Piezoelectric and Pyroelectric Materials and Structures for Energy Harvesting

Energy Harvesting 2016, 11th May

Chris Bowen
University of Bath

NE 10 | ME 68 | SI 14 | S 16

Novel Energy Materials: Engineering Science and Integrated Systems

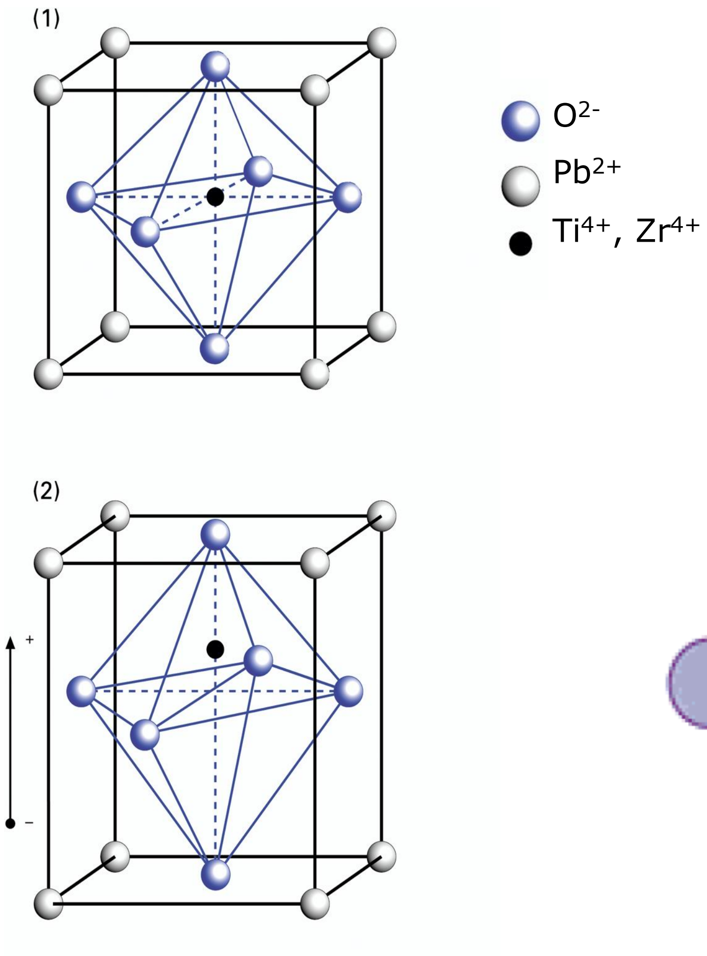
European Research Council
Established by the European Commission

Ferroelectric materials

Cubic and

Symmetrical

(above Curie T)

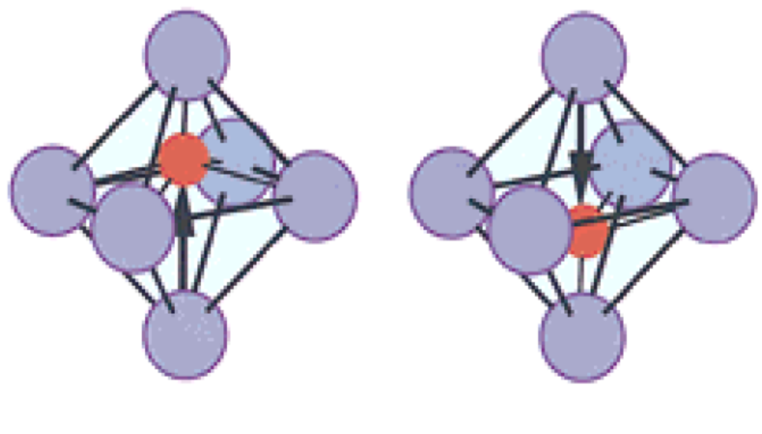


Tetragonal and

non-symmetrical

(below Curie T)

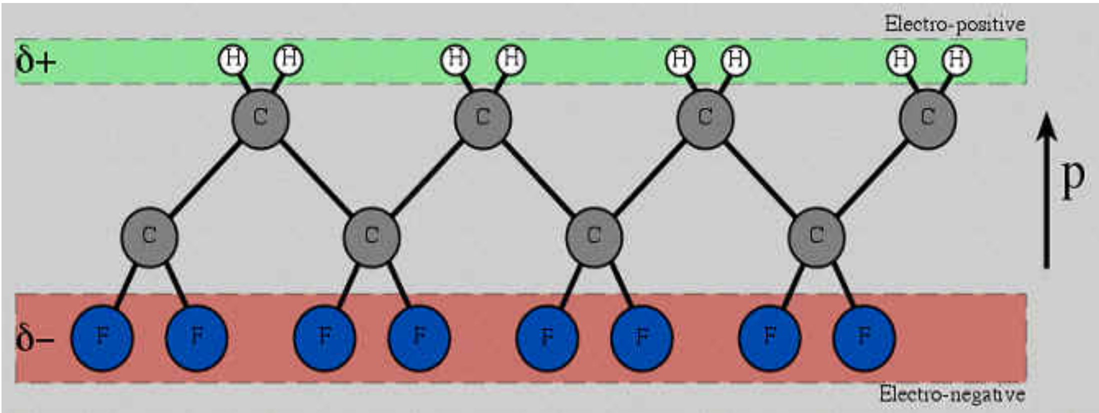
- Below the Curie temperate (T_c) the crystal structure distorts to tetragonal structure.
- Zr^{4+} or Ti^{4+} ion displaced from the centre, creating an electric dipole.



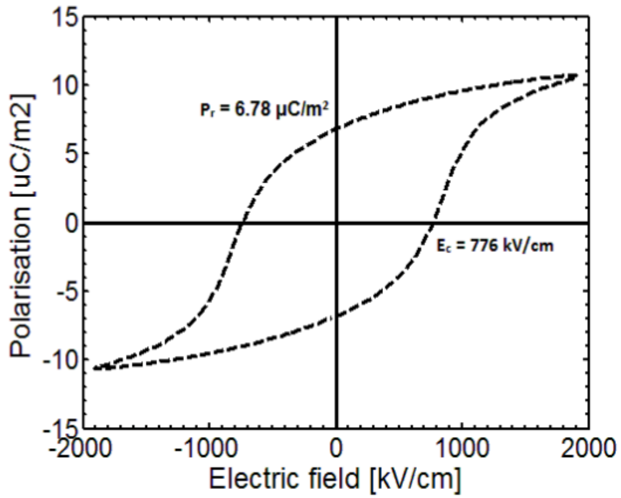
Polarization Up   Polarization Down

Polymer ferroelectrics

polyvinylidene fluoride (PVDF)

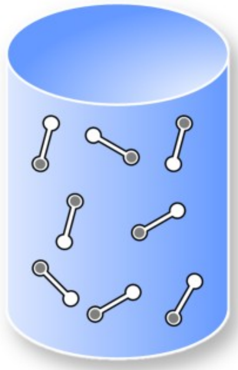


http://www.physics.montana.edu/eam/polymers/images/Piezoe5.jpg



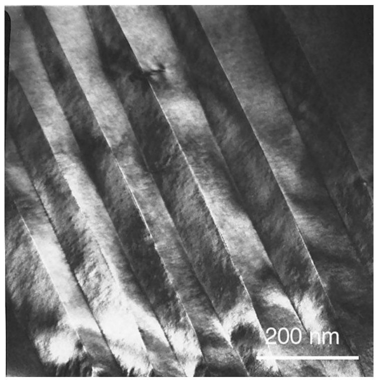
Daniel Zabek,* John Taylor, Emmanuel Le Boulbar, and Chris R. Bowen* , Advanced Adv. Energy Mater. 2015, 5, 1401891

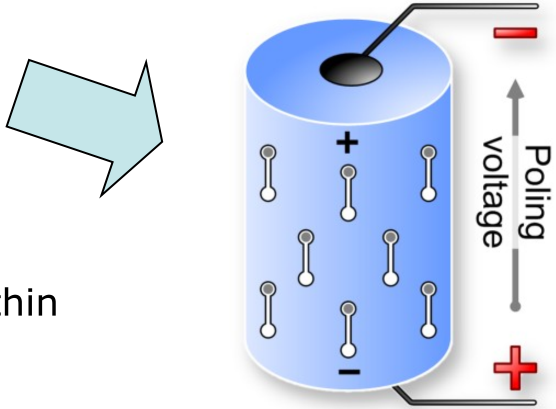
Poling – achieving piezoelectric response



Dipoles are orientated within domains.

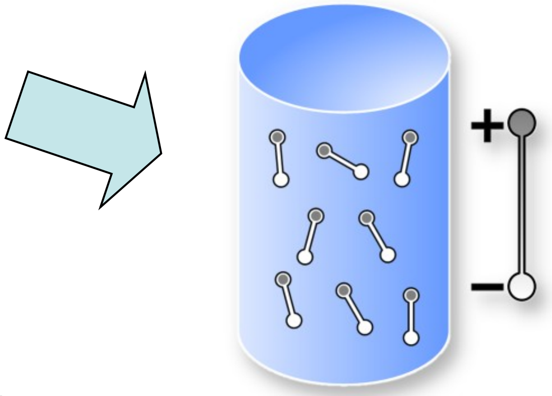
Dipoles randomly orientated.





To achieve net polarisation apply a high electric field at elevated temperatures.

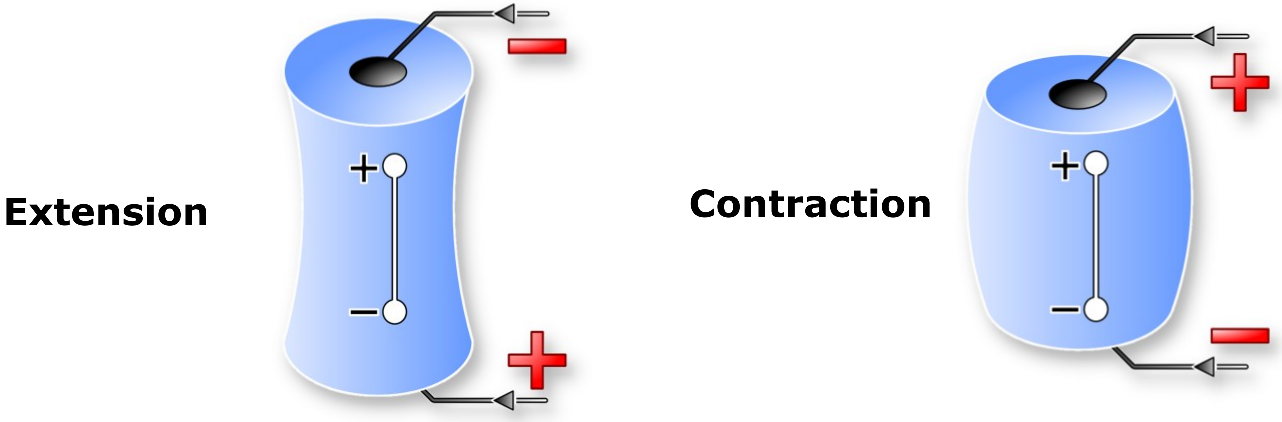
Cool to room temperature (with the electric field still applied).



This 'freezes in' the alignment of the domains, resulting in a net polarisation.

Converse piezoelectric effect

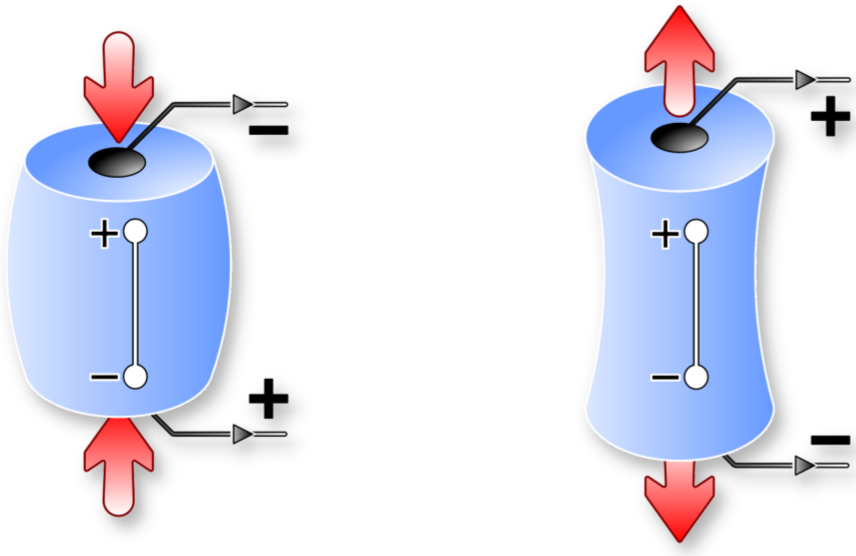
Electric field parallel to the poling direction (polar axis) extends the material.
Electric field opposite to the polar axis results in contraction.



This is the **actuato**r mode of operation.
Strains are **small** ~0.1-0.3%

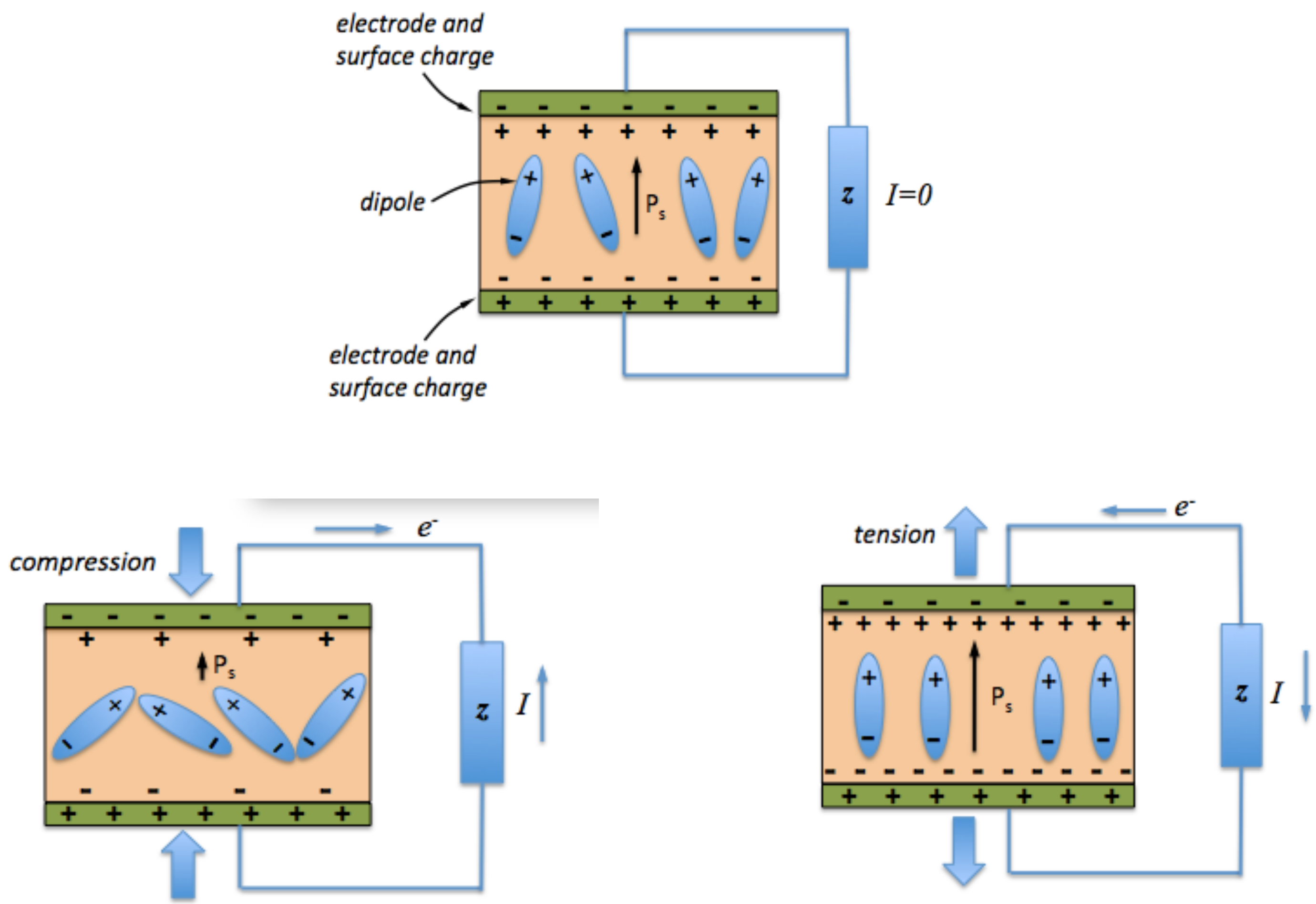
Direct piezoelectric effect

Tensile or compressive force parallel to the poling direction (polar axis) generates a potential difference across opposing faces.



