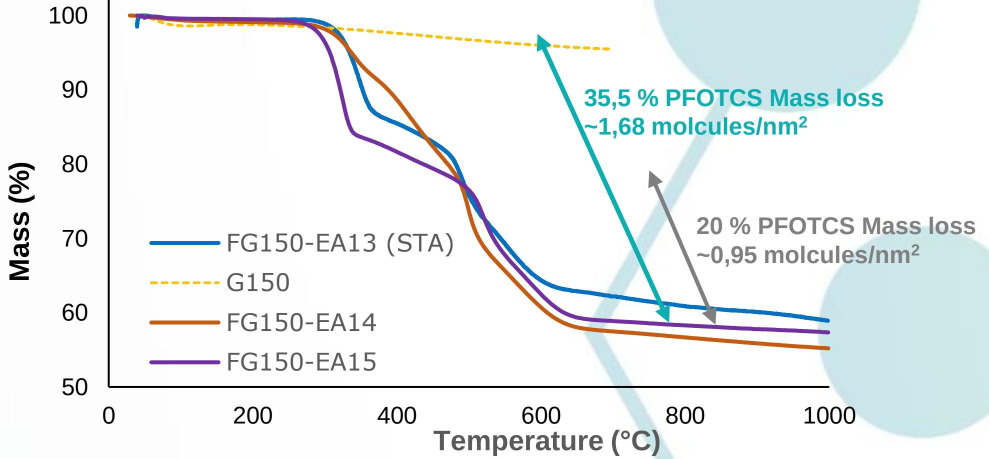
Solid state NMR



FTIR



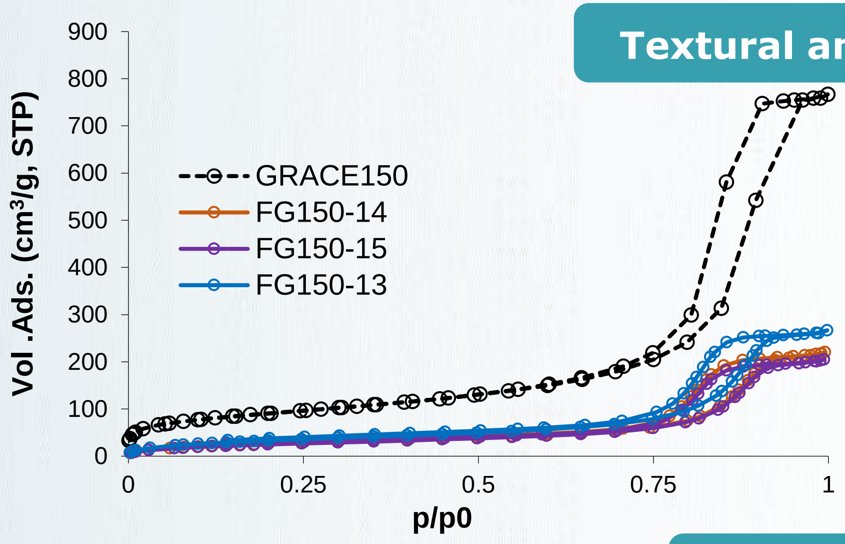
Thermogravimetric analysis

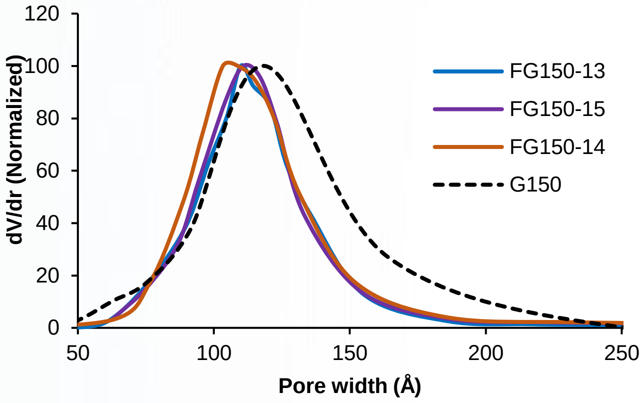


- **Confirmed covalent grafting by solid state NMR.**
- **Confirmed presence of Si-O-C bonds and CF3 groups.**
- **Variation of grafting CF3 silane molecules by mass per batch.**
- **Confirmed physiosorbed unreacted fluorosilanes (doble step mass loss).**
  - Easily removed by thermal activation of FG150 silica.

3. Materials – porous silicas

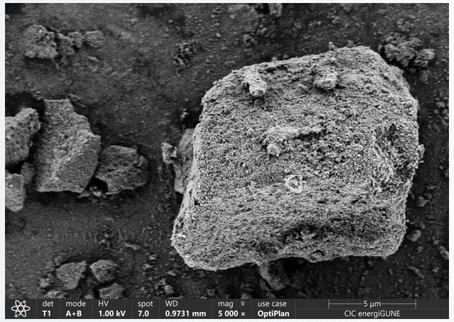
Textural analysis – N_2 adsorption

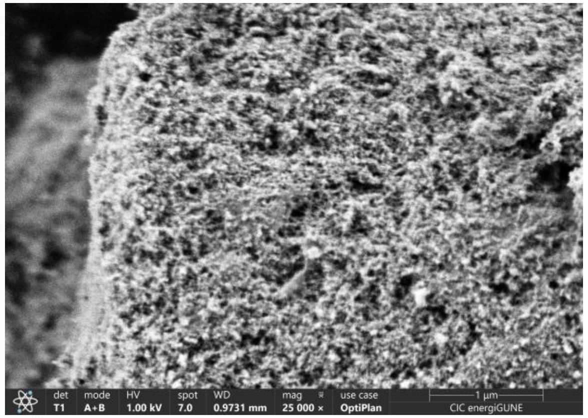


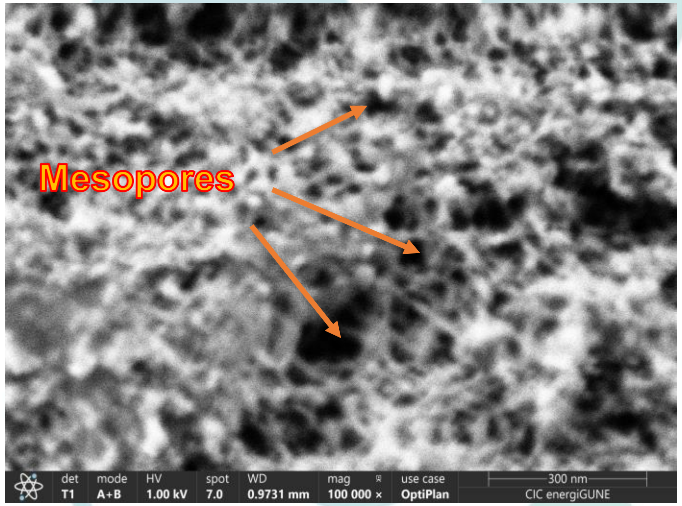


Material	S_{BET} (m^2/g)	Pore size BJH (nm)	Pore volume (cm^3/g)
G150	263 m^2/g	12 nm	1,161 cm^3/g
FG150-EA13	129 m^2/g	11 nm	0,410 cm^3/g
FG150-EA14	100 m^2/g	10,5 nm	0,336 cm^3/g
FG150-EA15	97 m^2/g	11 nm	0,314 cm^3/g

