



U.S. Army Research, Development and Engineering Command

# Energy-Storing Structures: Composite Capacitors and Batteries



***TECHNOLOGY DRIVEN. WARFIGHTER FOCUSED.***

**Dr. Danny O'Brien**

**Composite and Hybrid Materials Branch**

daniel.j.obrien58.civ@mail.mil 410-306-0851

**Army Research Laboratory**

RDRL-WMM-A

Aberdeen Proving Ground, MD 21005

**2<sup>nd</sup> Multifunctional Materials for Defense  
Workshop**

Arlington, VA

**30 July 2012**

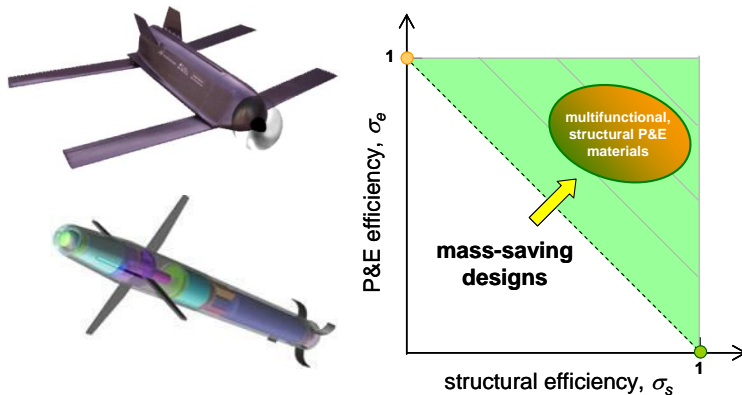
## Report Documentation Page

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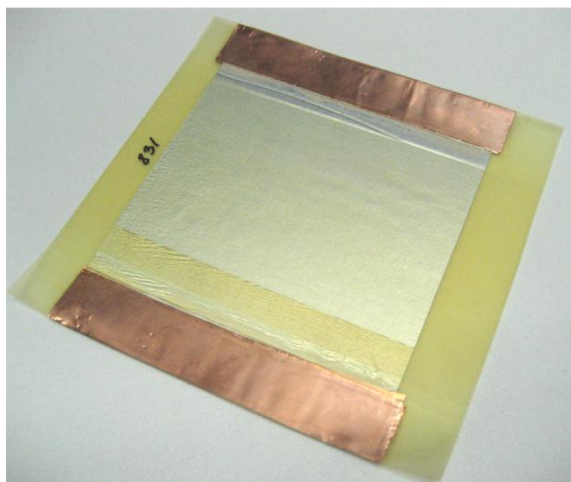
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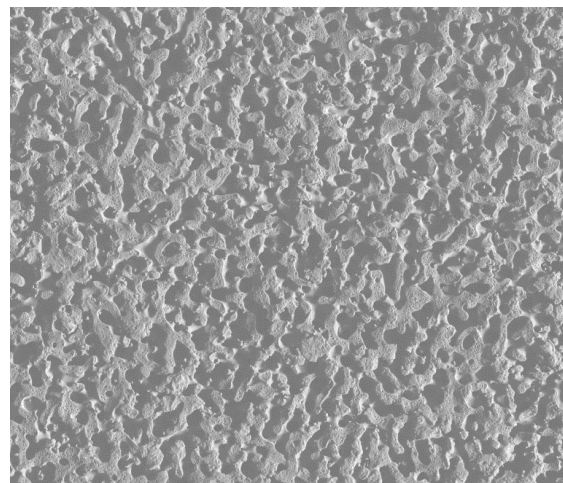
## Motivation and Approach



## Structural Capacitors

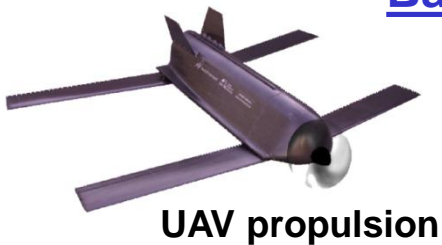


## Structural Batteries



ARL research team: Eric Wetzel, Jim Snyder, Danny O'Brien, Dan Baechle, Eddie Geinger, Oleg Yurchak, Wai Chin, Kris Behler

## Batteries



UAV propulsion

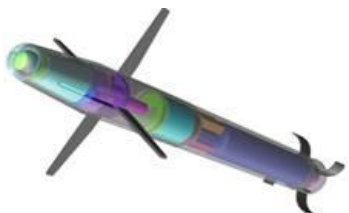
night vision goggles, radios



hybrid electric-combustion powerplants



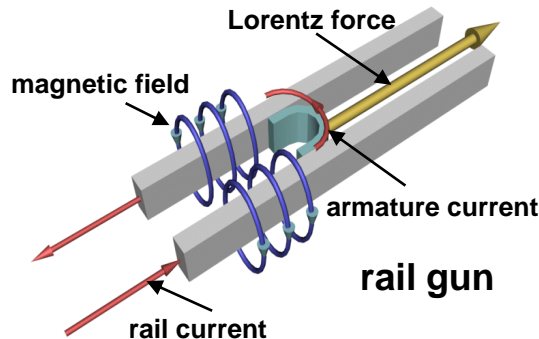
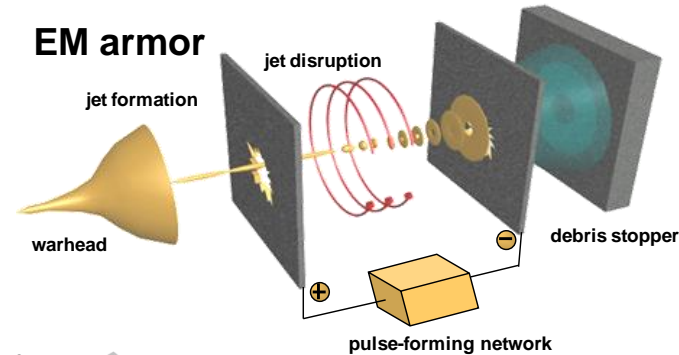
smart munition sensing, control, computation



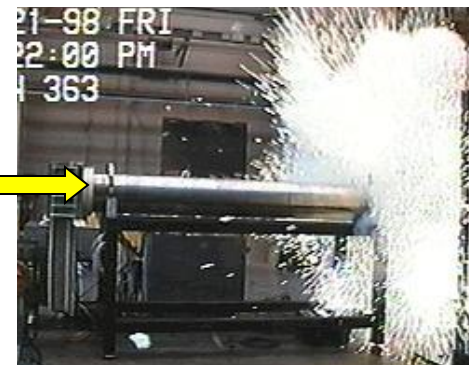
## Capacitors

*pulsed power applications*

EM armor

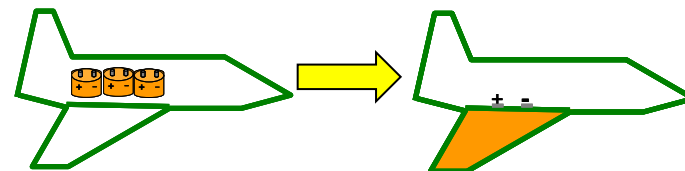
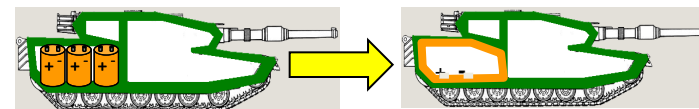


rail gun



## Objective

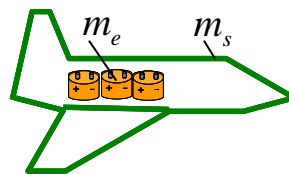
**Reduce system mass (or volume) by creating batteries and capacitors that can carry mechanical loads. Batteries / capacitors serve as structural or armor elements.**



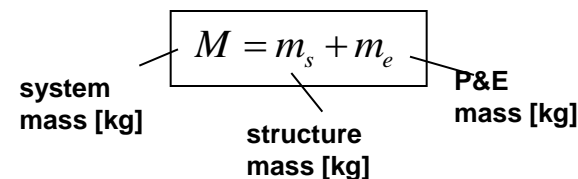
$\sigma_e$  → mass-normalized P&E efficiency  
 $\sigma_s$  → mass-normalized structural efficiency

$$\sigma_e = \frac{\bar{E}_{se}}{\bar{E}_e}$$

$$\sigma_s = \frac{\bar{S}_{se}}{\bar{S}_s}$$



## Conventional design



## Multifunctional design

$$M^* = m_s^* + m_e^* + m_{se}^* \quad \text{structural P\&E mass [kg]}$$

$$= (m_s - \sigma_s m_{se}^*) + (m_e - \sigma_e m_{se}^*) + m_{se}^*$$

$$= (m_s + m_e) + (1 - \sigma_s - \sigma_e) m_{se}^*$$

$$(M - M^*) = (\sigma_s + \sigma_e - 1) m_{se}^*$$

mass-savings can be achieved if:

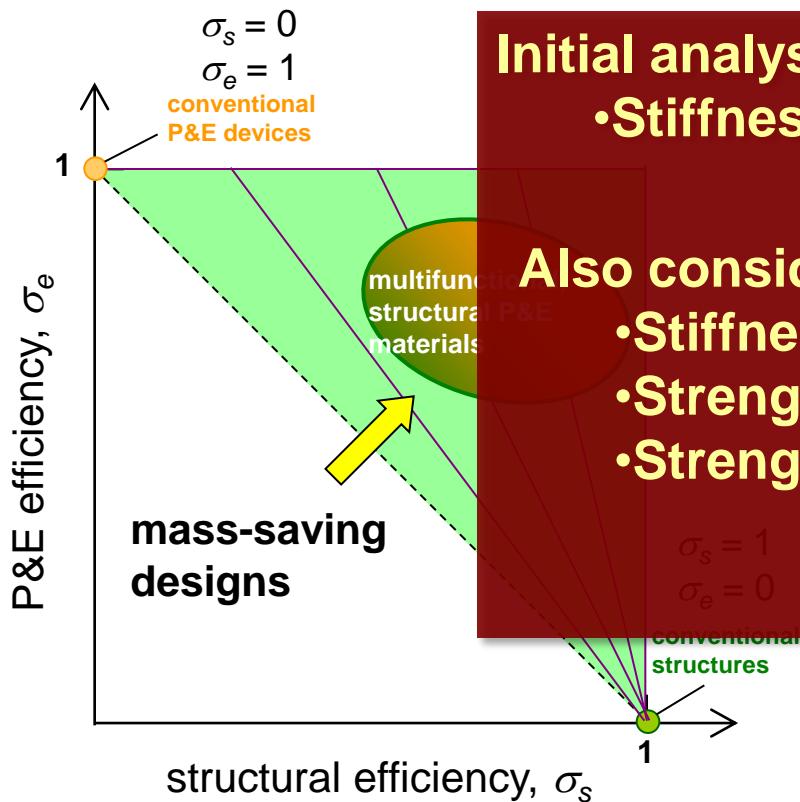
$$\sigma_{mf} \equiv \sigma_e + \sigma_s > 1$$

**Initial analysis driven by:**

- Stiffness / Mass

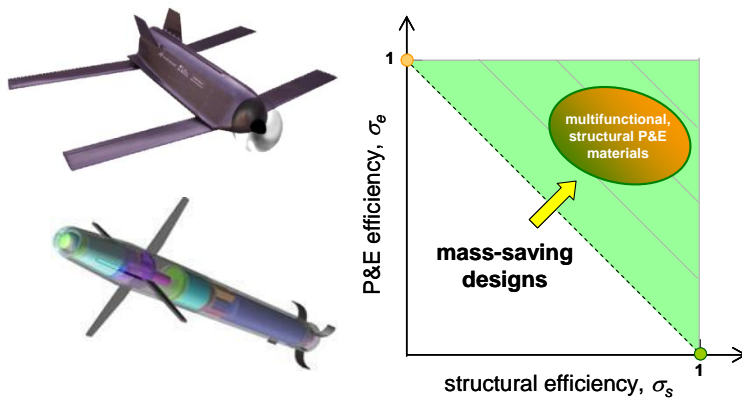
**Also consider:**

- Stiffness / Volume
- Strength / Mass
- Strength / Volume

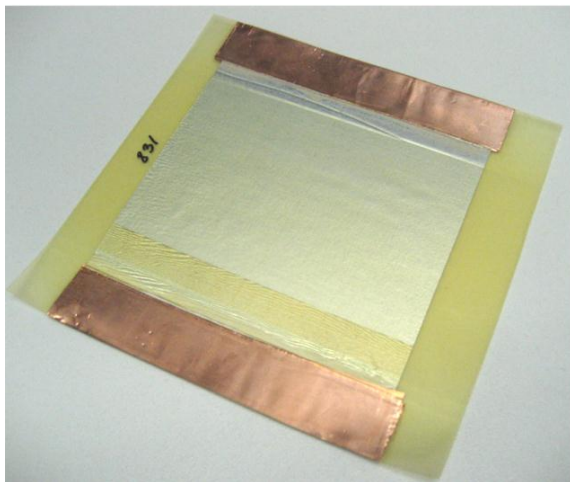


**Mass savings possible even if multifunctional material performs individual functions less efficiently than monofunctional materials.**