This is the **sensing**/generator mode of operation.

Direct piezoelectric effect



Novel Energy Materials: Engineering Science and Integrated Systems (NEMESIS)

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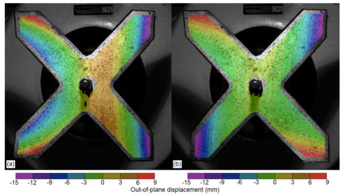
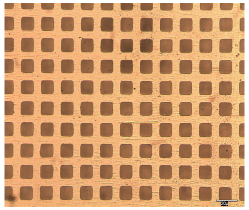


Peter Harris
Marcin Krazny



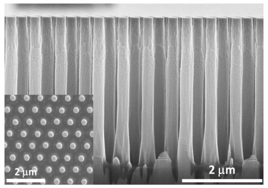
Dan Zabek

James Roscow
Andrew Avent

Vibration Harvesting
mechanical → electrical

Pyroelectric & Thermoelectric
temperature → electrical

Piezoelectric Ferroelectric



Water-Splitting
light → chemical
vibration → chemical

Solar-Cells
light → electrical

Vaia Adamaki
Mengying Xie

Oliver Weber
CDT - Chemistry

erc
European Research Council

@BowenNEMESIS

1. Materials development (Zabek, Roscow)
    - Micropatterned surfaces
    - Porous materials for harvesting

2. Materials applications (Harris, Krazny)

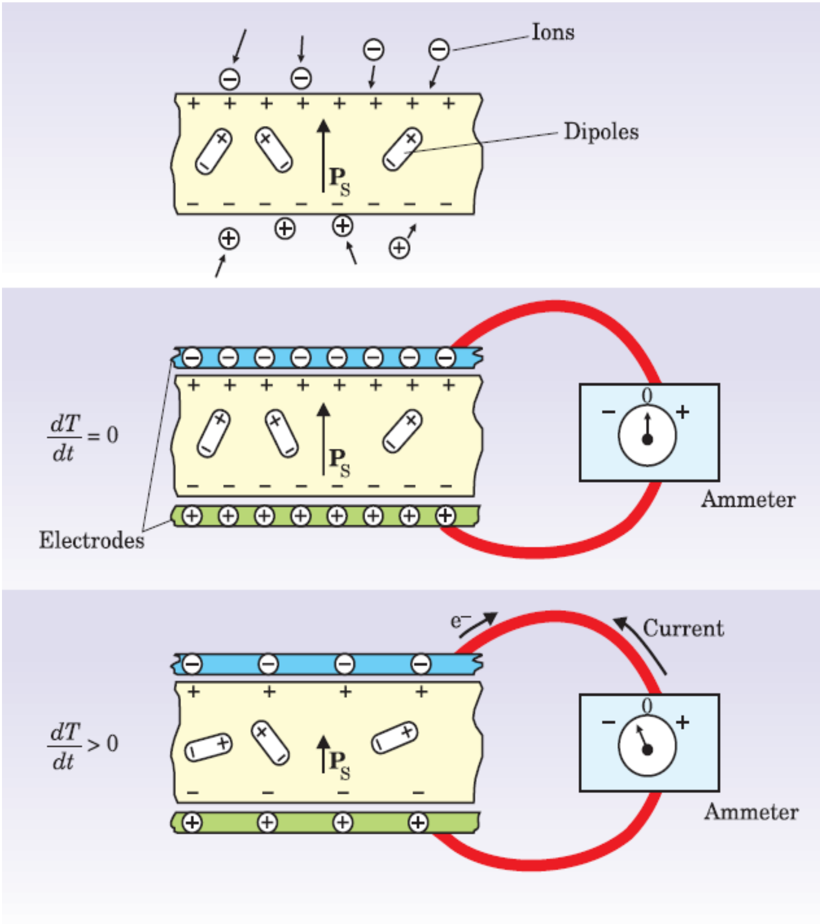
3. Water splitting (Adamaki, Xie)

Pyroelectric harvesting

Thermoelectric – harvesting temperature gradients

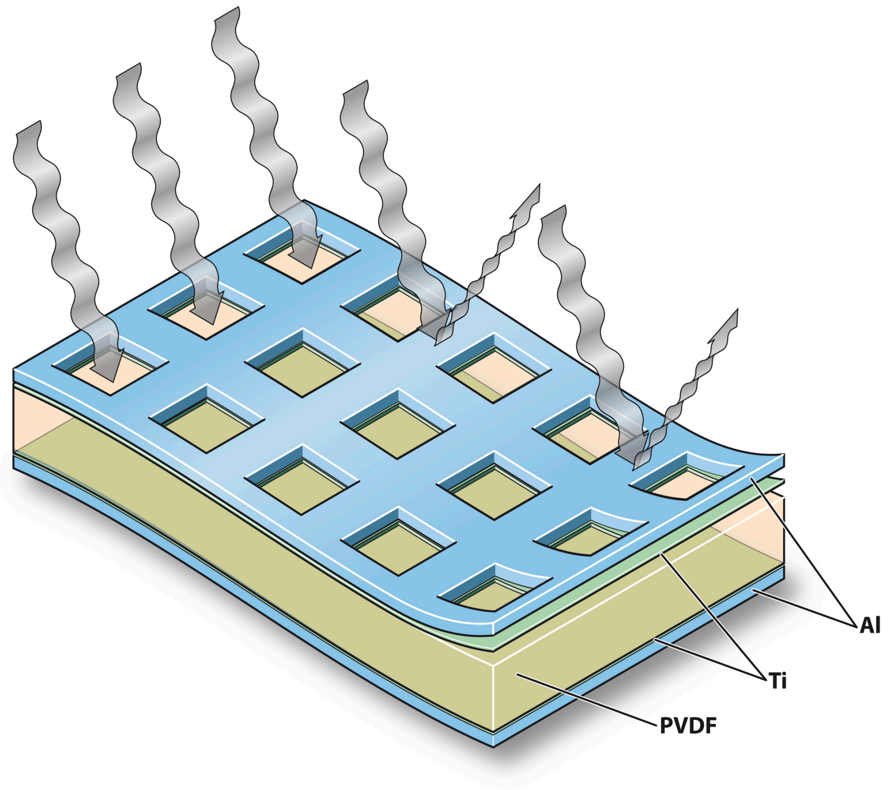
Pyroelectrics – harvesting temperature fluctuations

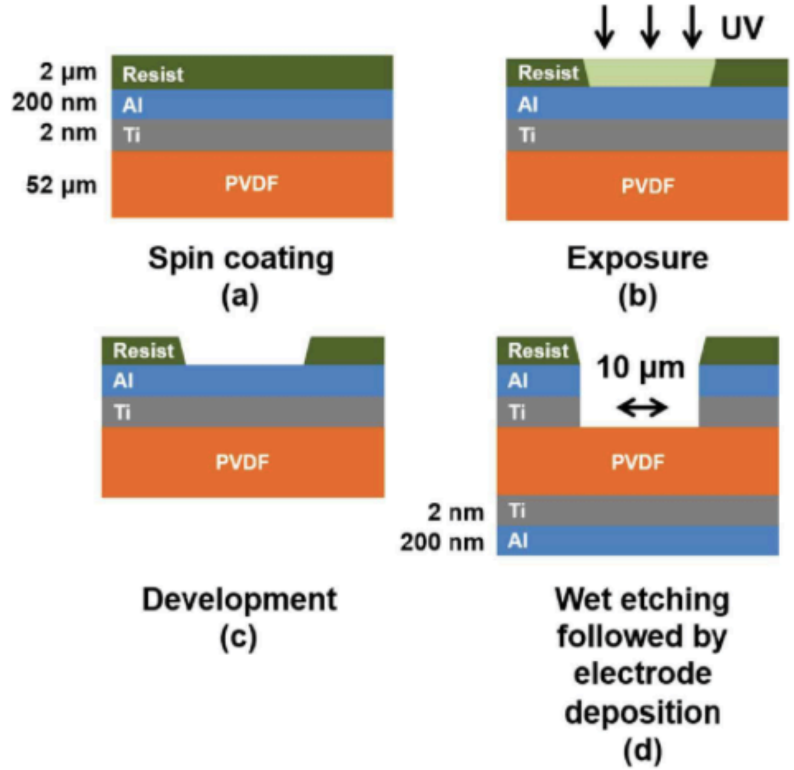
$$i_p = \frac{dQ}{dt} = A.p.\frac{dT}{dt}$$



Sidney Lang, Physics Today.

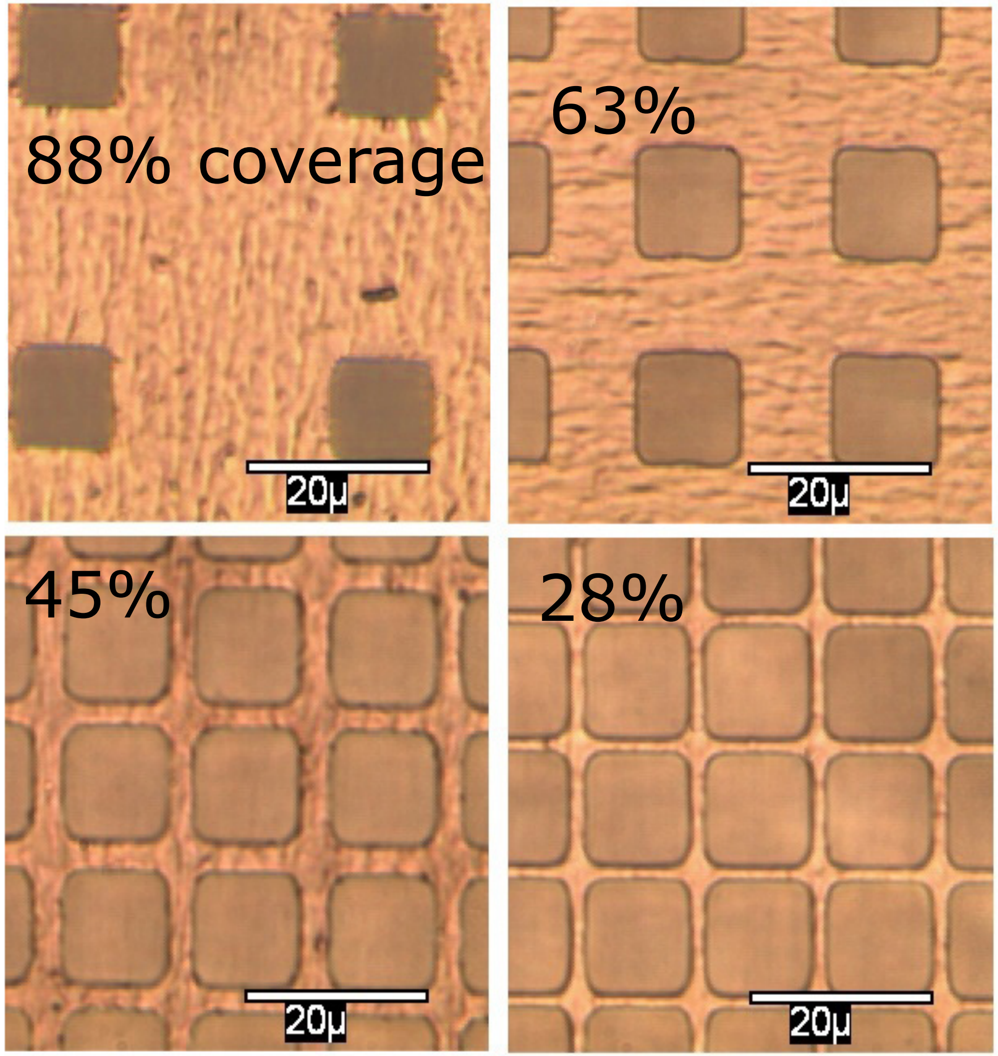
Micro-patterning of PVDF





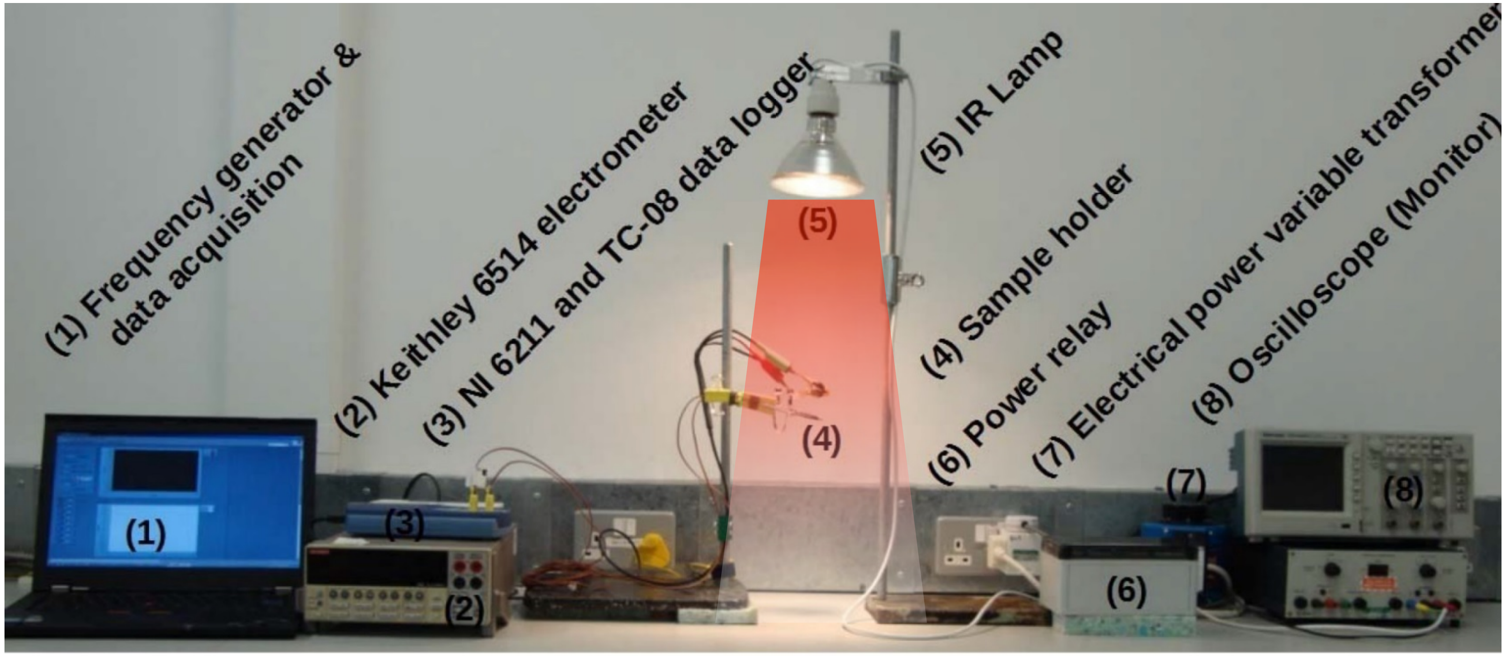
+ Direct heating of pyroelectric active material.
+ Decrease in radiative reflection.
+ Increase in surface area.

