東京大学
THE UNIVERSITY OF TOKYO

Solid-state Quantum Chemical Investigatin of a High-performance Fluorinated Polymer Electret

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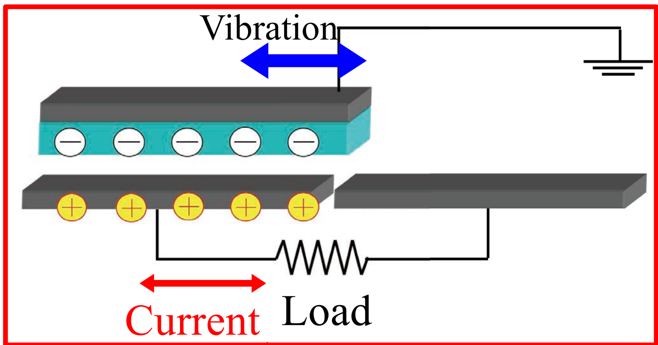
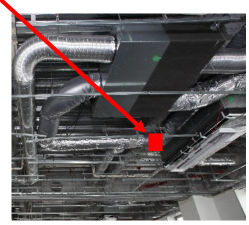
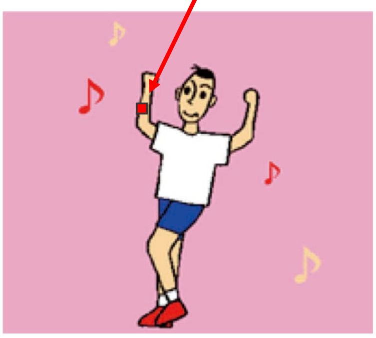
Kinetic Energy Harvesting Using Electret

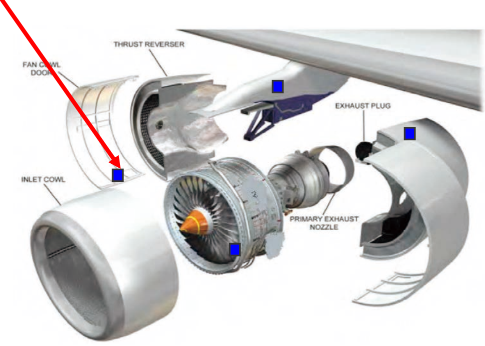




Air flow fluctuation, piping vibration

BEMS/HEMS





50 Hz @ Take-off

Automotive/Aviation

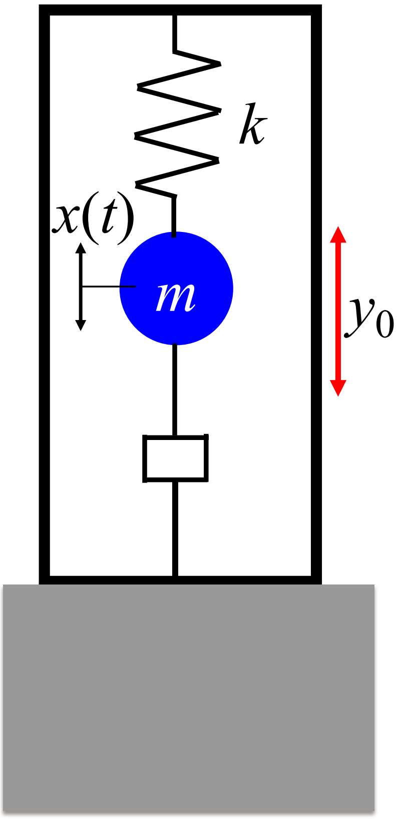
Tire pressure monitoring (TPMS)

Structural health monitoring (SHM)

Human/Animal motion

Biomedical, Agriculture

Mechanical Limit of Vibration EH



Energy Flow (2-step conversion)

Vibration energy in environment

1st step ⬇ **M→M**

Kinetic energy of mass

2nd step ⬇ **M→E**

Electricity

VDRG limit (P. Mitcheson et al., 2004)

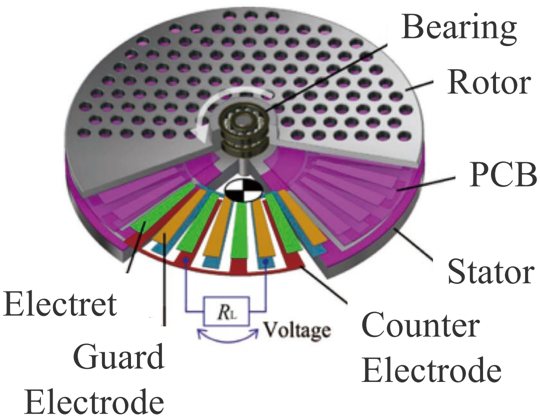
$$P_{max} = \frac{1}{2} m y_0 \omega_n^3 x_{max}$$

m: mass, ω_n: Resonant freq.