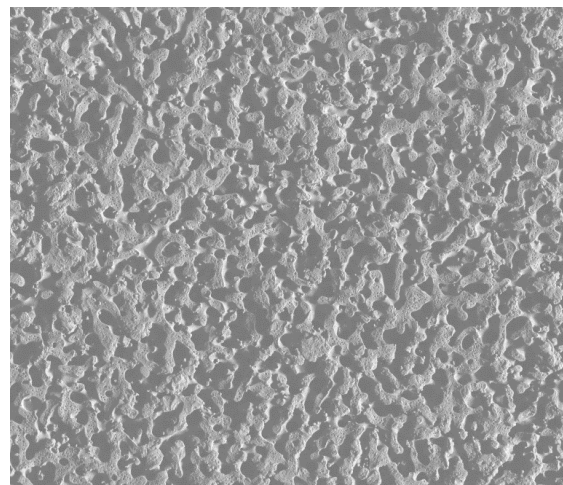
## Motivation and Approach



## Structural Capacitors

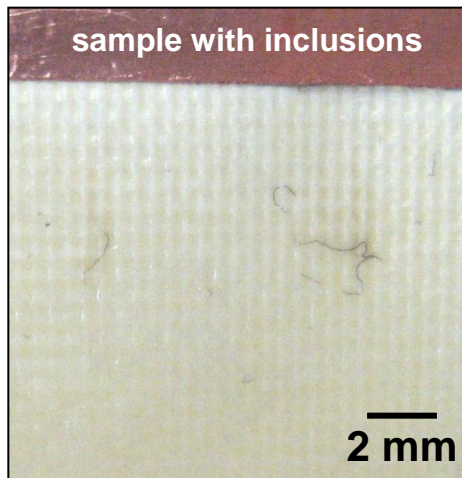


## Structural Batteries

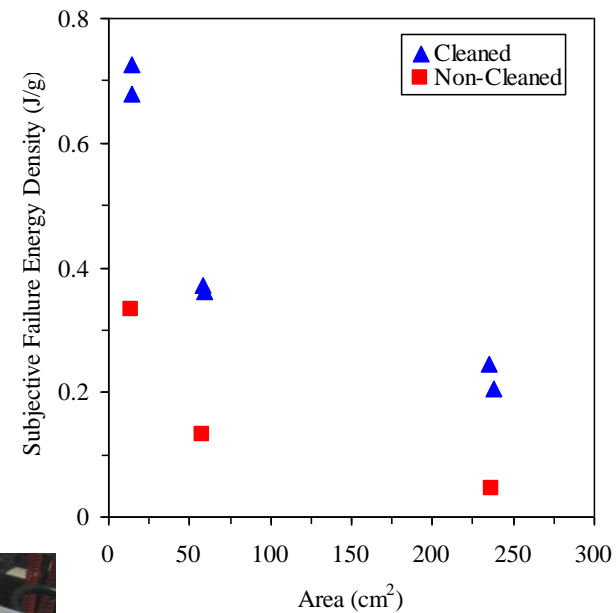




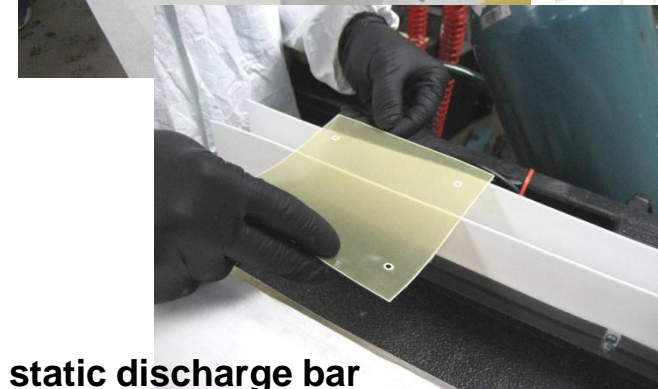
**laminar flow room**



**solvent wipe**

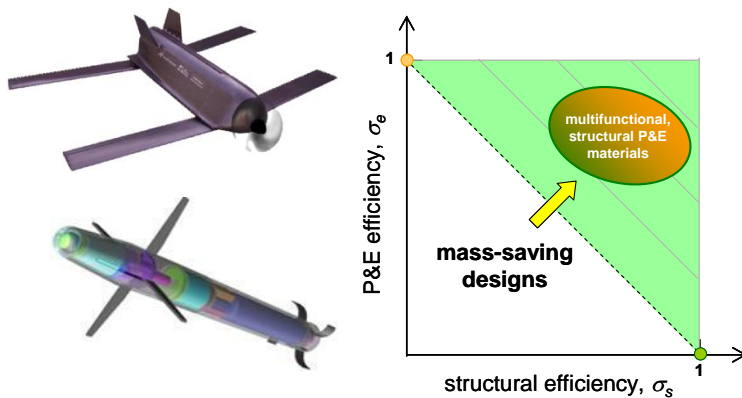


**dry nitrogen**

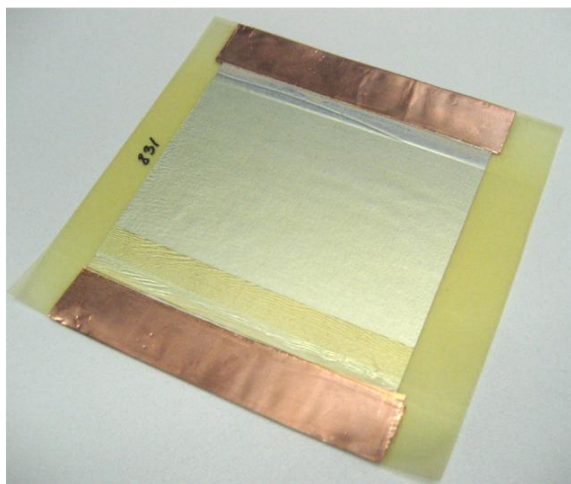


**static discharge bar**

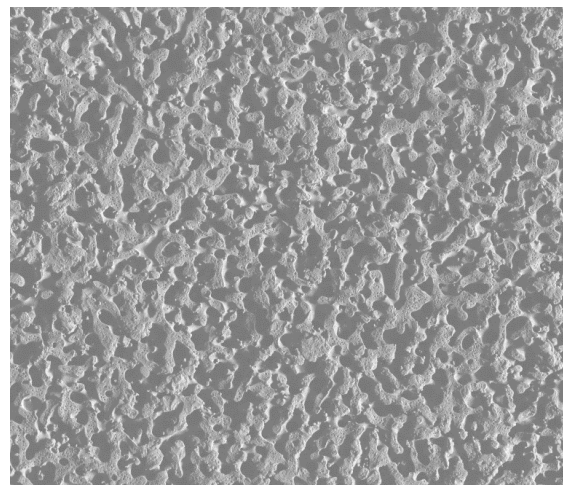
## Motivation and Approach



## Structural Capacitors



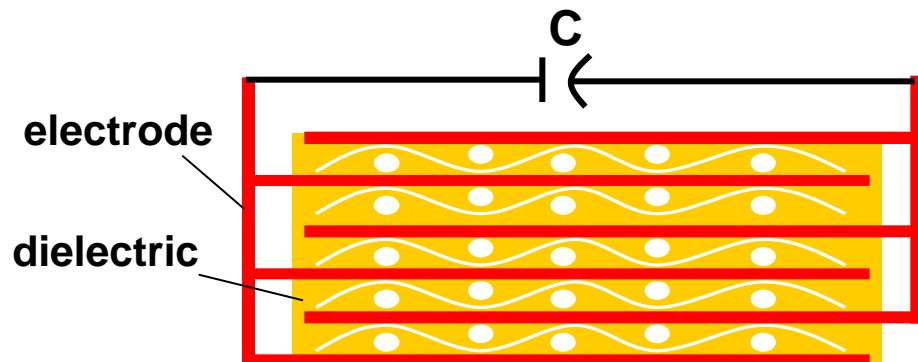
## Structural Batteries





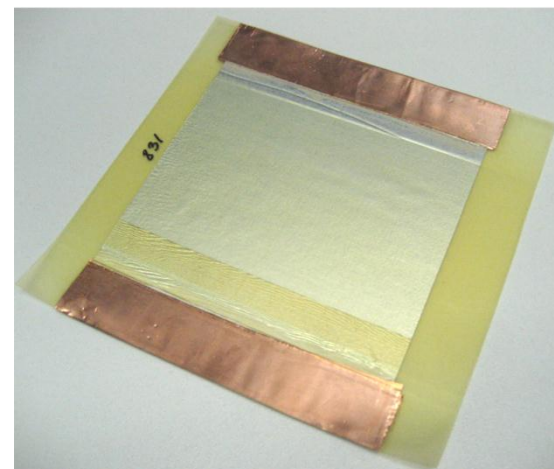
## Electrodes

- Metallized films and papers
- Examples: 100 nm Al on Kapton film, 20 nm Al on Kraft paper



## Composite dielectric

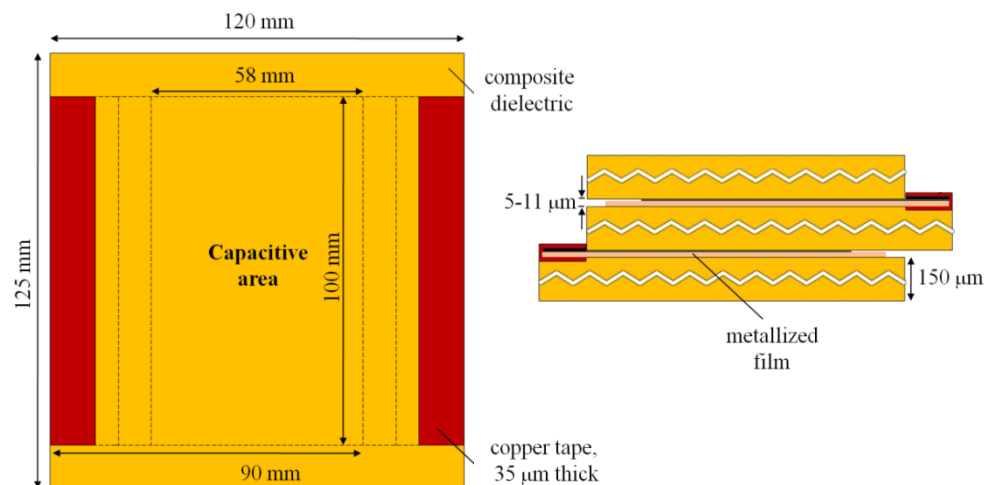
- Glass fiber-reinforced polymers
- Example: Nelcote printed circuit board (PCB) prepreg