Scanning electron microscopy

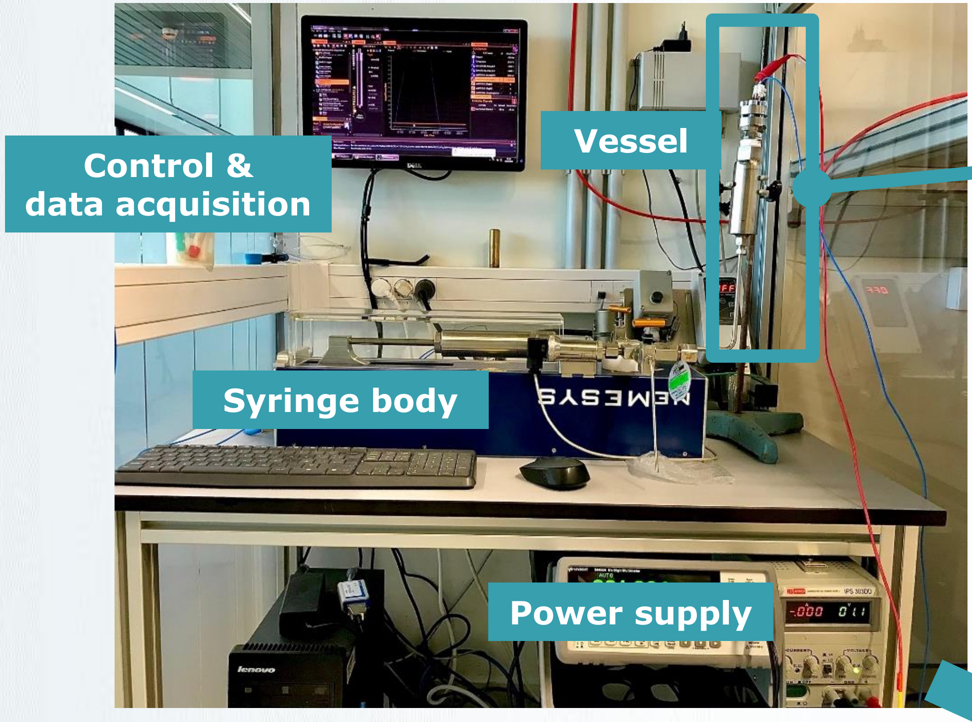




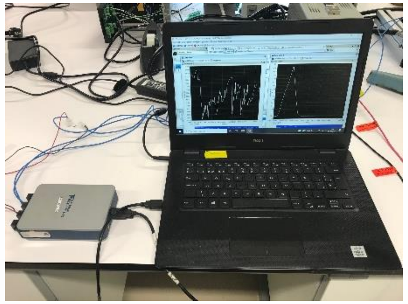


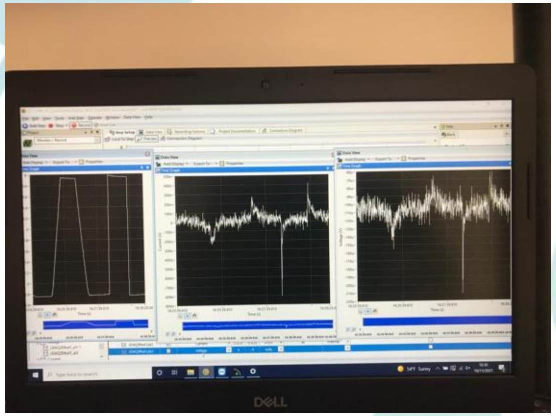
4. Recording triboelectrification

High pressure electrification setup



ADC & laptop

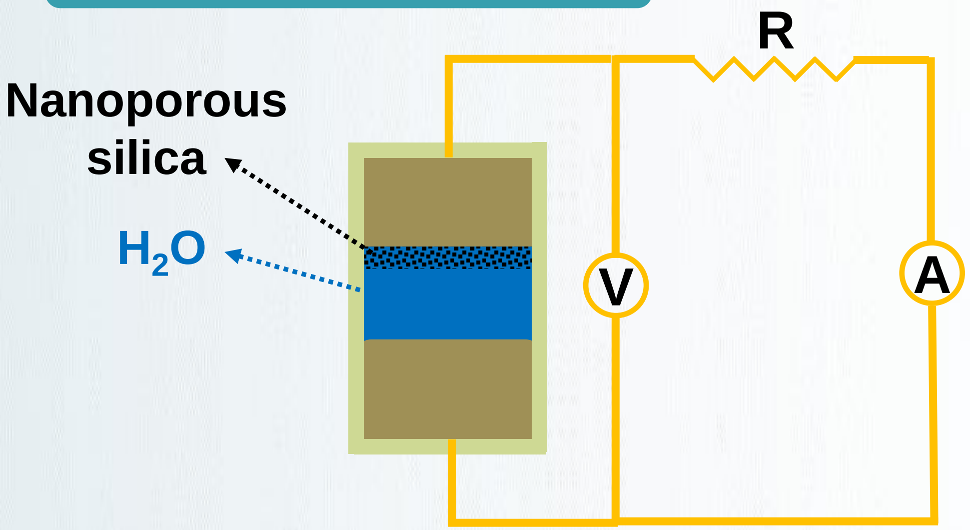




4. Recording triboelectrification

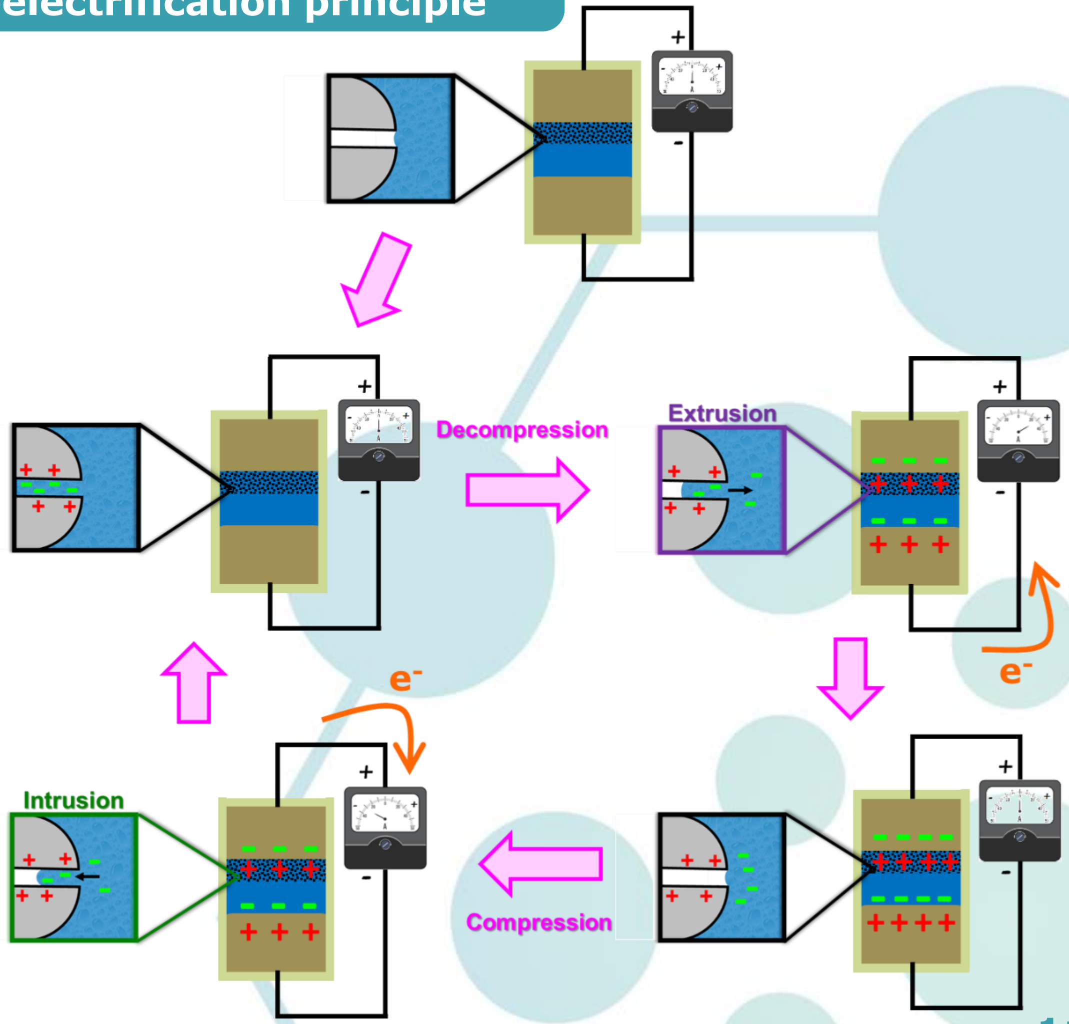
Passive configuration

Passive configuration



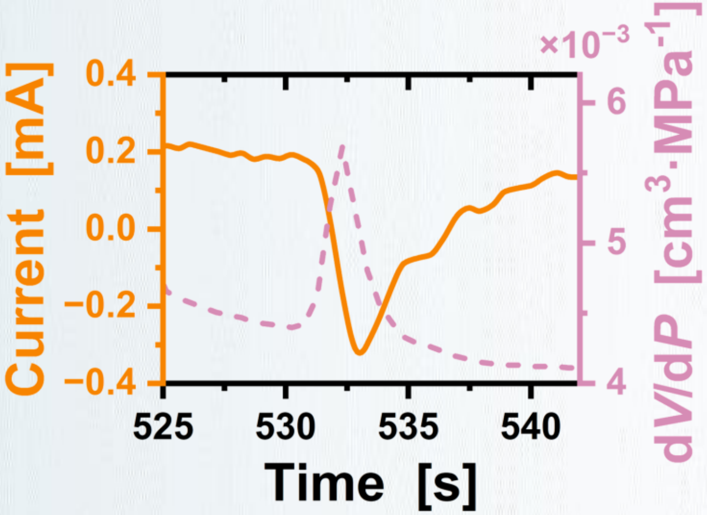
Compression/decompression tests

Intrusion-extrusion triboelectrification principle

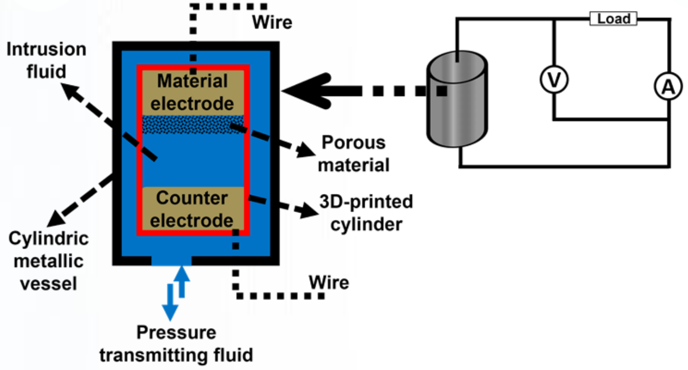


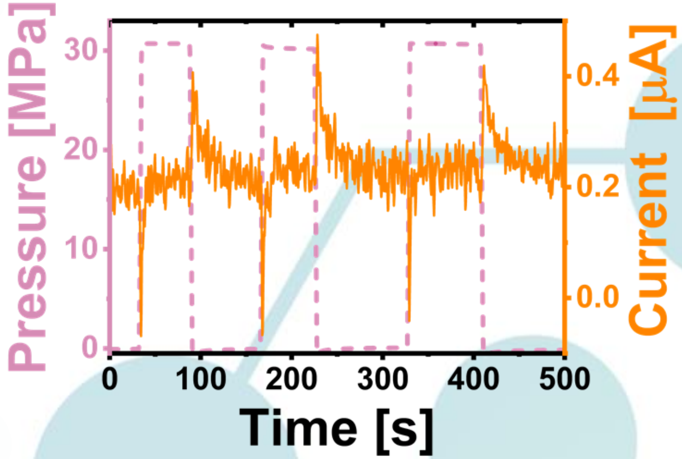
4. Recording triboelectrification
Passive configuration

