Aramid Nanofiber-Functionalized Graphene Electrodes for Structural Load-Bearing Energy Storage (FA9550-16-1-0230)

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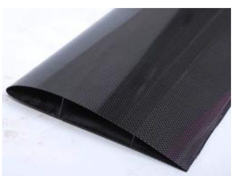
Structural energy and power systems simultaneously manage mechanical stress with energy and power needs. The unifying challenge in this area is to address both **electrochemical and mechanical needs** in a single **multifunctional** unit.



structural composite

\+

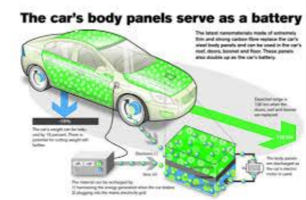
capacitor
(or battery)

Mechanical ⟷ (tradeoff) Energy

Q: **What factors control** mechanical properties, energy storage, and their tradeoff? (composition, architecture, porosity, chemistry, interfaces)

Relevance to AFOSR

- Integration into aircraft, satellites, vehicles
- Reduced mass and volume
- Costs savings
- Longer flight time



$$\eta_{mf} \equiv \eta_s + \eta_e > 1$$

Multifunctional Efficiency | Structural Efficiency | Energy Efficiency

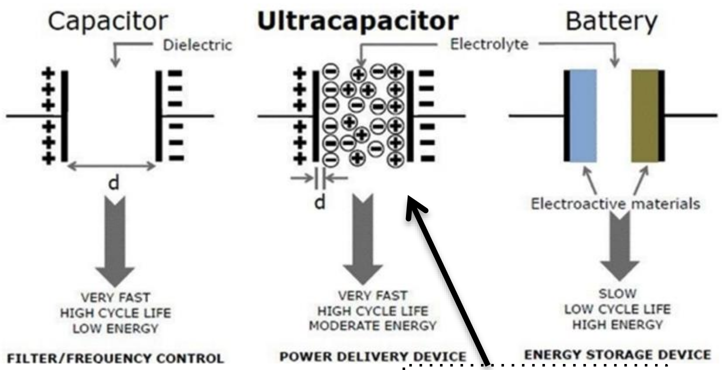
$$\eta_s = \frac{\text{Mechanical Property of M.F}}{\text{Mechanical Property of Norm}}$$

$$\eta_e = \frac{\text{Energy Property of M.F}}{\text{Energy Property of Norm}}$$

[1]Mass or volume-savings is possible when $\eta_{mf} > 1$

1. Wetzel et al. *J. Comp. Mat.* 2011

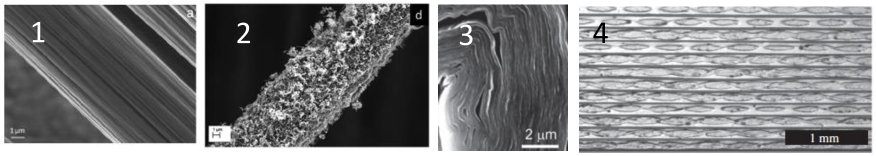
Literature Review



Most prevalent in literature

Structural Electrodes

- Carbon fibers[1]
- Carbon nanotubes w/carbon fibers[2]
- Reduced graphene oxide sheets[3]



Structural Electrolyte

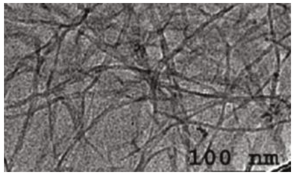
- Glass fiber[4]

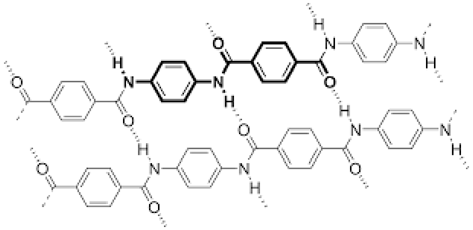
Challenge: Low capacitance, high stiffness
Or high capacitance, low stiffness

1. Qian et al. *JCIS* 2013; 2. Shirshova et al. *Farad. Diss.* 2014; 3. Ruoff et al. *Nano Lett.* 2008 and *Nature* 2007; 4. Wetzel et al. *J. Comp. Mat.* 2011

Aramid Nanofibers

- Nanoscale (40 nm dia.; >1 um length) version of Kevlar[5]
- Kevlar has high tensile modulus (156 GPa) and strength (4 GPa)

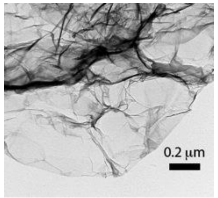


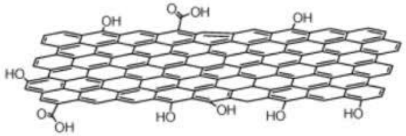


5. Kotov, N.A. et al., *ACS Nano* 2011

Reduced graphene oxide (RGO) sheets[3,6-7]

- High modulus (200 GPa)
- High capacity (RGO, 530 mAh/g)
- High conductivity (200 S/m)

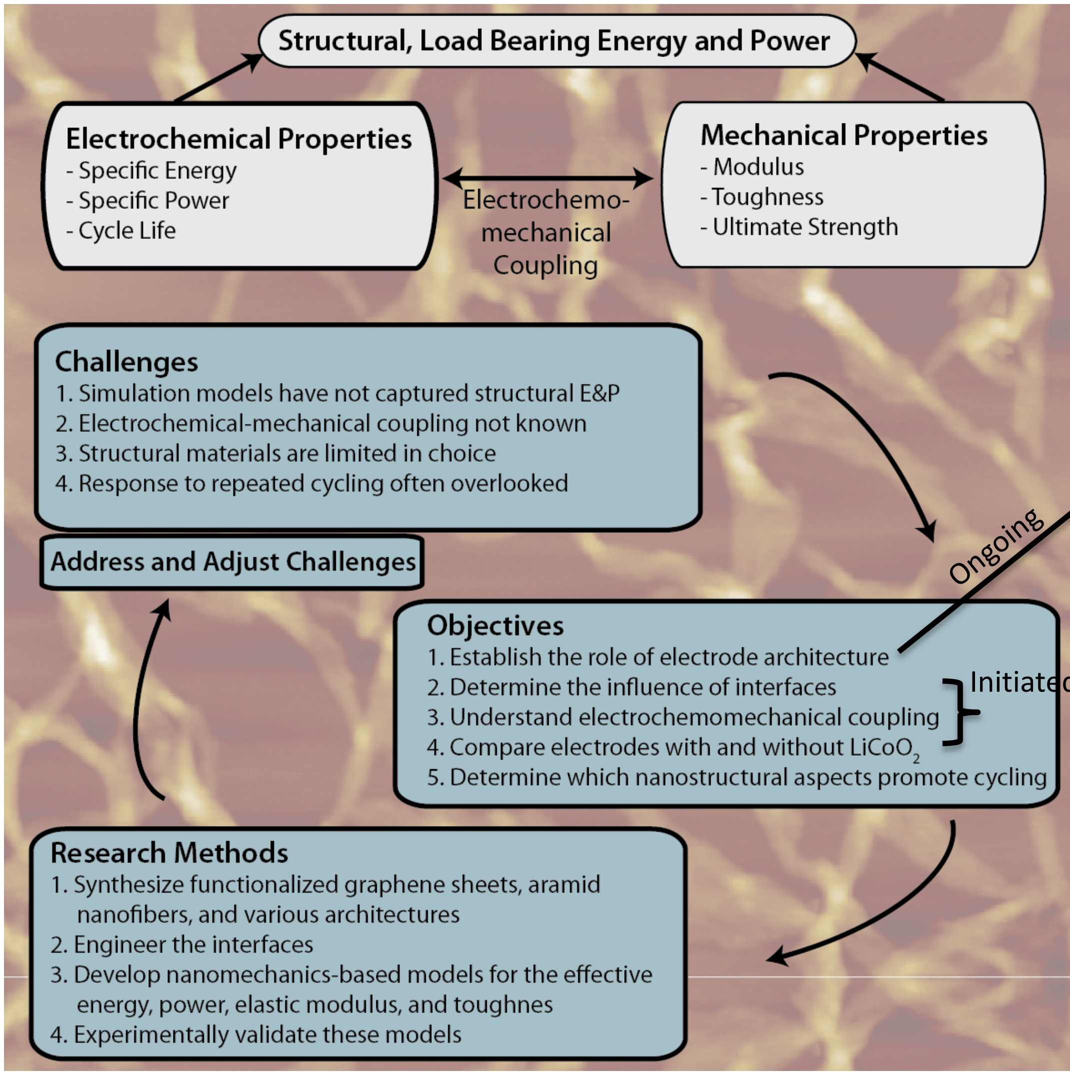




6. Ruoff, R.S. et al., *Carbon* 45 (7), 1558-1565 (2007);
7. Honma, I et al. *Nano Letters* 8 (8), 2277-2282 (2008)

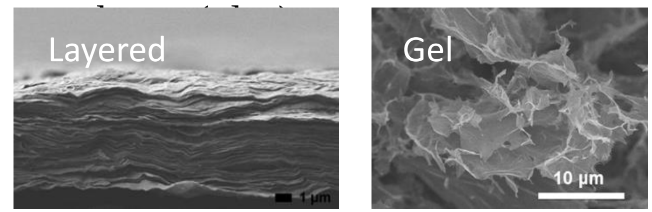
Overview of Activities

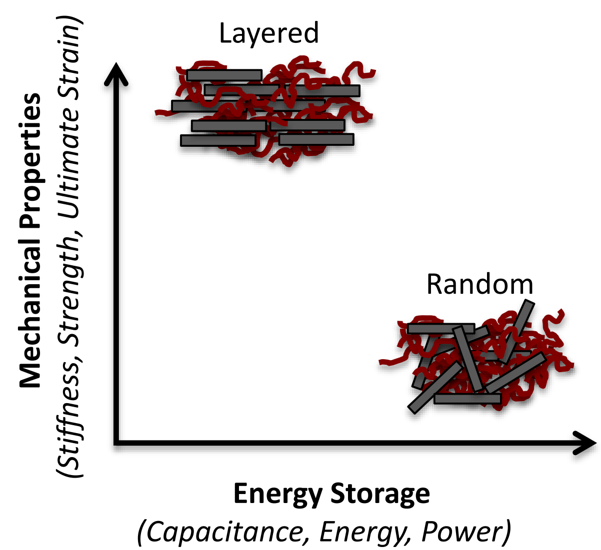
Q: Can the favorable qualities of **aramid nanofibers** and **graphene sheets** be designed for structural electrodes for energy and power?