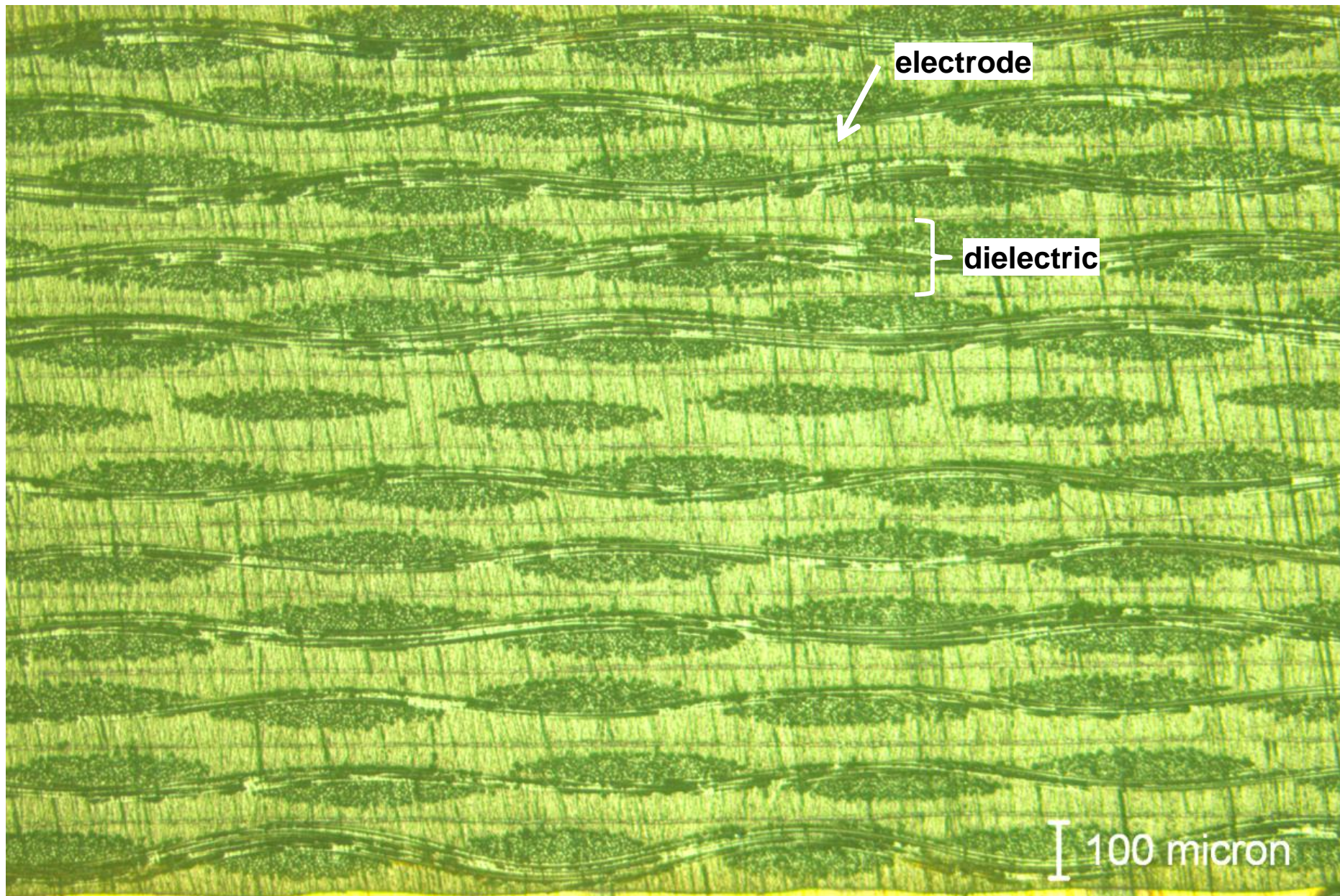


Autoclave-processed structural capacitor

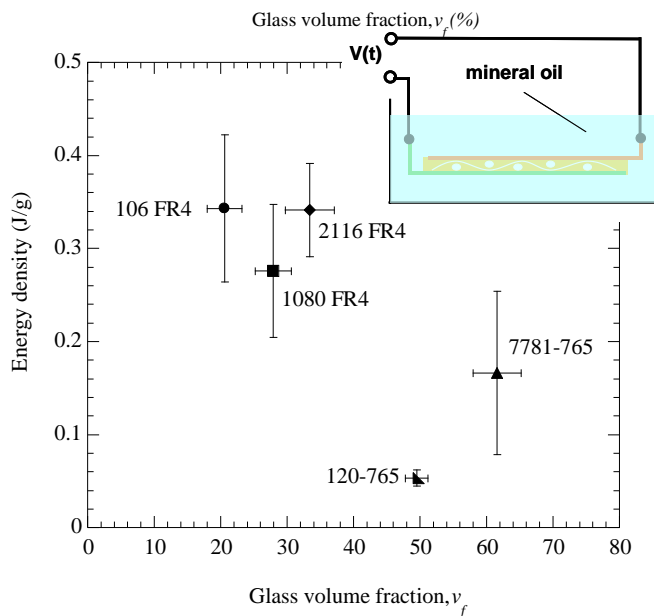
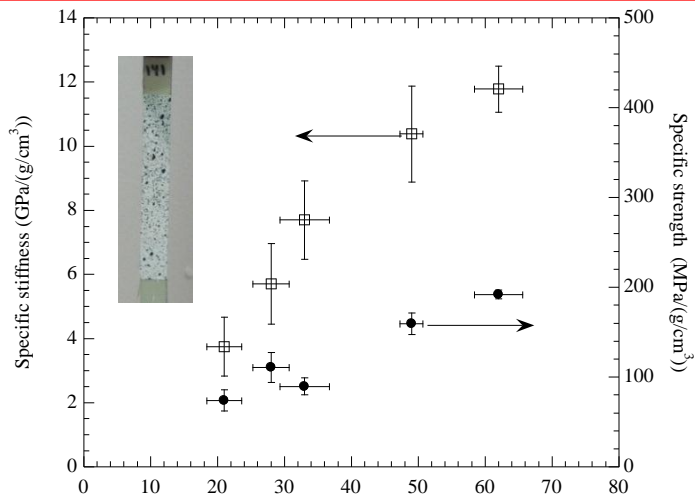
## Objective: High energy density, scalable structural capacitor

- High energy density
  - Vanishingly thin electrodes
  - Low void content
- Scaling
  - Clean processing
  - Self-clearing electrodes
  - Scalable assembly

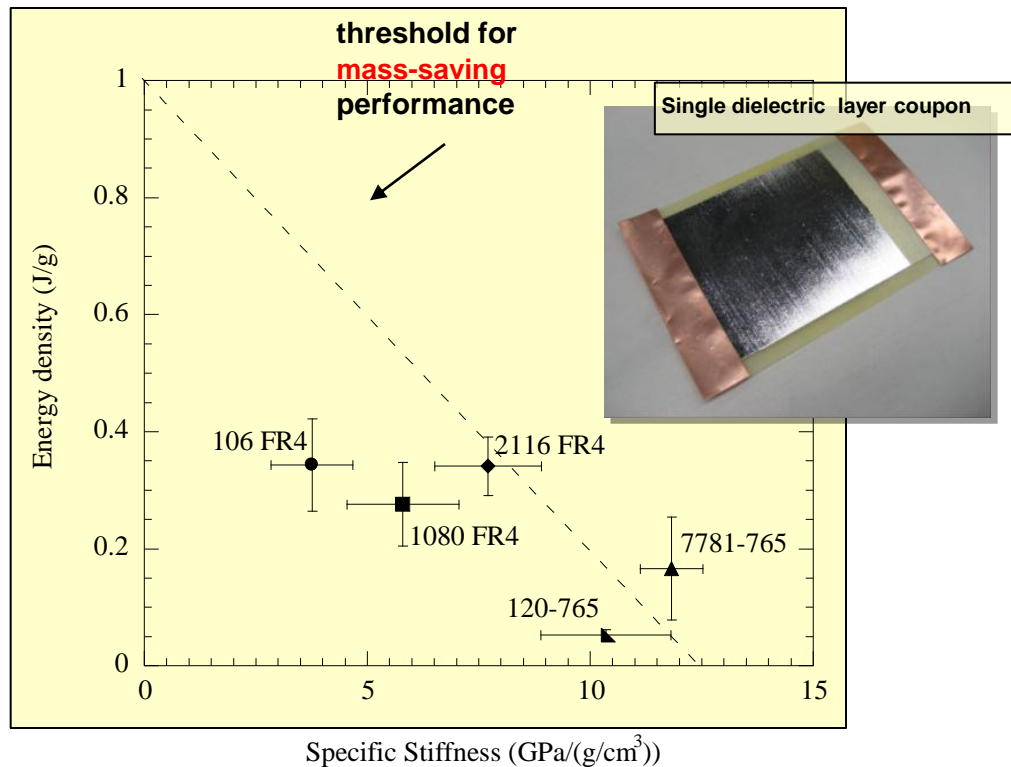


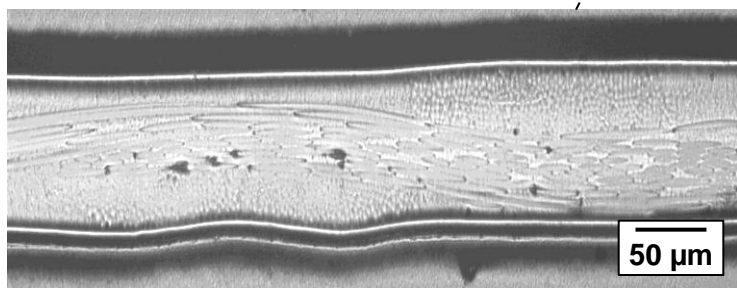
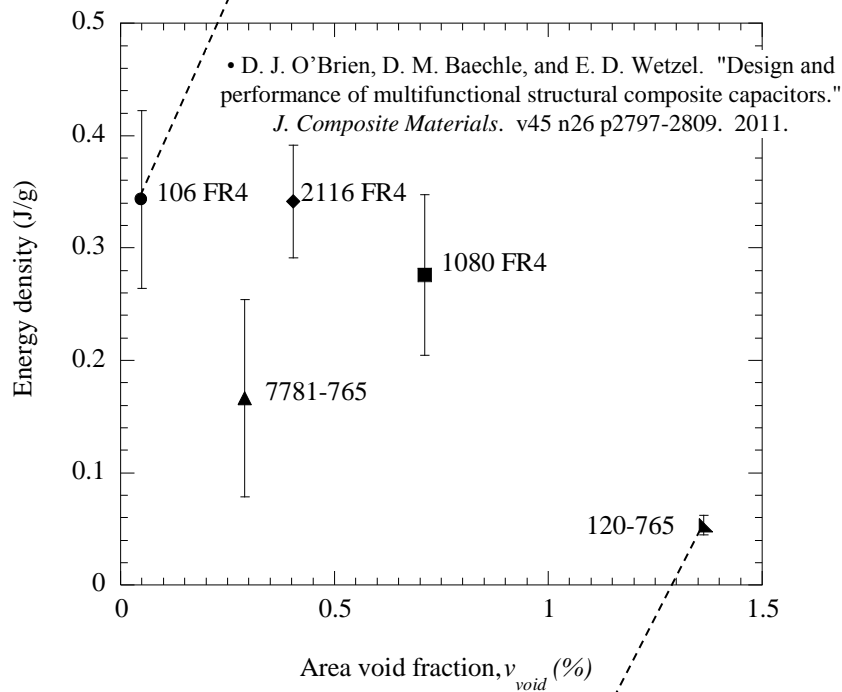
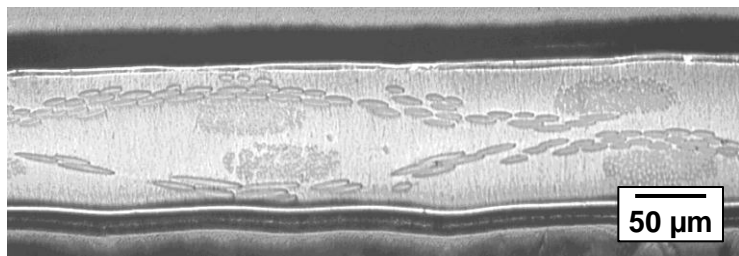


**Fiber volume fraction study showed that good multifunctional performance is obtained at high fiber volume fractions.**

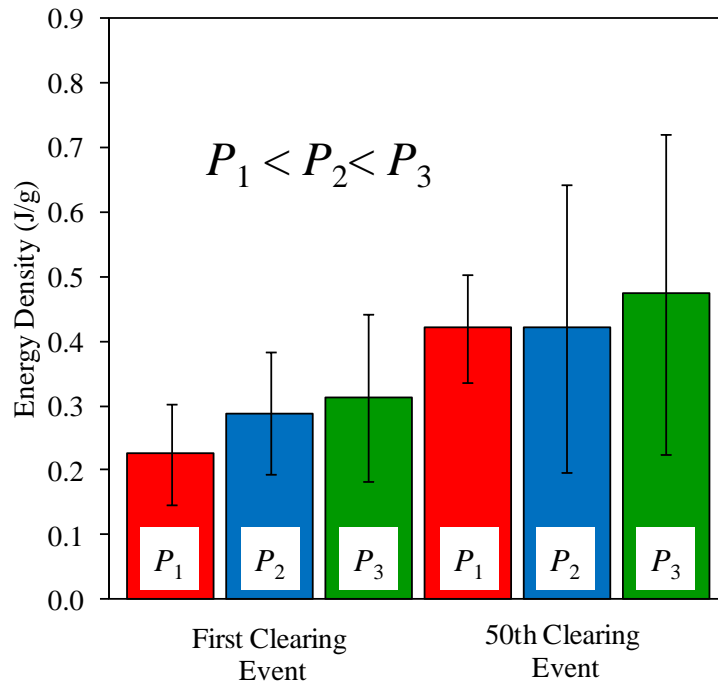


Group	Fabric type	Matrix type	Weave type	Fabric thickness (mm)	Areal density (g/m <sup>2</sup> )
1	106	FR4 (PCB)	Plain	0.04	25
2	1080	FR4 (PCB)	Plain	0.06	49
3	2116	FR4 (PCB)	Plain	0.10	109
4	120	765 (struct)	4H Satin	0.09	107
5	7781	765 (struct)	8H Satin	0.22	299

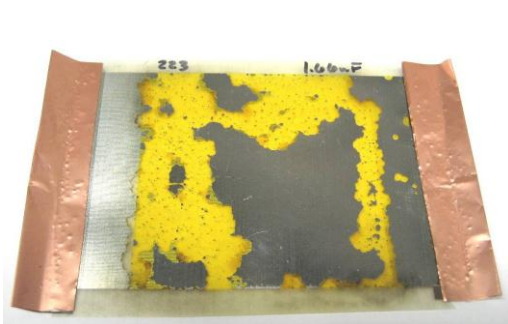




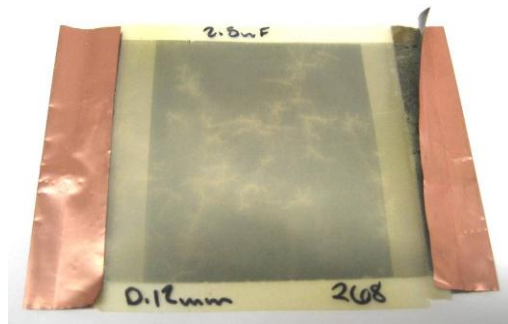
- **Energy density decreases with increasing void fraction**
  - Voids concentrate electric fields and reduce local dielectric strength
- **Processing needs to be optimized to minimize void generation, growth, and persistence**
  - High pressure processing
  - Minimize volatilization



## Self-clearing electrodes to enhance flaw tolerance

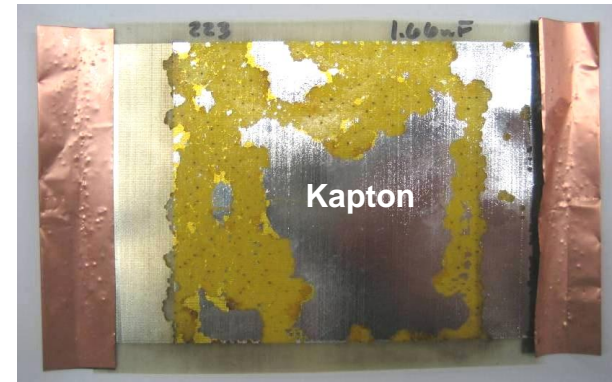


Kapton electrode



Kraft paper electrode

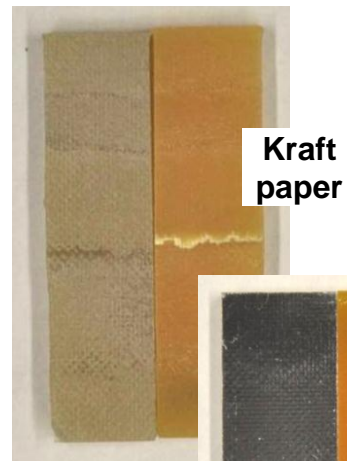
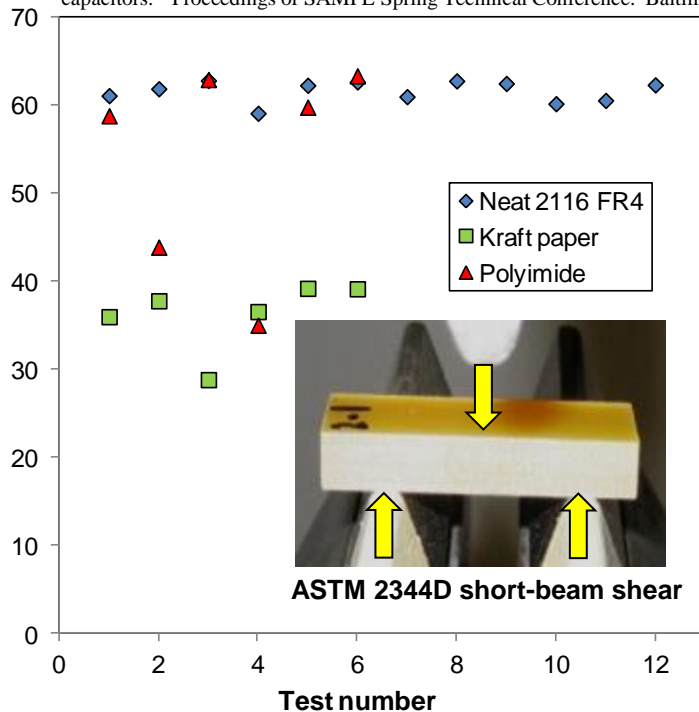
## Electrode connectorization