y_0: External amplitude

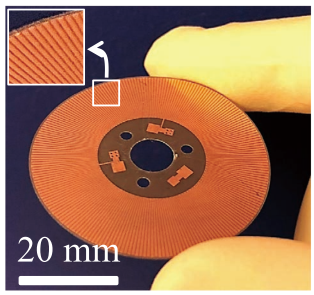
x_{lim}: Max. traveling distance

PCB-based Rotational Electret EH



Electret

- ✓ CYTOP EGG
- ✓ Surface potential: ~900V
- ✓ Spun onto PCB



Rotor

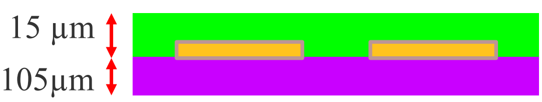
Glass-fiber-reinforced PCB

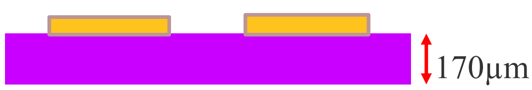
Minimize thermal deformation during curing process of electret

Stator

Low-permittivity PCB (ε=2.4)

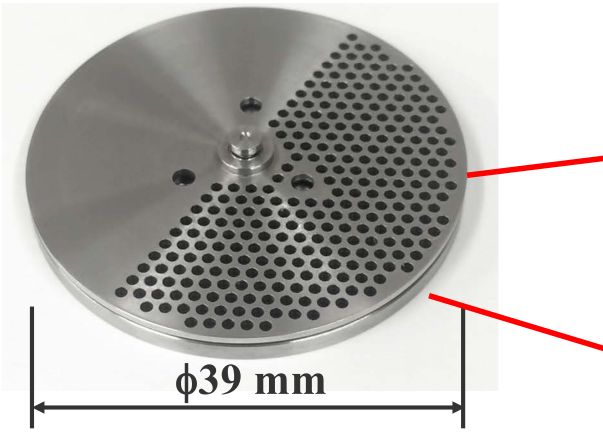
Reduce parasitic capacitance for higher output power



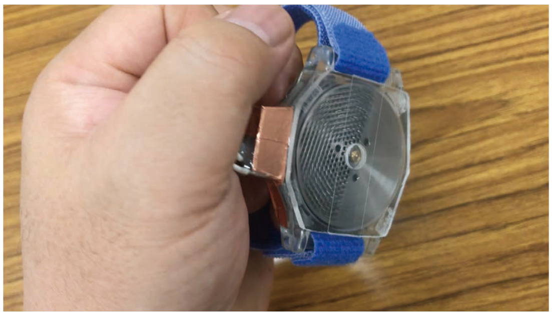


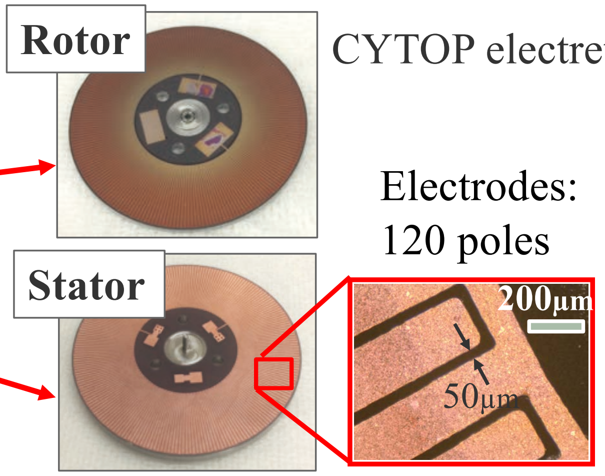
Adachi et al., PowerMEMS 2016; Miyoshi et al. IEEE MEMS 2017

Rotational Electret EH for Wearable Devices



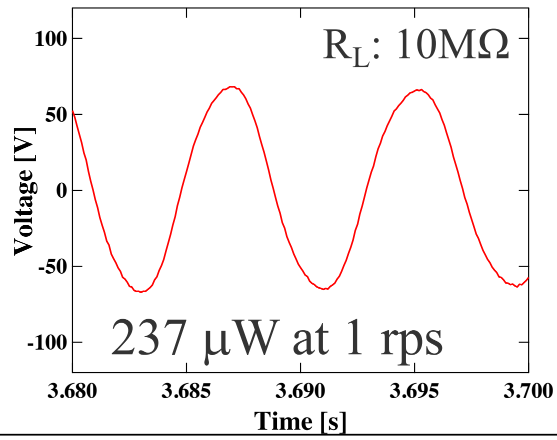
Only 2.7 mm in thickness!