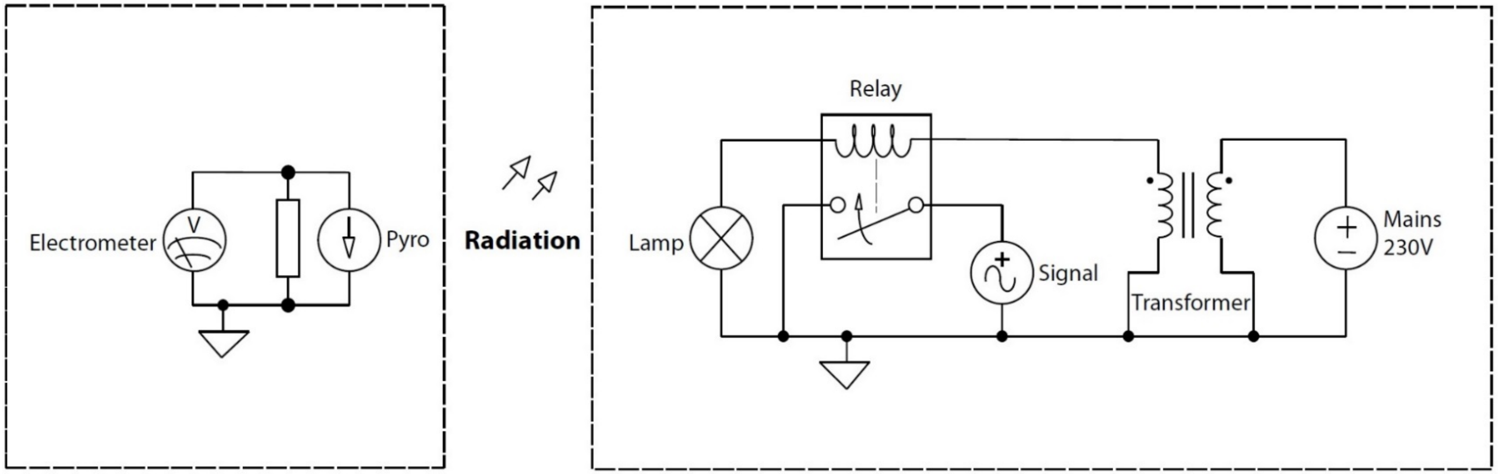
Micro-pattering PVDF



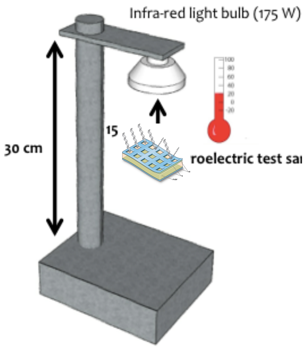
- **Pre-poled extruded PVDF**
- **Photolithographic process**
- **Physical vapour deposition of electrode**
- **Temperatures less than 60°C**
- **Variable geometry/substrate**
- **Durable electrode bonding**
- **Up-scaleable**
- **Pattern quality >95%**

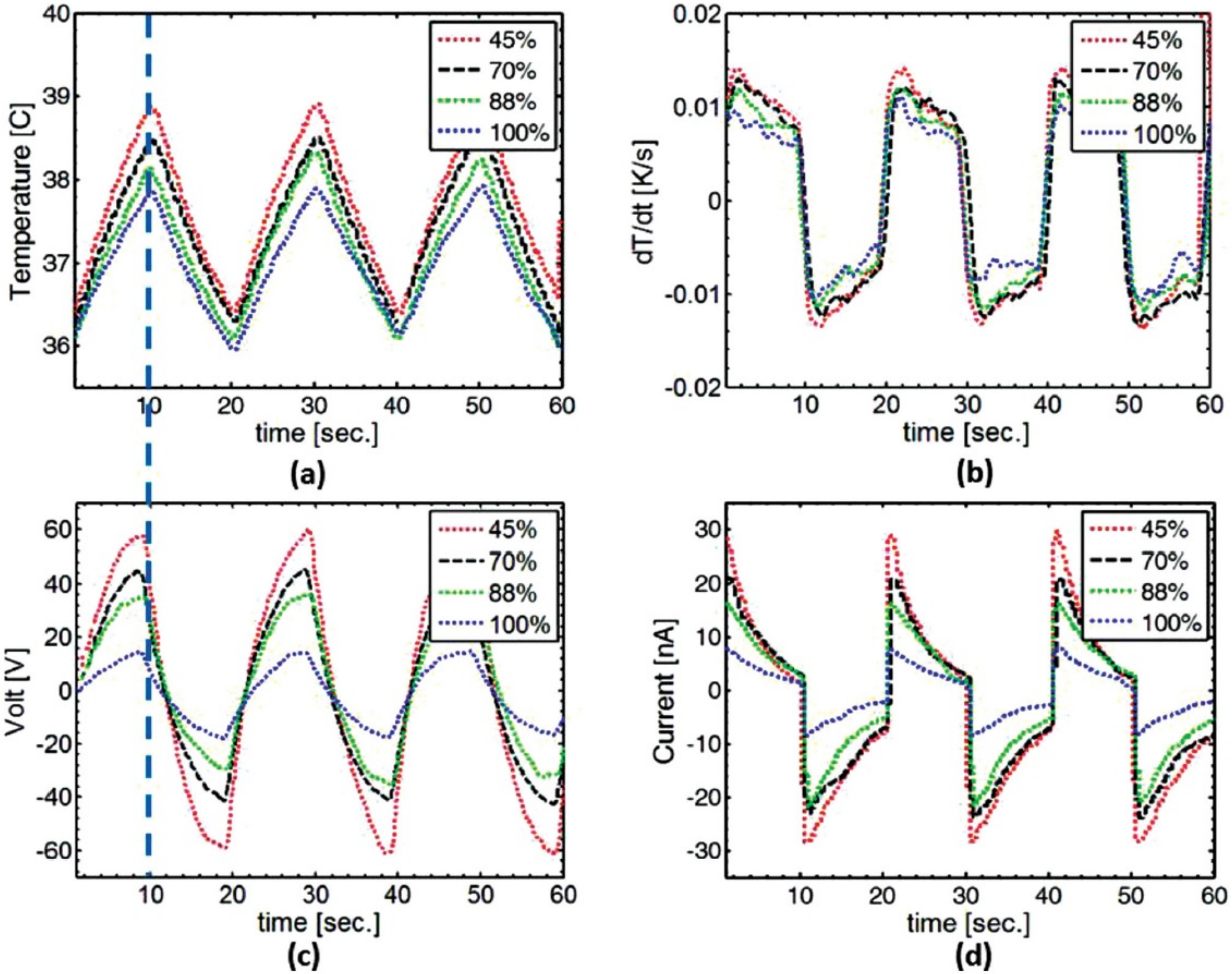
Harvesting thermal oscillations



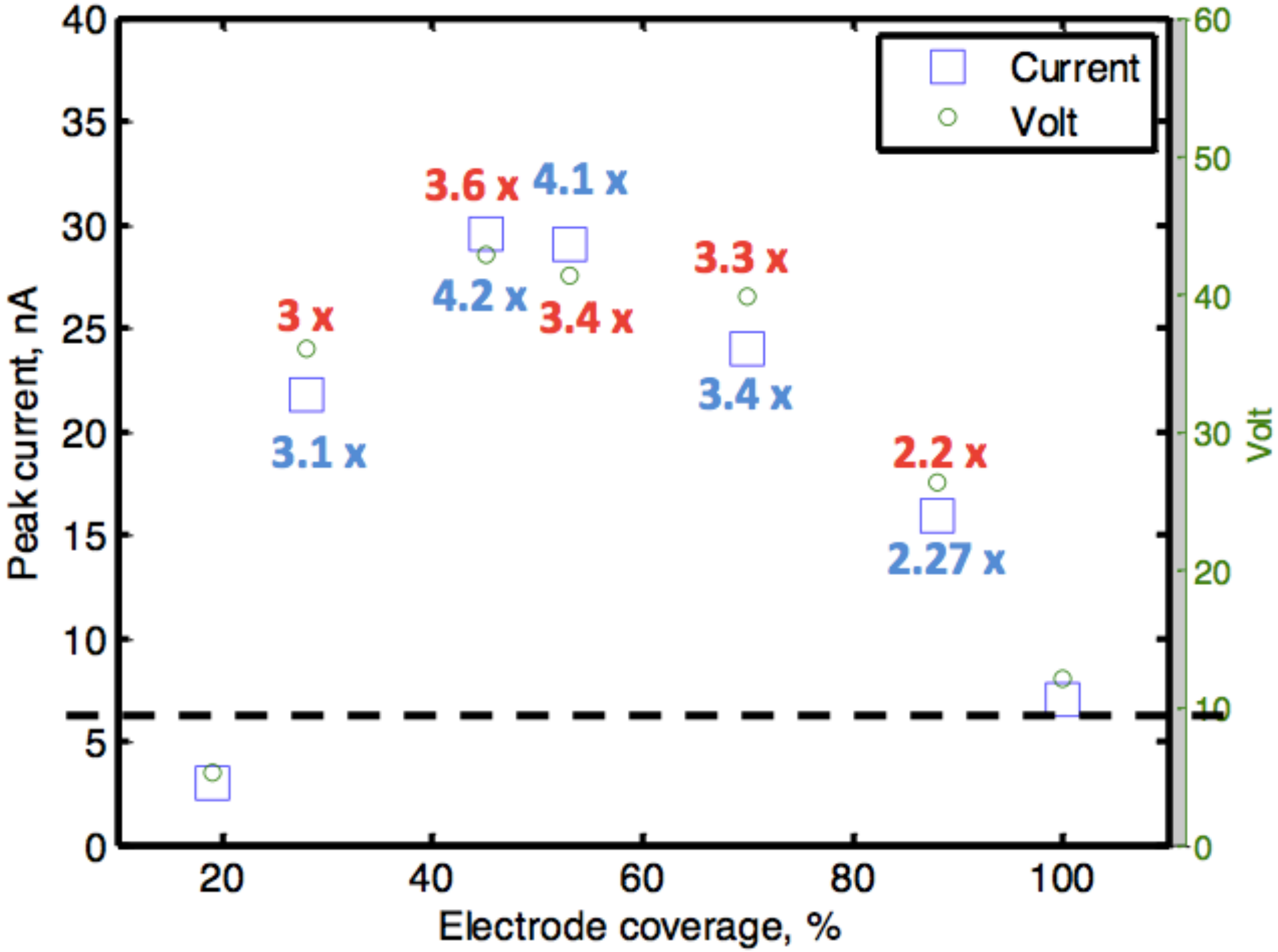


Temperature, closed circuit current, open circuit voltage



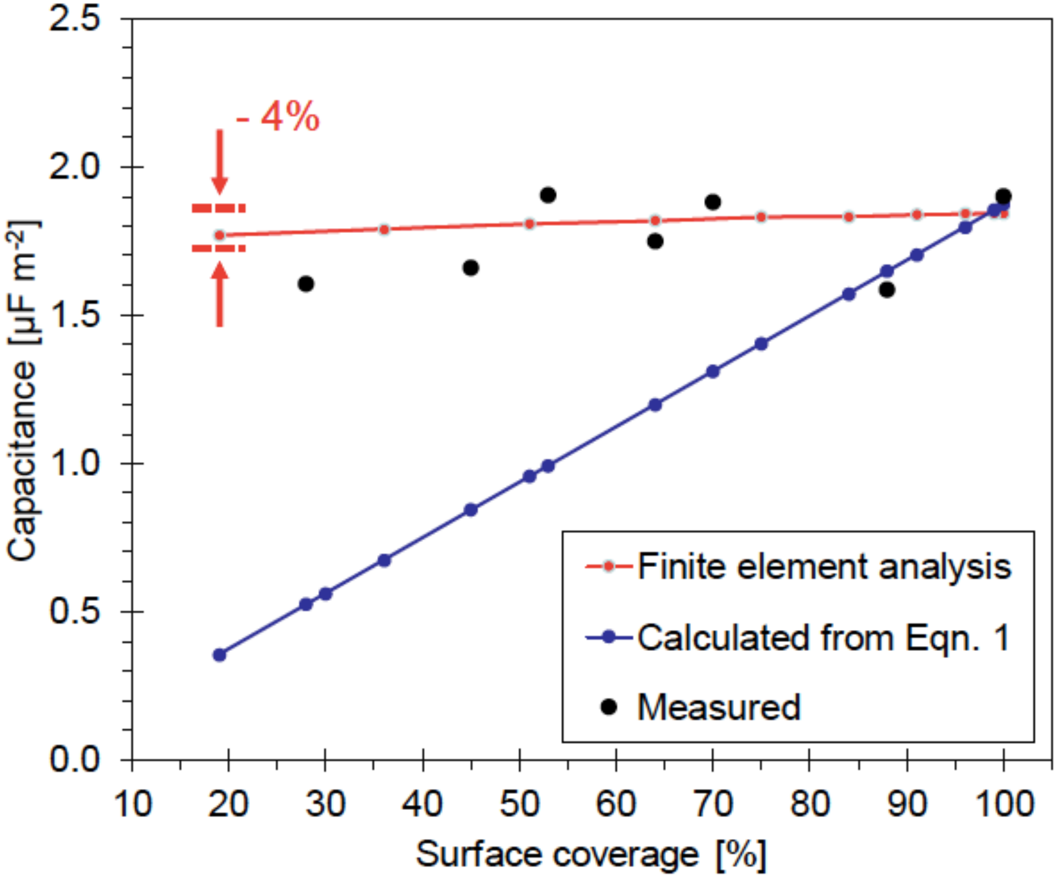


Optimum coverage

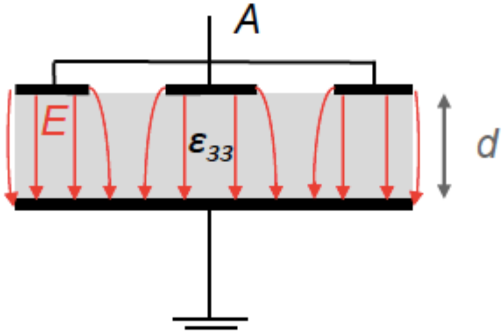


Zabek, D. Bowen, C. R. et al,. Micropatterning of flexible and free standing polyvinylidene difluoride (PVDF) films for enhanced pyroelectric energy transformation. ***Advanced Energy Materials***, 5 ,8 (2015)

Voltage up, what about capacitance?



