Processing science at scale to traverse the ‘valley of death’ from fundamental science to commercialization

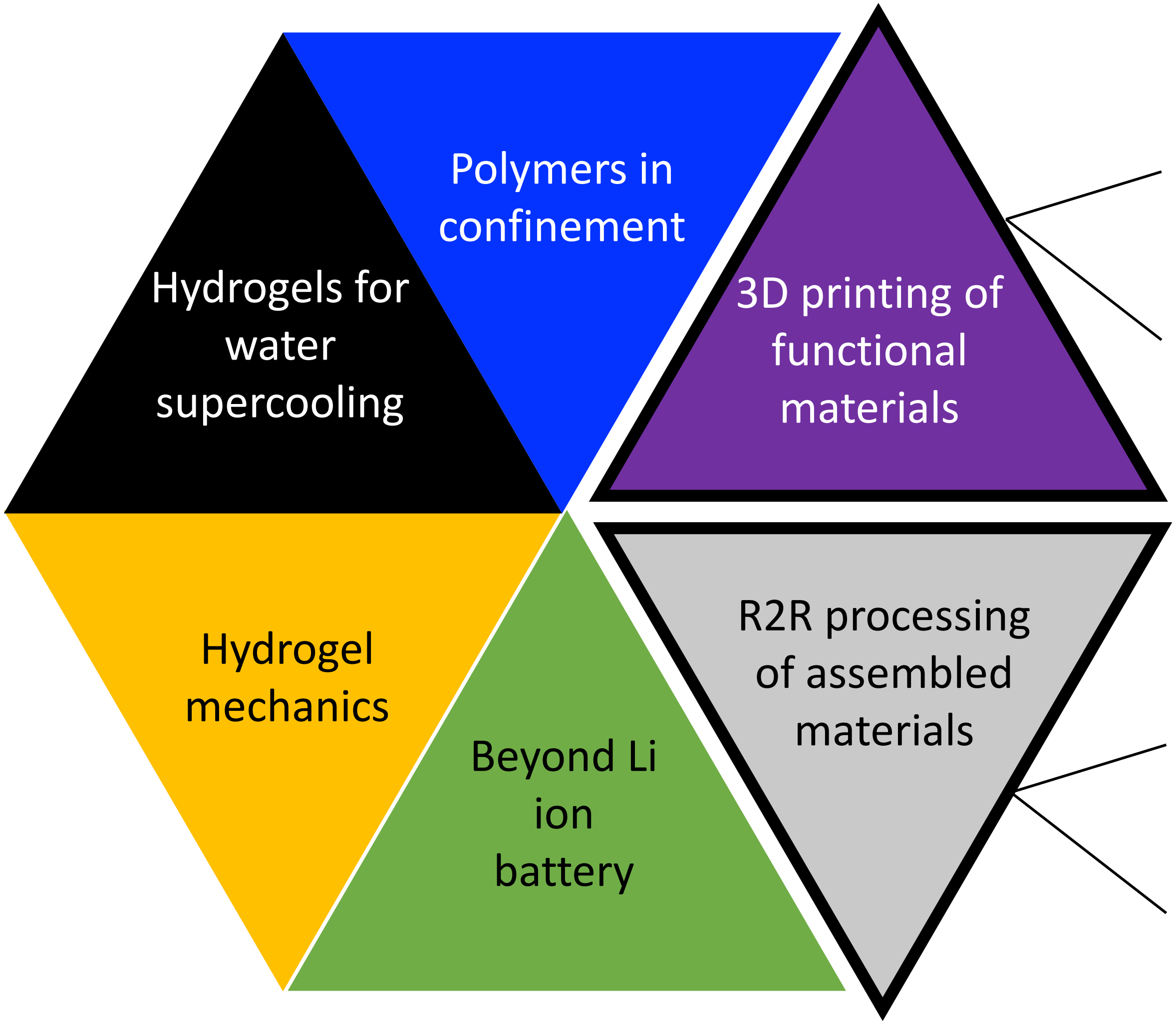
Bryan D. Vogt

Department of Polymer Engineering

University of Akron

Purdue University
26-Feb-2018

Vogt Research Group



Polymers in confinement

Hydrogels for water supercooling

3D printing of functional materials

Complex processing history
Design materials around process
Compatibility with existing tools
New properties imparted

Hydrogel mechanics

Beyond Li ion battery

R2R processing of assembled materials

Continuous processing
Large scale fabrication
Processing dependent structures

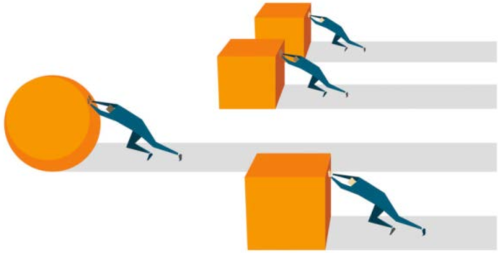
Focus on fundamental understanding that enable improved processes and properties
Process-structure-property relationships through advanced characterization