CYTOP electret

Electrodes:
120 poles

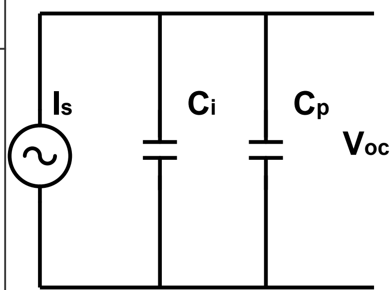


Miyoshi et al. IEEE MEMS 2018

SSHI: Electret versus Piezoelectric

Type	Piezoelectric EH (Liang et al, 2012)	Electret EH (Adachi et al, 2017)
I_s(μA)	87@30Hz	8.99@1rps
C_i(pF)	33740	46
C_p(pF)	<< C_i	128
C_0(pF)	33740	174
V_{oc}(V)	9	118

Generic circuit model



Characteristics of Electret EH

I_s: much lower

C_i: much lower (even lower than Cp)

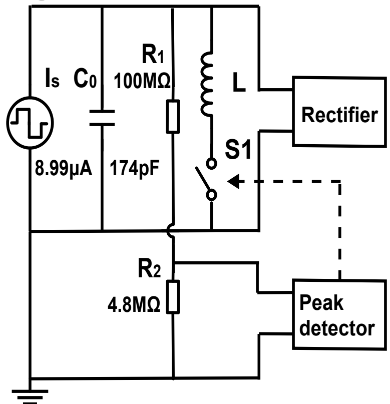
V_{oc}: much higher

Challenges of SSHI for Electret EH:

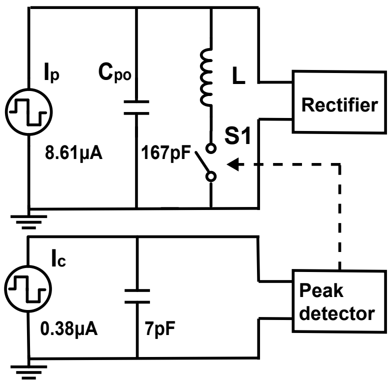
- Sensitive to leakage current
- Sensitive to external capacitance
- Large power consumption of the peak detection circuit

SSHI for Electret Generator

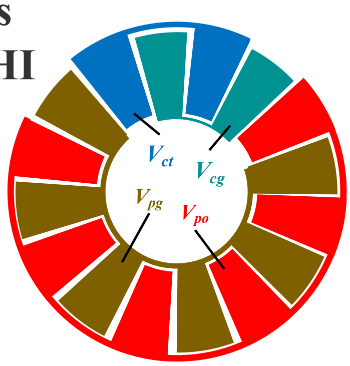
Voltage-divider SSHI

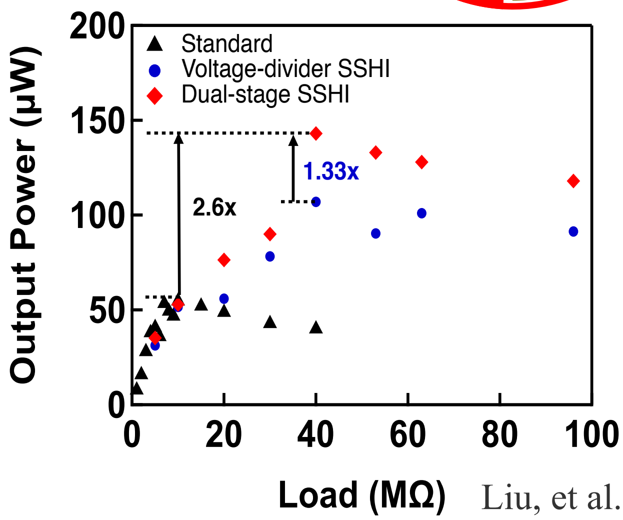


Dual-stage SSHI



Electrode patterns for dual-stage SSHI



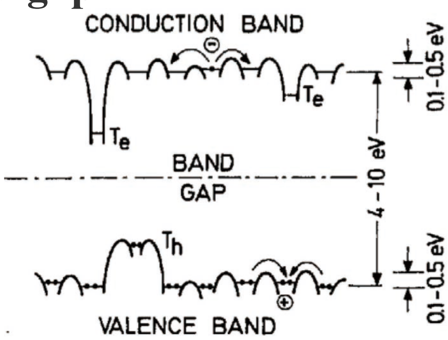


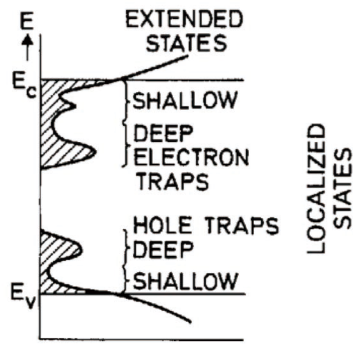
Liu, et al. (2019)