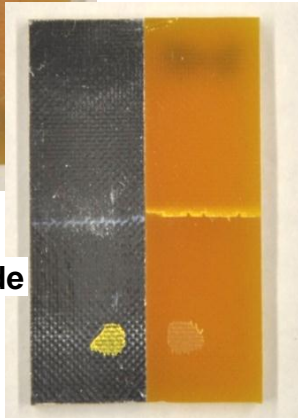
Kapton

## Mechanical performance

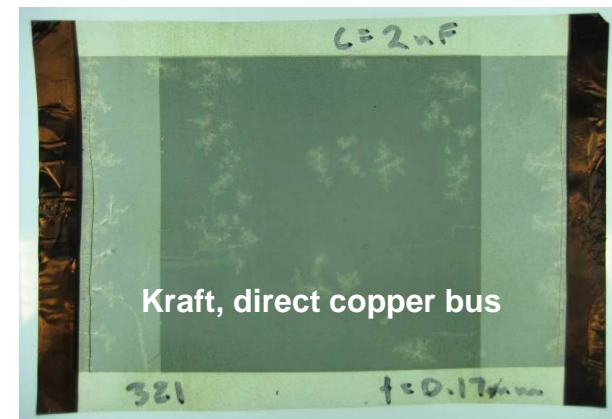
• O.B. Yurchak, D. J. O'Brien, D. M. Baechle, and E. D. Wetzel. "Shear properties of multifunctional structural capacitors." Proceedings of SAMPE Spring Technical Conference. Baltimore, MD. May 21-24, 2012.



Kraft paper



polyimide

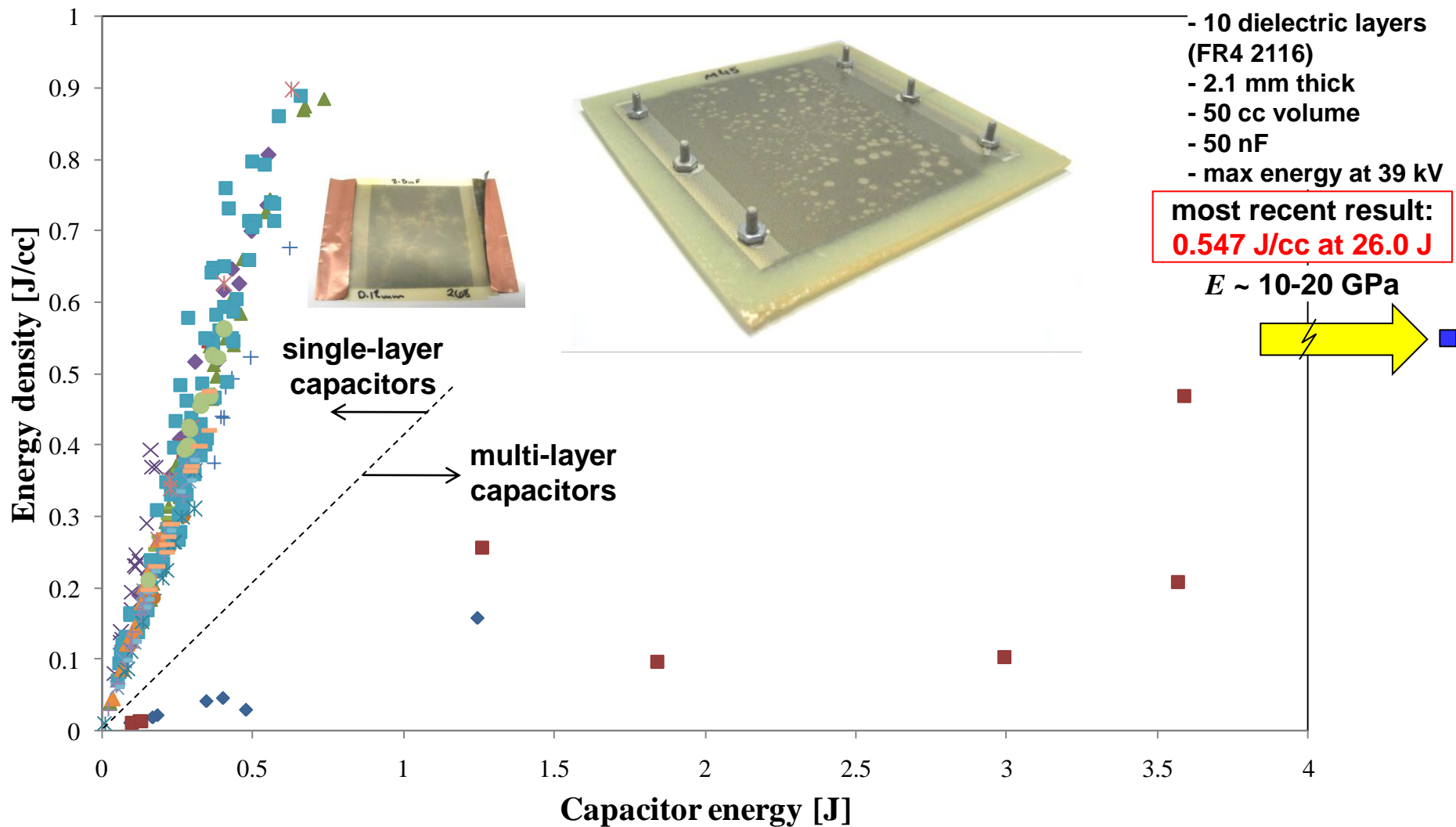


Kraft, direct copper bus

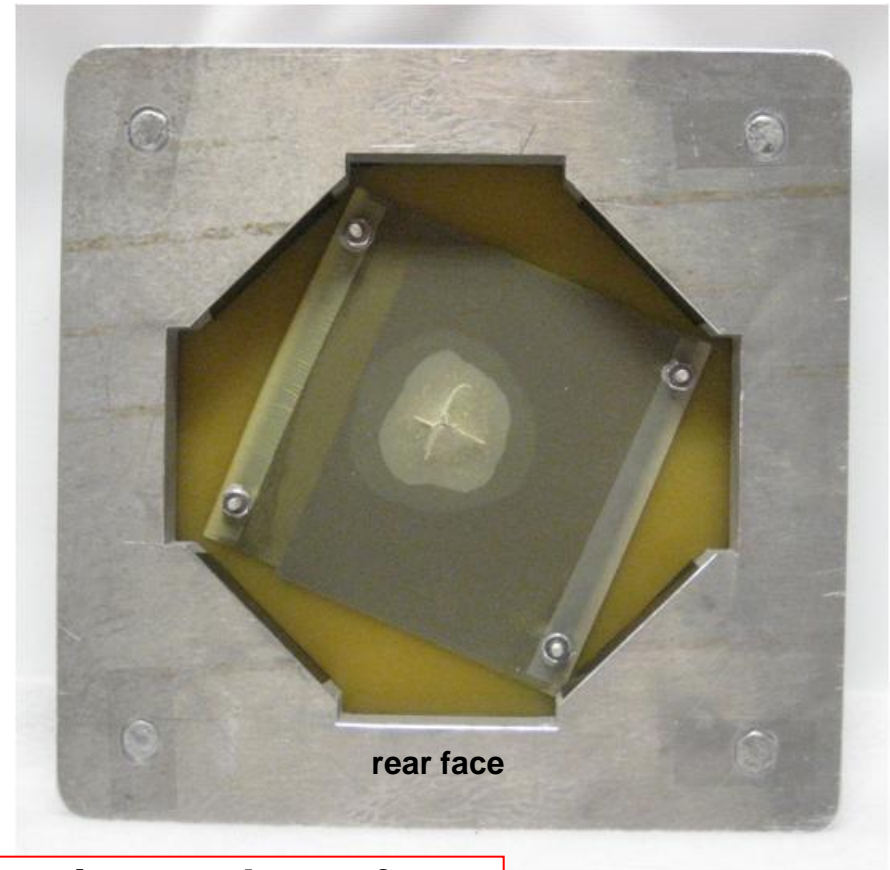
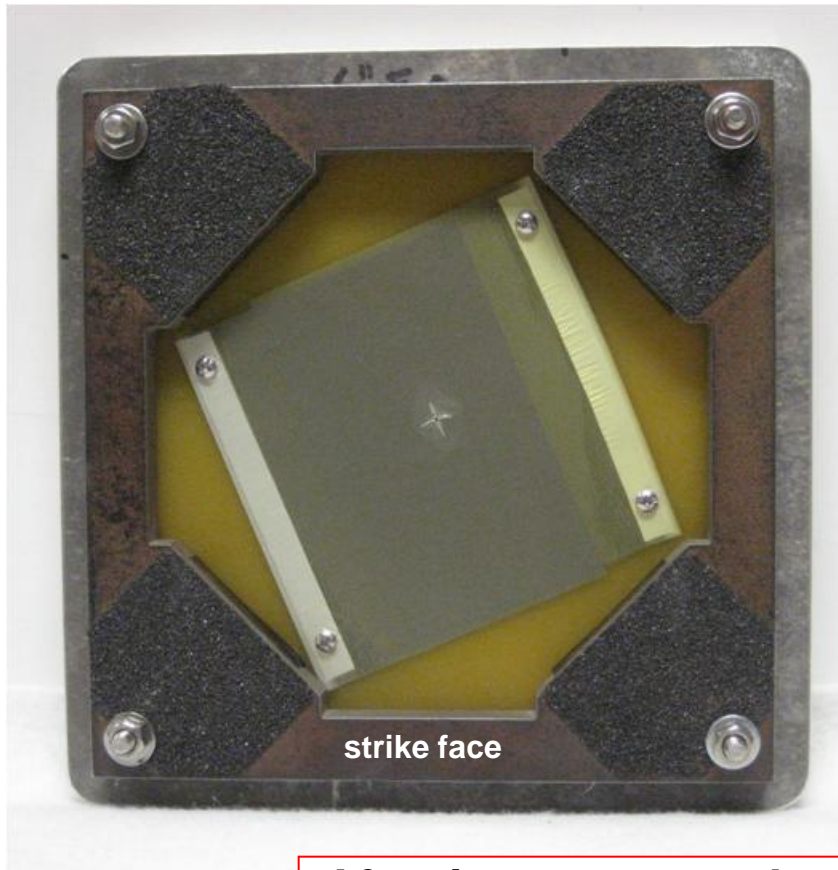


Kraft, silver paint / copper bus

- Developed **scalable assembly technique** for efficient stacking of many (dozens) electrode, dielectric, and bus layers
- Maintaining **excellent energy density** up to high energies (volume)

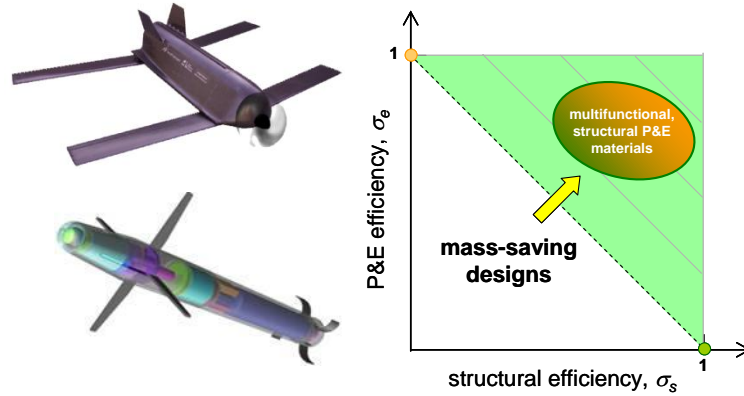


- **Ballistically impact** 4-dielectric layer, FR4-2116 composite panel **while energized at 15 kV**
  - 203 x 203 x 2 mm panels
  - Impacted with 0.22 cal steel sphere at 667 fps (penetration)

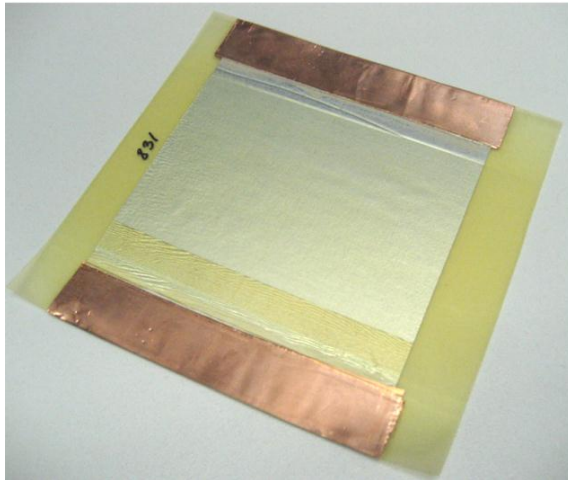


After impact... panel capacitance drops from 16.7 nF to **13.5 nF**, but **still holds 15 kV**.