Scalable (nano)manufacturing

<u>Key considerations</u>

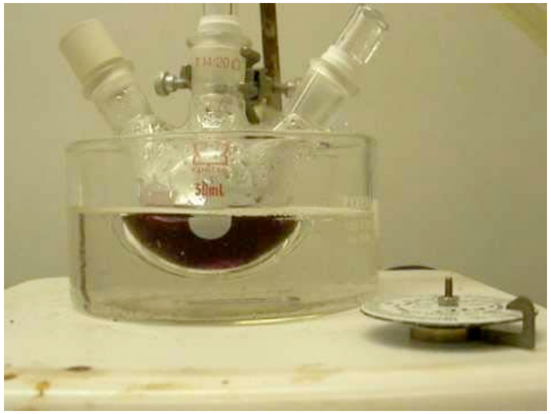
Low cost

Clear advantage



EH&S

How to go from



<100 mg

To this?

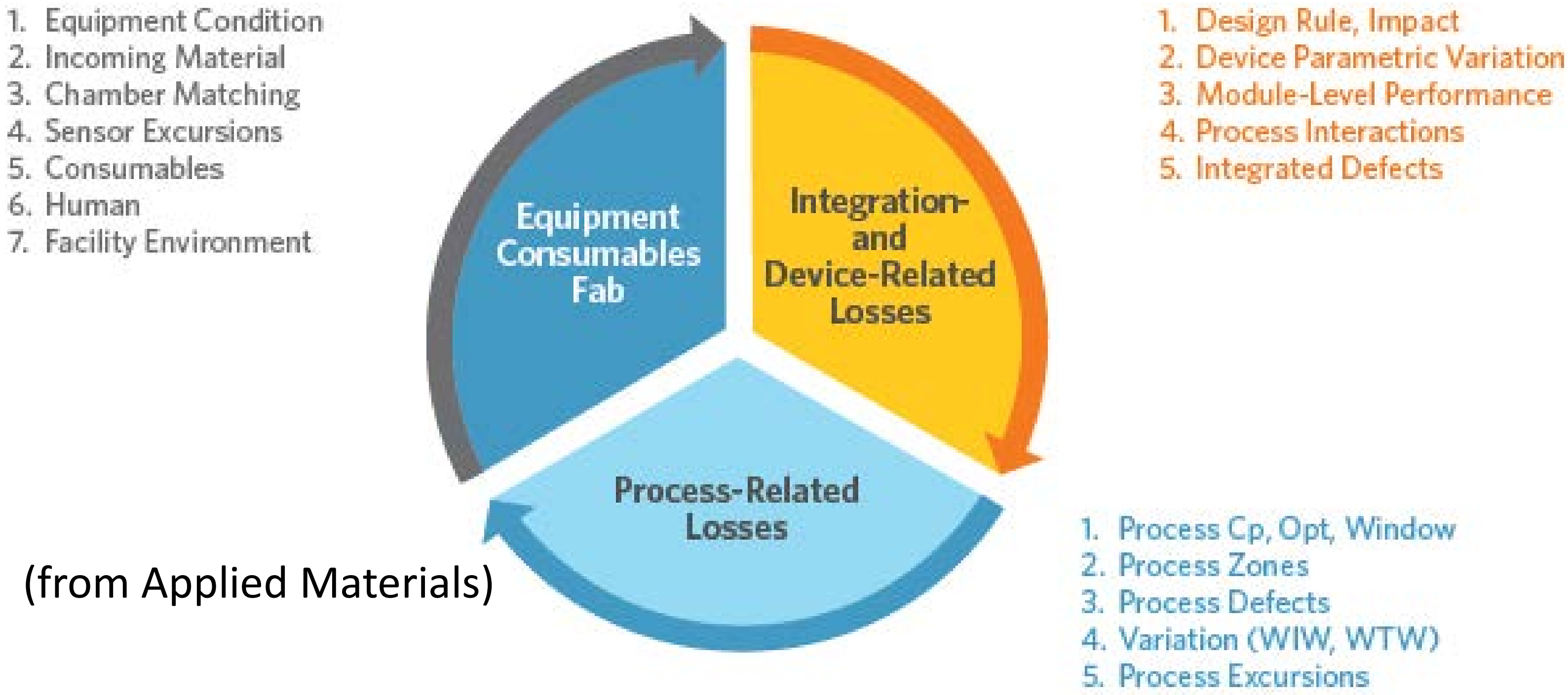
>> kg

Need to consider the entire manufacturing process!

Failure to launch… why “better” isn’t always enough

Can you reproducibly make it at scale? (manufacturability)

Integration with existing equipment?