Charge Trap in Polymer

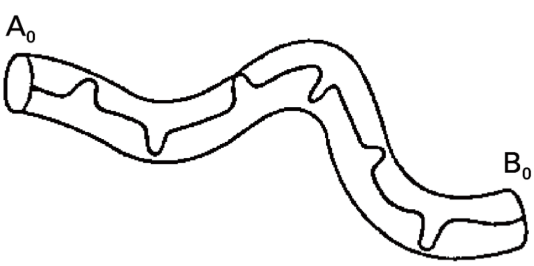
Band-gap

Sessler et al. 'Electret' (1998)



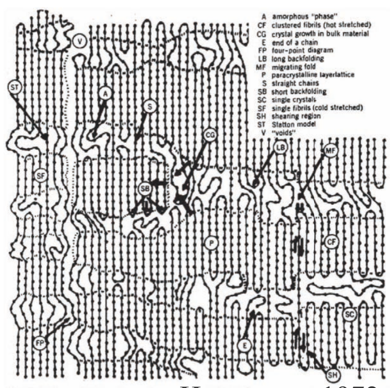


Focusing on a Single Molecule



Das-Gupta, 2001

Morphological Approach

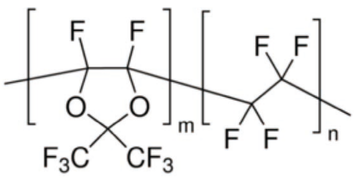


Hosemann. 1972

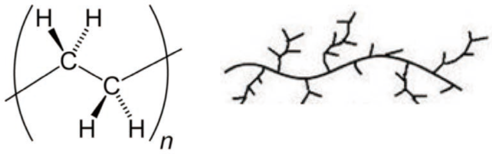
High-performance Polymer Electret

Output power ∝ $\Delta C\ V^2 f$

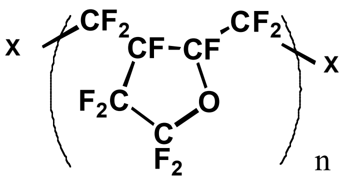
Teflon AF 0.5 mC/m^2 @ 15 μm
Chen et al. IEEE TDEI 1999
Hsieh et al. Transducers'97



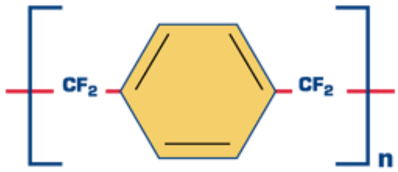
LDPE (Low-density PE)
0.43 mC/m^2@50 μm
Tao et al. (2015)



CYTOP EGG 2.0 mC/m^2 @ 15 μm
Sakane et al., JMM 2008
Kashiwagi et al., JMM 2011



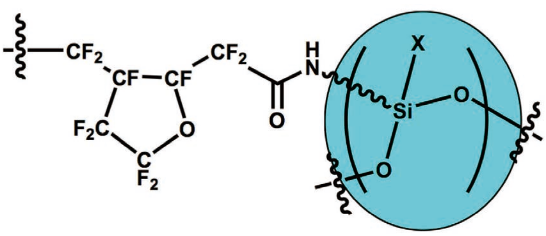
Parylene-HT 3.7 mC/m^2 @ 7.3 μm
Lo & Tai, JMM 2008

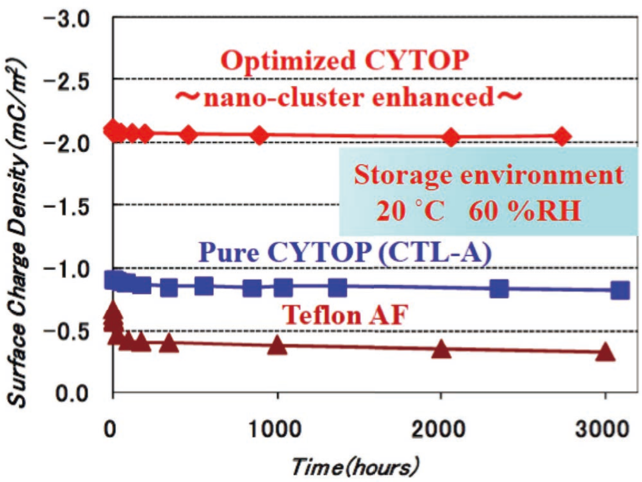


CYTOP:CYclic Transparent Optical Polymer

Nano-cluster-enhanced CYTOP Electret

- ✓ **Aminosilane additive**
- ✓ **σ=2 mC/m^2 for 15 μm-thick film (5+ times higher than Teflon AF)**
- ✓ **Improved thermal stability**