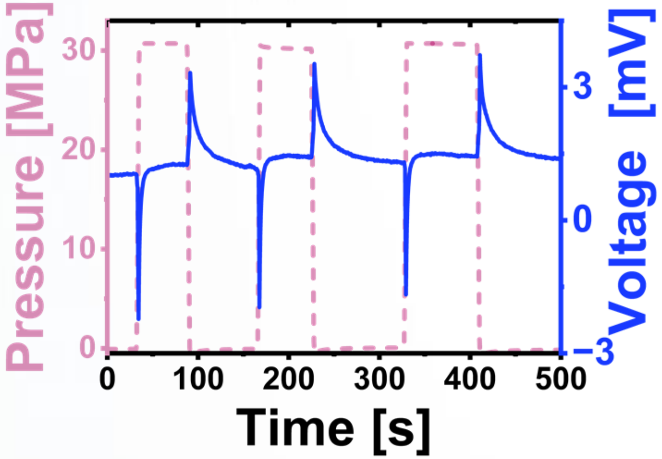
Triboelectrification results

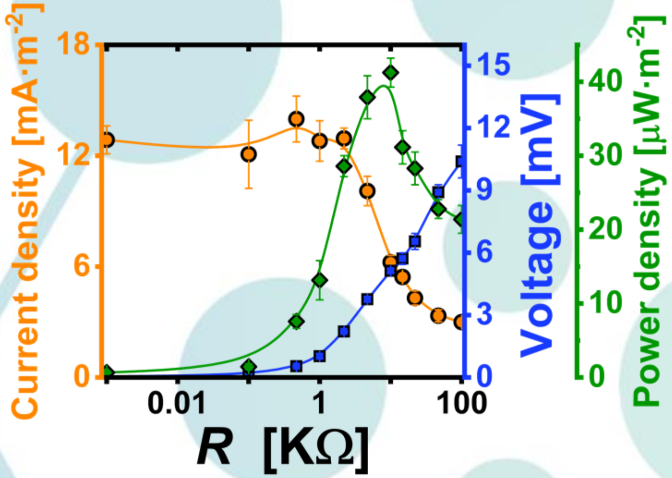


Intrusion and triboelectrification at the same time



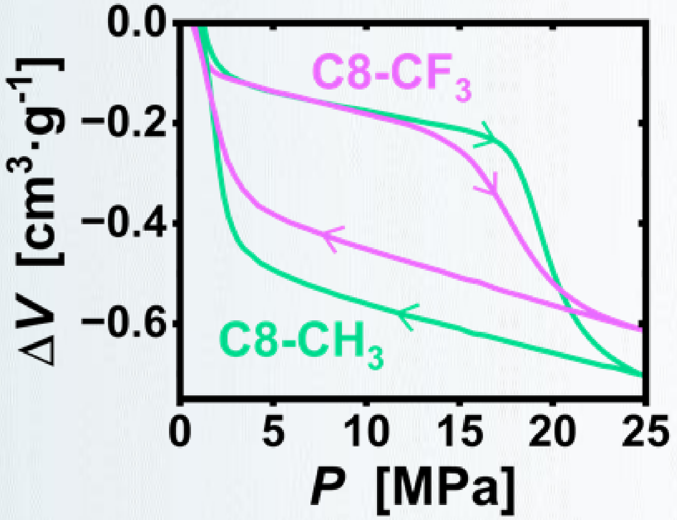




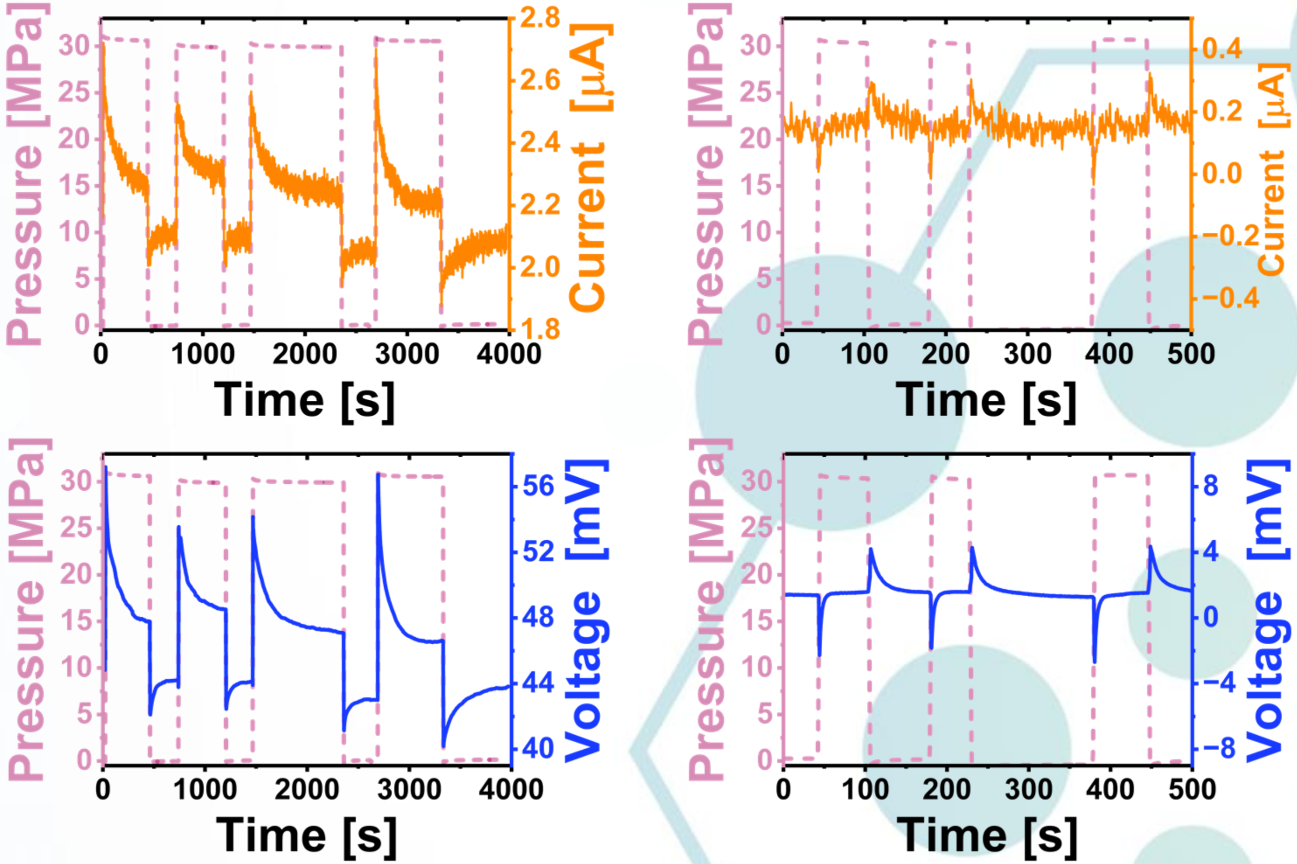


4. Recording triboelectrification
Passive configuration

Effect of grafting on triboelectrification