The Role of Architecture

- Layered RGO sheets
  - Layer-by-layer assembly
  - Flow-directed assembly
- Randomly oriented RGO

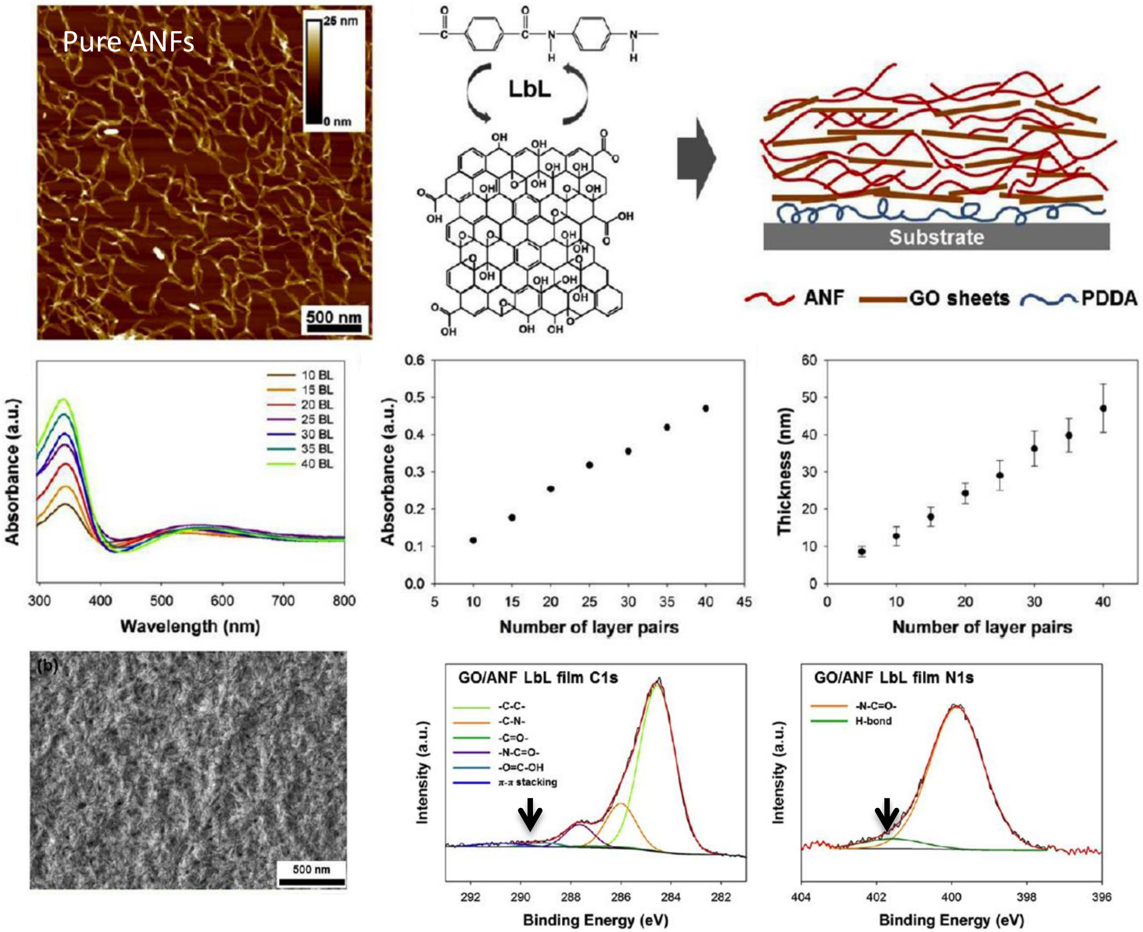




Experimental Investigation of Layered Electrode Architectures

Goal: Experimentally examine the role of **layered architecture** for aramid nanofiber/graphene composite capacitor electrodes

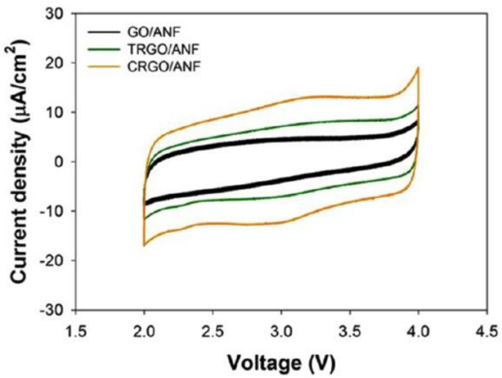
Approach: Layer-by-layer (LbL) assembly and vacuum filtration (flow-directed assembly) were explored

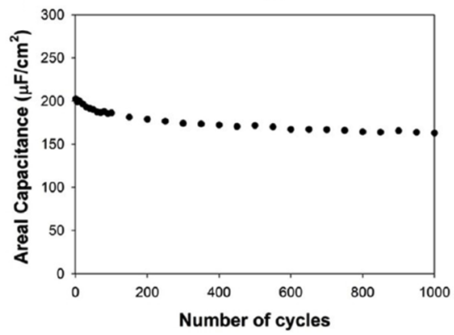


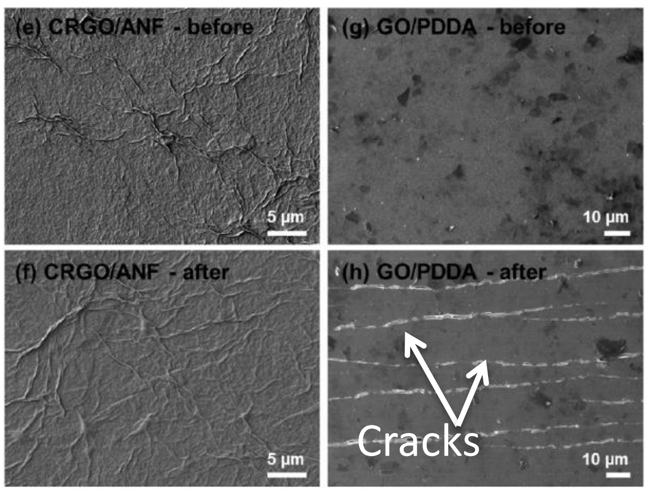
Layer-by-Layer Assembly

- A multilayer film was built up by alternate adsorption of ANFs and GO sheets
- The thickness increased linearly with the number of adsorption cycles (layer pairs)
- Chemically or thermal reducedtion to obtain ANF/RGO electrodes (75 wt% ANF)
- **ANFs were stable** during reduction process
- X-ray photoelectron spectroscopy show **favorable pi-pi and hydrogen bonding interactions**

Layer-by-Layer Electrodes, Continued







Layer-by-Layer Assembly: Mechanical Properties

- Nanoindentation showed mechanical properties intermediate to the two components (*Batteas, TAMU)
- Electrodes too thin for bulk mechanical testing
- Electrodes resisted cracking after 1000 cycles of flexure (a control showed extensive cracking)

Layer-by-Layer Assembly: Energy Storage

- Chemical reduction gave best performance (221 uF/cm^2 or 78 F/cm^3)
- Excellent capacitance retention over 1000 cycles

Key Discoveries

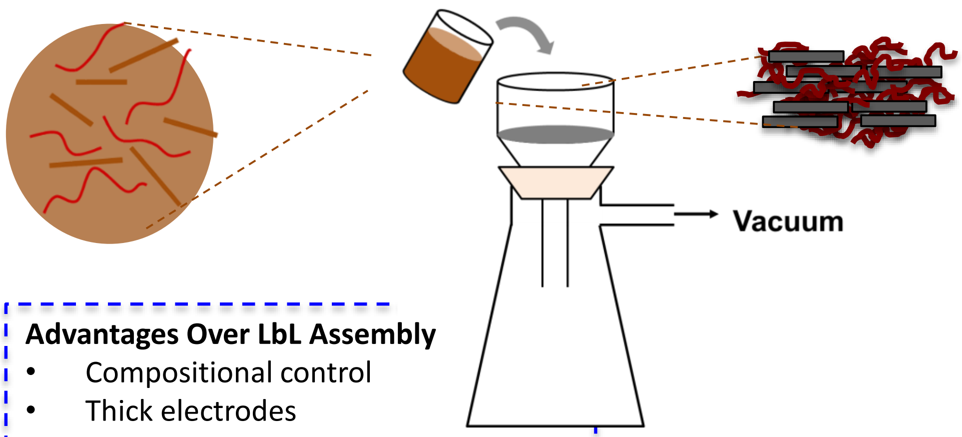
ACS Applied Materials & Interfaces, Just Accepted, 2017