$E = \frac{1}{2} C V^2$

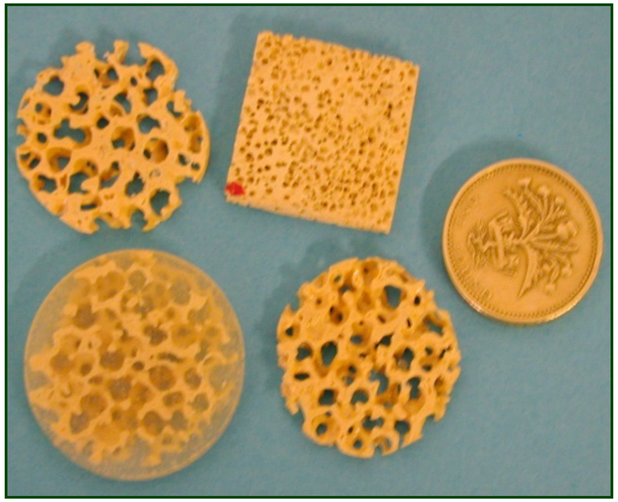


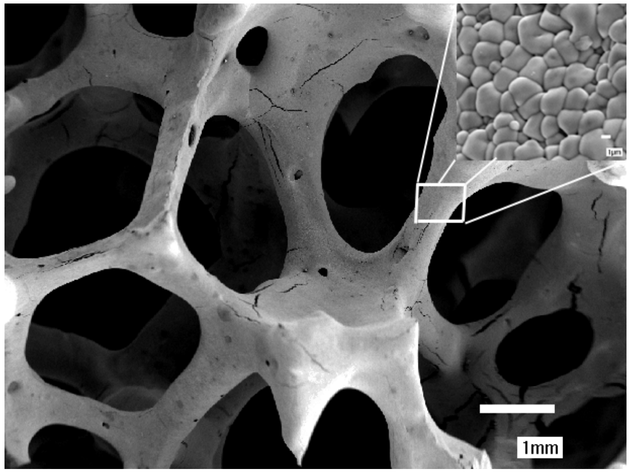
Topics: Materials development

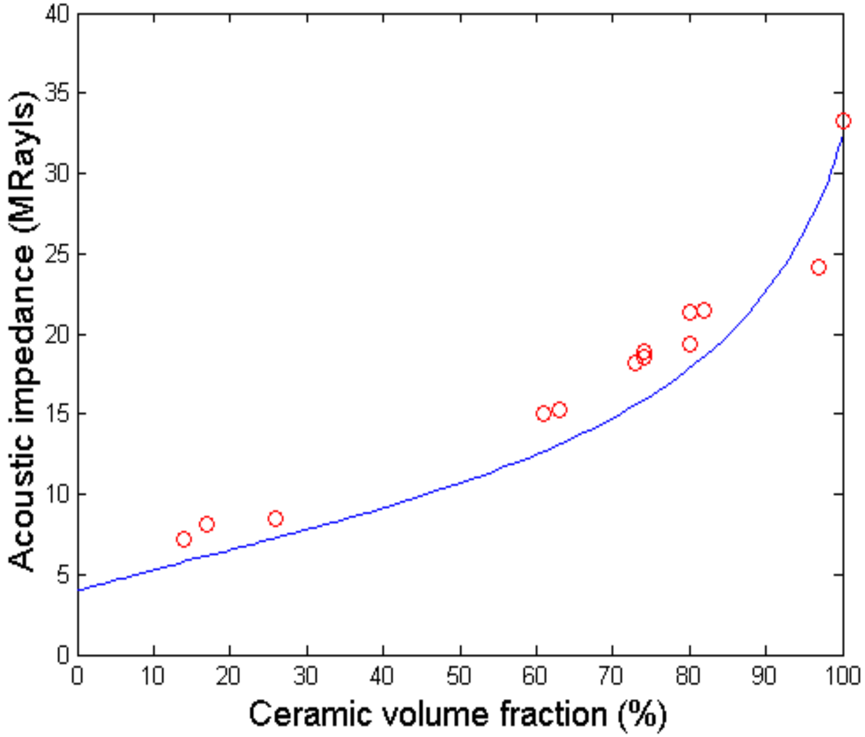
1. Porous ferroelectrics for piezoelectric harvesting (James Roscow)

2. Porous ferroelectrics for pyroelectric harvesting (Yan Zhang, Hunan University)

Porous ferroelectrics







Benefits of porosity in vibration energy harvesting ?

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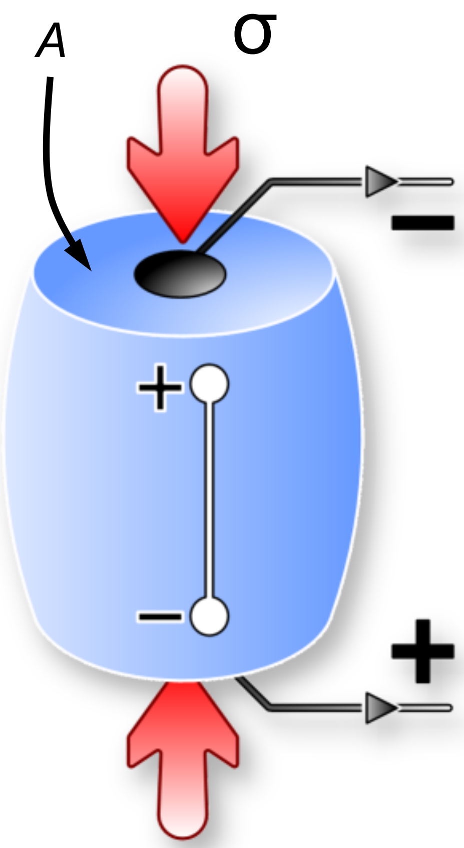
$$E = \frac{1}{2} C V^2$$

$$Q = CV$$

$$Q = d_{33} . F$$

$$C = \frac{A . \varepsilon_{33}}{t}$$

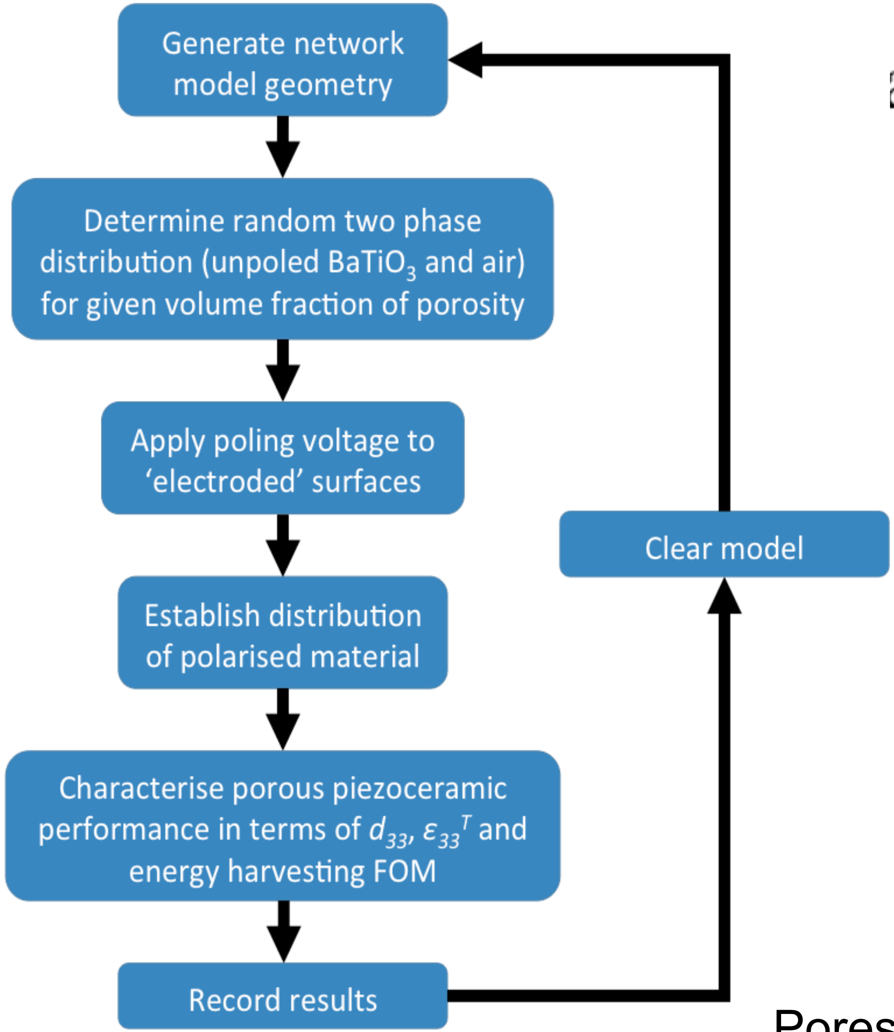
$$E = \frac{1}{2} \frac{d_{33}^2}{\varepsilon_{33}} . A . t . \sigma^2$$

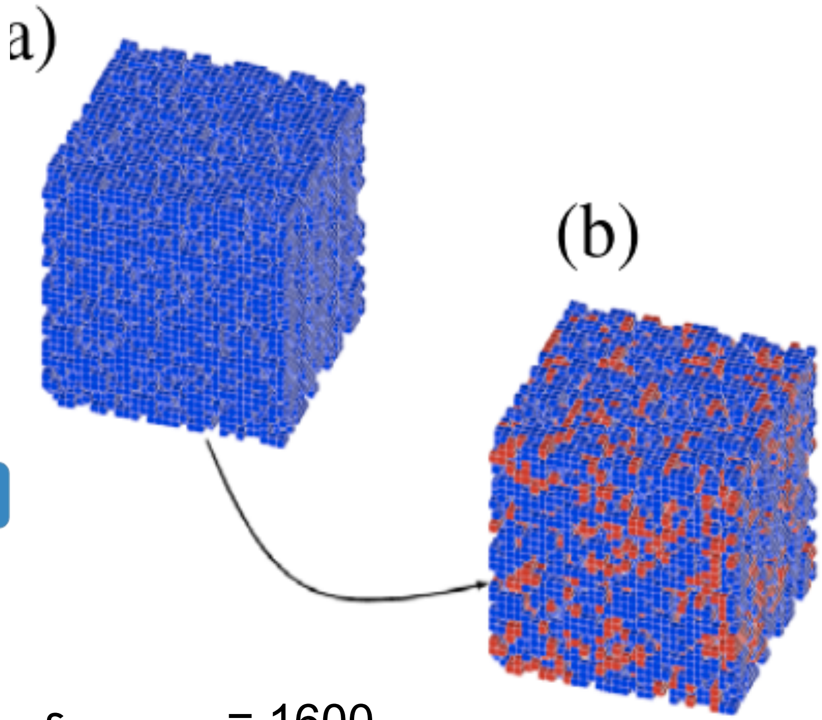


E - Energy
C - Capacitance
Q - Charge
V – Voltage
σ – Stress (F/A)
d_{33} charge per unit force (C/N)
ε_{33} permittivity

Figure of Merit $FOM_{33} = \frac{d_{33}^2}{\varepsilon_{33}}$

Porous ferroelectric finite element model



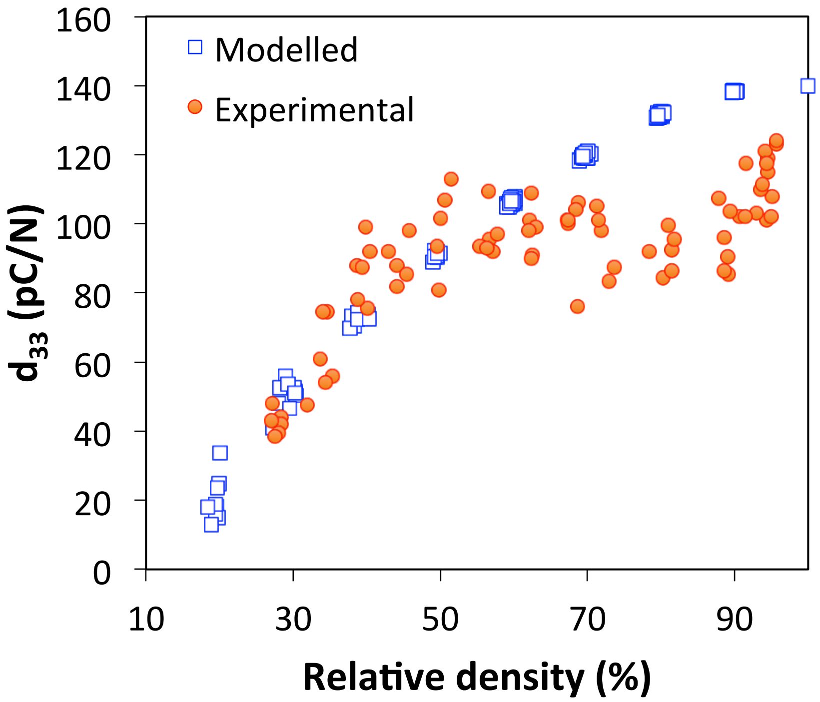


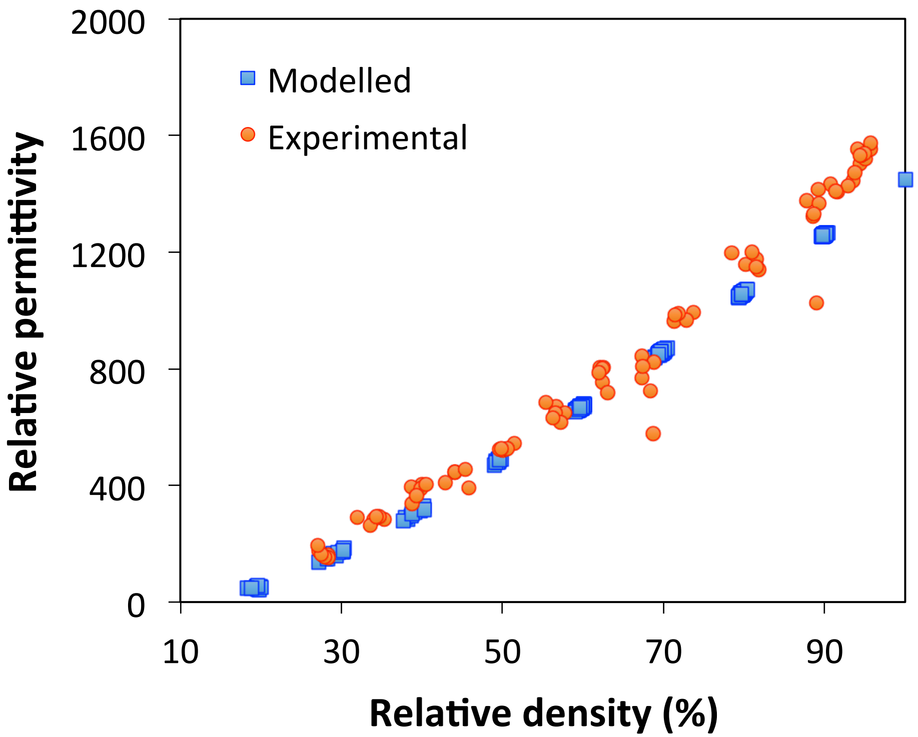
$\varepsilon_{33\ BaTiO3} = 1600$

$\varepsilon_{33\ air} = 1$

Pores lead to complex electric field distribution (contrast in permittivty)