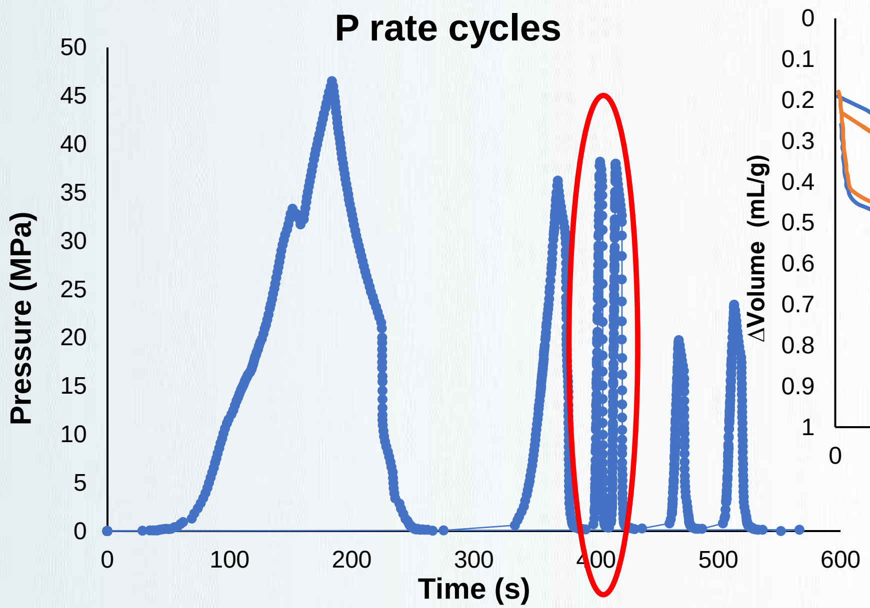
$C8\text{-}CF_3$ and $C8\text{-}CH_3$

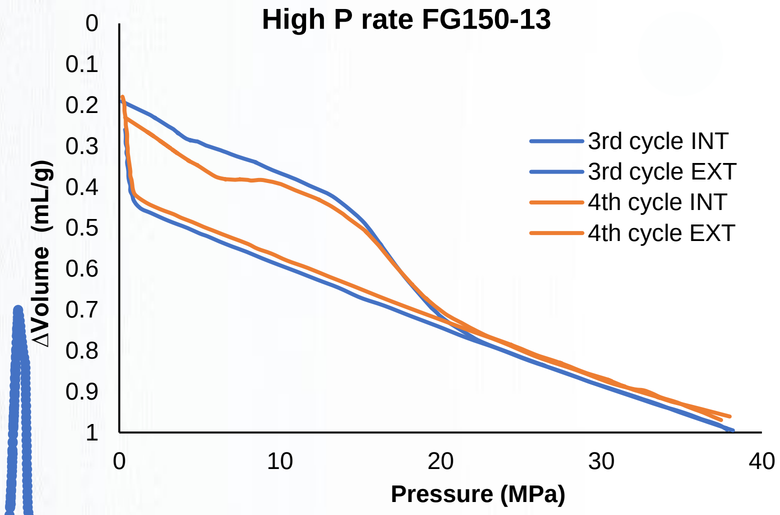


4. Recording triboelectrification

Passive configuration

High frequency PV tests

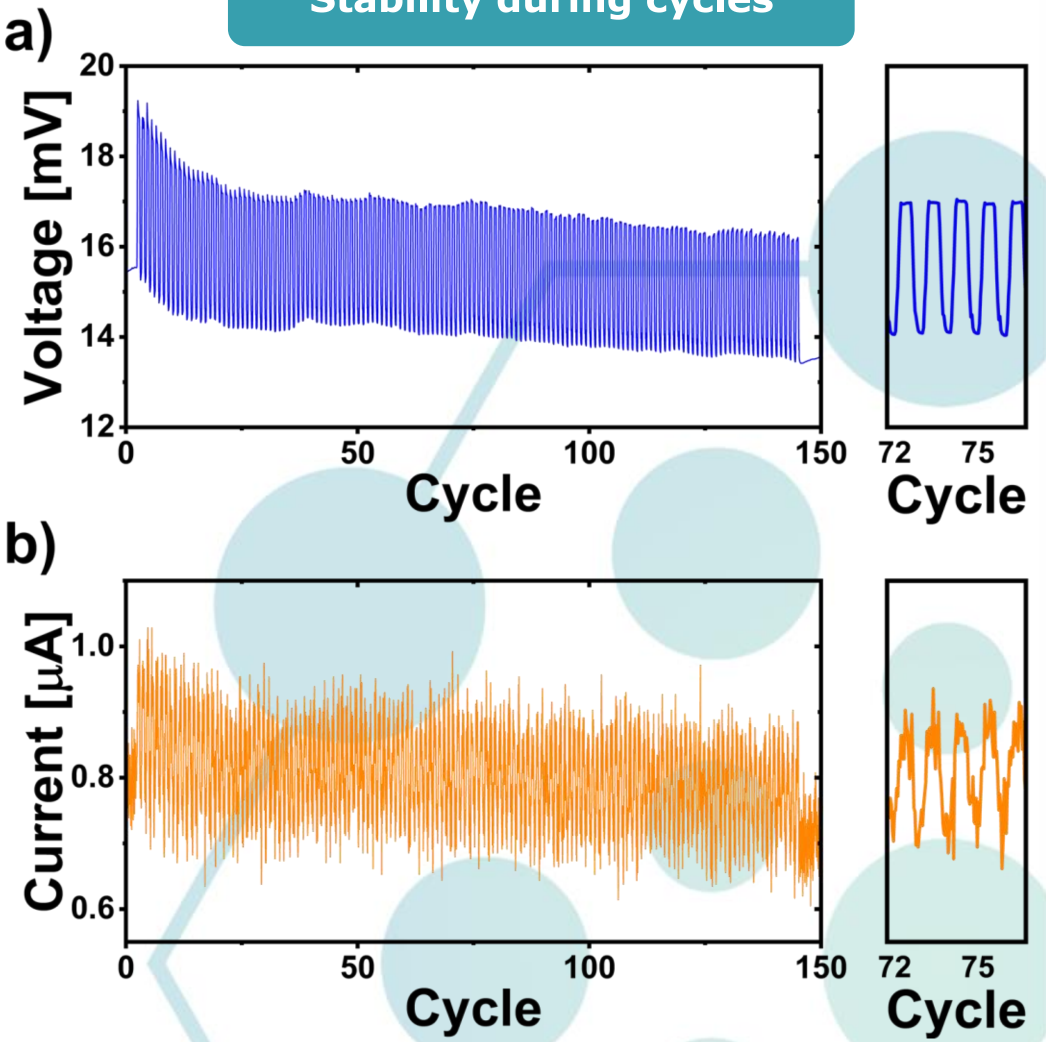




P_{rate}	Compression	Decompression
3rd cycle	195,07 Mpa/min	345,87 Mpa/min
Pause (s)	2,4 s	
4th cycle	418,07 Mpa/min	213,82 Mpa/min