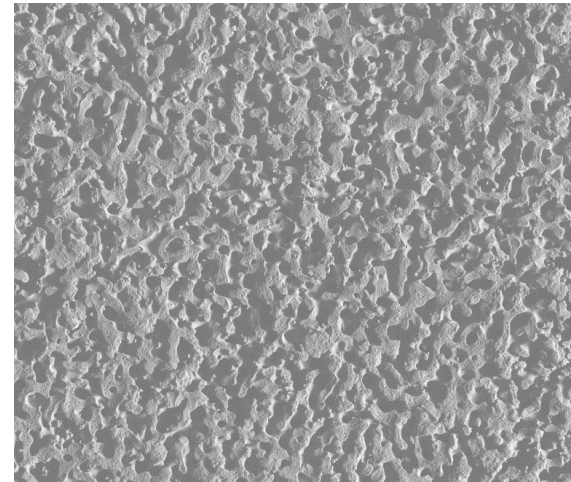
## Motivation and Approach



## Structural Capacitors



## Structural Batteries





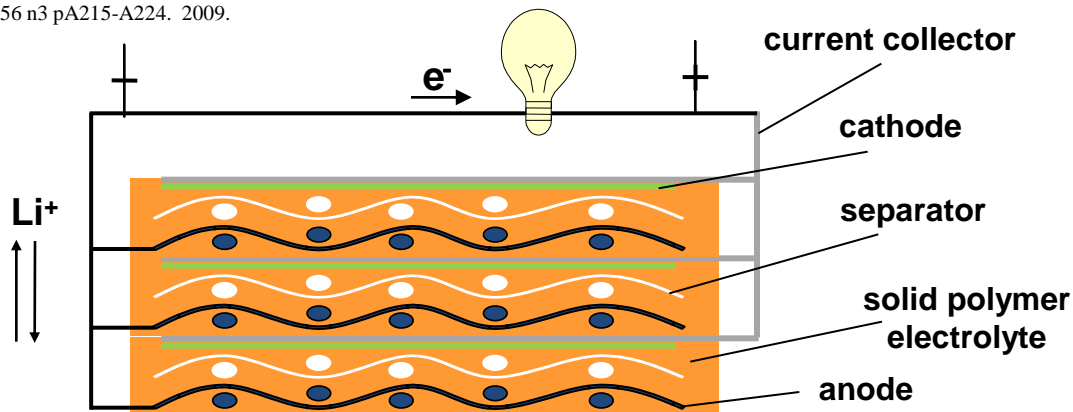
## Anodes

- **Intercalates** Li ions and provides structural reinforcement
- **Example:** T-300 PAN-based carbon fiber fabric

## Separator

- Provides **electrical insulation** while permeable to electrolyte and ions
- **Examples:** glass veil cloth, Celgard<sup>®</sup> porous polypropylene

J. F. Snyder, E. L. Wong, and C. W. Hubbard. "Evaluation of commercially available carbon fibers, fabrics, and papers for potential use in multifunctional energy storage applications." *J. Electrochem Soc.* v156 n3 pA215-A224. 2009.



## Cathode

- Comprised of current collector + active cathode material
- Reacts with Li ions, busses electrons, and provides structural reinforcement
- **Example:** Perforated stainless steel foil coated with  $\text{LiFePO}_4$  + acetylene black + binder

## Electrolyte

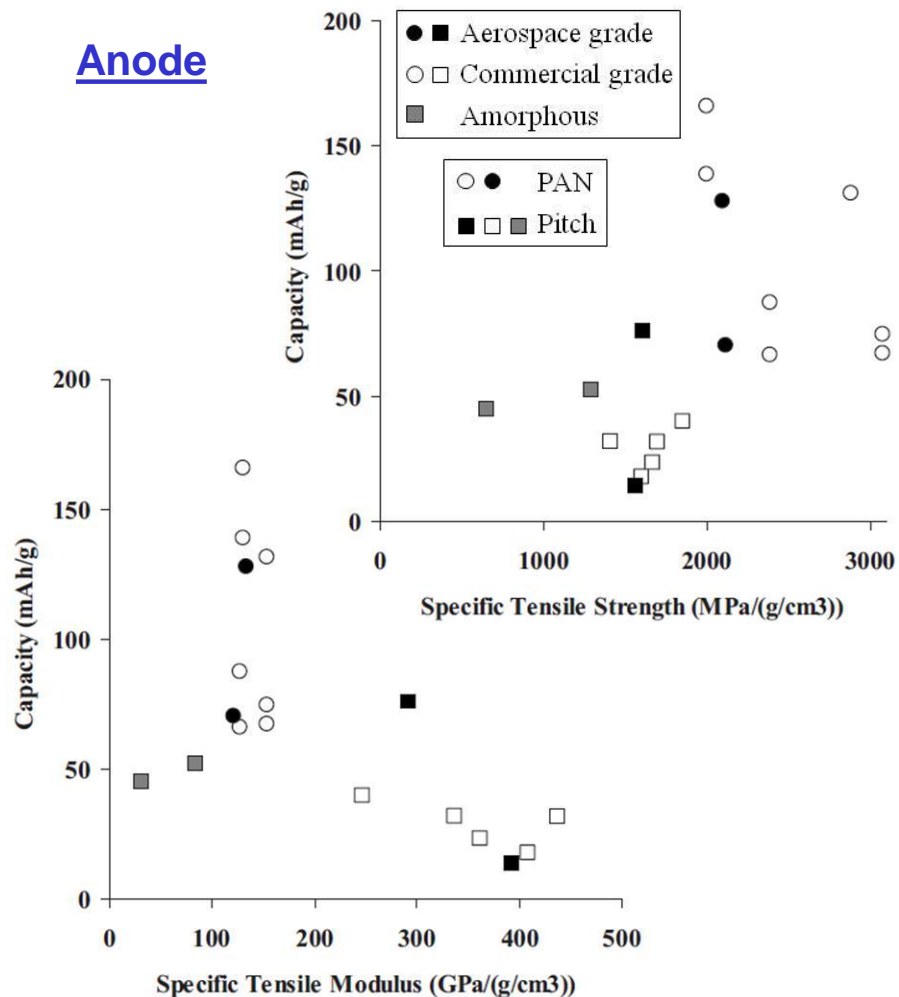
- **Solid polymer electrolyte** → provides balance of mechanical properties and ion conductivity

**Most critical technical / scientific challenge**

• E.B. Gienger, J.F. Snyder, E.D. Wetzel, and K. Xu. "Multifunctional structural composite supercapacitor development and evaluation." Proceedings of SAMPE Spring Technical Conference. Baltimore, MD. May 21-24, 2012.

← (these electrolytes are also needed for structural **supercapacitors**)

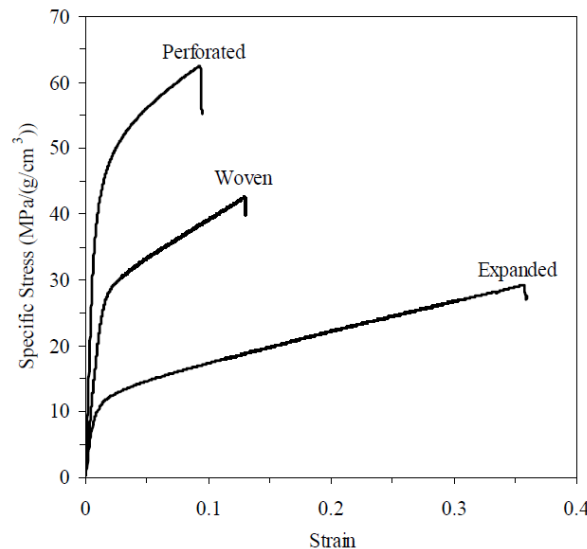
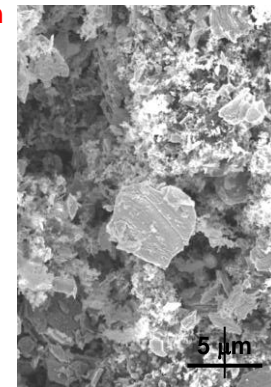
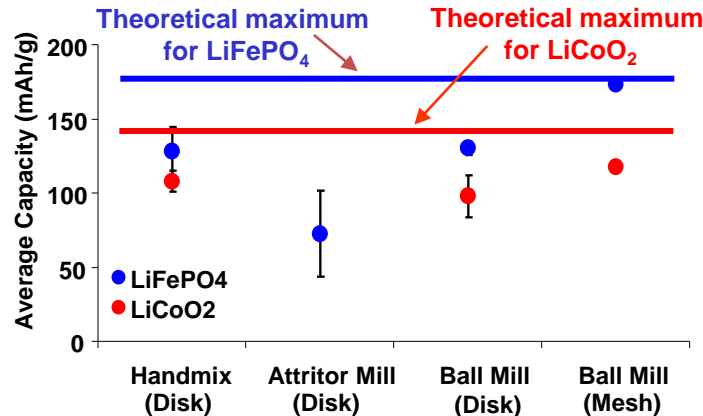
## Anode



**Traditional structural carbon fiber reinforcement should provide excellent anodic functionality.**

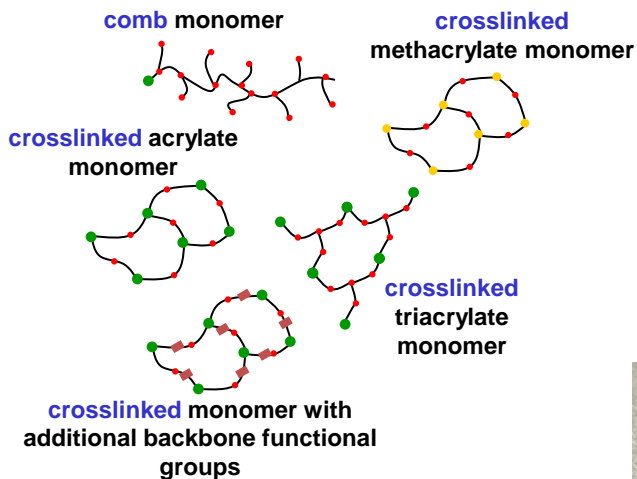
J. F. Snyder, E. L. Wong, and C. W. Hubbard. "Evaluation of commercially available carbon fibers, fabrics, and papers for potential use in multifunctional energy storage applications." *J. Electrochem Soc.* v156 n3 pA215-A224. 2009.

## Cathode



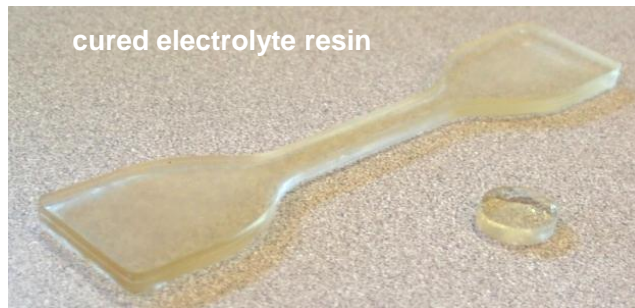
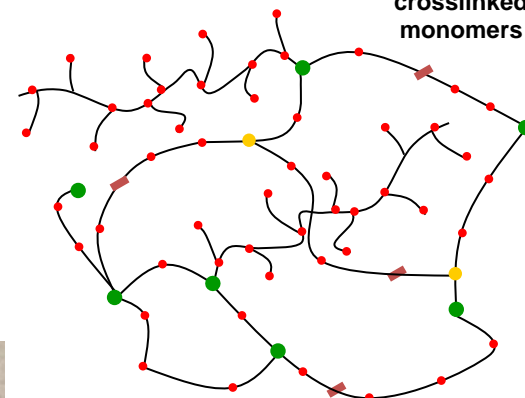
**Cathode and current collector components provide good performance... but challenging to integrate.**

## Homopolymers

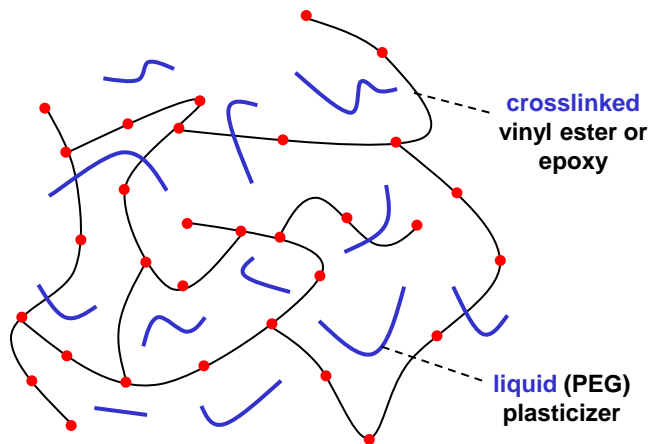


## Copolymers

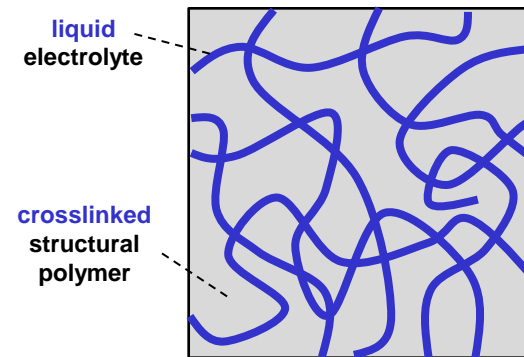
copolymer of comb monomers and crosslinked monomers