d_{33} and permittivity with porosity





Vibration harvesting figure of merit

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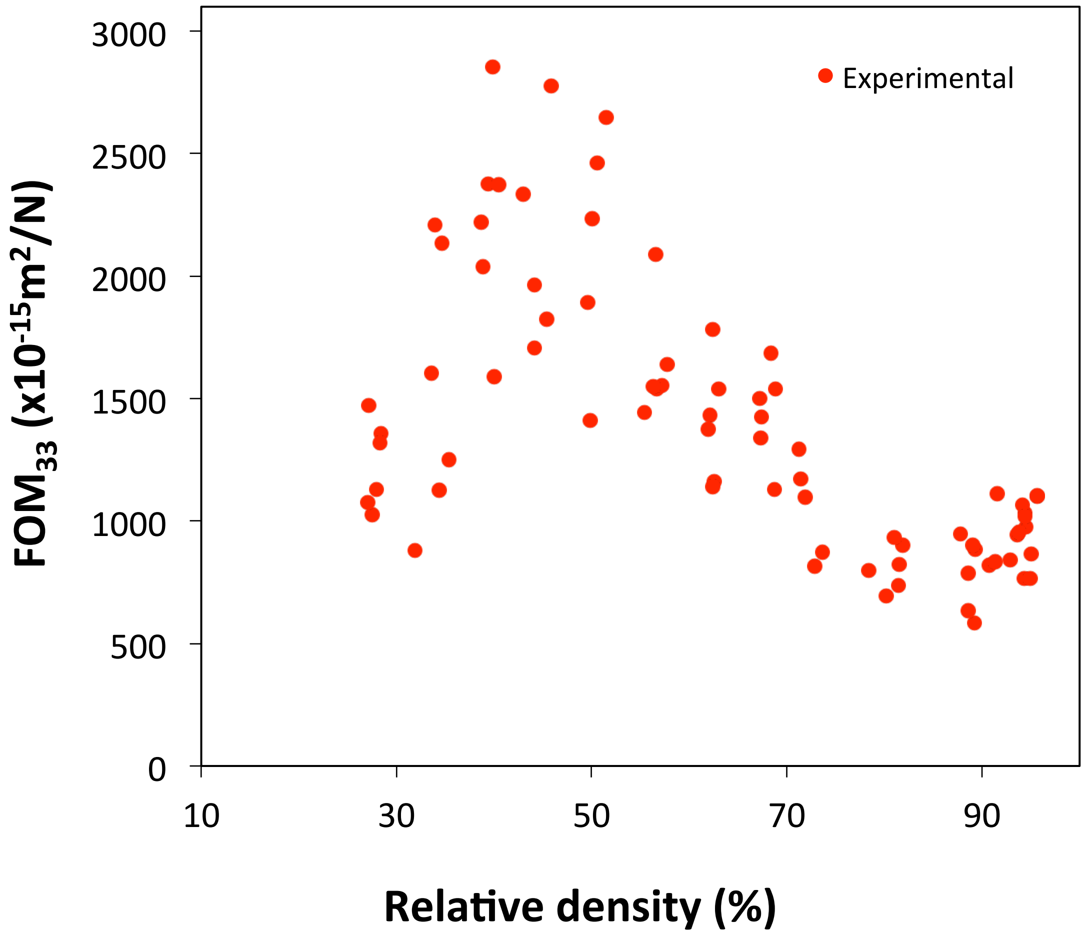
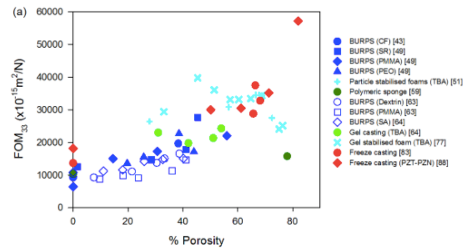
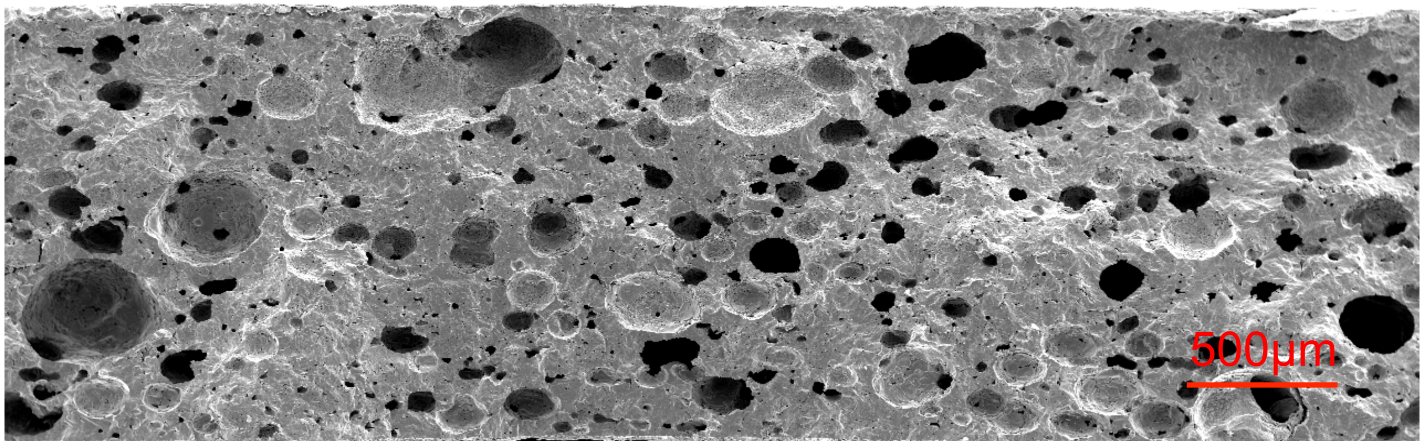




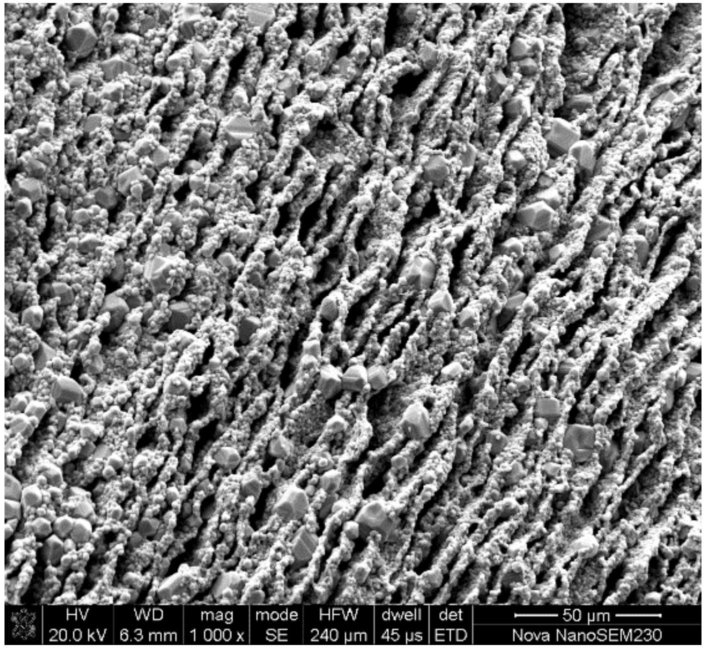
J. Roscow, Y.Zhang, C.R.Bowen et al., Porous ferroelectrics for energy harvesting applications, accepted **Euro. Phys. J. Special Topics**.

Evaluation of effect of porous structures on key properties

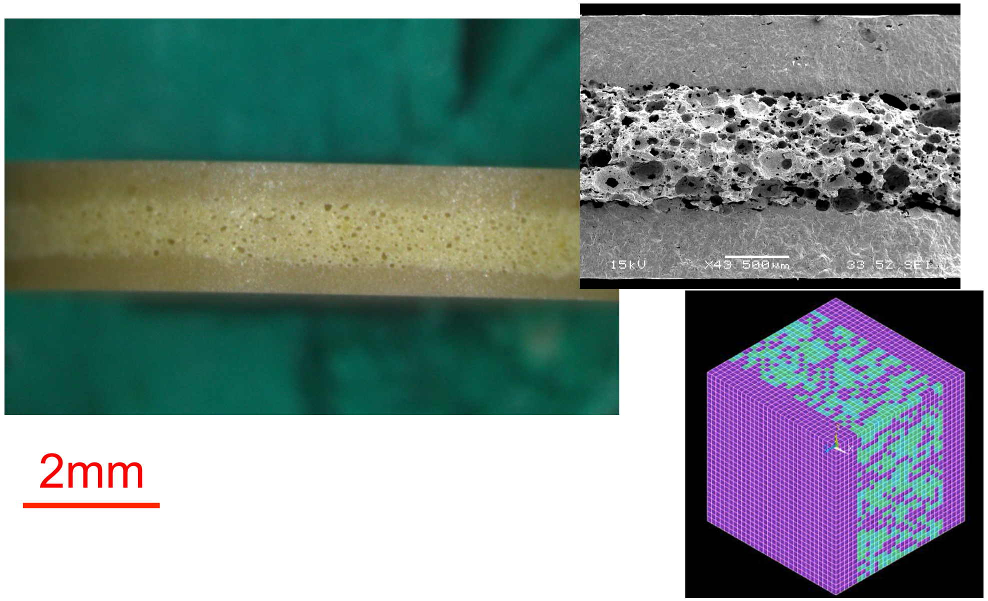
BURPS



Freeze casting



Porous sandwich layers



Benefits for porosity in pyroelectric energy harvesting ?

$$\Delta T = \frac{W.\Delta t}{c_E.h}$$

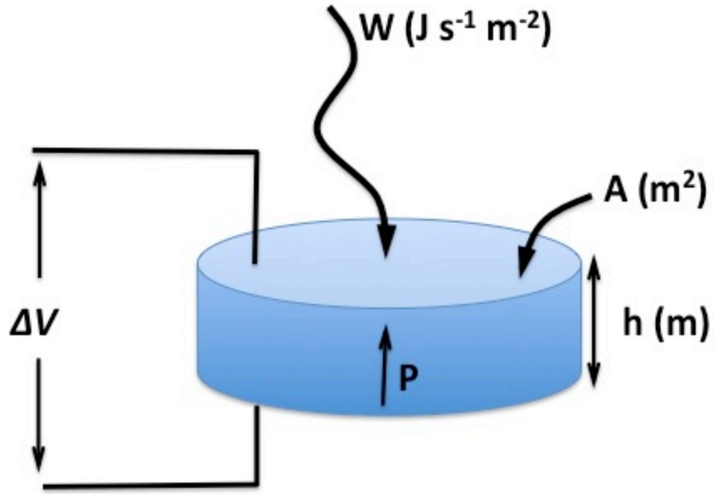
$$Q = p.A.\Delta T$$

$$\Delta V = \frac{p}{\varepsilon_{33}^{\sigma}}.h.\Delta T$$

$$E = \frac{1}{2}CV^2$$

$$E = \frac{1}{2}.\left[\frac{p^2}{\varepsilon_{33}^{\sigma}.(c_E)^2}\right].\left[\frac{A}{h}\right].(W.\Delta t)^2$$

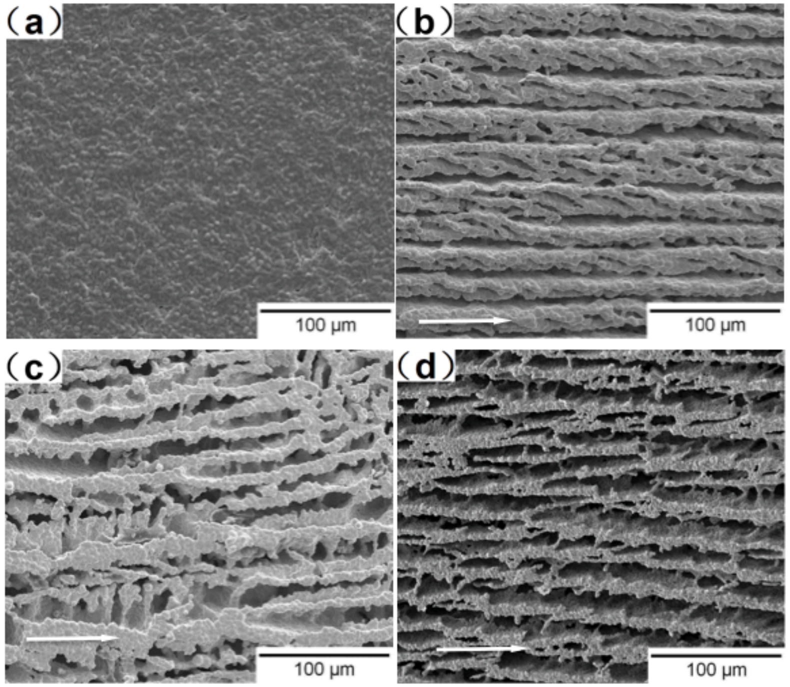
$$F_E' = \frac{p^2}{\varepsilon_{33}^{\sigma}.(c_E)^2}$$

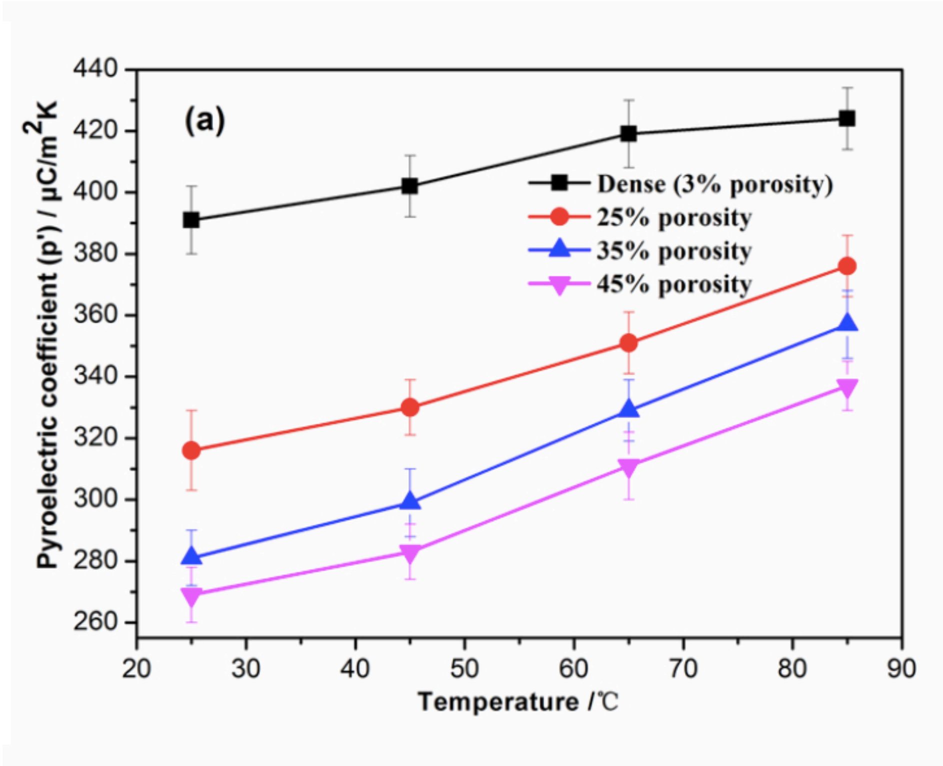


W - thermal flux ($J\ s^{-1}\ m^{-2}$)
ΔT - temperature change
Δt - time change
p - pyroelectric coefficient ($C\ m^{-2}\ K^{-1}$)
c_E - volume heat capacity ($J\ m^{-3}\ K^{-1}$)
Q - charge
E - Energy *C* - Capacitance *V* - Voltage
ε_{33} - permittivity

Bowen et al. 2015. A modified figure of merit for pyroelectric energy harvesting. Materials Letters, 138, pp. 243-246.