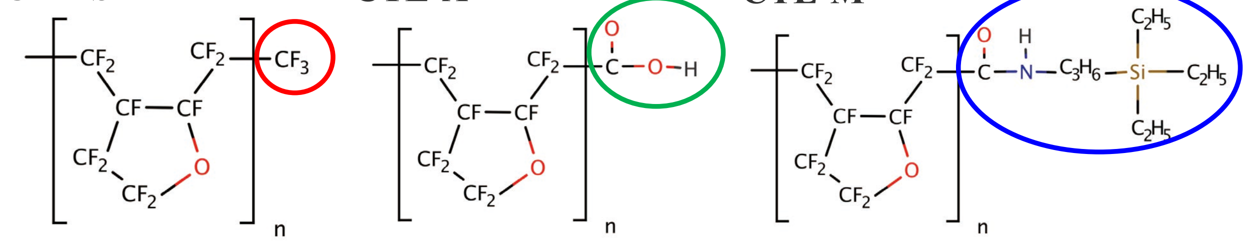
"CYTOP EGG"

Kashiwagi et al., JMM 2011

Possible Approach for Further Improvement

- **Multiple Layers**
  - e.g., Zhang and Sessler (2001), Chen et al. (1999)
- **Porous Polymer**
  - e.g., Xia et al. (2001), Behrendt et al. (2006)
- **Additives/Blends**
  - e.g., Mohmeyer et al. (2007), Erhard et al. (2010)
- **Surface Treatment**
  - e.g., Rychkov and Gerhard (2011)
- **Molecular Structure**
  - Quantum Chemical Analysis
    - Kim et al., STAM (2018), Kim et al. (2018)

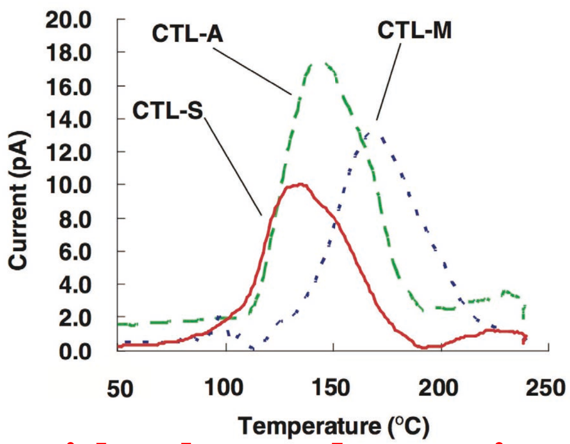
Effect of End Group on CYTOP Electret



amorphous polymer, 500-1000 repeat units

	End group	Surface charge density after 200h
CTL-M	Aminosilane	-1.3 mC/m²
CTL-A	COOH	-0.87 mC/m²
PTFE		-0.84 mC/m²
CTL-S	CF_3	-0.37 mC/m²