- RGO/ANF electrodes **resist cracking** during mechanical flexure
- Capacitance is slightly lower than bulk-like carbon-based electrodes

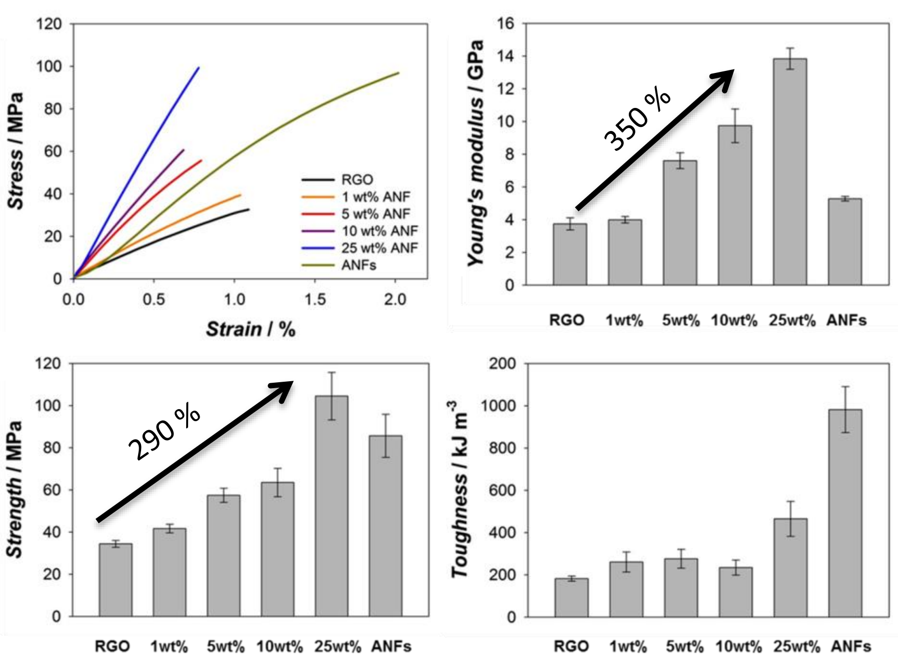
Impact

- LbL assembly enables crack-free RGO/ANF electrodes as thin films or coatings

Flow-Directed Assembly

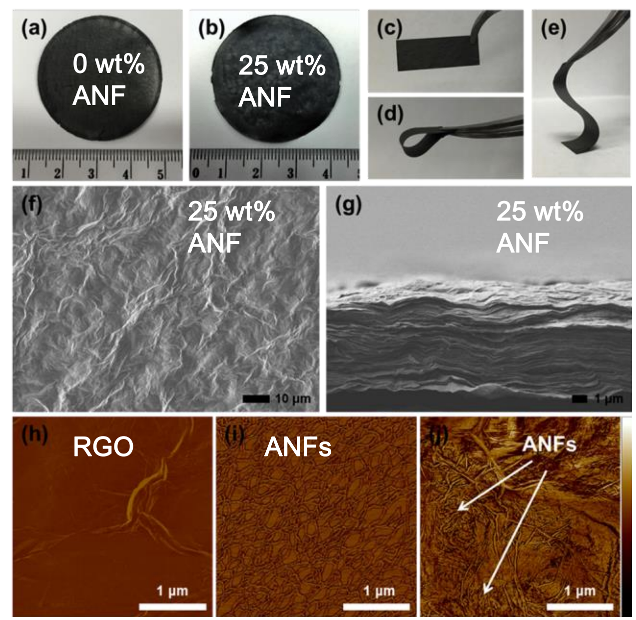


Advantages Over LbL Assembly
- Compositional control
- Thick electrodes
- Densely packed and layered structure



Flow-Directed Assembly Process
- GO and ANF suspensions were mixed and then vacuum filtered
- The electrode was isolated and thermally reduced

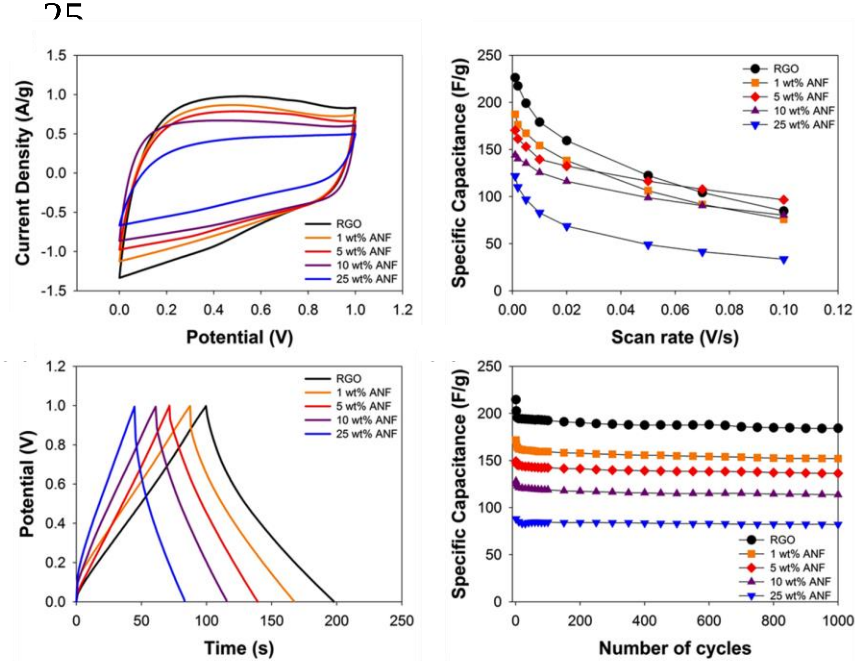
Flow-Directed Assembly: Mechanical Properties
- **Stiffness and tensile strength** increased with ANF content
- Max Young's modulus of 13.0 GPa and max strength of 100.6 MPa for 25 wt% ANF



Flow-Directed Assembly

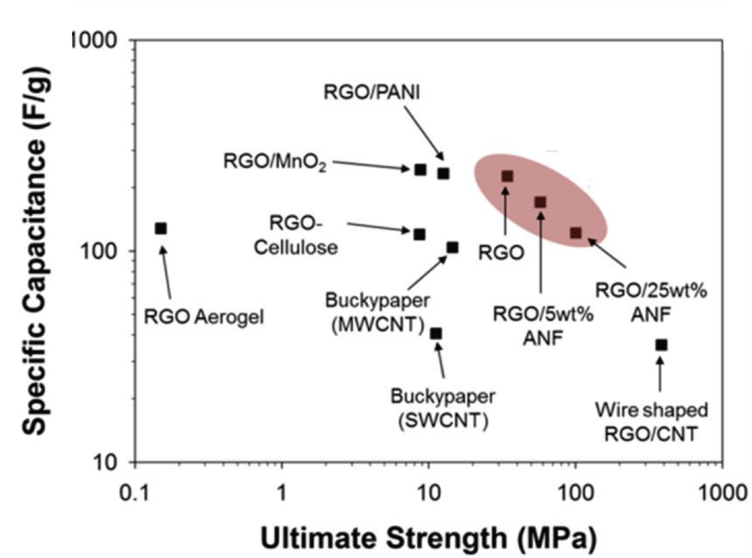
Flow-Directed Assembly: Energy Storage

- **Electrochemically stable** at all ANF contents
- **Tradeoff** in capacitance with ANF content
- 207 → 93 F/g as ANF% increased from 0 → 25



Multifunctional Comparison with Lit.

- ANF/RGO electrodes (shaded) have the **highest ultimate strength** among other systems
- Higher capacitance systems use pseudocapacitive materials



<u>Key Discoveries:</u> Electrodes made by vacuum filtration exhibit **enhanced stiffness, strength, and toughness** because of the brick-and-mortar structure and interfacial interactions

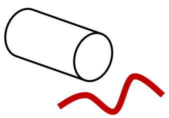
<u>Impact:</u> The layered architecture enables structural energy power

Submitted and In Revision

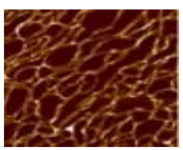
Micromechanical Modeling of Tensile Moduli

Goal: Create and validate a micromechanics model to predict **elastic moduli** of ANF/RGO composites. Experimental results show enhanced tensile moduli with increasing ANF content. **Micromechanical modeling may explain the major controlling factors** (spatial architecture, waviness, composition)

Micromechanical Modeling Approach



Inclusion (ANF)



AFM image of ANFs

Properties from literature

↓

Introduce waviness (a/λ)

↓

Introduce in-plane random orientation

↓

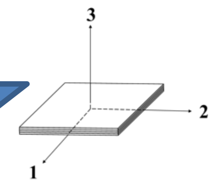
Stiffness matrices of ANF or rGO

↓

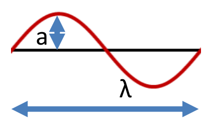
Mori-Tanaka method

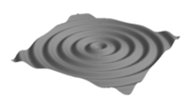
↓

Effective elastic moduli of composites



Matrix (RGO)





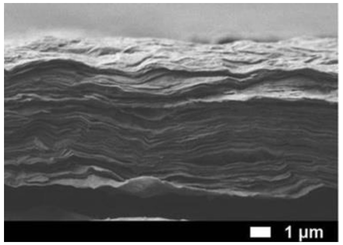
Combines ANF and RGO

Example: RGO

Properties from Literature:

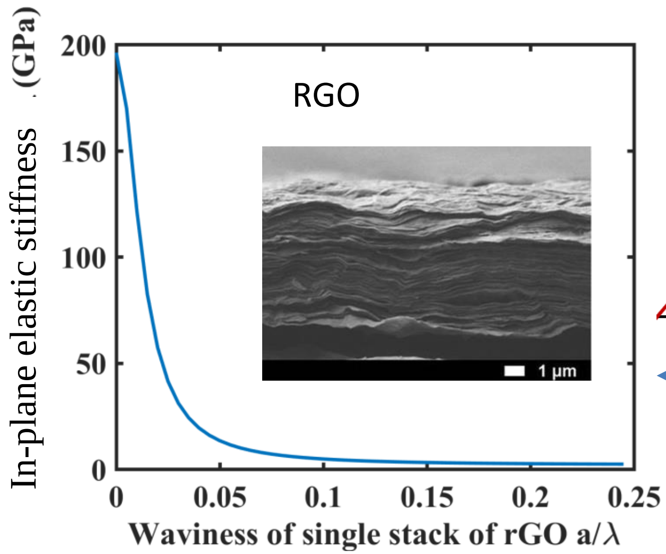
Property Symbol	Input Value
E_1 (GPa)	200
E_3 (GPa)	1.2
G_{13} (GPa)	1.2
Poisson's Ratio	0.2

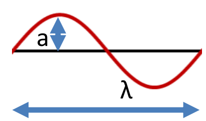
Introduce waviness (a/λ) as about 1/16

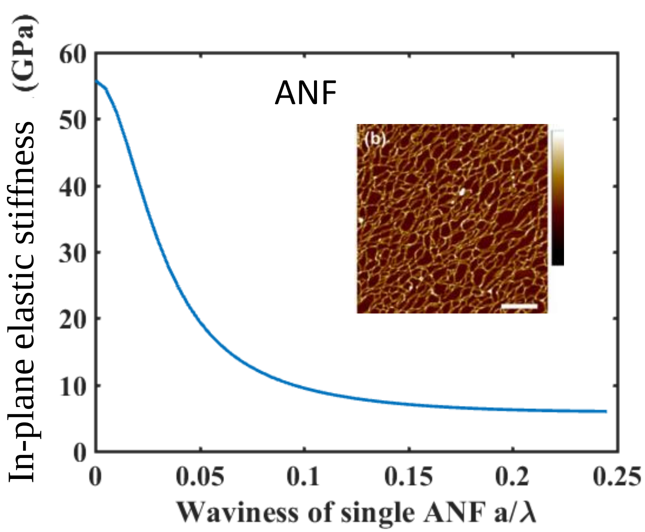


Parametric Study on Waviness and Extension to Composite

Waviness (a/λ) is the **main cause** of in-plane elastic modulus decrease of RGO and ANF

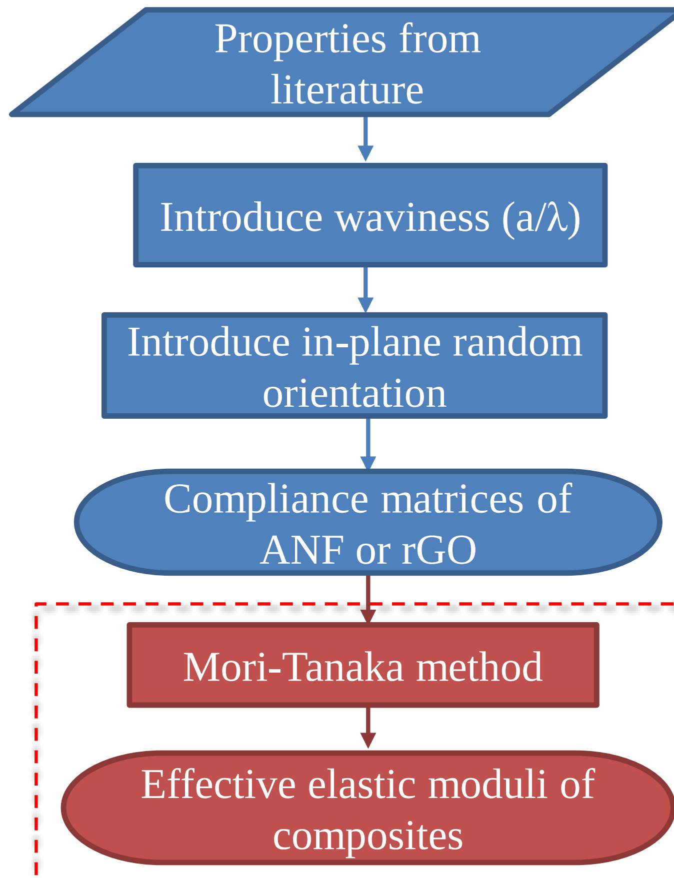






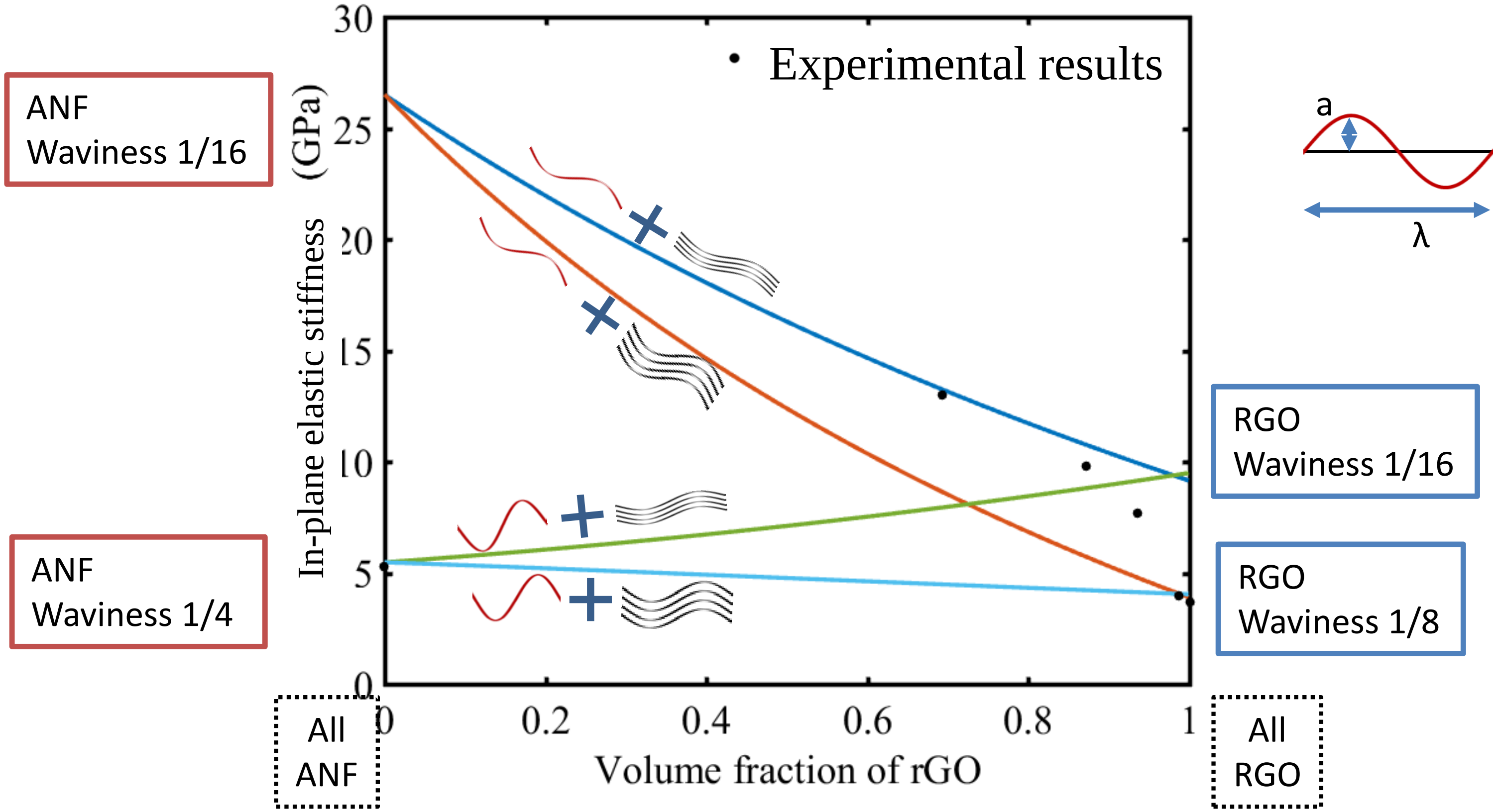
ANF/RGO Composite Micromechanical Modeling Approach

- Mori-Tanaka model with randomly oriented inclusions was used to account for inhomogeneity and non-dilute inclusions



ANF/RGO Composite Micromechanical Modeling Results

Effective tensile modulus as a function of RGO volume fraction and combinations of ANF (red) and RGO (black) waviness



Key Discoveries: Waviness of neat ANF and RGO **decreases** their **tensile moduli**

Interpretation of experiments using the model implies that waviness is a function of volume fraction: Higher RGO volume fraction (up to 100%) results in higher RGO waviness and lower modulus