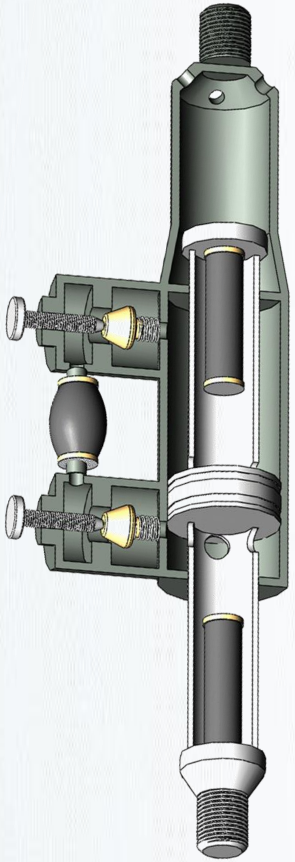
National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute"

Stability during cycles



5. Material for shock-absorbers

Car shock-absorber prototype

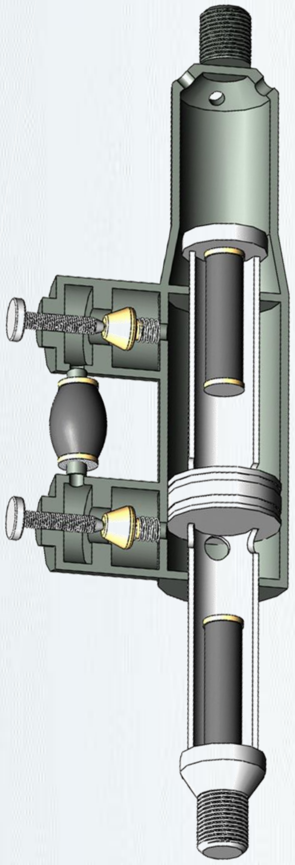


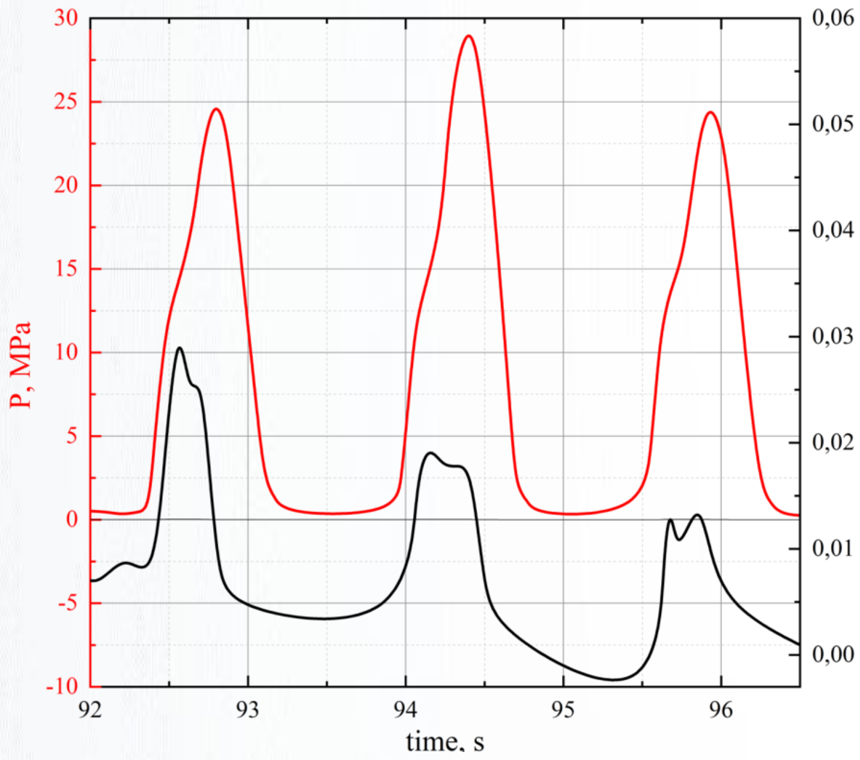
Prof. Victor Stoudenets Team

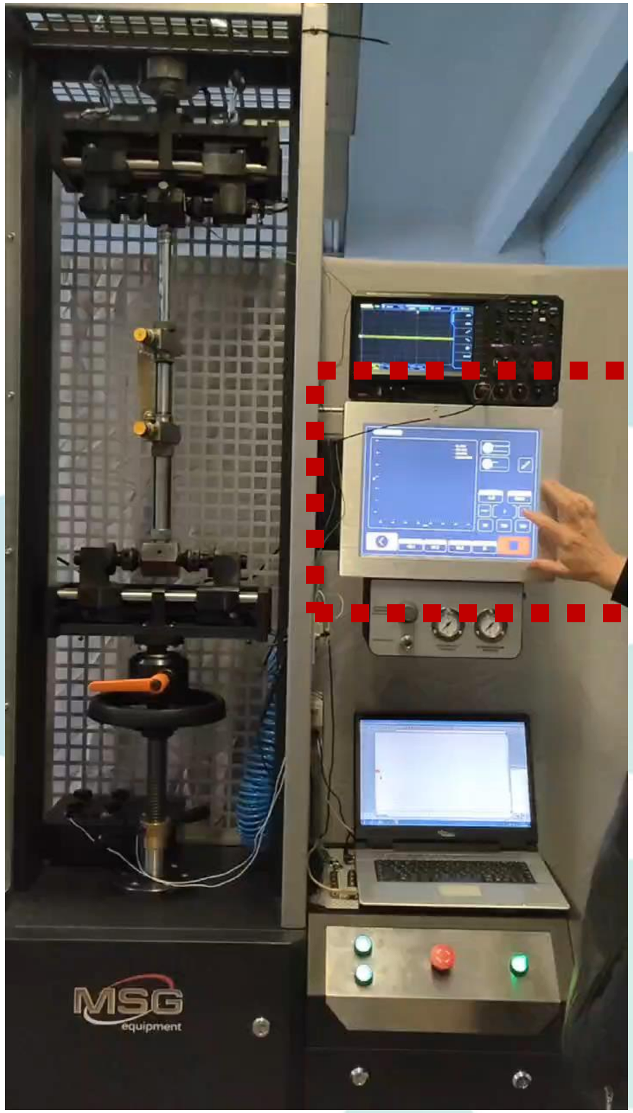
National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute"

5. Material for shock-absorbers

Car shock-absorber prototype







National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute"

6. Porous conductive approach

Conductive monolithic porous silica preparation

Formation of porosity

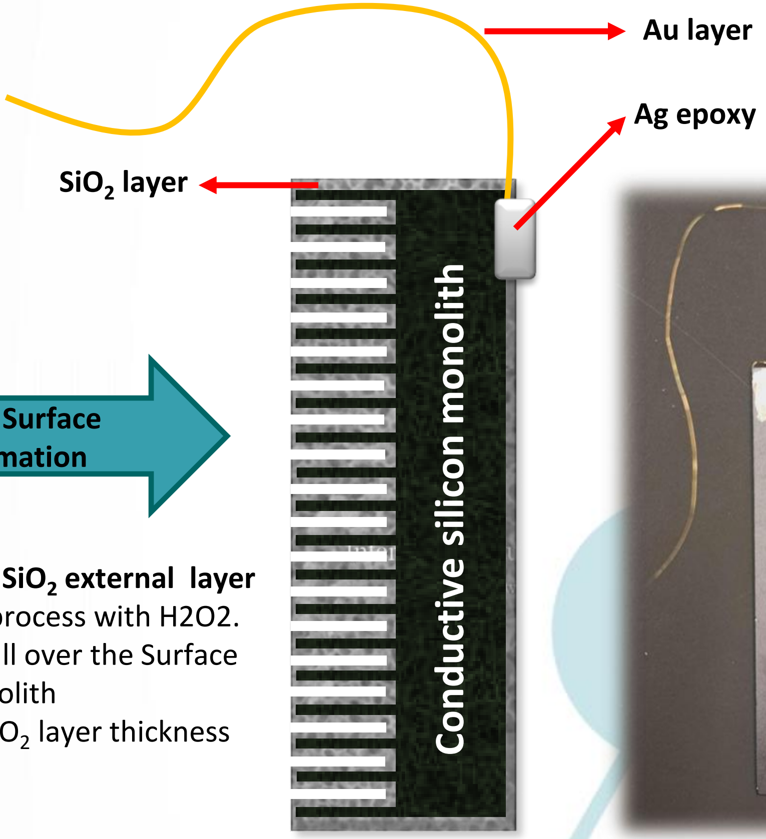
Porosity formation applying electric current

- Formation of vertical pores
- Pore sizes depending on Intensity (7-12 nm)
- Porosity: 45-55%
- ≈7 nm of pore wall
- 10-33 µm of porous thickness

SiO_2 Surface formation

Formation of SiO_2 external layer

- Oxidation process with H2O2.
- Oxidation all over the Surface of the monolith
- ≈1 nm of SiO_2 layer thickness



Grafting portocol

TUHH Patrick Huber's group

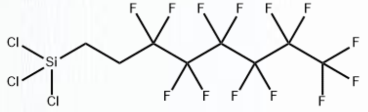
Why Si monoliths?