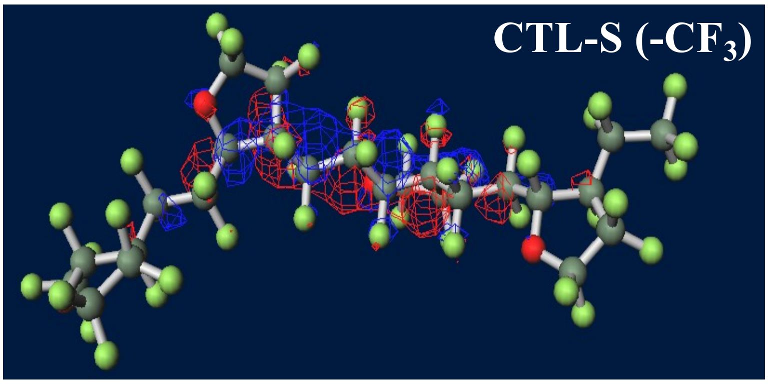
15 μm-thick samples, corona charging

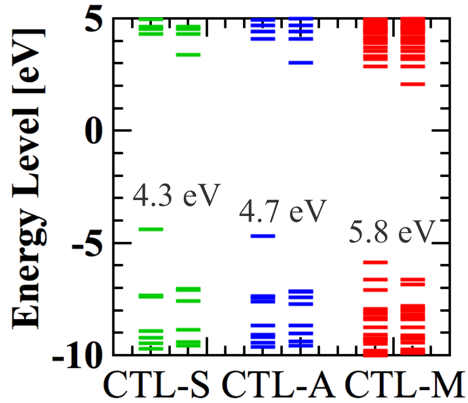


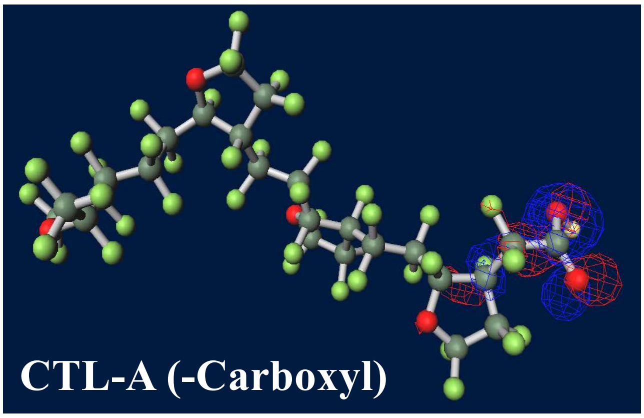
Improvement might be possible with other end group!

Sakane et al. J. Micromech. Microeng (2008), Kashiwagi et al. J. Micromech. Microeng. (2011)

DFT of Charge Trap in CYTOP Electret







- Trend of the energy level is in accordance with surface charge density/TSD data.

LEIPS:
Low-energy Inverse Photocurrent Spectroscopy

S. Kim et al. ISE16, STAM (2018)

Objectives

Develop a new high-performance electret based on solid-state quantum chemical analysis

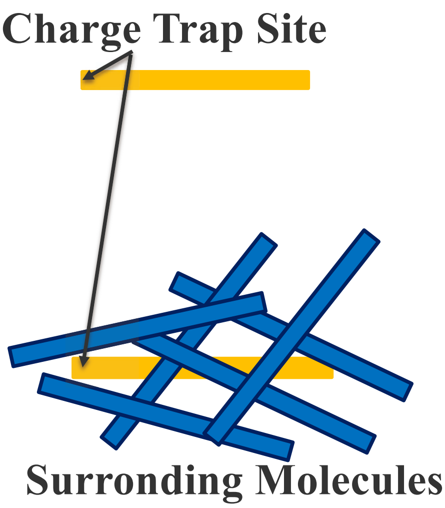
Approach

- **Solid-state quantum chemical analysis of CYTOP**

- Direct comparison with experiments
- Evaluate electron affinity for different end group
- Propose a new high-performance electret

- **Synthesize the new high-performance electret materials**

Solid State Analysis



Single Molecular Analysis

○ Low computational cost

△ 0 K, vacuum state

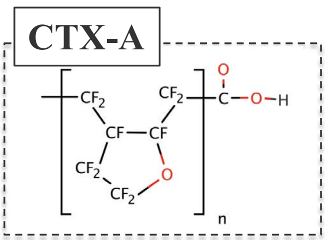
△ Influence of surrounding molecules neglected

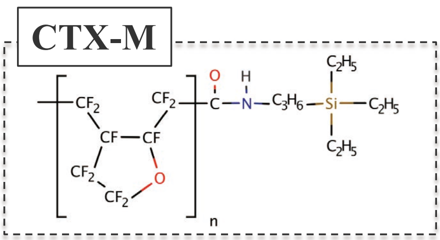
Solid State Analysis

MD Parameter Fitting ⇨ MD Simulation ⇨ QM Calculation & Multipole Analysis ⇨ Solid State Electron Affinity

Search for End Group for Higher EA

CYTOP





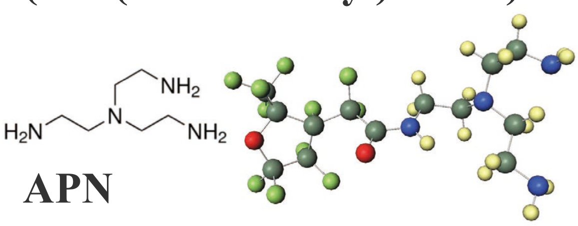
Base material

CYTOP CTX-A

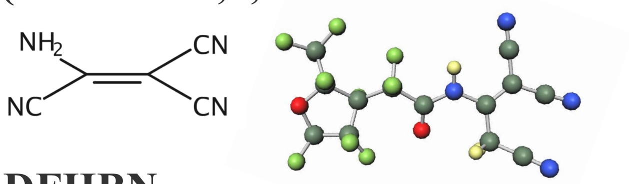
Candidate additives

- **NH_2**
- **CN**

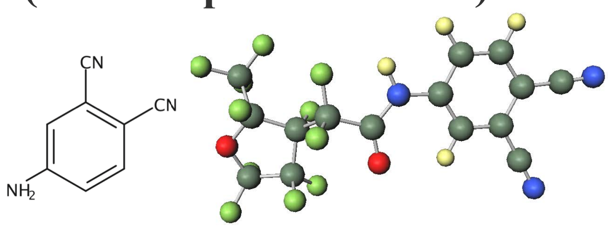
TAA
(Tris(2-aminoethyl)amine)