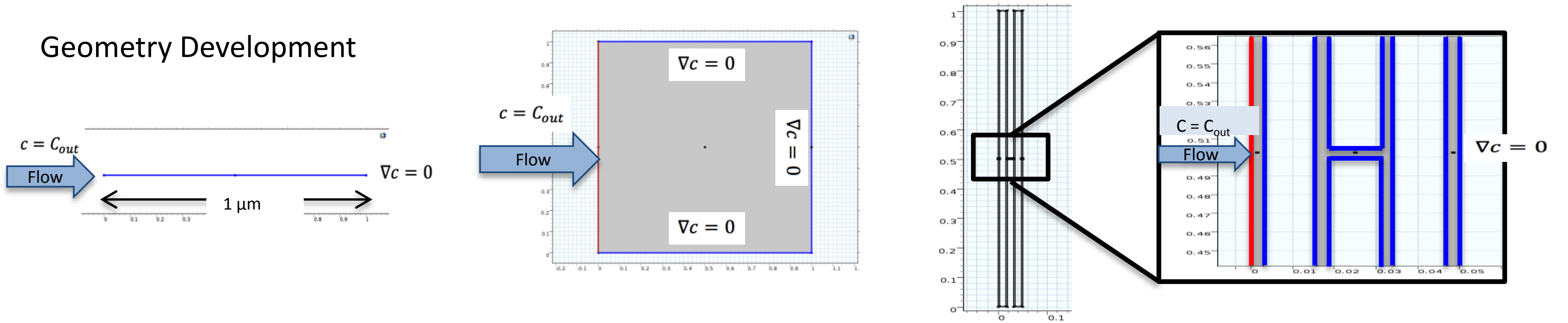
Impact: Model **enables systematic design** of ANF/RGO composites with tailored properties

Ionic Diffusivity in Layered RGO/ANF Composite Electrodes

Goal: Develop a diffusion model to investigate the ionic diffusivity of ANF/RGO composite electrodes based on RGO arrangement (staggered vs. perfect) and waviness utilizing COMSOL Multiphysics

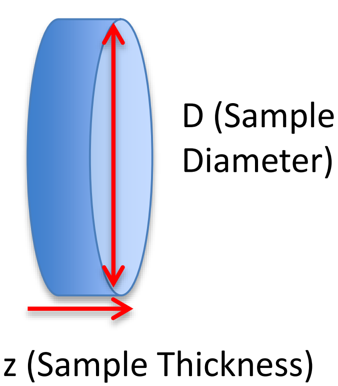
Motivation: Ion diffusion directly impacts power and capacitance

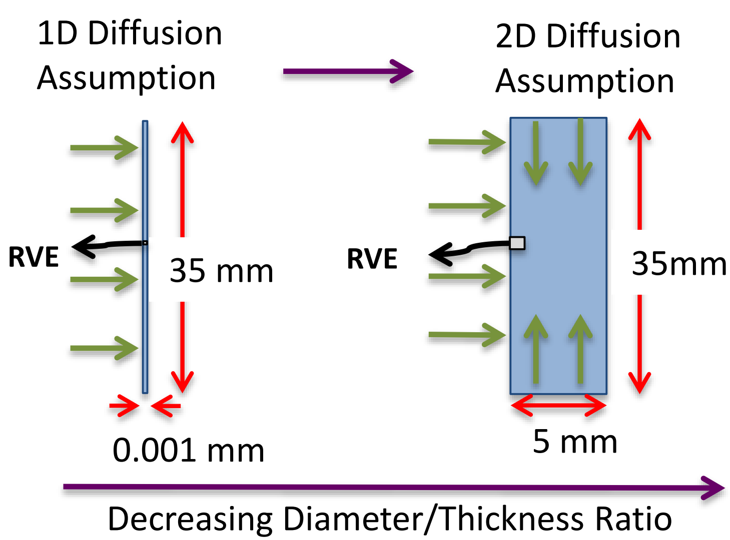
Geometry Development

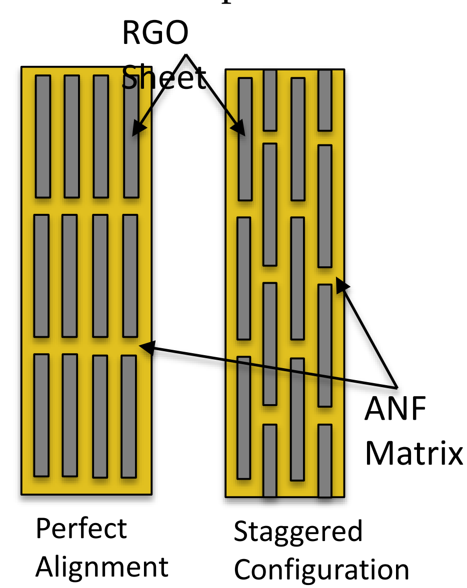


- 2-D diffusion model will provide a basis to analyze the microstructural alignment of components
- Different configurations of ANF/RGO may lead to different diffusion rates

Fickian Diffusion $\frac{\partial c}{\partial t} + \nabla(D\nabla c) = 0$



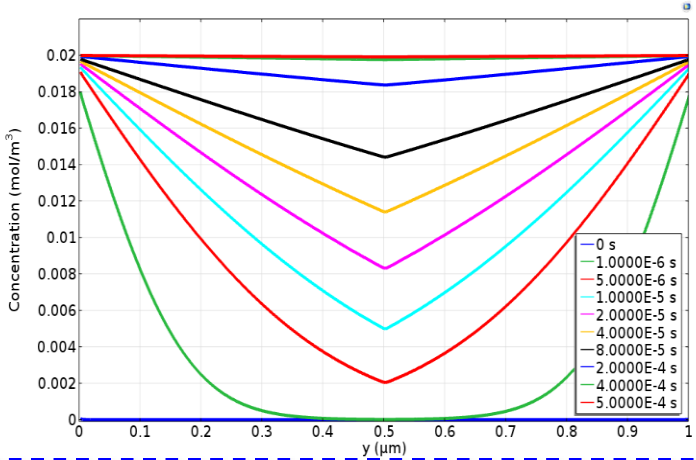




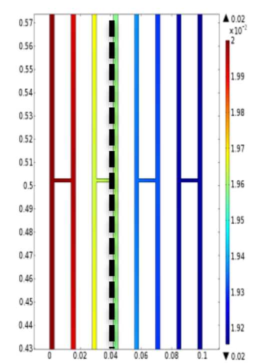
J. Crank, 1975, Clarendon Press, Oxford

Ion Concentration Development and Waviness

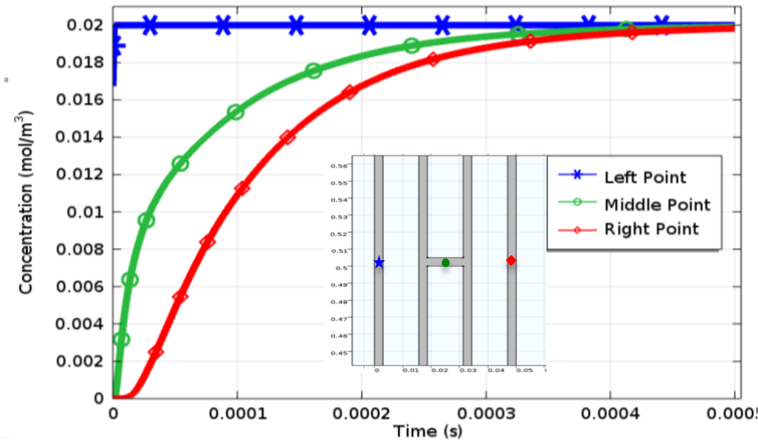
Concentration plot along a graphene sheet (black line) RGO/25wt% ANF