- Improve electrification contact → Enhance charge transfer
- Material susceptible for our grafting protocol.

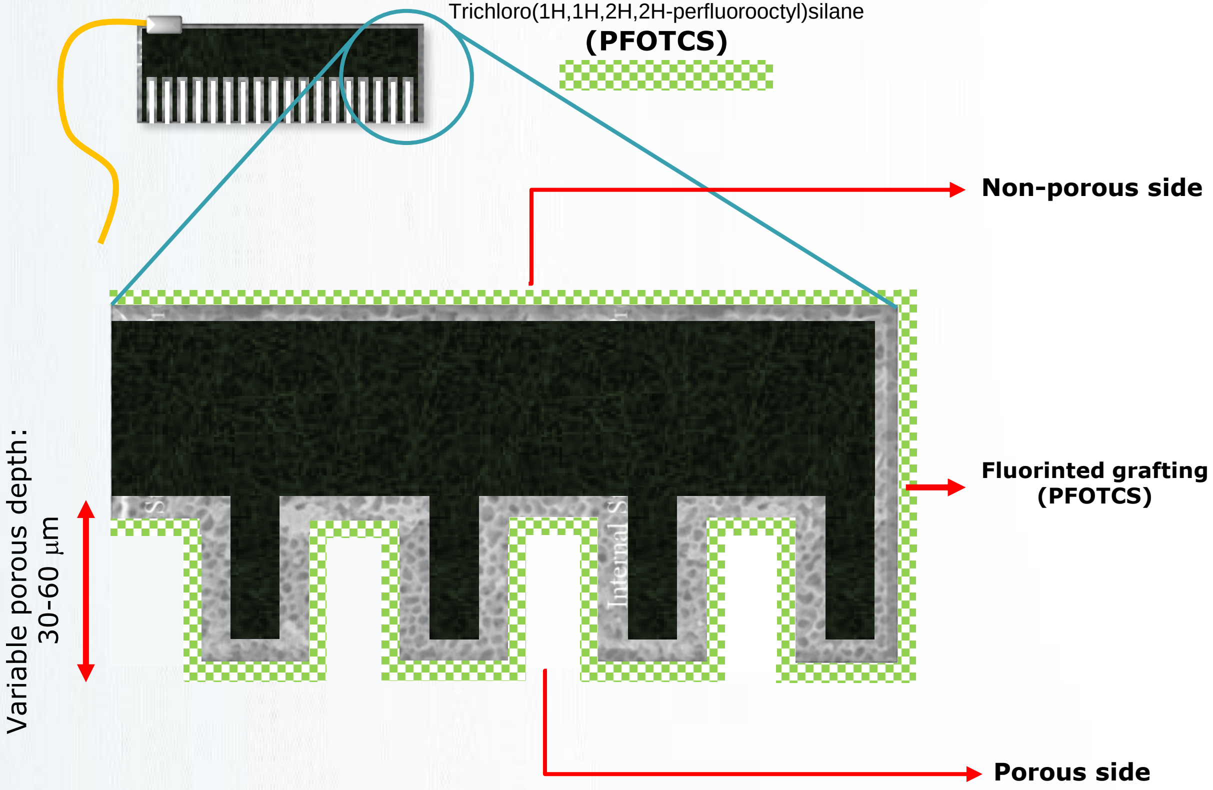
6. Porous conductive approach

Conductive monolithic porous silica preparation

- 120 h in non-aqueous ethanolic ammonia solution // 50 ºC// CF_3 grafting density: 5 molecules/nm^2
  - Si monolith with porous SiO_2 (pore sizes: 7-12 nm)

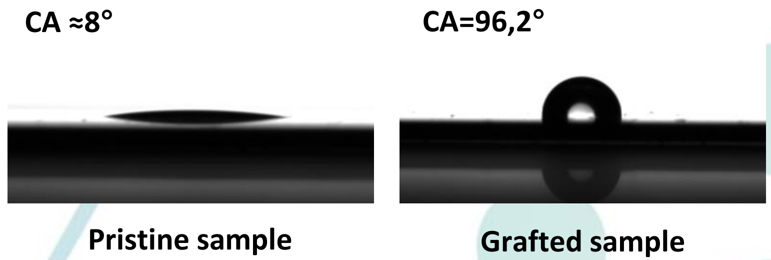


Trichloro(1H,1H,2H,2H-perfluorooctyl)silane
(PFOTCS)