(from Applied Materials)

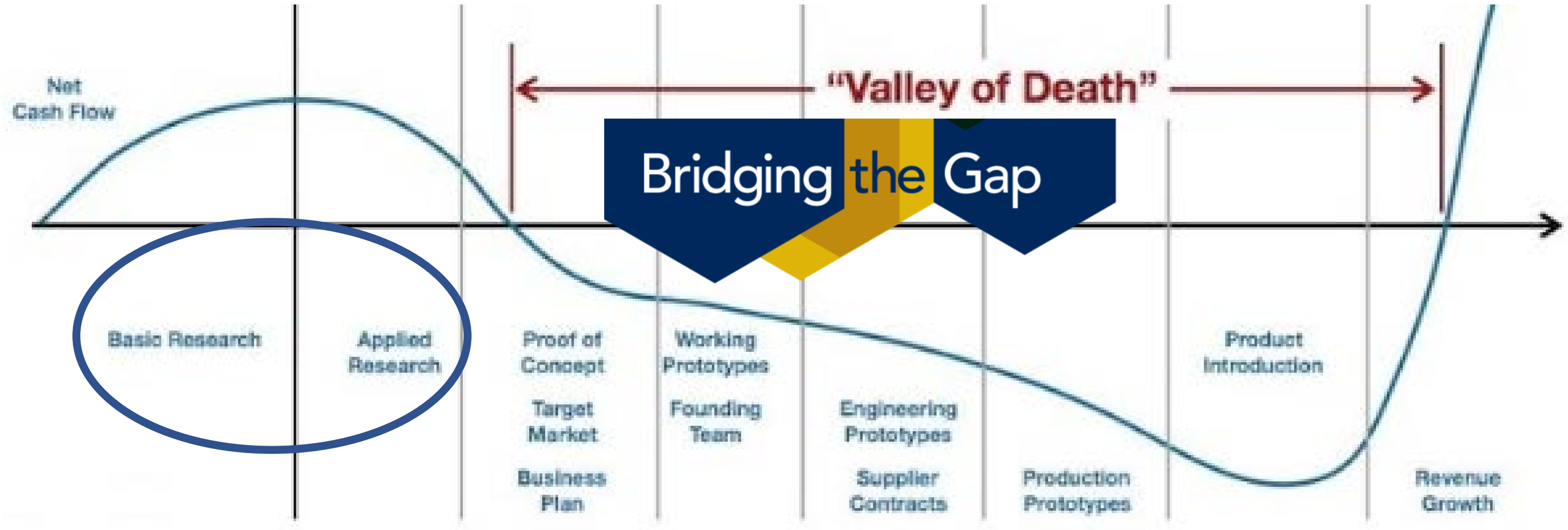
From production of devices, the material is only a small component in determining yield

What is the cost differential to replacement material?

Is there really a market?