## Gels



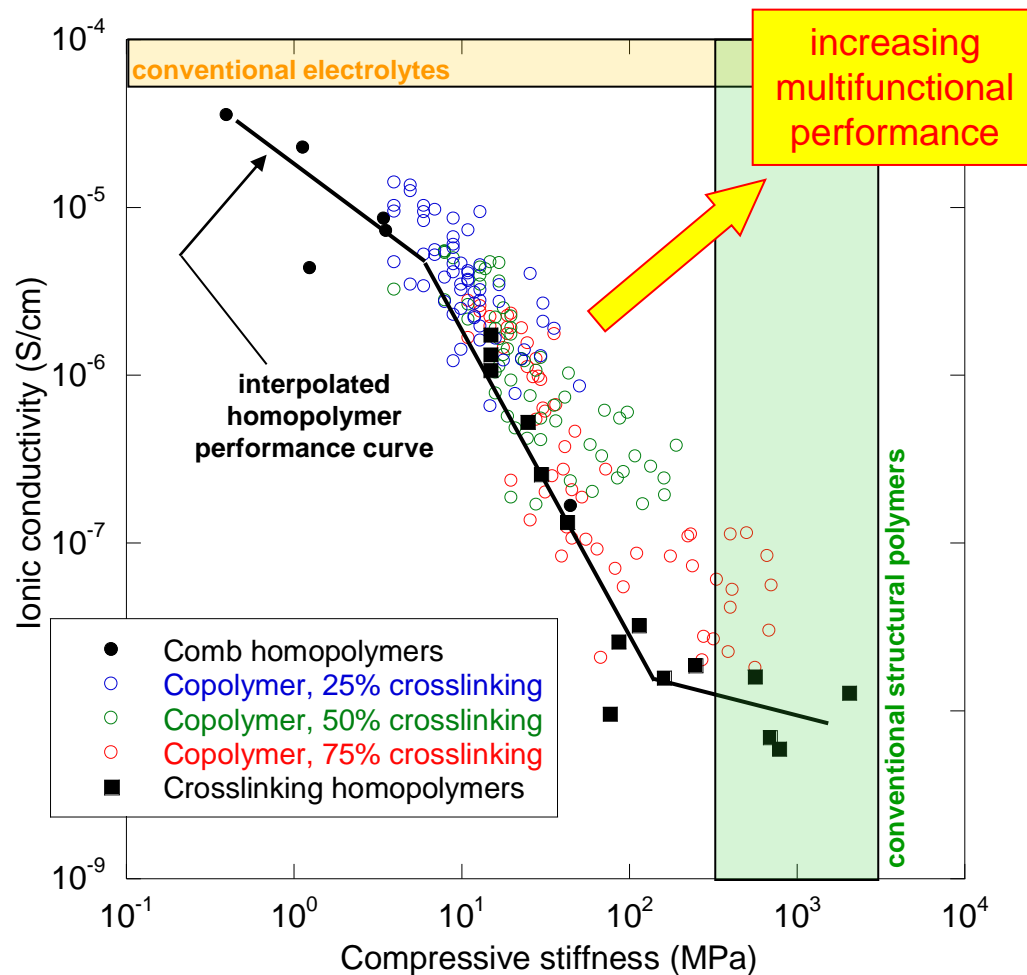
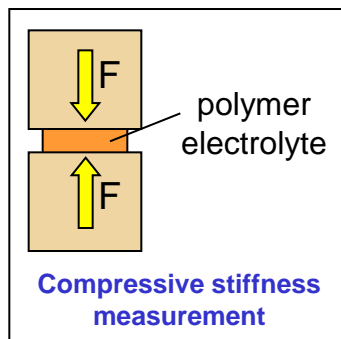
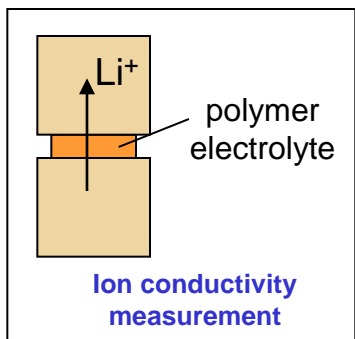
## Micro-foams



1-100  $\mu\text{m}$

• J. F. Snyder, R. H. Carter, E. D. Wetzel. "Electrochemical and mechanical behavior in mechanically robust solid polymer electrolytes for use in multifunctional structural batteries." *Chem. Mater.* v19 n15 p3793-3801. 2007.  
 • J. F. Snyder, C. Watson, and E. D. Wetzel. "Improving multifunctional behavior in structural electrolytes through copolymerization of structure- and conductivity-promoting monomers." *Polymer.* v50 p4906-4916. 2009.

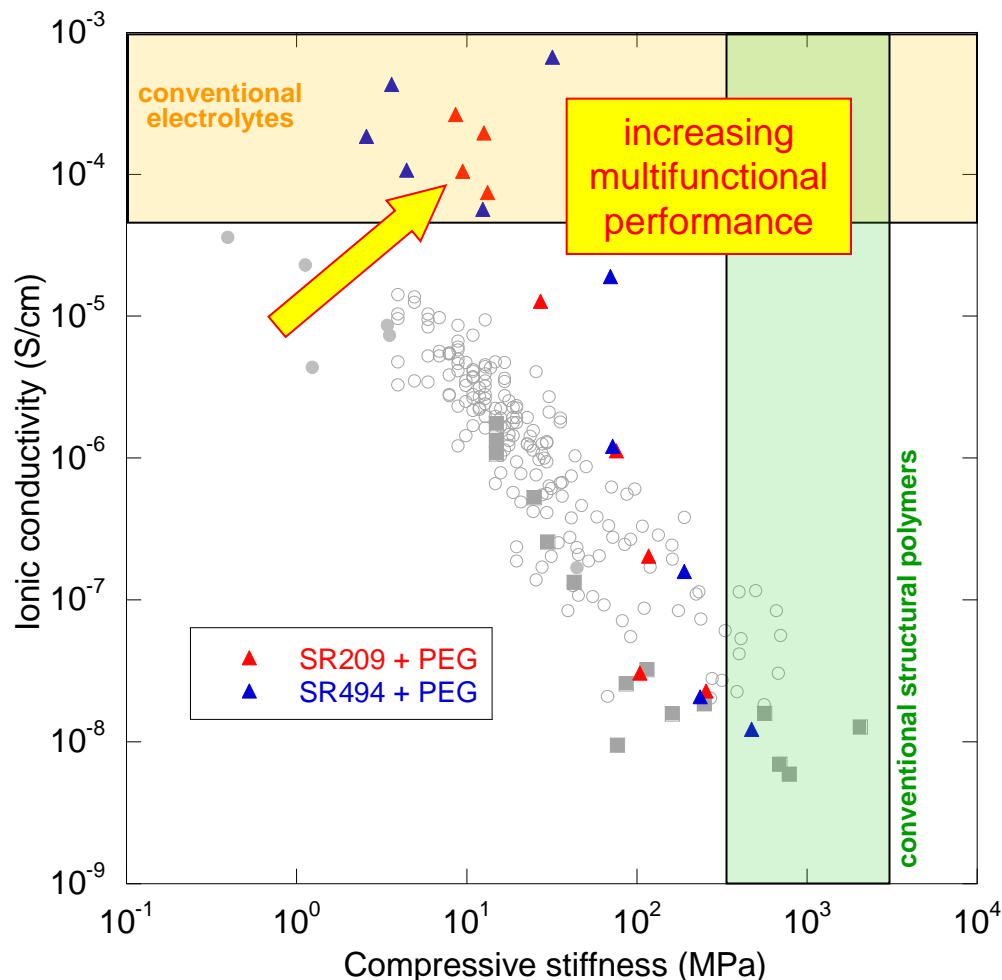
- Vinyl ester backbones
- PEG combs / plasticizers
- Variations in
  - Nature, number of reactive groups
  - PEG length and concentration
  - Endgroups (combs)
  - Crosslinking groups (networks)
- Polymers complexed with lithium triflate for ionic conductivity



- Clear **inverse correlation** between **mechanical properties** and **conductivity**
  - **Copolymers show improved multifunctionality** versus homopolymers

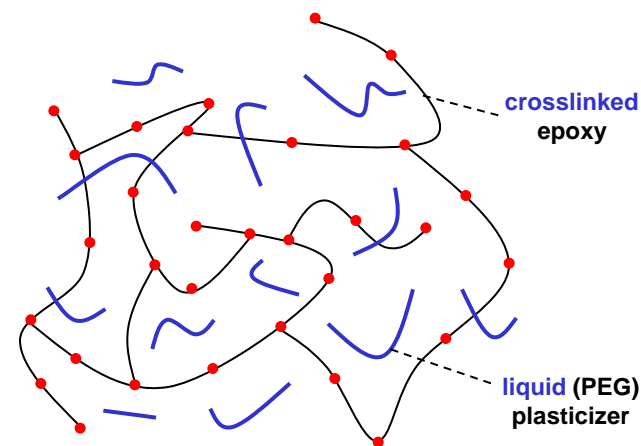
P. T. Nguyen and J. F. Snyder. "Multifunctional properties of structural gel electrolytes."  
*ECS Transactions*. v11 n32. 2007.

- Gel electrolytes provide greatly **enhanced multifunctional performance**

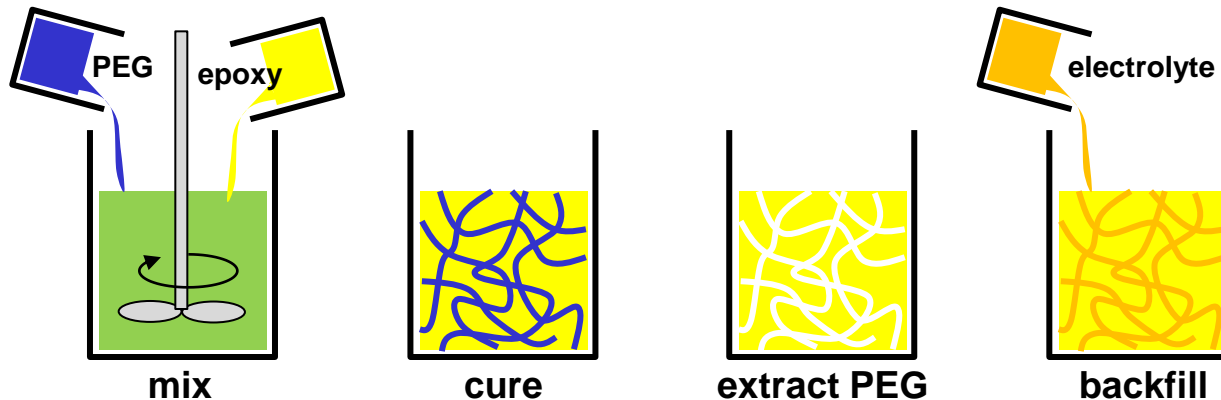


Gel electrolytes provide good balance of mechanical performance and ion conductivity

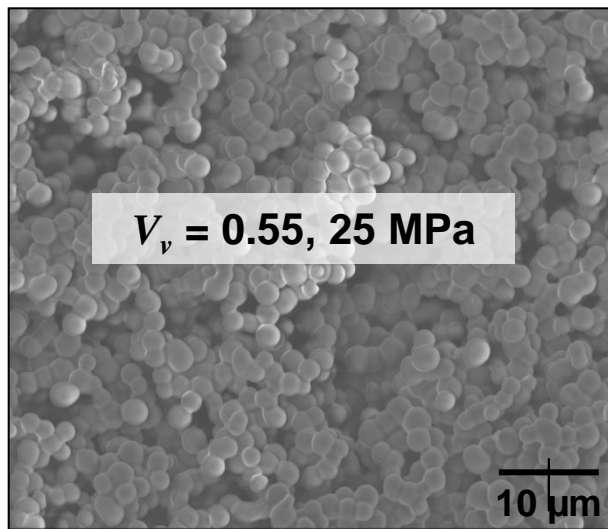
Example epoxy-based electrolyte:  
EPON 828 epoxy plasticized with 80% liquid electrolyte  
( $C_2HF_6NO_4S_2$  dissolved in 50:50 ethylene carbonate and dimethyl carbonate)



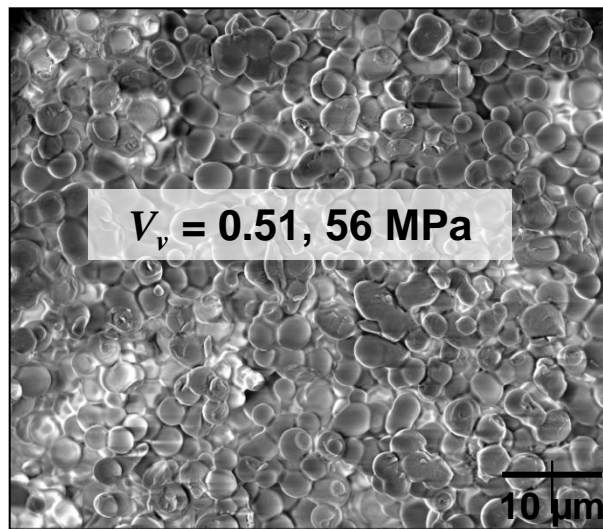
- Processing approach
  - PEG (e.g. 70% v/v) mixed with epoxy pre-polymer (e.g. 30%v/v)
  - System cured → phase-separates, leaving micro-sized epoxy/PEG interpenetrating network
  - Sonicate in water, dry in oven to remove PEG
  - Soak in liquid electrolyte to back-fill pores



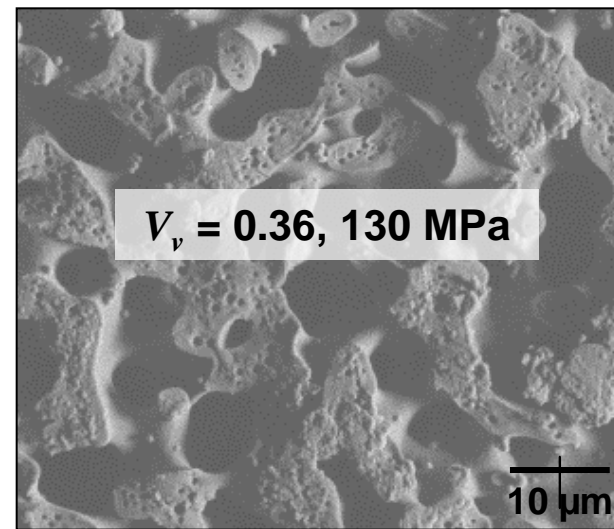
- Tailorable microstructure → PEG/epoxy ratio, cure temperature, surfactant
- Advantages relative to gel electrolytes
  - Process base resin without electrolyte
    - Avoid salt contamination effects
    - Prevent evaporation of electrolyte during vacuum / heating
  - Independent selection / engineering of liquid porogen and liquid electrolyte → more design / processing flexibility
  - Minimize likelihood of plasticization of structural polymer