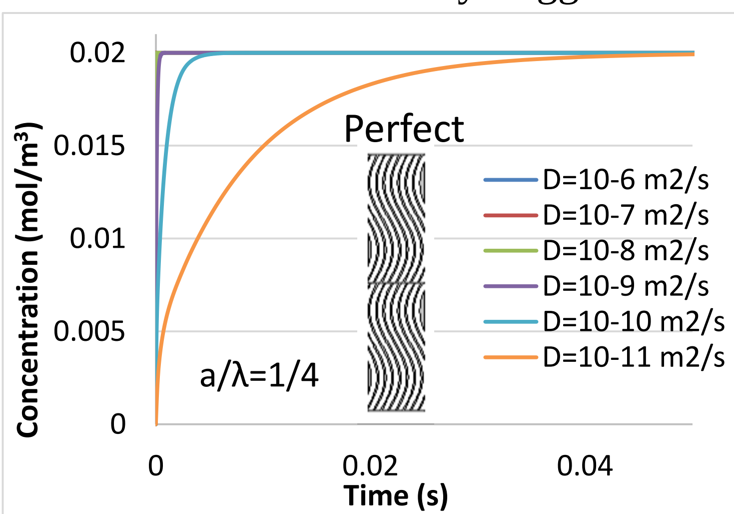
Flat, staggered

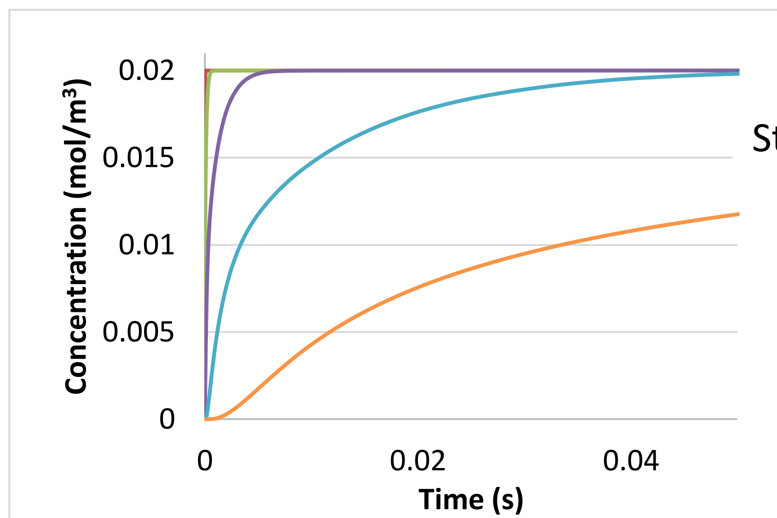


Concentration plot for 3 points shown in the geometry RGO/25wt% ANF



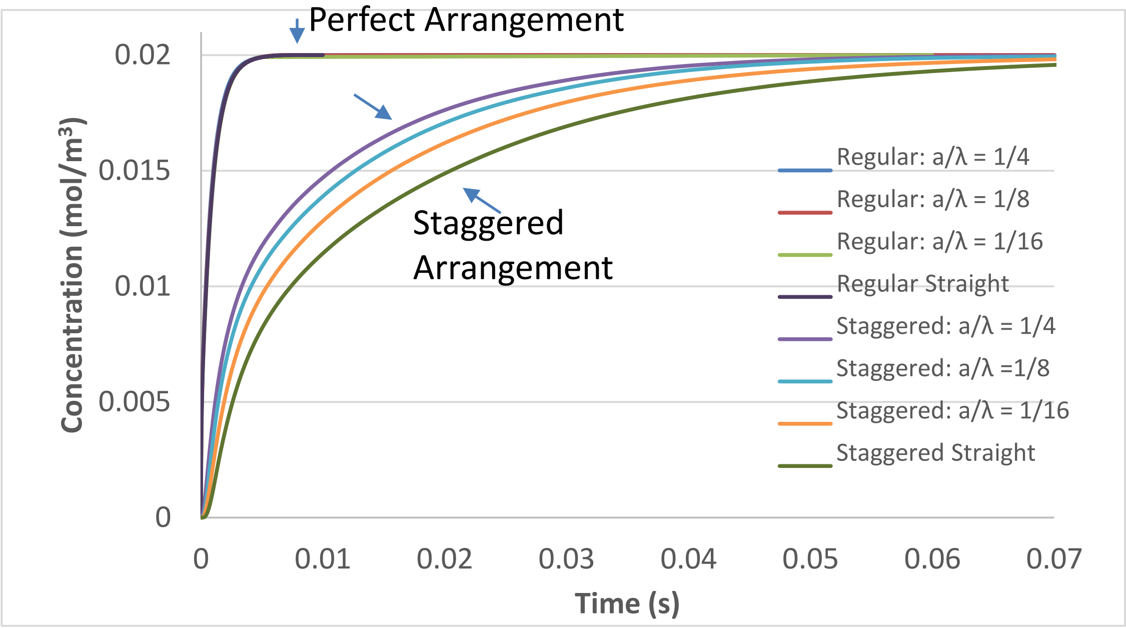
- The wavy staggered arrangement takes a longer time to reach equilibrium

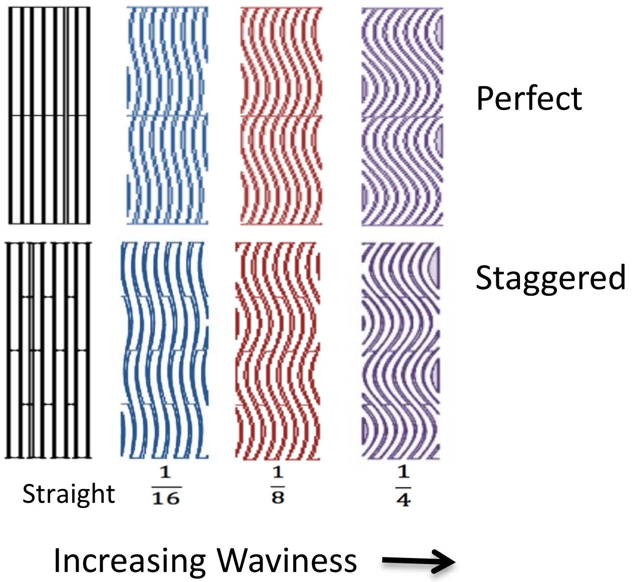




Staggered

The Effect of Waviness and Arrangement on Diffusion Time Scale





Key Discoveries:

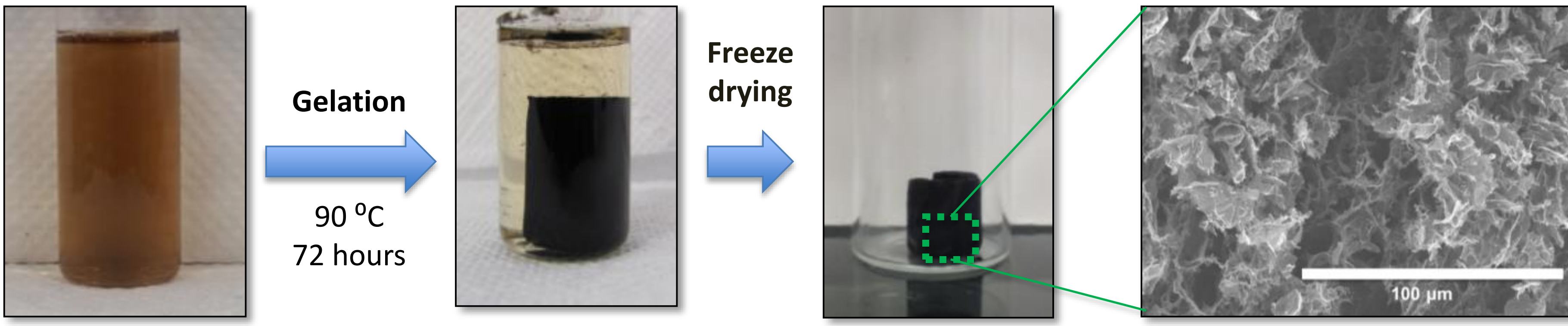
Waviness in staggered arrangement affects ion diffusion: higher waviness leads to shorter time needed to reach the steady state condition. Perfect arrangemenet is less sensitive to waviness.

Impact: Model enables the prediction of ionic diffusion with consideration of spatial arrangement and waviness

Examine Role of Electrode Architecture

Goal: Synthesize 3D reduced graphene oxide (RGO) **random** architecture to achieve high surface area and better ion diffusion properties for supercapacitor application

Research Activities



Aq. GO dispersion + NH_4OH | RGO hydrogel | RGO aerogel | SEM: RGO aerogel

Achievements

Advantages:

- One-pot synthesis of self-assembled gel structure
- Ammonia aids in formation of covalent bonds between GO sheets, providing structural integrity
- Freeze drying retains porous structure of RGO **random** hydrogel

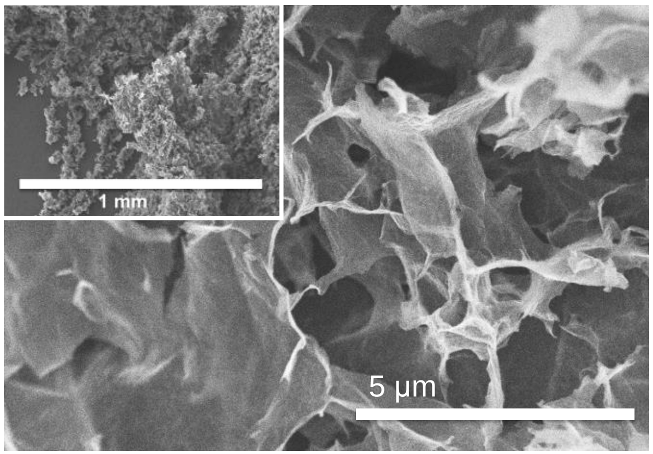
Challenges:

- Long synthesis time (relative to vacuum filtration) required for gel formation

Examine Role of Electrode Architecture

Synthesize 3D reduced graphene oxide (RGO) architecture to **achieve high surface area and better ion diffusion properties** for supercapacitor application

SEM Micrographs of rGO aerogel

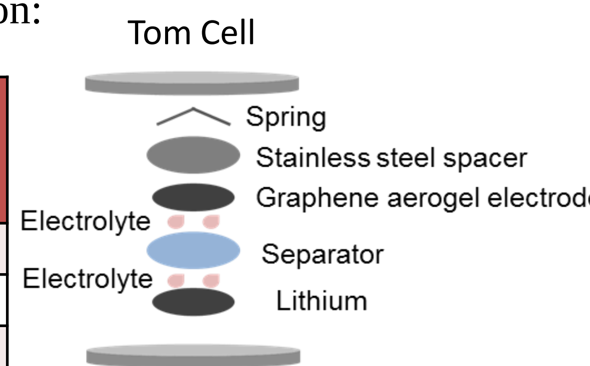


Research Activities

Brunauer–Emmett–Teller (BET) surface area analysis: 1648 m^2/g

Electrochemical characterization:

Current Density (A/g)	Charge Capacitance (F/g)	Discharge Capacitance (F/g)
0.05	711	755
0.5	470	471
5	197	191



Achievements

Advantages:

- These **random** gels have very high surface area in comparison to stacked-layered architectures
- SEM shows the presence of macro- and micro-pores which improve ion diffusion properties
- Electrodes made from these porous RGO gels show high capacitance over a wide range of current densities

Challenges:

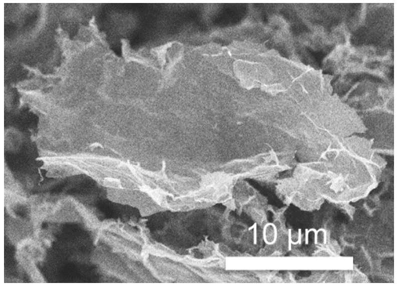
- High porosity comes at the cost of mechanical strength

Examine Role of Electrode Architecture

Synthesis of functional graphene oxide sheets for improved mechanical and electrochemical performance

Modified Hummers' Method

- Chemical oxidation approach to synthesize graphene oxide nanosheets



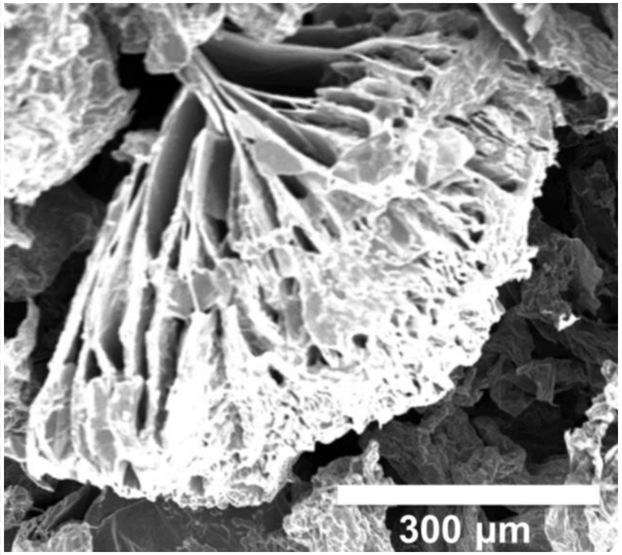
RGO made from Modified Hummers Method

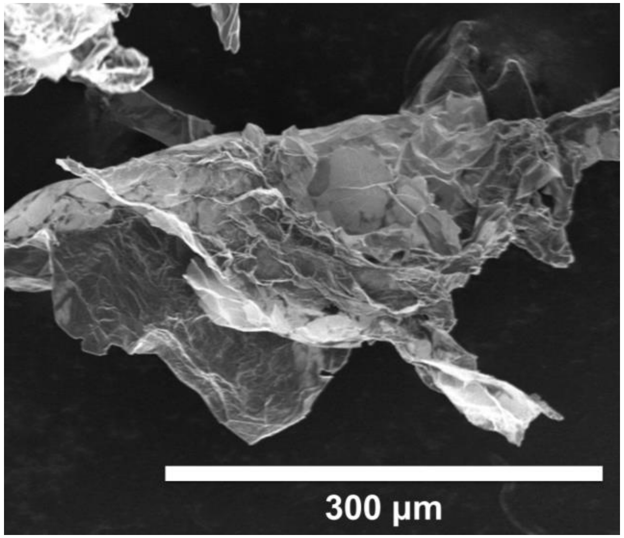
Lateral size: 10-15 μm
Time-consuming synthesis

Electrochemical Exfoliated Graphene (EEG)

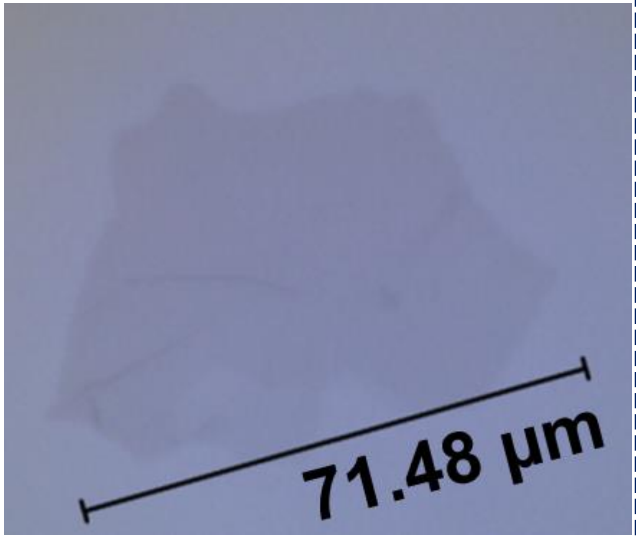
- Developed scalable in-house electrochemical exfoliation approach to synthesize GO sheets
- Low cost graphene powder
- Large lateral size (10-100 μm)
- More rapid synthesis

SEM Micrographs of EEG





Optical Image of EEG

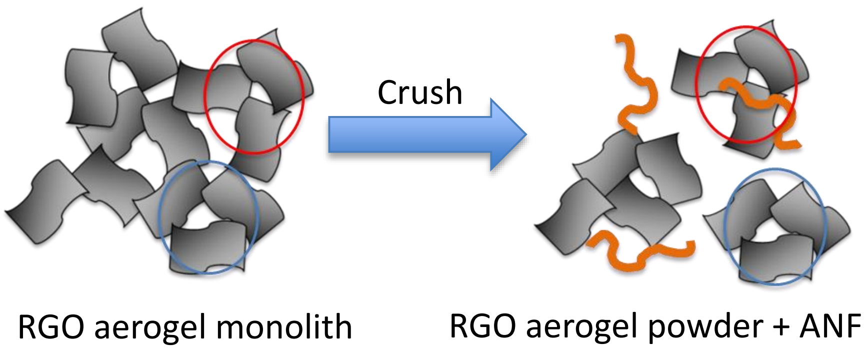


Examine Role of Electrode Architecture

Future Work: **Incorporate aramid nanofibers (ANFs)** to improve mechanical properties of 3D RGO gel architectures

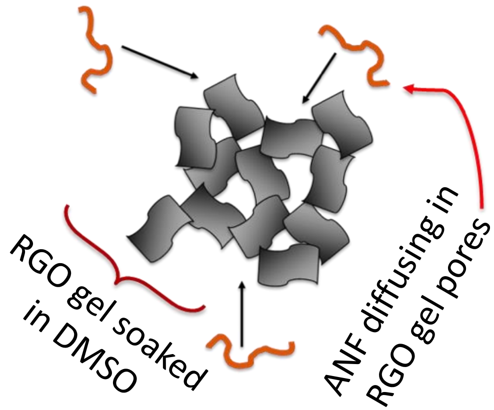
Aerogel as Filler

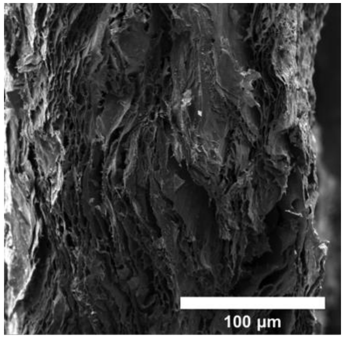
- Create RGO aerogel monoliths
- Crush these monoliths into a powder that retains high surface area
- Use as conductive binder in ANF electrodes



Aerogel as Monolith

- Infuse GO gel (soaked in DMSO) with ANFs dispersed in DMSO+KOH
- Coagulate the ANF infused GO in water to form monolithic composite
- Cold press to form electrodes





3D morphology stays intact after cold pressing RGO gel

Key Discoveries:

GO gelation generates a 3D macro- and microporous structure with high surface area, and high capacitance at a wide range of current densities

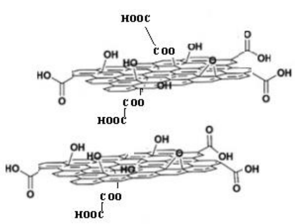
Impact:

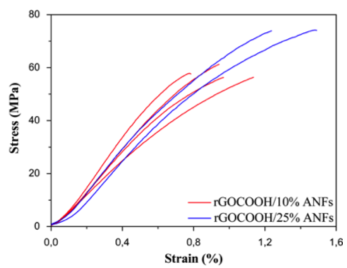
Highly porous structure of the RGO gel provides **high surface area** for better energy storage

Future Experimental Plans

Experimental Manipulation of Interfacial Interactions

Functionalize graphene sheets (with COOH and NH_2 groups) to enhance **interfacial interactions** with aramid nanofibers

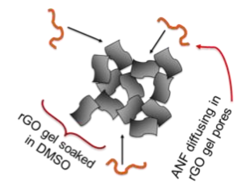




& waviness

Experimental Structure and Properties of RGO/ANF Aerogel

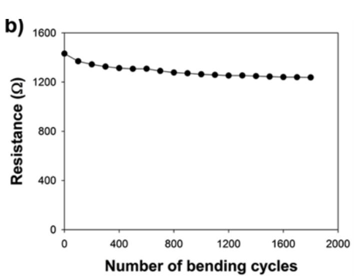
Integrate **aramid nanofiber** inside the porous RGO gel and translate new structure/properties to **micromechanical modeling**



Enhanced capacitance, surface area, ion diffusion

Electromechanical Coupling

Obtain **electrical properties during mechanical deformation** to enable **micromechanical modeling**