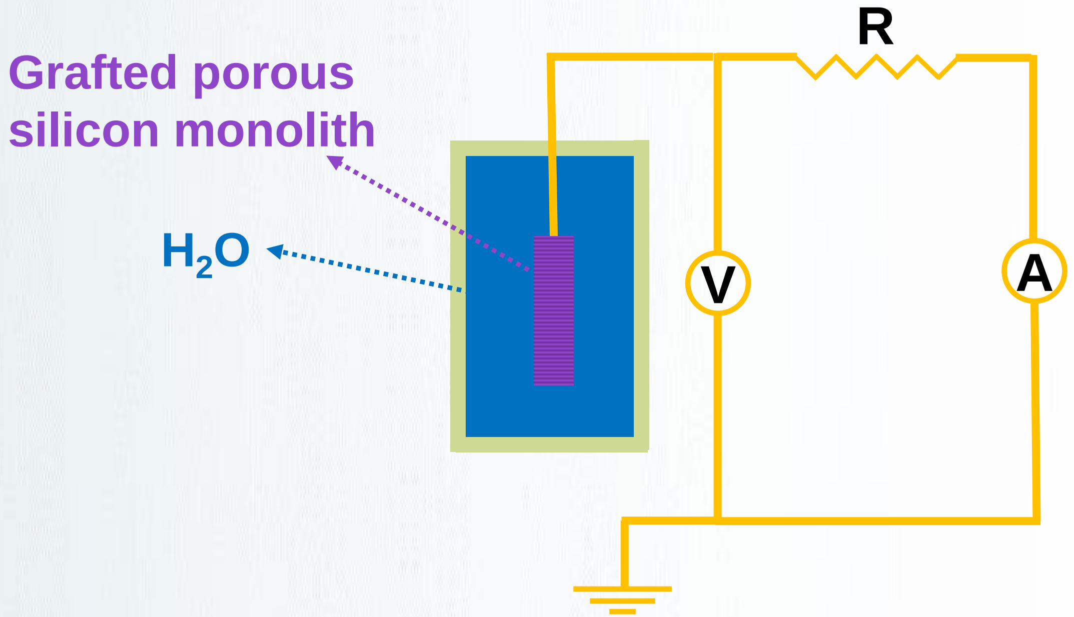
Contact Angle: non-porous side

Contact Angle: porous side

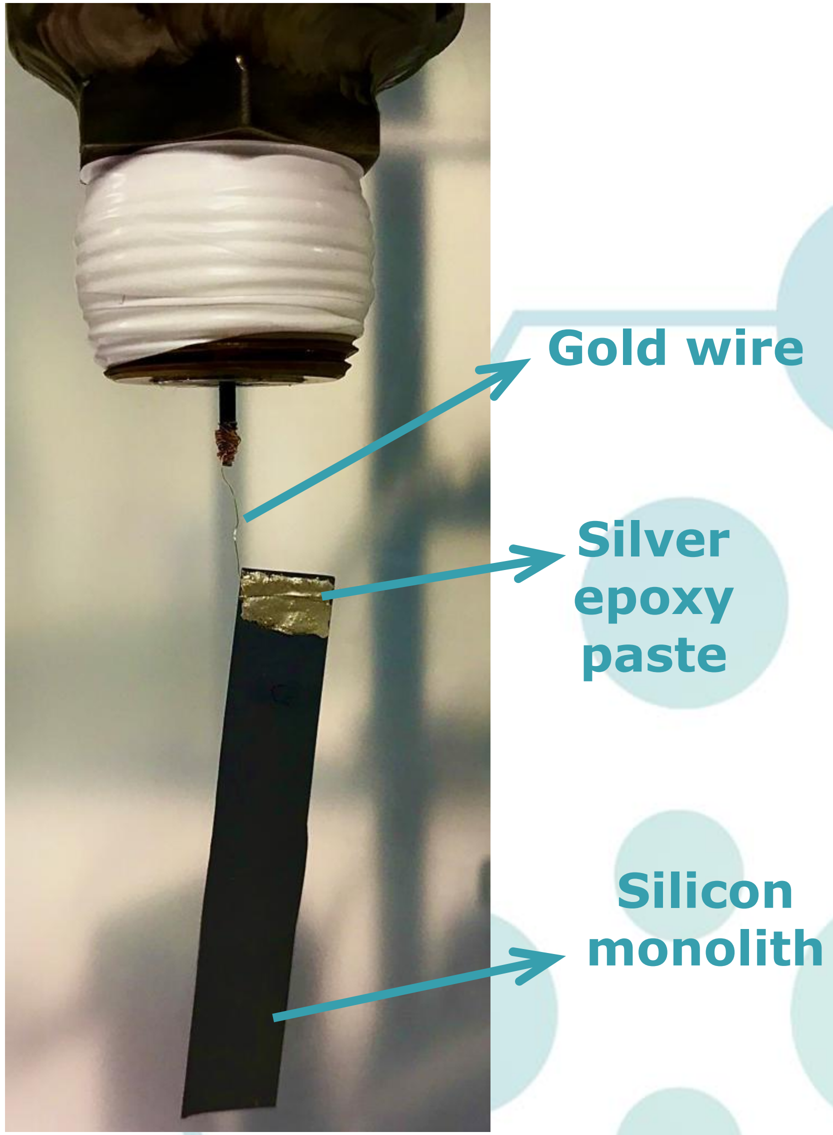


6. Porous conductive approach
Monolith configuration

Si monolith configuration



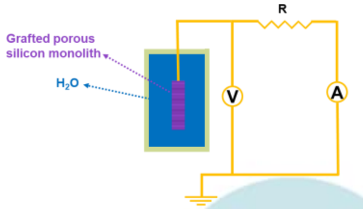
Compression/decompression tests

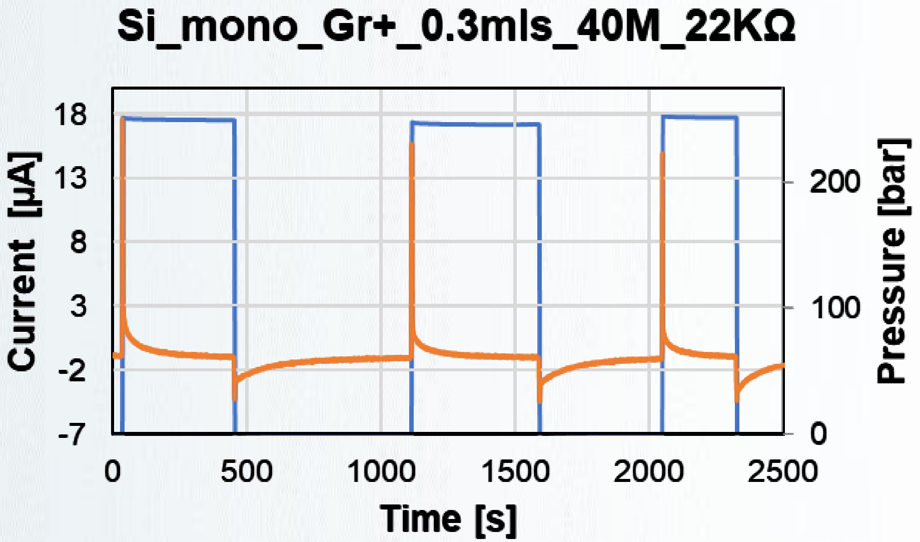


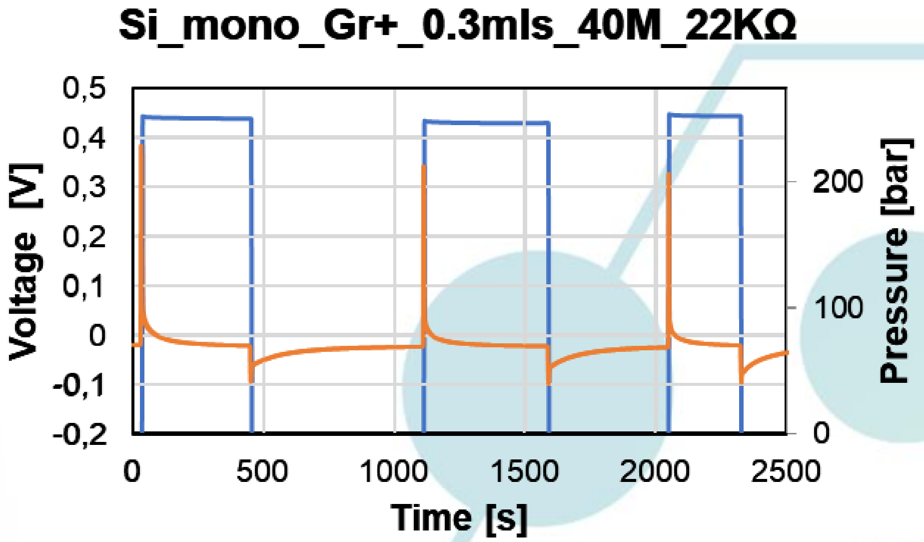
6. Porous conductive approach

Monolith configuration

Current and voltage results



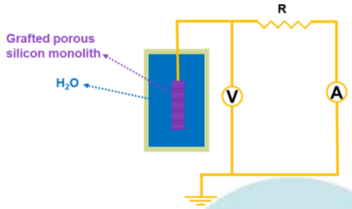


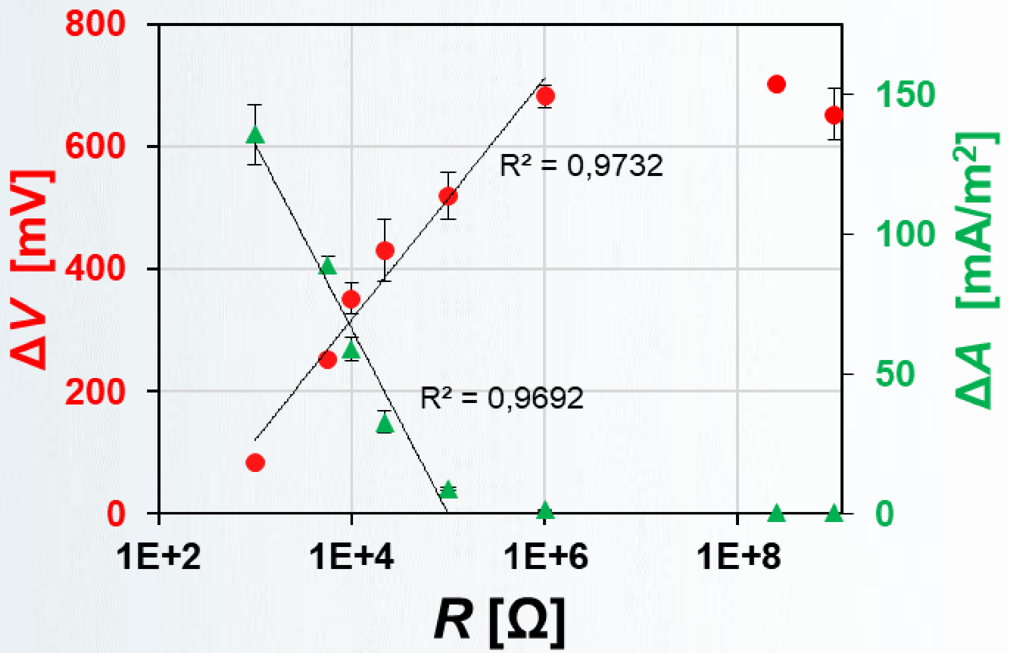


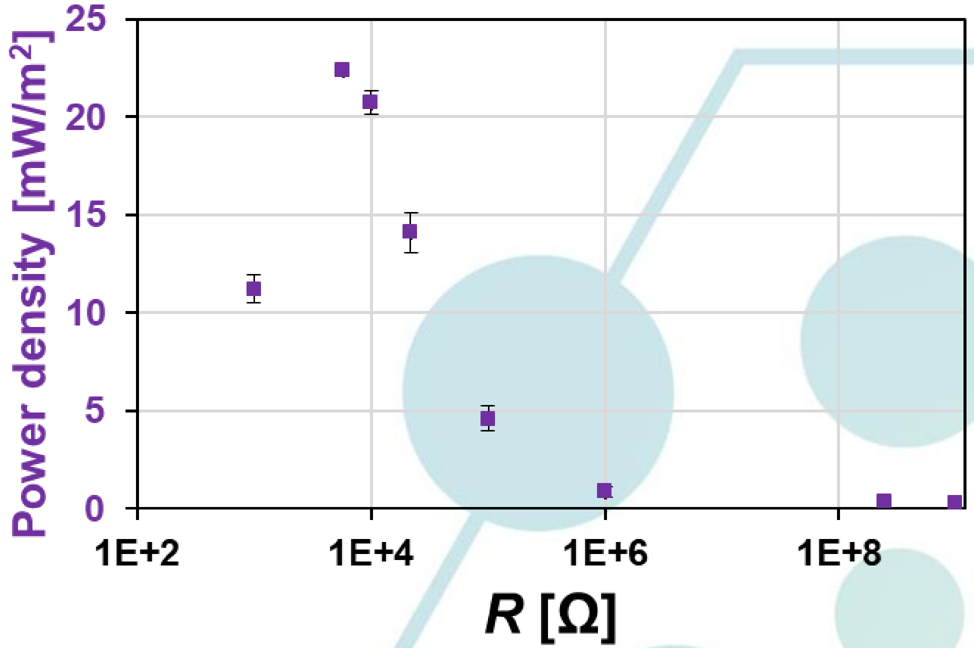
6. Porous conductive approach

Monolith configuration

Peak amplitudes & power density







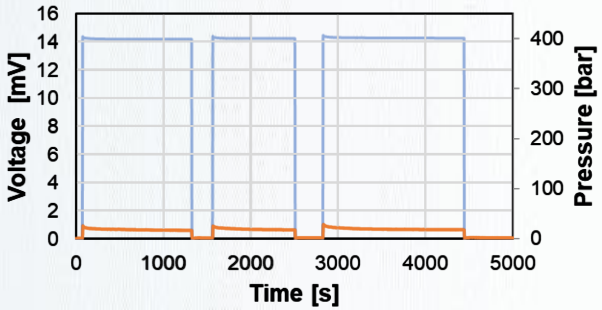
Maximum power density at ~8 KΩ (optimal load)

6. Porous conductive approach

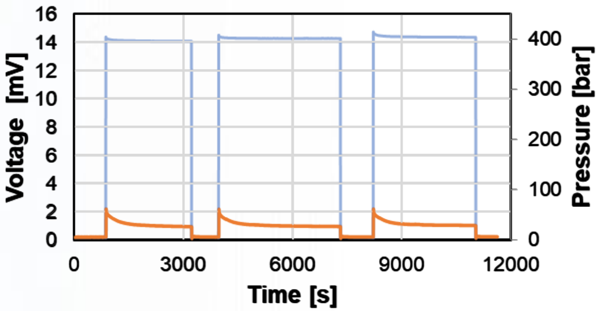
Monolith configuration

Testing different liquids

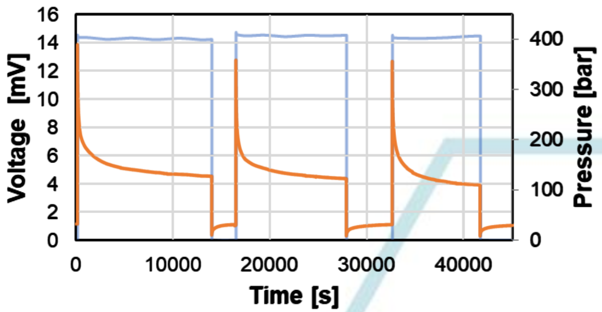
Si-mV_En_Gr+_0.3mls_40MPa_10KΩ



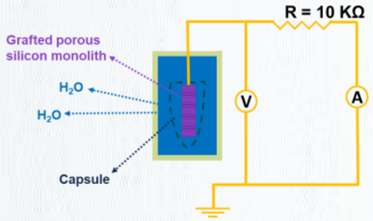
Si-mV_EnD$_2$O_0.3mls_40MPa_10KΩ



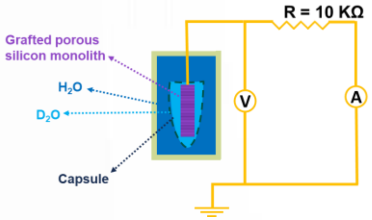