25% epoxy + 75% PEG



30% epoxy + 70% PEG

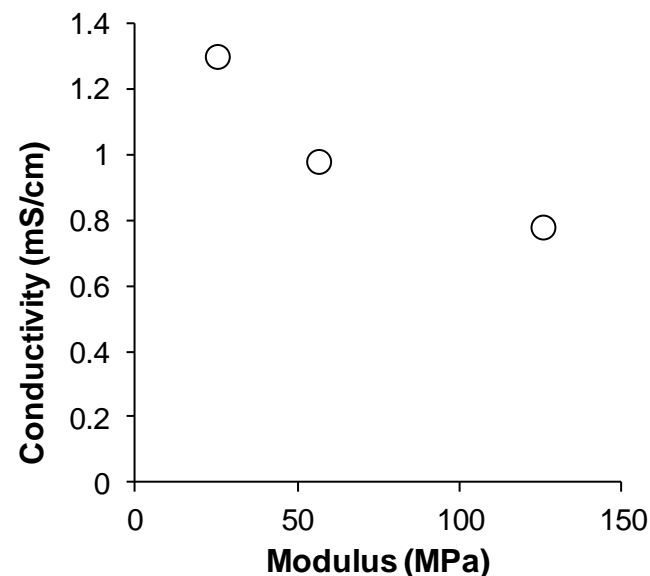


35% epoxy + 65% PEG

(all samples: Epon 828 + PACM, 160C cure, 5% PEG-PPG-PEG surfactant, backfilled with 1 M LiTFSI / propylene carbonate electrolyte)

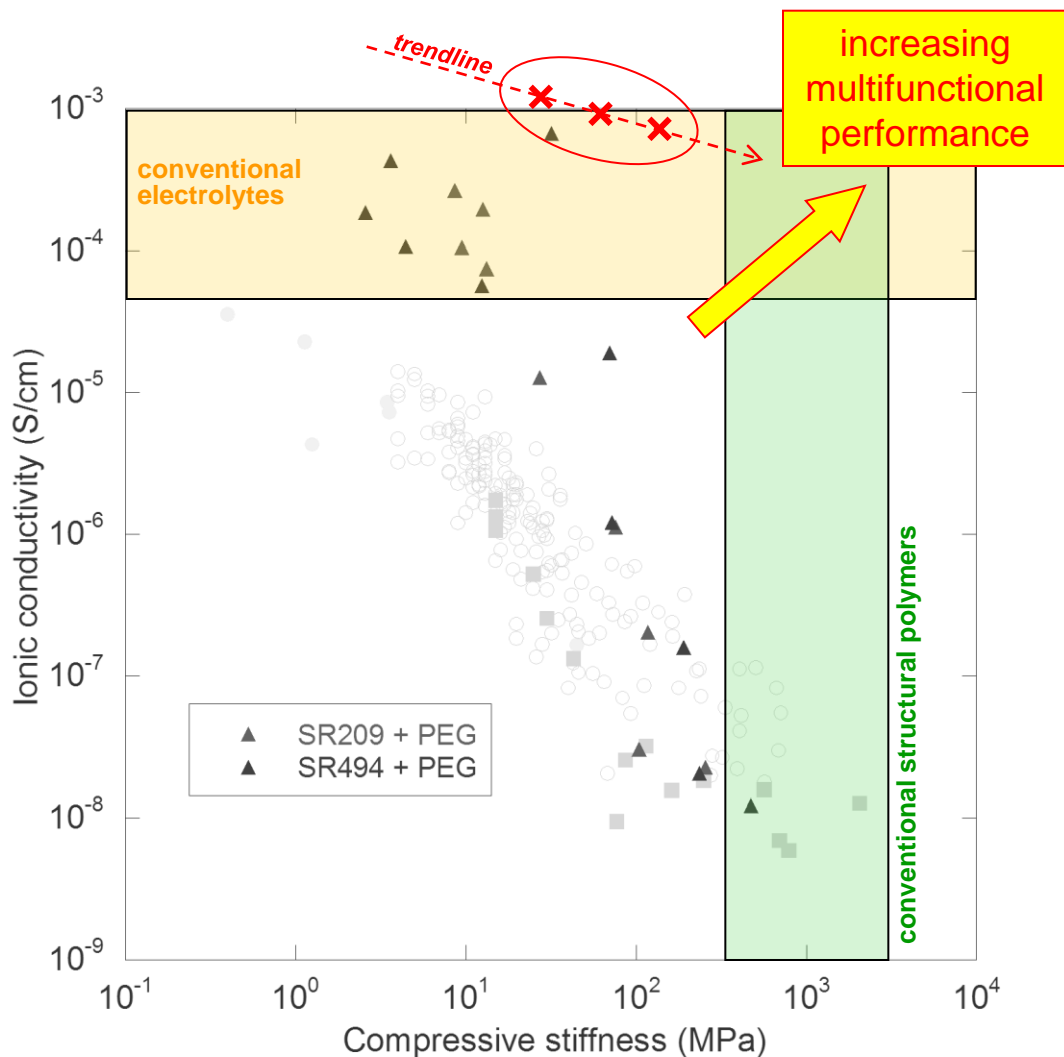
% Epoxy (original mixture)	Void volume fraction	Electrolyte uptake	Conductivity	Compressive modulus
			(mS/cm)	(MPa)
25%	55%	128%	1.3	25.3
30%	51%	105%	0.98	56.5
35%	36%	60%	0.78	125.6

**Co-continuous structure (e.g. 35% epoxy) provides best multifunctional performance.**

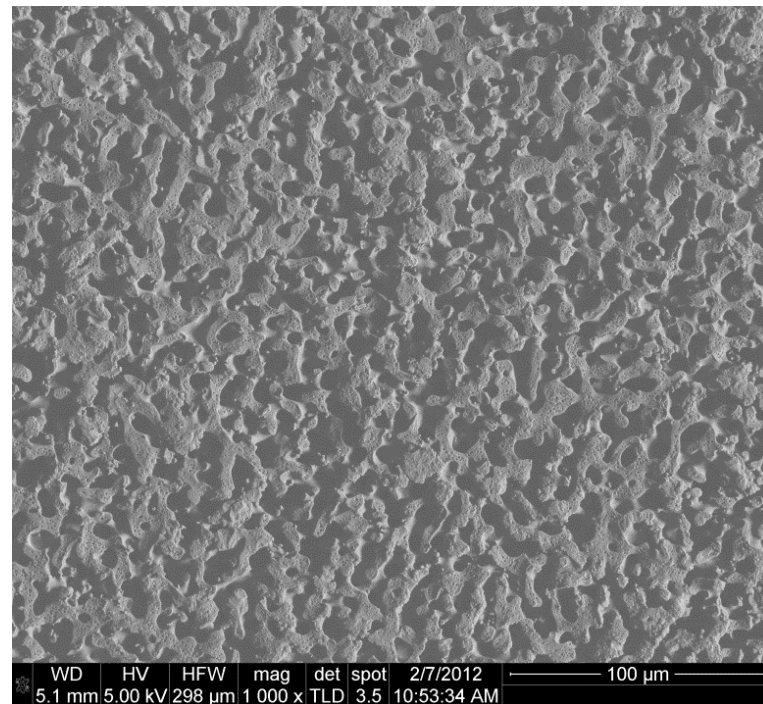


Co-continuous structured postulated as idealized multifunctional structures by e.g. Torquato et al. *J. App. Phys.* v94 n9 p5748. 2003.

- Microfoam electrolytes provide best **multifunctional performance** to date → a **leading candidate** for structural batteries



- Additional **processing advantages** of microfoam electrolytes are also attractive
- Next challenge → **Controlling microstructure near surfaces / interfaces**





Technical community is **converging towards practical, mass-saving structural power and energy composites.**

## Continuing Work

- **Capacitors**
  - Continued **scaling** (lab safety limit → 100 J)
  - Beyond commercial FR4 prepreg → high **dielectric additives, super-clean prepregging**
  
- **Batteries**
  - Further exploration of polymer foam electrolytes
    - Achieve goal of **1 GPa and 0.1 mS/cm**
    - Designed, **self-assembling electrolyte-electrode interfaces**
    - Scaled fabrication
  - Highly **structural cathodes**
  - Integrated packaging

# Effect of Electrode Thickness on Capacitance and Energy Density

## Thin, Flat Electrode (e.g. metallized film)



$\epsilon_0$  → permittivity of free space  
 $\kappa$  → matrix relative dielectric constant  
 $d$  → electrode spacing  
 $h$  → electrode waviness amplitude  
 $l, w$  → length, width of unit cell  
 $C$  → capacitance  
 $\bar{C}$  → volume - normalized capacitance  
 $V$  → voltage  
 $S$  → matrix dielectric strength

## Wavy Electrode (e.g. carbon fabric electrode)



$$C_o = \epsilon_0 \kappa \frac{lw}{d} \quad \bar{C}_o = \frac{C_o}{Vol} \rightarrow \bar{C}_o = \frac{\epsilon_0 \kappa}{d^2}$$

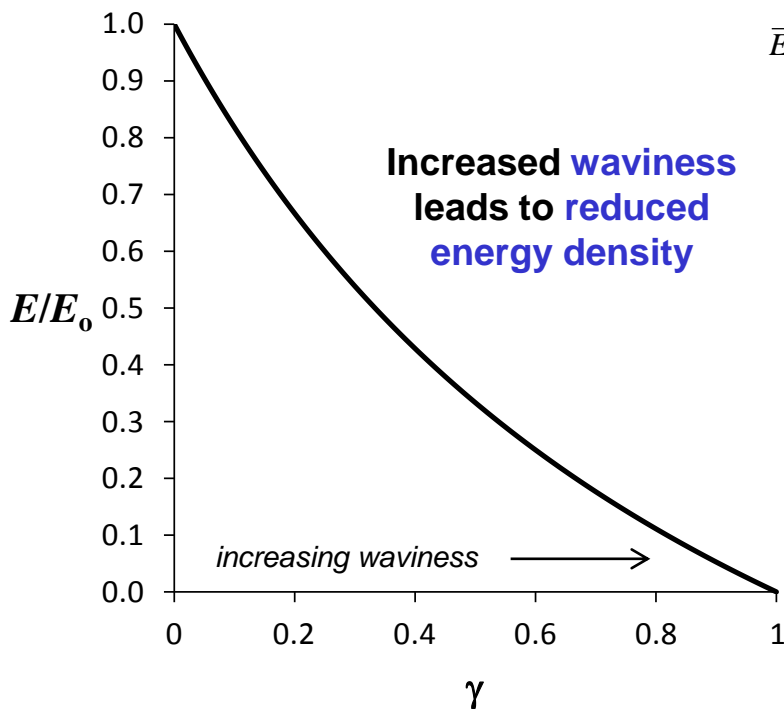
$$C = \epsilon_0 \kappa l w \left( \frac{1}{2} \frac{1}{d+h} + \frac{1}{2} \frac{1}{d-h} \right) \quad \bar{C} = \frac{C}{Vol} = \frac{\epsilon_0 \kappa}{d^2} \frac{1}{(1-\gamma^2)} \rightarrow \bar{C} = \bar{C}_o \frac{1}{(1-\gamma^2)}$$

$$\bar{E}_o = \frac{1}{2} \bar{C}_o V^2 = \frac{1}{2} \bar{C}_o (S \cdot d)^2 = \frac{1}{2} \frac{\epsilon_0 \kappa}{d^2} (S \cdot d)^2$$

$$\bar{E} = \frac{1}{2} \bar{C} V^2 = \frac{1}{2} \bar{C} (S \cdot (d-h))^2 = \frac{1}{2} \frac{\epsilon_0 \kappa}{d^2} \frac{1}{(1-\gamma^2)} (S \cdot (d-h))^2$$

$$\bar{E}_o = \frac{1}{2} \epsilon_0 \kappa S^2$$

$$\bar{E} = \frac{1}{2} \epsilon_0 \kappa S^2 \frac{(1-\gamma)}{(1+\gamma)} \rightarrow \bar{E} = \bar{E}_o \frac{(1-\gamma)}{(1+\gamma)}$$

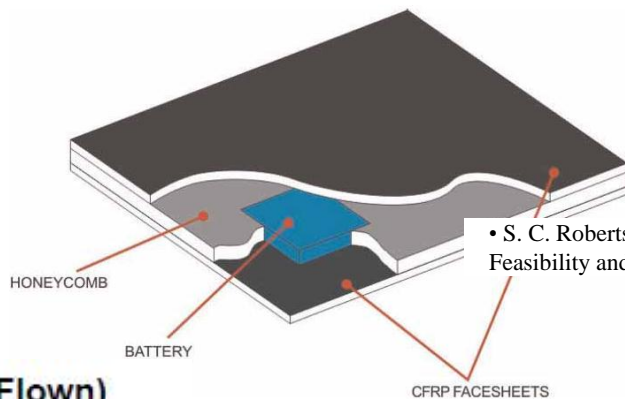
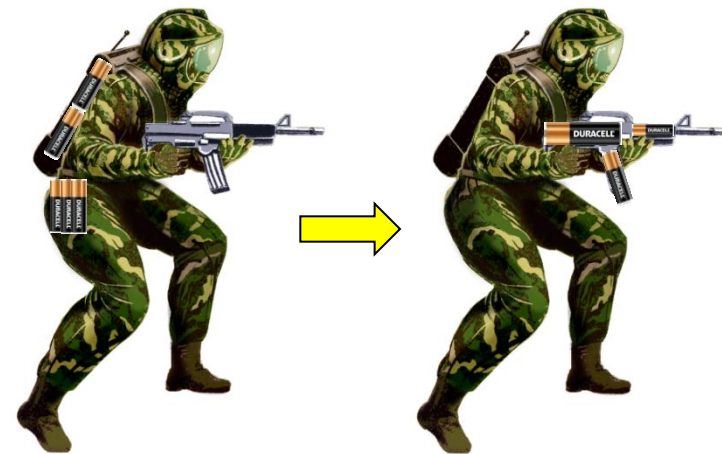


Increased waviness leads to reduced energy density

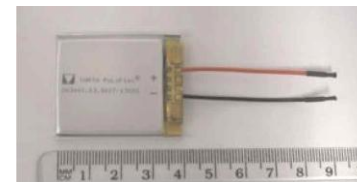
Thin, flat electrodes should be used to achieve maximum energy density.