Experimental: Freeze cast porous PZT





$$F'_E = \frac{p^2}{\varepsilon_{33}^{\sigma}.(c_E)^2}$$

Pyroelectric coefficient decreases with increasing porosity ☹

But…so does permittivity and volume specific heat ☺

Yan Zhang[1], Yinxiang Bao[2], Dou Zhang[2] and Chris R. Bowen
[1]Modern Engineering Training Center, Hunan University, Changsha
[2]State Key Laboratory of Powder Metallurgy, Central South University

Porosity on pyroelectric FOMs

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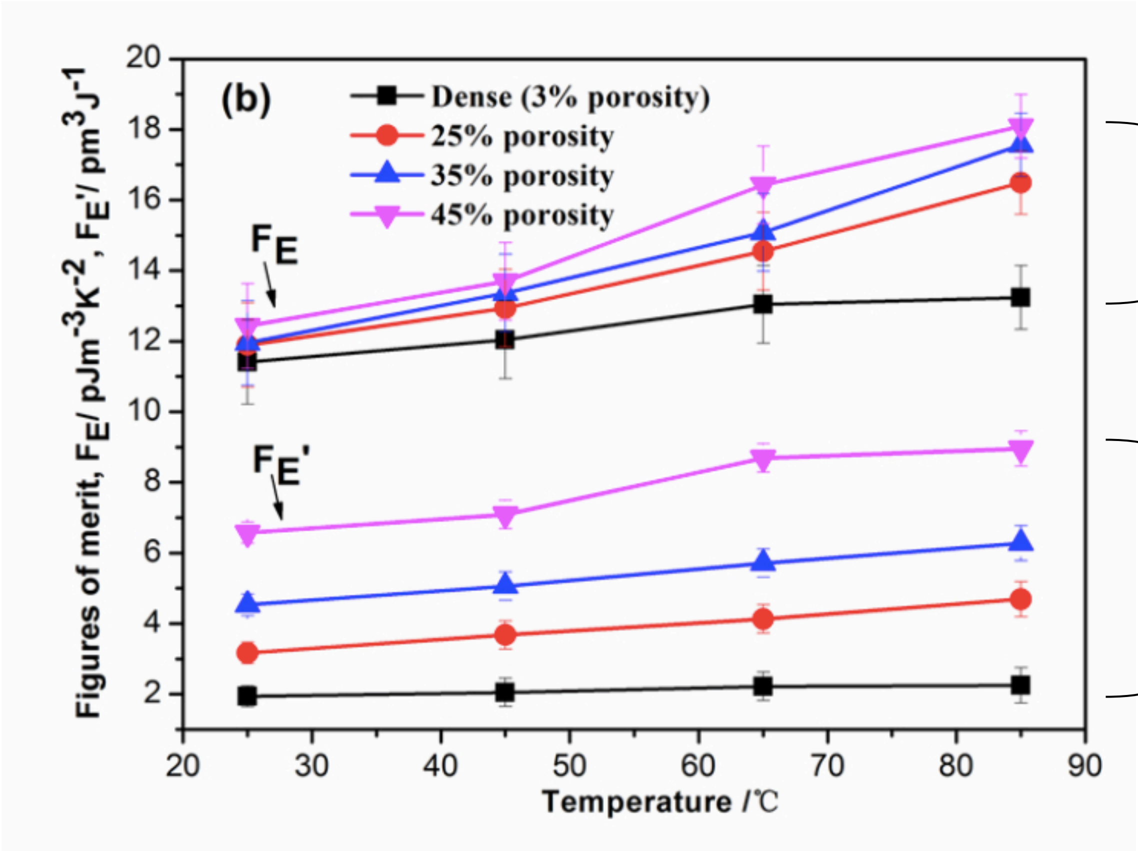

$$F_E = \frac{p^2}{\varepsilon_{33}^{\sigma}}$$

$$F_E' = \frac{p^2}{\varepsilon_{33}^{\sigma}.(c_E)^2}$$

Porosity to tailor:

- ε_{33}
- p
- d_{33}
- c_E
- k

J. Am. Ceram. Soc. DOI: 10.1111/jace.13797

Yan Zhang[1], Yinxiang Bao[2], Dou Zhang[2] and Chris R. Bowen

[1]Modern Engineering Training Center, Hunan University, Changsha

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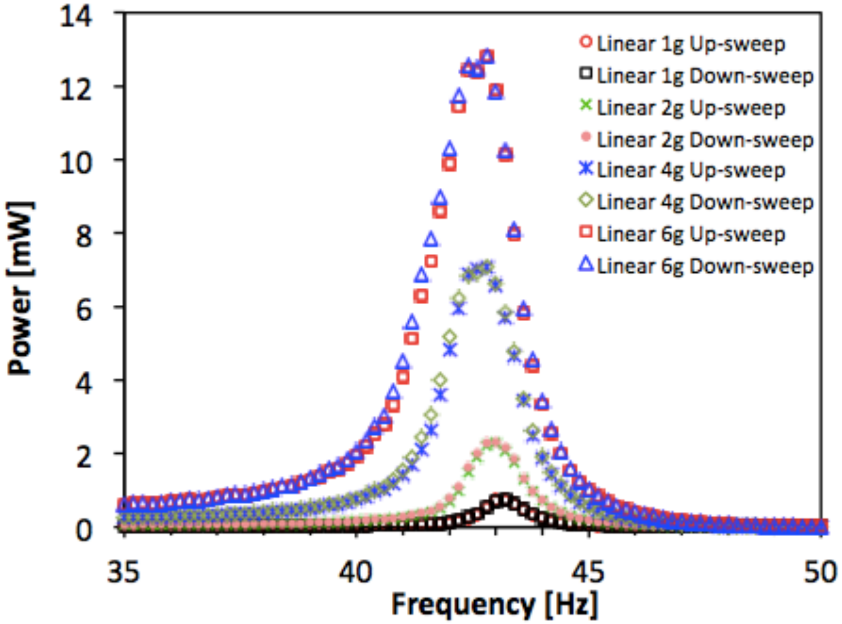
1. Materials development (Zabek, Roscow)
    - Micropatterned surfaces
    - Porous materials for harvesting

2. Materials applications (Harris, Krazny, Avent)

3. Water splitting (Adamaki, Xie)

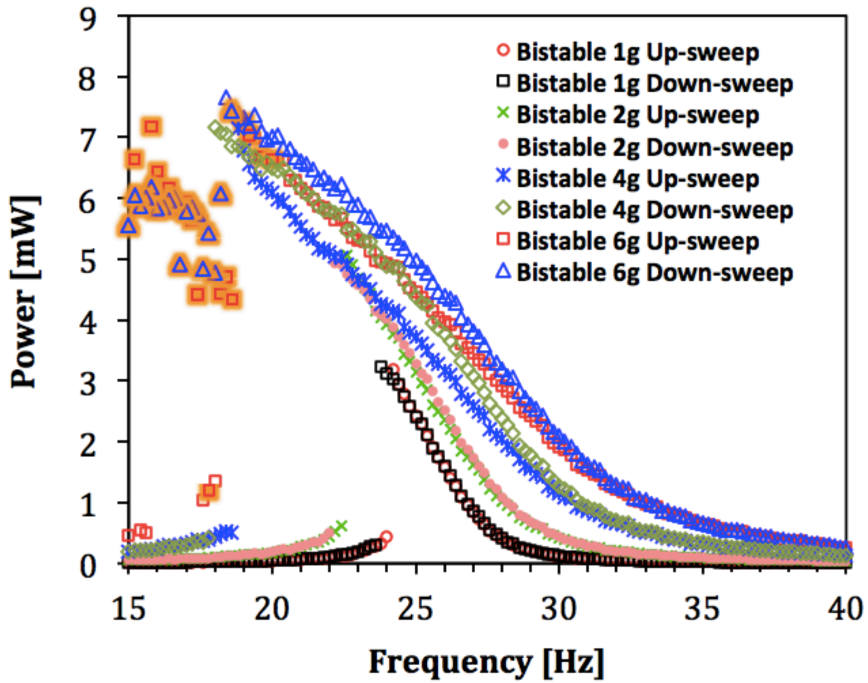
Bistable lay-up $[90/90/0/0]_T$ Peter Harris

$[90/0/0/90]_T$ Linear

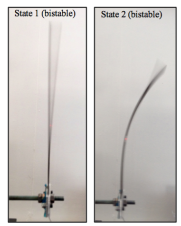


FWHM @1g 0.8Hz, Peak power 0.74mW
FWHM @6g 1.8Hz, Peak power 12.8mW

$[90/90/0/0]_T$ Bistable



FWHM @1g 1.6Hz, Peak power 7.3mW
FWHM @6g 8.2Hz, Peak power 12.8mW



Schematic of a thermoacoustic energy harvester
Andrew Avent

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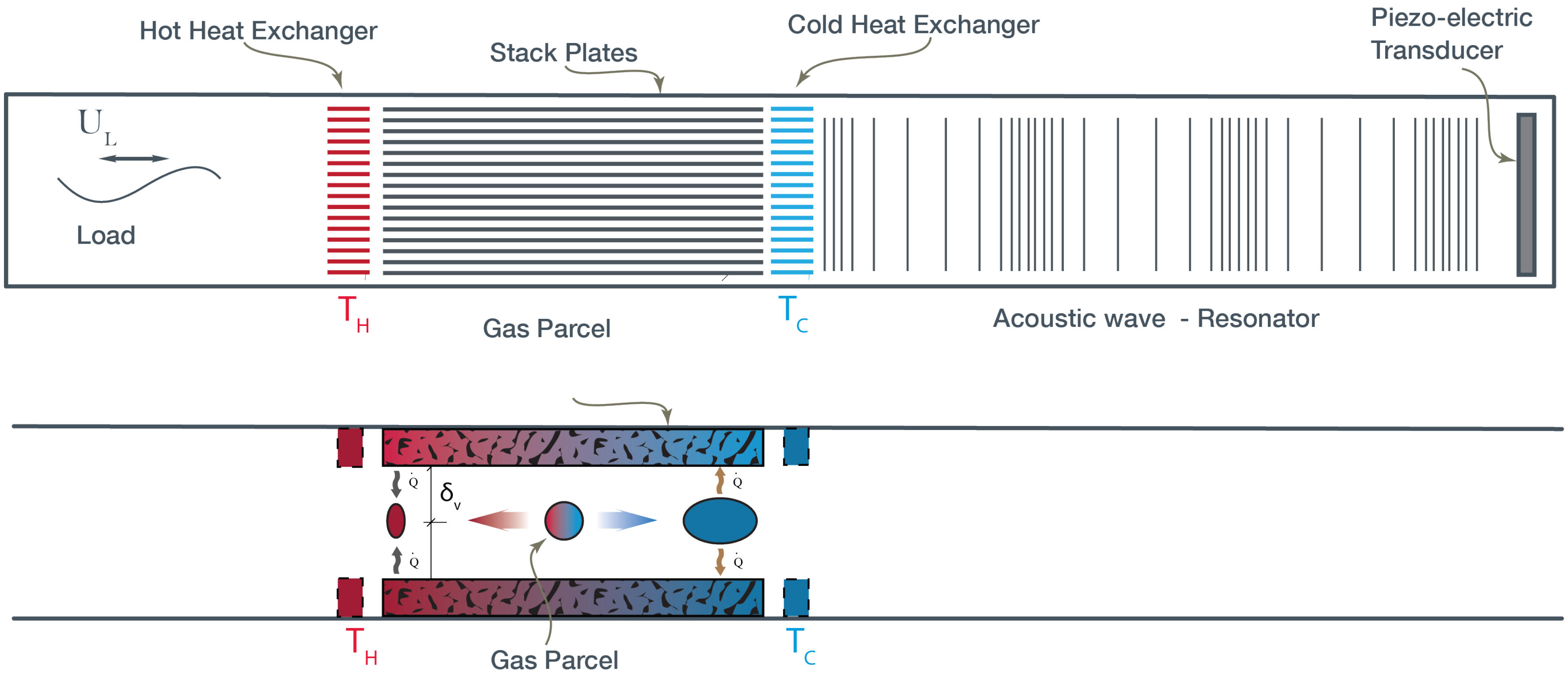

NE 10 ME 68 SI 14 S 16
Novel Energy Materials: Engineering Science and Integrated Systems

PROJECT: THERMAE THERMOACOUSTIC ENERGY

erc European Research Council

Thermoacoustic energy harvester

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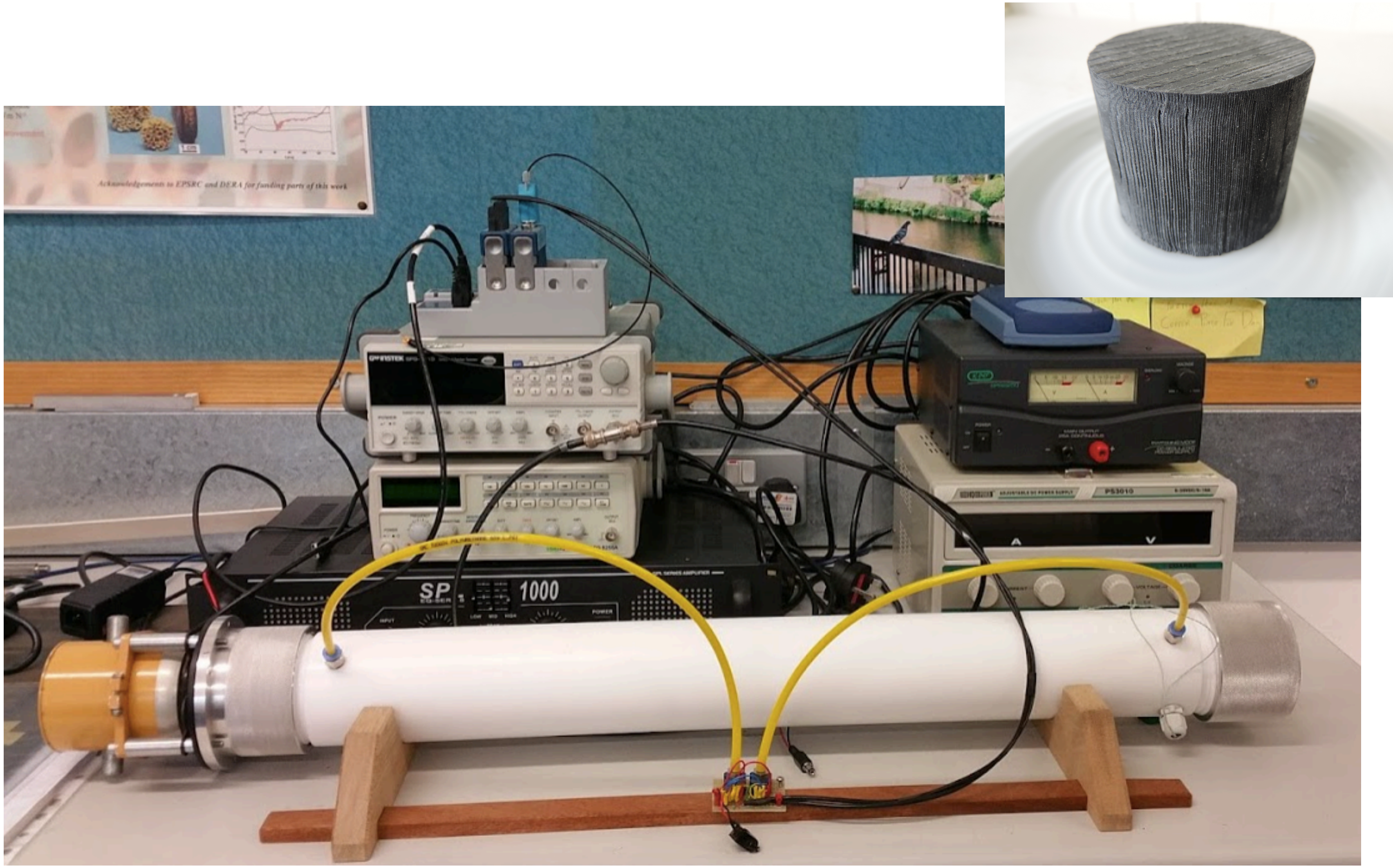

High Temperature Piezo Materials Measurement System
Marcin Krazny

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High temperature measurement system for characterisation of piezoelectric harvesting materials