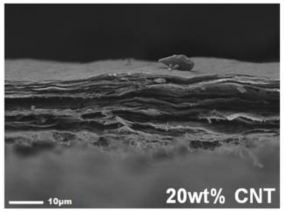


- RGO/25wt% ANF
- Flexed between radii of 4.4 mm and 3.6 mm

& waviness

Role of Third Components CNTs or $LiCoO_2$

Integrate **CNTs** or **$LiCoO_2$** as a third component

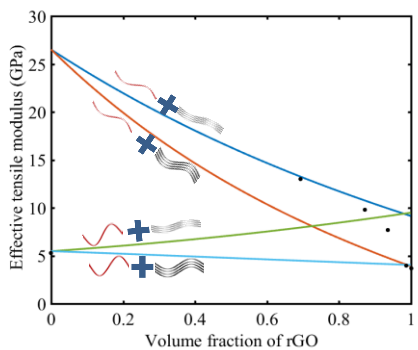


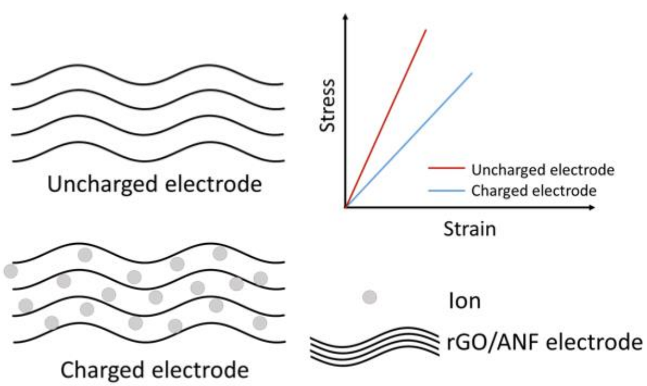
- 76 wt% RGO, 4 % ANF, 20 % CNT
- **CNTs** for porosity and mechanical properties
- **$LiCoO_2$** for battery cathodes, enhanced capacity and energy

Future Modeling Plans

Micromechanical Modeling

- Update Mori-Tanaka method with RGO waviness as a function of RGO volume fraction
- Model effective resistance and capacitance
- Model coupling of mechanical and electrical properties

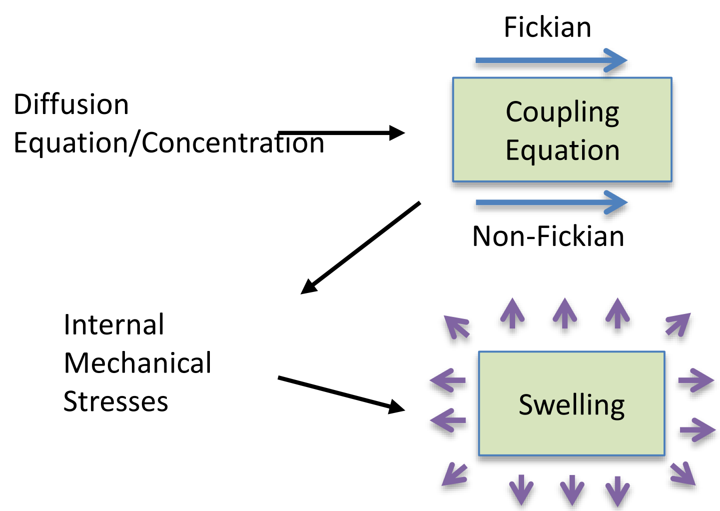




Ion Diffusion Modeling

- Develop the model for lower ANF wt%
- Investigate the ionic conductivity for different configurations
- Coupling diffusivity and mechanical properties to investigate internal insertion stresses[1,2,3]

$$\frac{\partial c}{\partial t} = D\left(\nabla^2 c - \frac{\Omega}{RT}\nabla c \cdot \nabla \sigma_h - \frac{\Omega c}{RT}\nabla^2 \sigma_h\right)$$



1. Christensen, Newman, J. *Solid State Electrochemistry.* (2006); 2. Christensen, *J. The Electrochemical Society* (2010); 3. Zhang et al. *J. The Electrochemical Society* (2007) .

Publications and Presentations Planned

Papers in published, submitted, or in preparation:

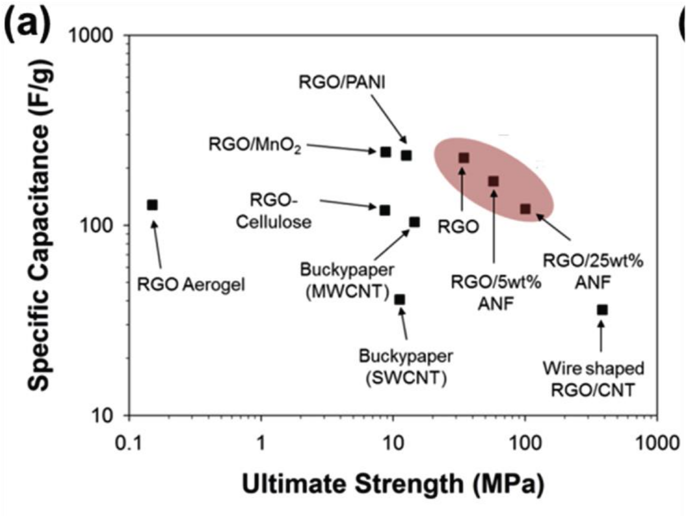
1. "Robust and Flexible Aramid Nanofiber/Graphene Layer-by-Layer Electrodes," *ACS Applied Materials & Interfaces* 2017*, Just Accepted*. **Lutkenhaus.**
2. "Mechanically Strong Graphene/Aramid Nanofiber Composite Electrodes for Structural Energy and Power," *Submitted and In Revison.* **Lutkenhaus and Boyd**.
3. "Micromechanics Modeling of In-plane Modulus of Aramid Nanofiber-Functionalized Graphene Composites," *In Preparation.* **Lagoudas, Boyd, Lutkenhaus**
4. "Micromechanics Modeling of Electrical Conductivity of Aramid Nanofiber-Functionalized Graphene Composites," *In Preparation.* **Lagoudas, Lutkenhaus, Boyd**
5. "Modeling Ionic Diffusion in rGO/ANF Electrode in Supercapacitors and Batteries," *In Preparation*. **Ardebili, Lutkenhaus**
6. "Composites of Aramid Nanofibers and Porous Reduced Graphene Oxide Gels for Obtaining Tougher Battery Electrodes," *In Preparation.* **Green, Lutkenhaus**

Conference abstracts submitted:

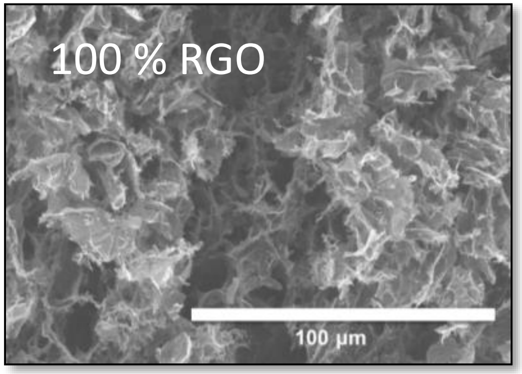
1. "Micromechanics Modeling of Aramid Nanofiber-Functionalized Graphene Composite Electrodes," Society of Engineering Science (SES) 54th Annual Technical Meeting, Boston, MA, USA, Jul 25-28, 2017
2. "Manufacturing, Characterization And Micromechanics Modeling Of Aramid Nanofiber-functionalized Graphene Electrodes," 21st International Conference on Composite Materials (ICCM), Xi'an, China, Aug 20-25, 2017
3. "Fabrication, Characterization and Modeling of Aramid Nanofiber-Functionalized Graphene Composite Electrodes," Conference on Smart Materials, Adaptive Structures and Intelligent Systems (SMASIS), Snowbird, UT, USA, Sept 18-20, 2017
4. "Manufacturing, Characterization and Modeling of Aramid Nanofiber-Functionalized Graphene Electrodes," American Society for Composites (ASC) 32nd Annual Technical Conference, West Lafayette, IN, USA, Oct 23-25, 2017
5. "Crumpled graphene nanosheets and their assembly into crosslinked networks," AIChE Annual Meeting, San Francisco, CA, Nov 2016
6. "Crumpled graphene nanosheets and their assembly into crosslinked networks," ACS Regional, Galveston, TX Oct 2016

Selected Technical Highlights

- Layered electrodes made by flow-directed assembly exhibit **enhanced stiffness and strength** because of the brick-and-mortar structure and interfacial interactions. (Max Young's modulus of 13.0 GPa and max strength of 100.6 MPa for 25 wt% ANF)

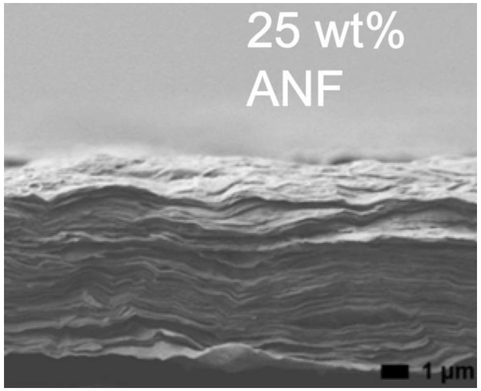


- Random RGO gels have high capacitance (755 F/g at 0.05 A/g)



- First micromechanical and ion diffusion models to capture effects of RGO waviness in this composite

- Waviness strongly affects stiffness



Closing Thoughts

Challenges

- Experimental work is further along, but still trial and error
  - Simulation models are needed to capture structural energy and power
- Electrochemical or mechanical properties are measured separately
  - Electrochemical – mechanical coupling should be considered
- Structural materials limited in choice
  - Expand the materials portfolio
  - Interfaces offer infinite possibilities
    - "God made the bulk; surfaces were invented by the devil" - W. Pauli
- Durability to repeated electrochemical or mechanical cycling
  - Understand failure modes

Broader Applications

- The end-application drives the design criteria
  - Flexible → Wearables
  - Stretchable → Wearables, biometrics
  - High-impact/toughness→ Protection, body armor
  - Stiffness and strength → Structural
- No single materials system simultaneously covers all of these end-applications, yet each offers an opportunity space for new multifunctional energy and power platforms