- In dielectric capacitor, electrodes bus power, but do not store energy → therefore their mass should be minimized
- The dielectric body possesses maximum energy when uniformly polarized at limiting dielectric strength → flat electrodes provide uniform electric fields

- Battery packaging used as structure, or structure used as packaging to protect / ruggedize battery
  - Active battery elements see negligible mechanical loads
- Typical: embed COTS batteries into composite structures



• S. C. Roberts and G. S. Aglietti. "Satellite multifunctional power structure: Feasibility and mass savings." Proc. IMechE. Part G. v222 n1 p41-51. 2008.

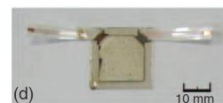


PLI Wasp I (Flown)

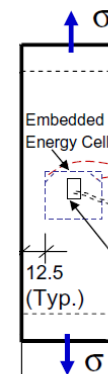
4x  
24.5 g



3-Layer PLI Cell



(d)

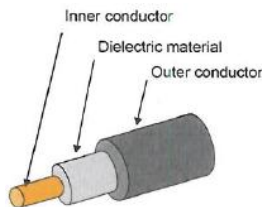
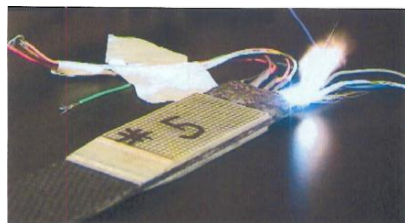


• J. P. Thomas and M. A. Qidwai. "The design and application of multifunctional structure-battery materials systems." JOM. v57 n3 p18-24. 2005.

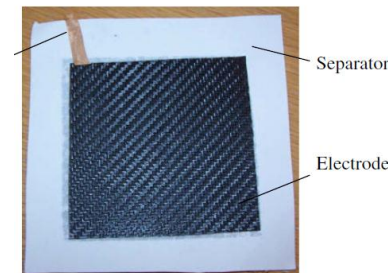
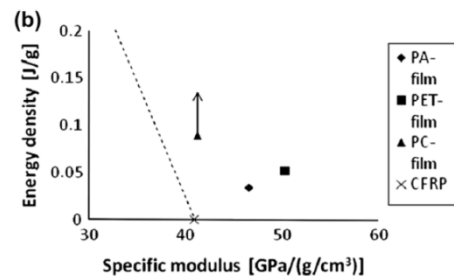
• T. Pereira, Z. Guo, S. Nieh, J. Arias, and H. T. Hahn. "Embedding thin-film lithium energy cells in structural composites." Comp. Sci. Tech. v68 p1935-1941. 2008.

J. F. Snyder, D. J. O'Brien, and E. D. Wetzel. "Structural batteries, capacitors, and supercapacitors." *Handbook of Solid State Batteries & Capacitors*. Eds: N. Dudney, W. West, J. Nanda. To appear.

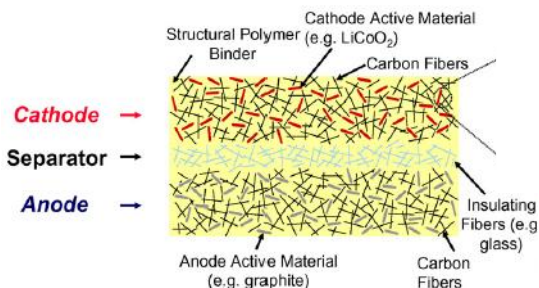
- **Active energy-storing materials directly bear mechanical loads**
  - Requires development of **structural electrolytes, dielectric, electrodes, separators, etc.**
- **Structural capacitors more advanced than structural batteries**



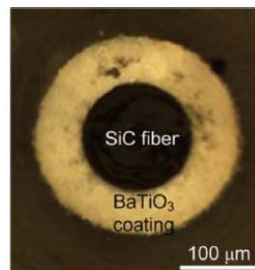
• W. Baron and D. Zeppetella. "Multifunctional airframe structure for energy storage using load bearing coaxial capacitor." *Proc. of ASME-SMASIS*. SMASIS08-435. 2008.



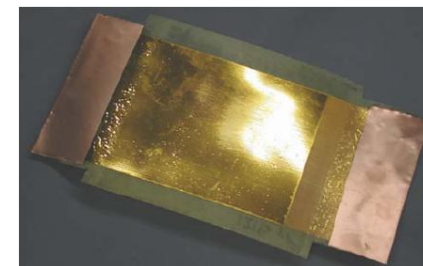
• T. Carlson, D. Ordeus, Maciej Wysocki, and L. E. Asp. "Structural capacitor materials made from carbon fibre epoxy composites." *Comp. Sci. Tech.* v70 n7 p1135. 2010.



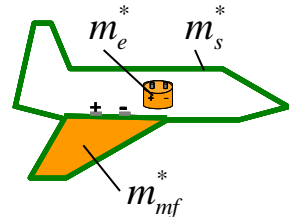
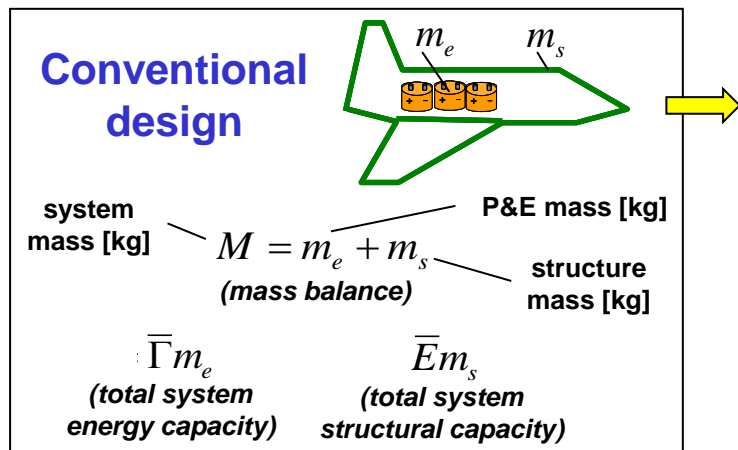
• P. Liu, E. Sherman, and A. Jacobsen. "Design and fabrication of multifunctional structural batteries." *J. Power Sources*. v189 p646. 2009.



• Y. Lin and H. A. Sodano. "Characterization of multifunctional structural capacitors for embedded energy storage." *J. App. Phys.* v106 n114108. 2009.



• J. F. Snyder et al. "Structural composite capacitors, supercapacitors, and batteries for U.S. Army applications." *Proc. of ASME-SMASIS*. SMASIS08-315. 2008.



## Multifunctional design

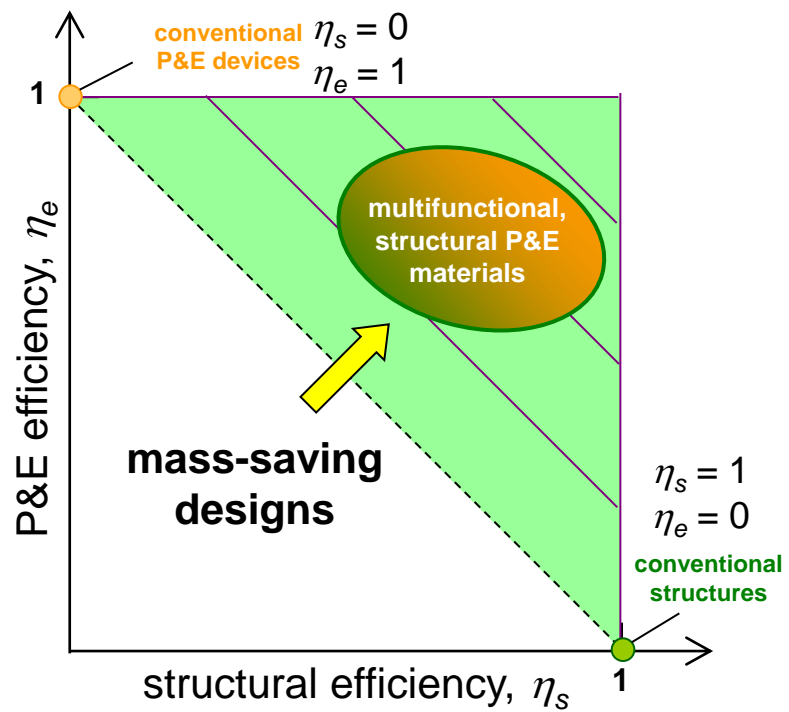
$M^* = m_e^* + m_s^* + m_{mf}^*$  structural P&E mass [kg] (mass balance)

$\bar{\Gamma}m_e^* + \bar{\Gamma}_{mf}m_{mf}^* = \bar{\Gamma}m_e$  (maintain total system energy capacity)

$\bar{E}m_s^* + \bar{E}_{mf}m_{mf}^* = \bar{E}m_s$  (maintain total system structural capacity)

$(M - M^*) = \left( \frac{\bar{\Gamma}_{mf}}{\bar{\Gamma}} + \frac{\bar{E}_{mf}}{\bar{E}} - 1 \right) m_{mf}^*$

• D. J. O'Brien, D. M. Baechle, and E. D. Wetzel. "Design and performance of multifunctional structural composite capacitors." *J. Composite Materials*. v45 n26 p2797-2809. 2011.



mass-savings can be achieved if  $M^* < M$ :

$\therefore \frac{\bar{\Gamma}_{mf}}{\bar{\Gamma}} + \frac{\bar{E}_{mf}}{\bar{E}} > 1 \implies \eta_{mf} \equiv \eta_e + \eta_s > 1$

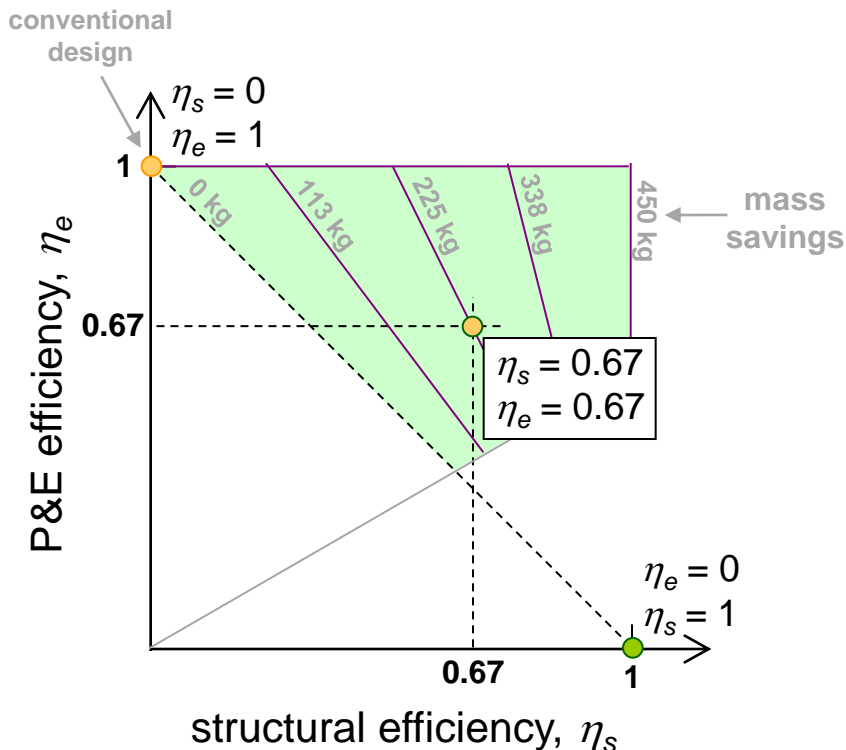
$\eta_e = \frac{\bar{\Gamma}_{mf}}{\bar{\Gamma}} = \frac{\text{energy density of multifunctional structure}}{\text{energy density of conventional P\&E}}$

$\eta_s = \frac{\bar{E}_{mf}}{\bar{E}} = \frac{\text{specific stiffness of multifunctional structure}}{\text{specific stiffness of conventional structure}}$

**Mass savings possible even if multifunctional material performs individual functions less efficiently than monofunctional materials.**

Prius : 21 kW, 202V, 45kg NiMH battery pack, 1300 kg curb weight

**Tesla Roadster: 215 kW, 375 V, 450 kg Li-ion battery pack, 1220 kg curb weight**



## Conventional design

770 kg structure ( $\eta_e = 0, \eta_s = 1$ )  
 + 450 kg battery ( $\eta_e = 1, \eta_s = 0$ )  
**1220 kg** total system weight



## Multifunctional design

320 kg structure ( $\eta_e = 0, \eta_s = 1$ )  
 + 675 kg structural battery ( $\eta_e = 0.67, \eta_s = 0.67$ )  
**995 kg** total system weight

**System weight reduced by 18%**



Underside of the Tesla Roadster's carbon fiber rear panel.

www.teslamotors.com

Tesla roadster uses RTM-ed, epoxy carbon fiber composite body panels with a glass fiber / polypropylene interlayer.