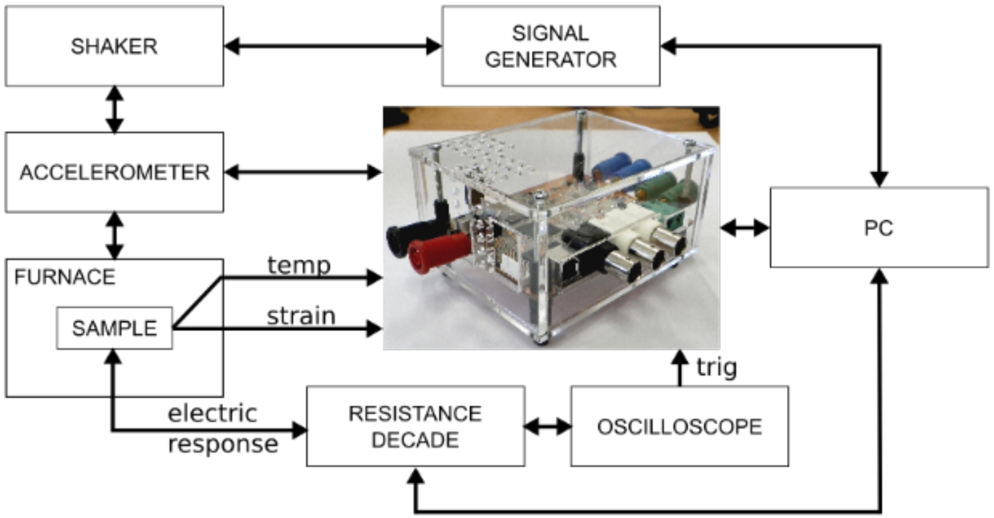


Fig. Measurement system diagram

Rig parameters:

- temperature range: 20-1000°C
- frequency range: 1-125 kHz
- sample's strain measurement with 16 and 24 bit resolution
- accelerometer with +/- 2G to +/- 16G ranges

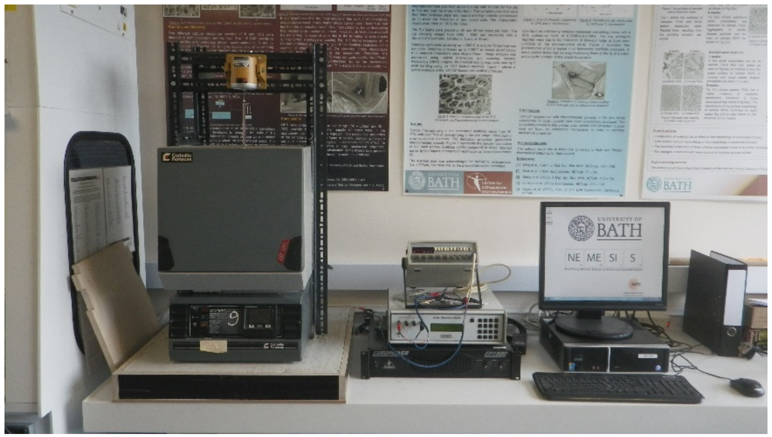
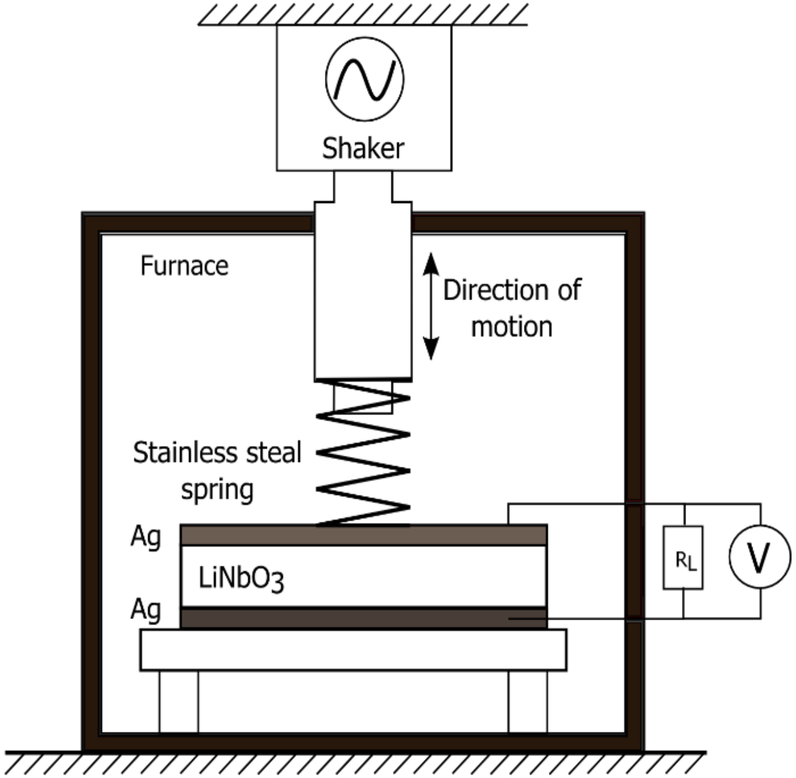
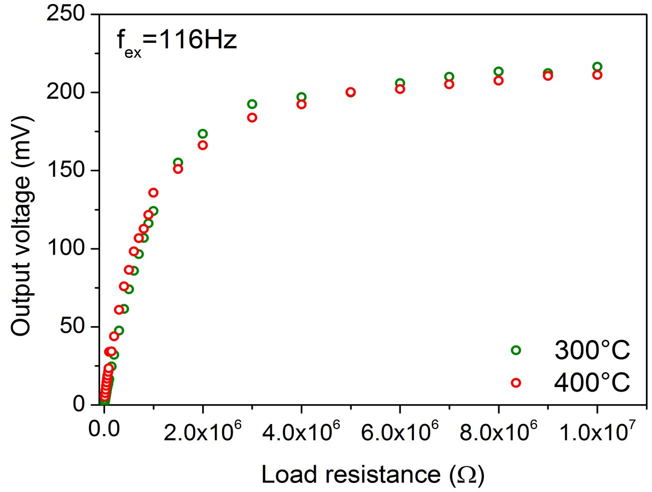


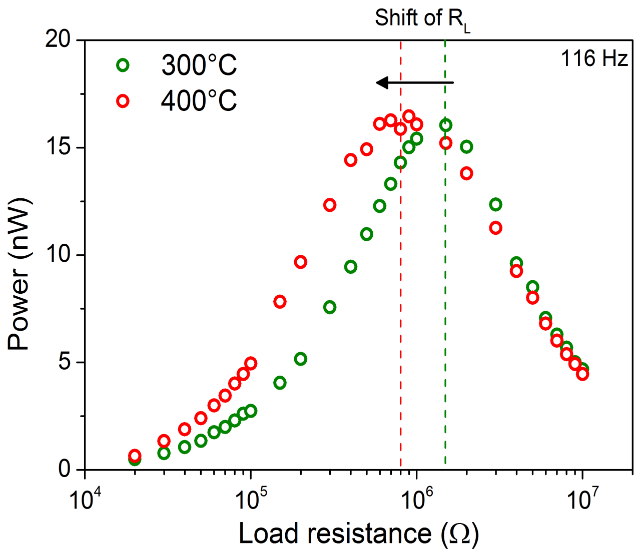
Fig. Measurement system –lab setup

The measurement system will be presented in the form of a poster at International Conference on Nanotechnology Applications in September 2016, Valencia, Spain.

High temperature harvesting





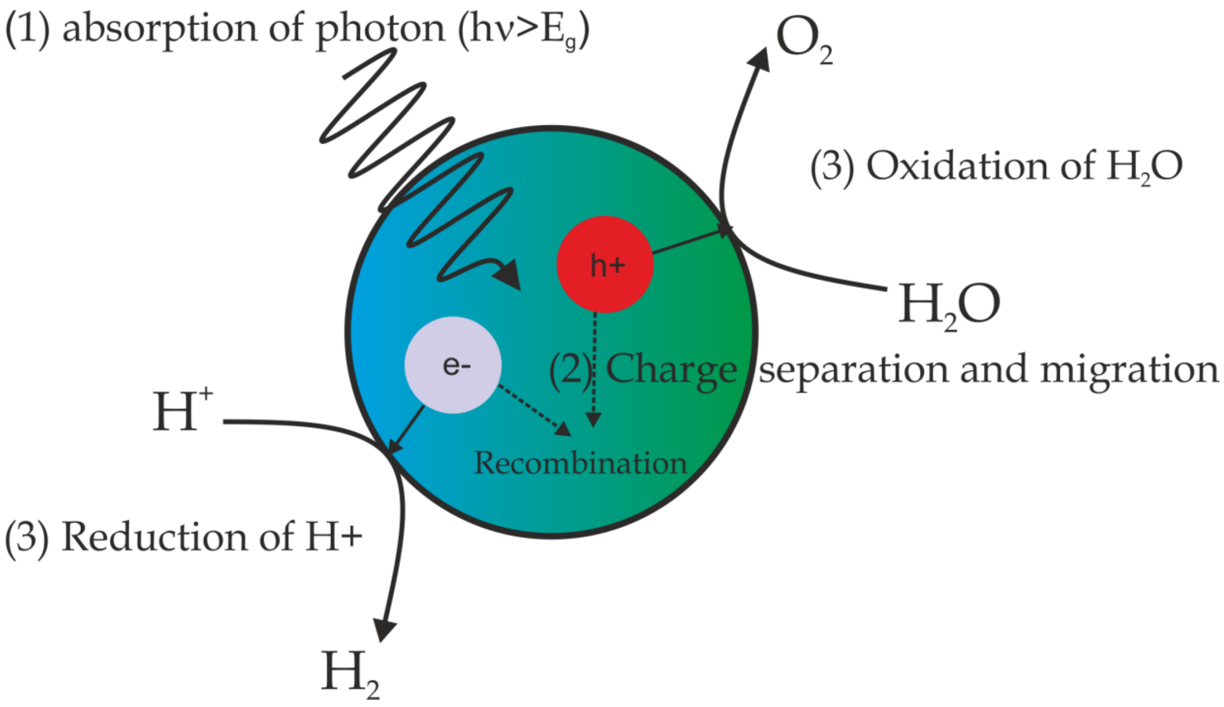


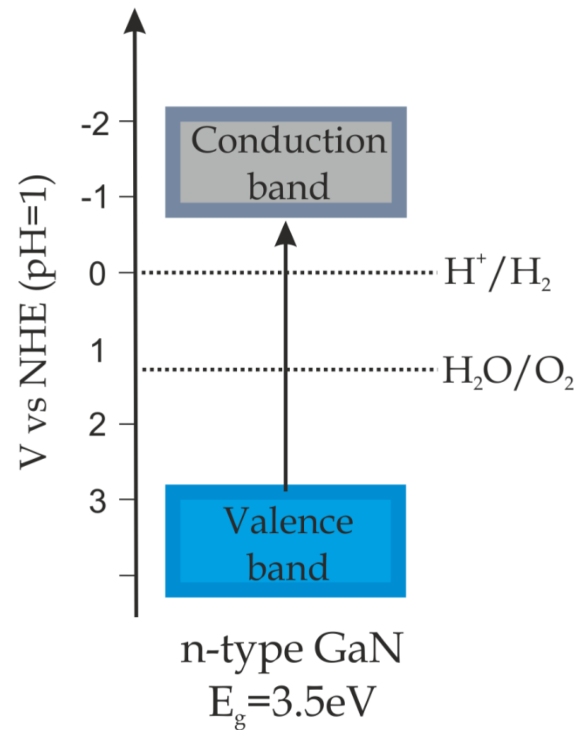
1. Materials development (Zabek, Roscow)
   - Micropatterned surfaces
   - Porous materials for harvesting

2. Materials applications (Peter Harris, Marcin Krazny, Andrew Avent)

3. Water splitting (Adamaki, Xie)

Photo-electrochemical splitting

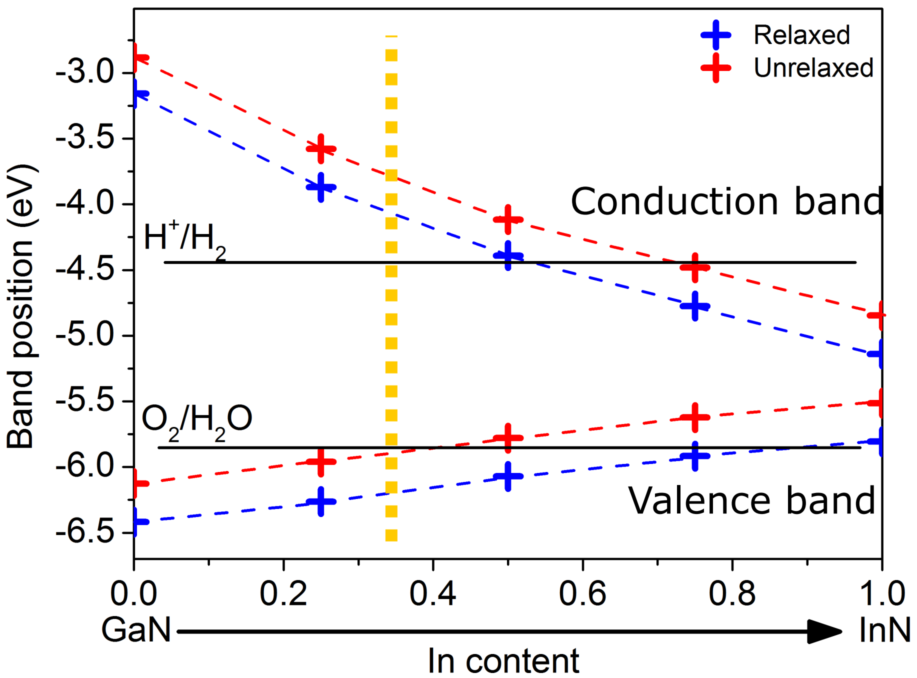


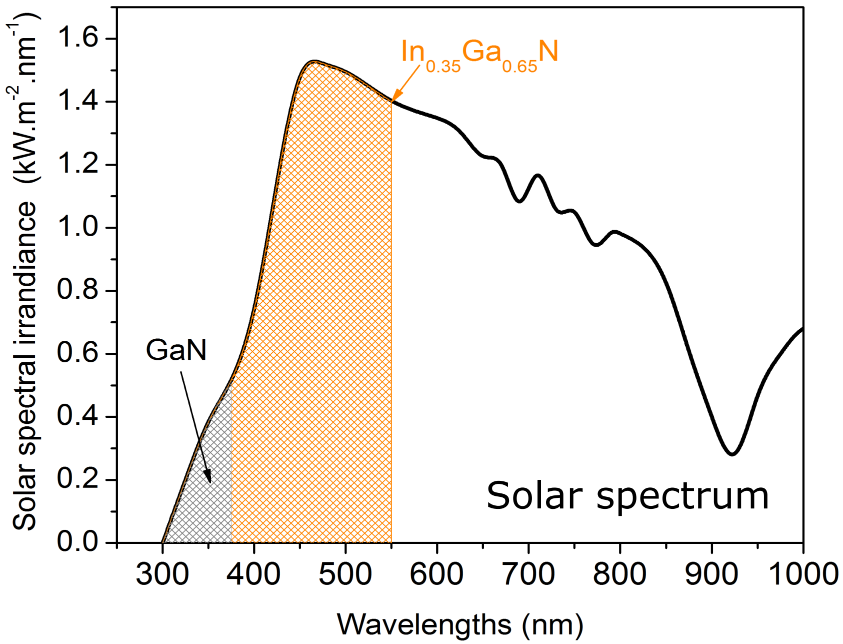


- Suitable valence / conduction band positions
- Bottom CB < 0 V and top of VB > 1.23 V
- GaN suitable for photo-electrochemical splitting

[1] A.B.Murphy et al. International Journal of Hydrogen Energy (2006) **31**, 1999-2017