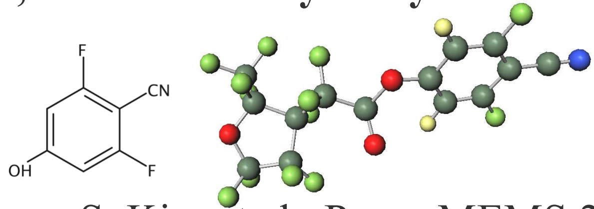
AETCN
(2-Amino-1,1,2-ethenetricarbonitrile)



APN
(4-Aminophthalonitrile)

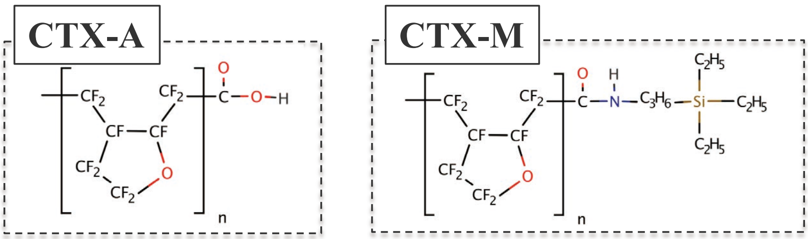


DFHBN
(2,6-Difluoro-4-hydroxybenzonitrile)