Si-mV_EnPEI_0.3mls_40MPa_10KΩ



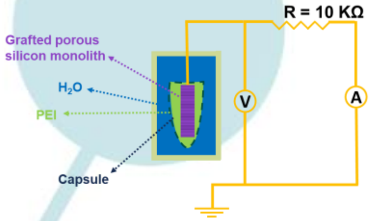
H_2O

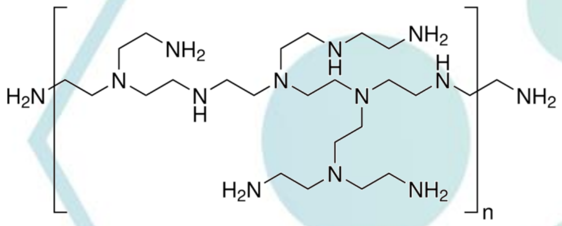


D_2O



PEI



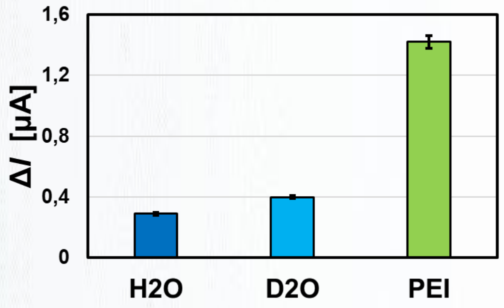


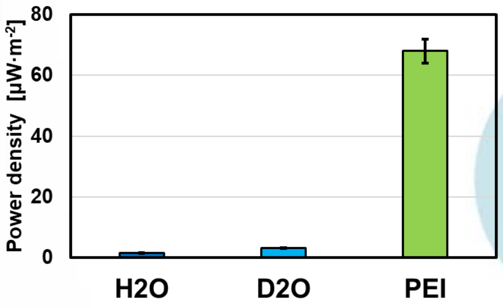
6. Porous conductive approach

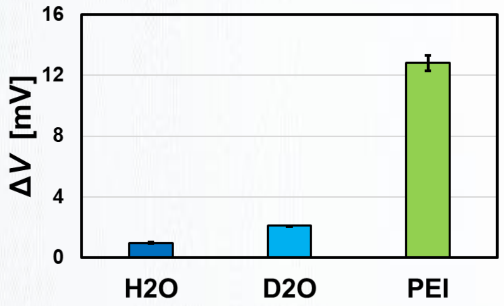
Monolith configuration

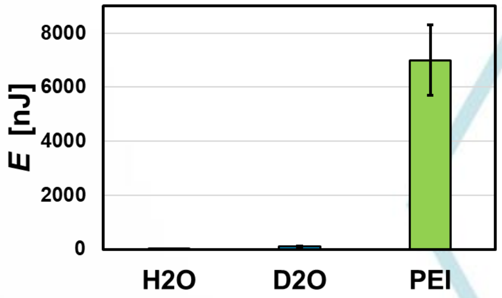
Testing different liquids

	H_2O	D_2O	PEI
ΔI [μA]	0.29±0.01	0.40±0.01	1.42±0.04
ΔV [mV]	0.96±0.05	2.1±0.01	12.8±0.5
Power density [μW·m^{-2}]	1.6±0.08	3.18±0.08	68±4
E_1 [nJ]	17±5	110±5	7000±1300









Electric output:
H_2O < D_2O < PEI

7. Conclusions

- Liquid intrusion-extrusion into-from nanopores is accompanied by triboelectrification

- Intrusion-extrusion process allows TENGs with 100-1000 m^2/g contact area

- Charge transfer in intrusion-extrusion TENGs is a challenge

Thanks for your attention!

This project leading to this application has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101017858.

ELECTRO INTRUSION

CIC energiGUNE

MEMBER OF BASQUE RESEARCH & TECHNOLOGY ALLIANCE