InGaN alloys: band alignment / solar spectrum absorption





- Straddle of redox potential available up to $In_{0.35}Ga_{0.65}N$

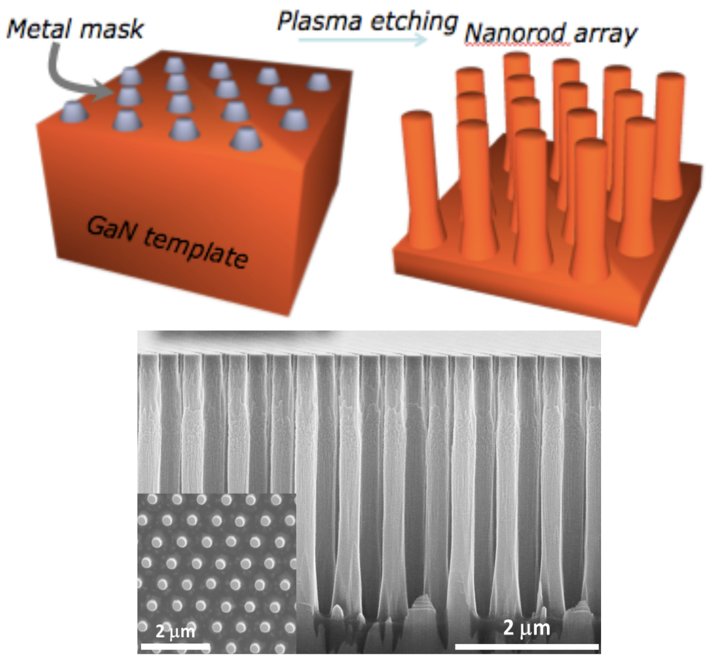
  - Valence band below O_2/H_2O
  - Conduction band above H^+/H_2

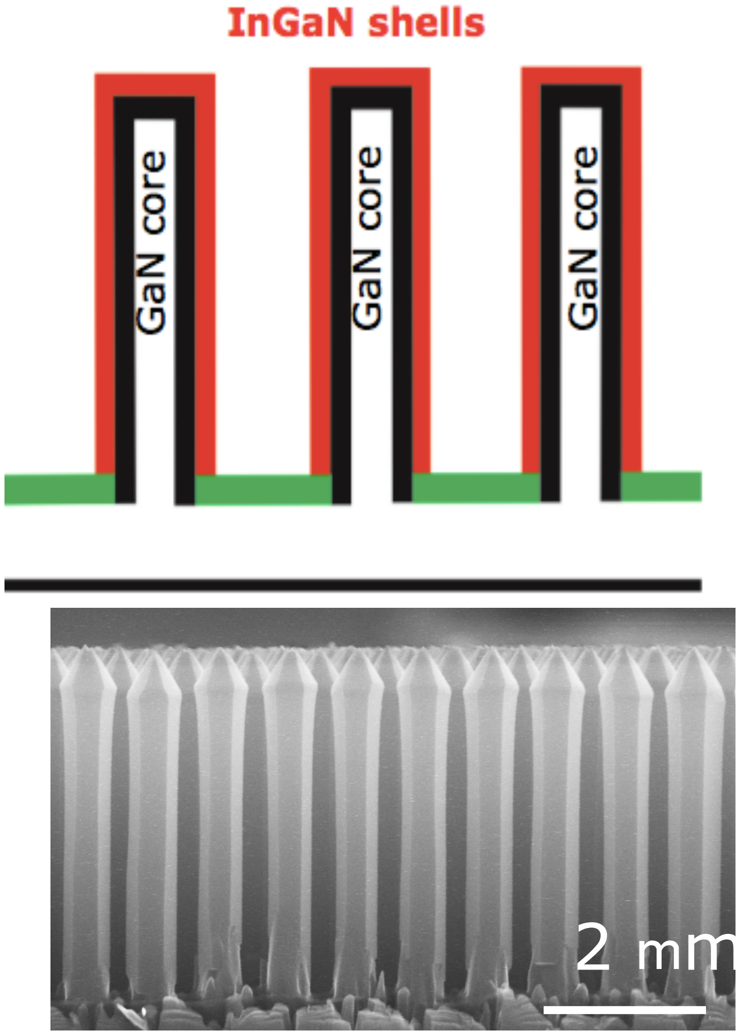
- Extending solar spectrum absorption down to 550nm

[2] P.G. Moses, C.G. Van de Walle, "Band bowing and band alignment in InGaN alloys" Appl. Phys. Lett. (2010) **96**, 021908

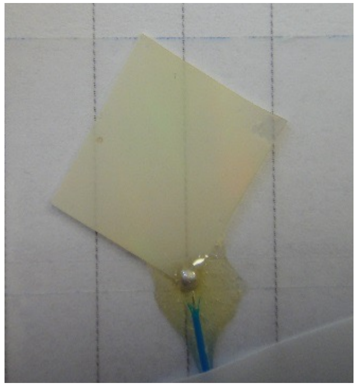
Core-shell structure for water splitting

- Large surface area
- Non defective material
- Wide spectrum absorption

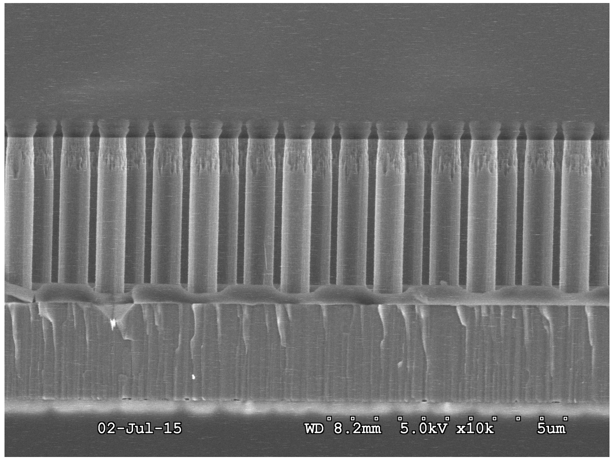




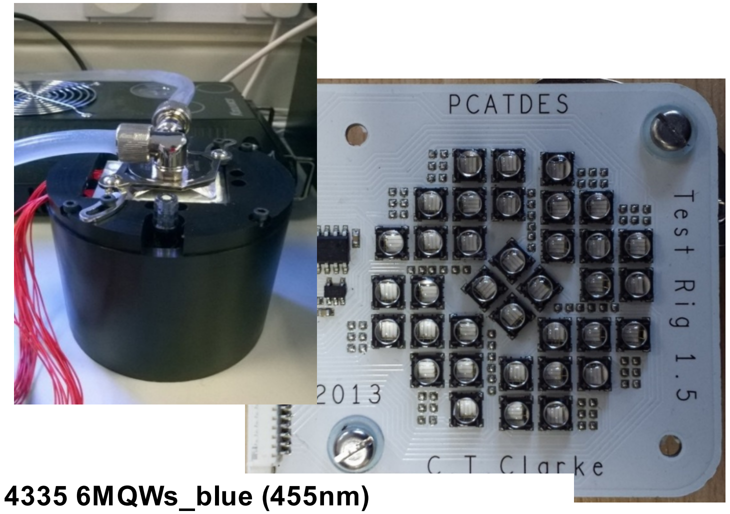
InGaN nanorods for water splitting



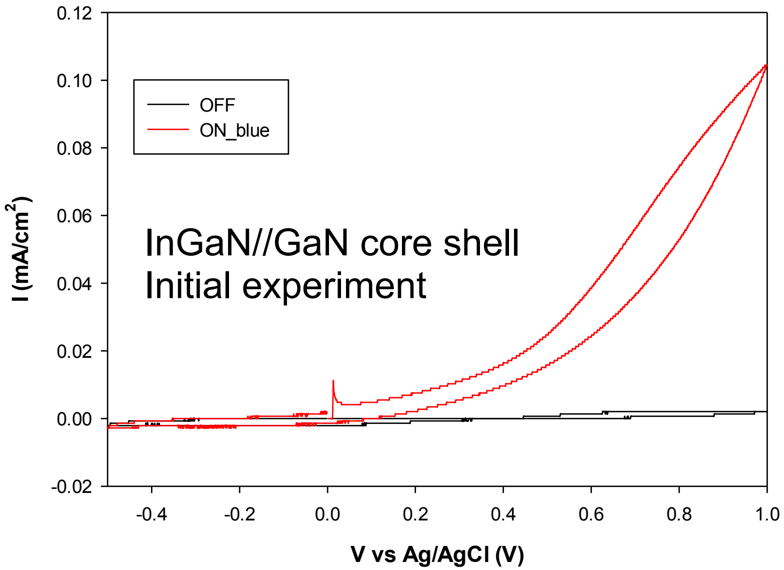
Working electrode in $0.1M\ Na_2SO_4$

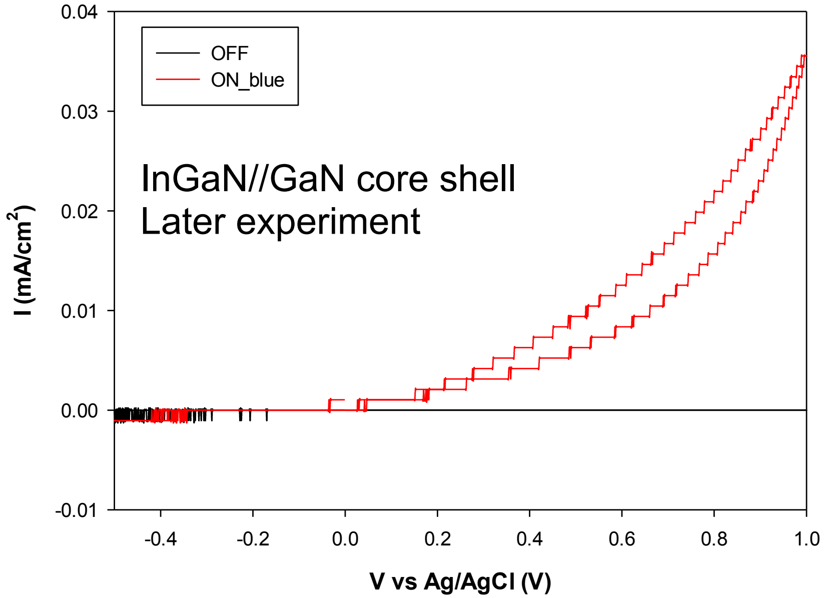


4326 SQW_blue (455nm)



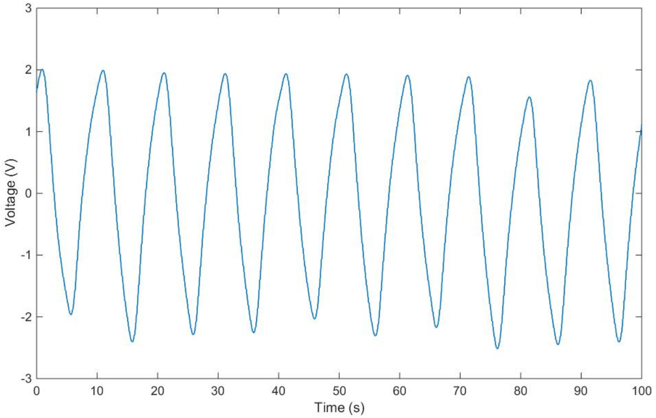
4335 6MQWs_blue (455nm)



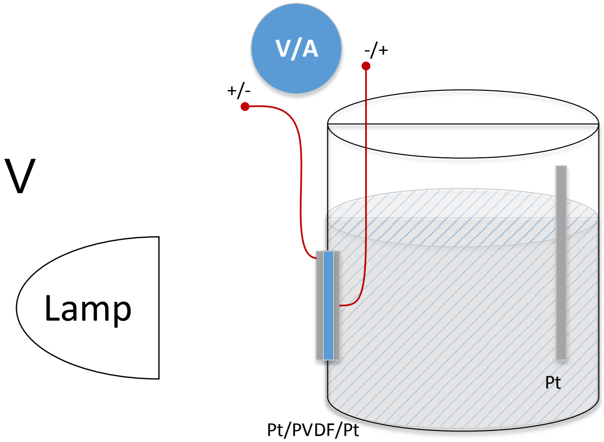


Pyro-water splitting

- Pyroelectric energy harvesting
  - Temperature fluctuation

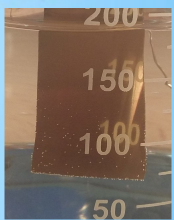


+/-0.4°C → +/-2 V

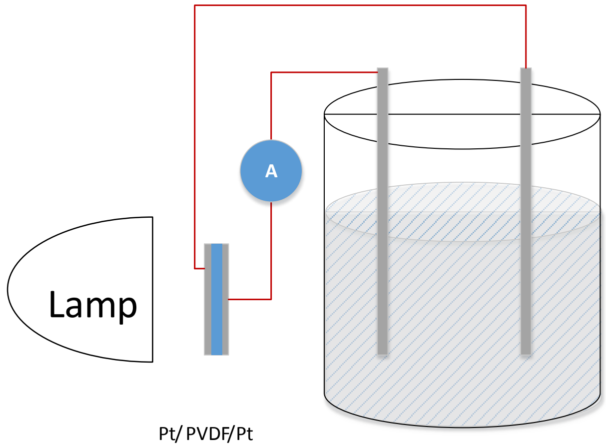


- Water splitting

$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$



$4OH^- \longrightarrow 2H_2O + O_2 + 4e^-$



Acknowledgment

European Research Council

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Letter

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An Explanation of the Photoinduced Giant Dielectric Constant of Lead Halide Perovskite Solar Cells

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ABSTRACT: A photoinduced giant dielectric constant of $\sim 10^6$ has been fou
impedance spectroscopy measurements of lead halide perovskite solar cells. We
similar effects in measurements of a porous lead zirconate titanate (PZT) s
saturated with water. The principal effect of the illumination of the solar cell and
introduction of water into the pore volume of the PZT sample is a significant incre
conductivity and dielectric loss. This is shown to exhibit low frequency powe
dispersion. Application of the Kramers–Kronig relationships show the large mea
values of permittivity to be related to the power law changes in conductivity and die
loss. The power law dispersions in the electrical responses are consistent with an ele
network model of microstructure. It is concluded that the high apparent valu
permittivity are features of the microstructural networks and not fundamental effe
the two perovskite materials.

CRYSTAL GROWTH & DESIGN

Article

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Structural and Optical Emission Uniformity of *m*-Plane InGaN Single Quantum Wells in Core–Shell Nanorods

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European Research Council

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Bedtime reading:

C. R. Bowen, H. A. Kim, P. M. Weaver and S. Dunn, Piezoelectric and ferroelectric materials and structures for energy harvesting applications, ***Energy and Environmental Science*** , 1, 25-44 (2014)

C. R. Bowen, J. Taylor, E. LeBoulbar, D. Zabek, A. Chauhan and R. Vaish, Pyroelectric materials and devices for energy harvesting applications, ***Energy & Environmental Science***, 7 (12), pp. 3836-3856 (2014)

J. Zhang, C. Wang and C. Bowen, Piezoelectric effects and electromechanical theories at the nanoscale, ***Nanoscale***, 6 (22), 13314-13327, (2014)

C. R. Bowen and M. H. Arafa, Energy Harvesting Technologies for Tire Pressure Monitoring Systems, ***Advanced Energy Materials*** *5, 1401787 (2015)*

A Chauhan, S Patel, R Vaish, CR Bowen, Anti-Ferroelectric Ceramics for High Energy Density Capacitors, ***Materials***, 2015, 8 (12), 8009-8031

D. J. Wales,   J. Grand,   V. P. Ting,   R. D. Burke,c   K. J. Edler   C. R. Bowen,   S. Mintova, A. D. Burrows, Gas sensing using porous materials for automotive applications, ***Chem. Soc. Rev.***,,44, 4290-4321 (2015)

A Chauhan, S Patel, R Vaish, CR Bowen, A review and analysis of the elasto-caloric effect for solid-state refrigeration devices: Challenges and opportunities, ***MRS Energy & Sustainability***, 2, E16 (2015)

J. Roscow, Y.Zhang, C.R.Bowen et al., Porous ferroelectrics for energy harvesting applications, accepted ***Euro. Phys. J. Special Topics.,*** 224, 2949-2966 (2015)

A. Avent and C.R. Bowen, Principles of thermoacoustic energy harvesting, ***Euro. Phys. J. Special Topics,*** 224, 2967-2992 (2015)