S. Kim et al., PowerMEMS 2018

Screening End Group for Higer EA

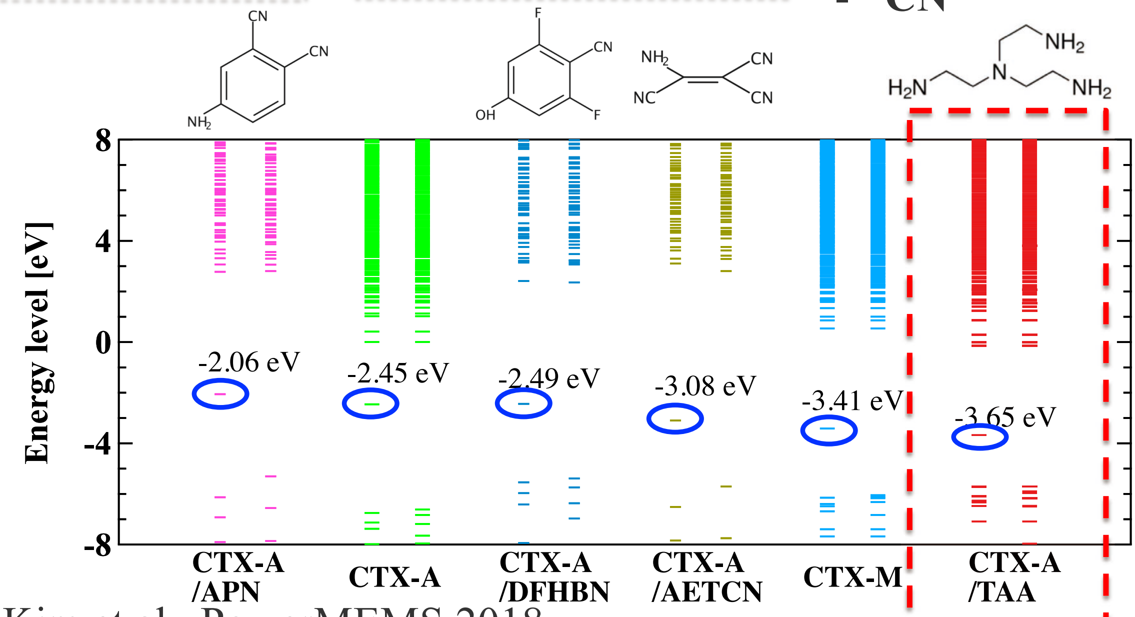


Base material

CYTOP CTX-A

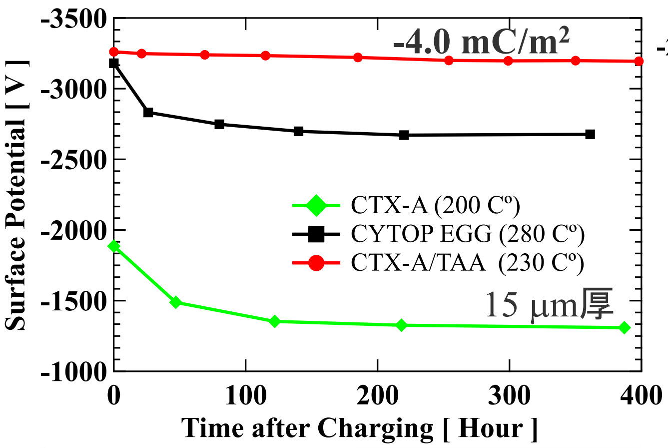
Candidate additives

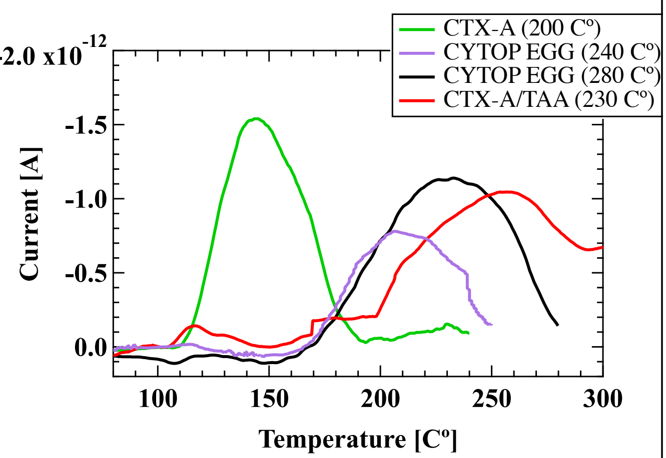
- **NH_3**
- **CN**

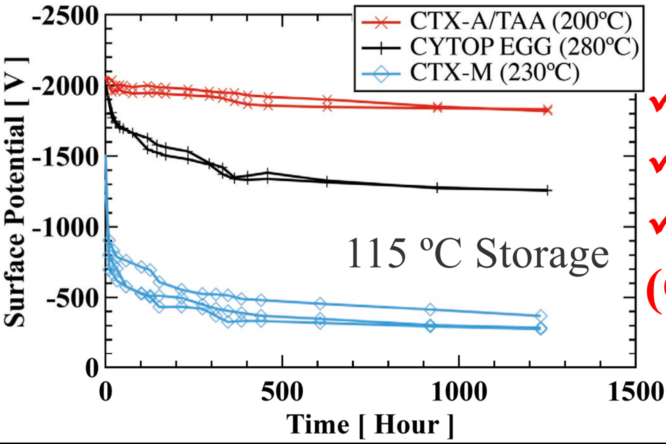


S. Kim et al., PowerMEMS 2018

Charging Performance of New Electret







- ✓ **4.0 mC/m² @ 15μm**
- ✓ **Higher thermal stability**
- ✓ **Lower curing temperature**

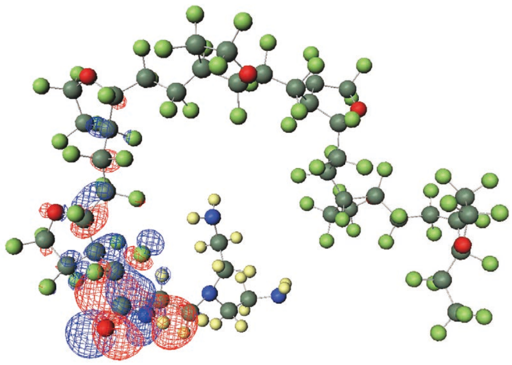
(Good for polymer substrate!)

S. Kim et al., PowerMEMS 2018

Advantages of CYTOP CTX-A/TAA

CYTOP CTX-A

- Inherent high breakdown voltage
- Amorphous fluorinated polymer (no grain boundary)
- Large molecular weight (~ 1000 repeat units)



+TAA

- Localized excess electron near the end group
- High electron affinity
- Long distance between neighboring charge trap (~10^1 nm) to avoid charge hopping
- Relatively-low reaction temperature between TAA and the carboxyl group for low curing temperature

Summary

- ✓ **EA with solid-state quantum chemical analysis is in good accordance with the measured data with LEIPS.**
- ✓ **Among the end groups examined, TAA gives the higest electron affinity when it is combined with CYTOP CTX-A.**
- ✓ **New CYTOP electret (CTX-A/TAA) has been synthesized. Generation of amide bond is confirmed with FT-IR.**
- ✓ **Surface charge density up to -4 mC/m^2 has been obtained. Thermal stability is higher than CYTOP EGG even with lower curing temperature.**