Integrating scalability into fundamental science/engineering

lab to commercial product - minimizing Valley of Death

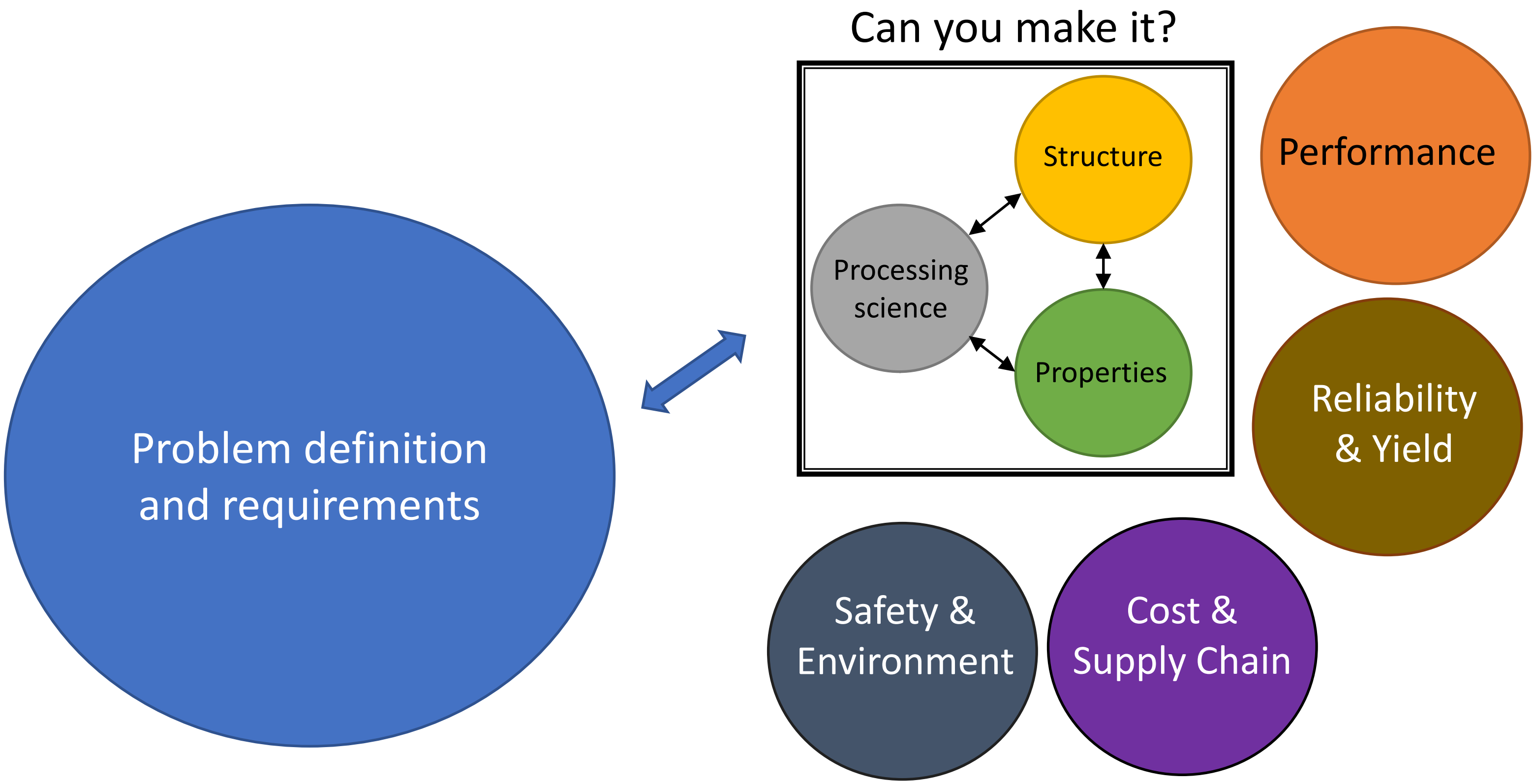


Use of scalable fabrication methods improves ability to translate/commercialize
Early considerations of manufacturability can shorten time for developing prototypes

<u>Added advantages of using easily scaled fabrication:</u>

1. More materials in less time for trial studies
2. Enables new potential applications to be examined (esp. if high material demand)
3. Promotes collaborations as student time cost for providing materials is low

Developing scalable solutions



Problem definition and requirements

Can you make it?

Processing science

Structure

Properties

Performance

Reliability & Yield

Safety & Environment

Cost & Supply Chain

Considerations of processing and manufacturing can lead to early decisions to assist the ability to translate to commercialization

3 vignettes on scalability considerations

- Stretchable dry electrodes
  - Problem: Motion sickness during virtual reality (VR) use
  - Requirements: Tunable areas and surface structures for contact with skin
- 3D printing
  - Problem: Trade-off between mechanical properties and dimensional accuracy
  - Requirements: Use commercial materials and compatible with existing 3D printers
- Room temperature sodium sulfur batteries
  - Problem: Polysulfide shuttling degrades lifetime
  - Requirements: low cost precursors and highly reproducible

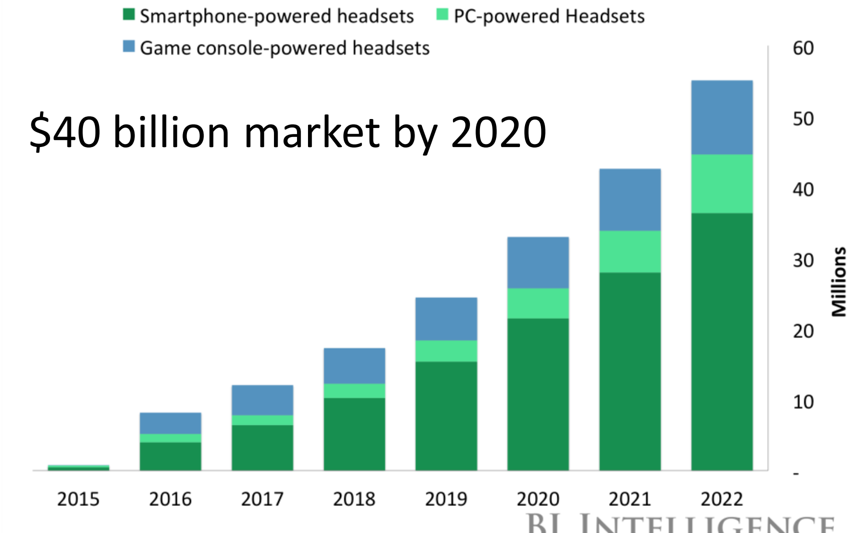
OFMJC

Federal Research Network

Virtual reality

FORECAST: Global VR Headset Shipments

By Category

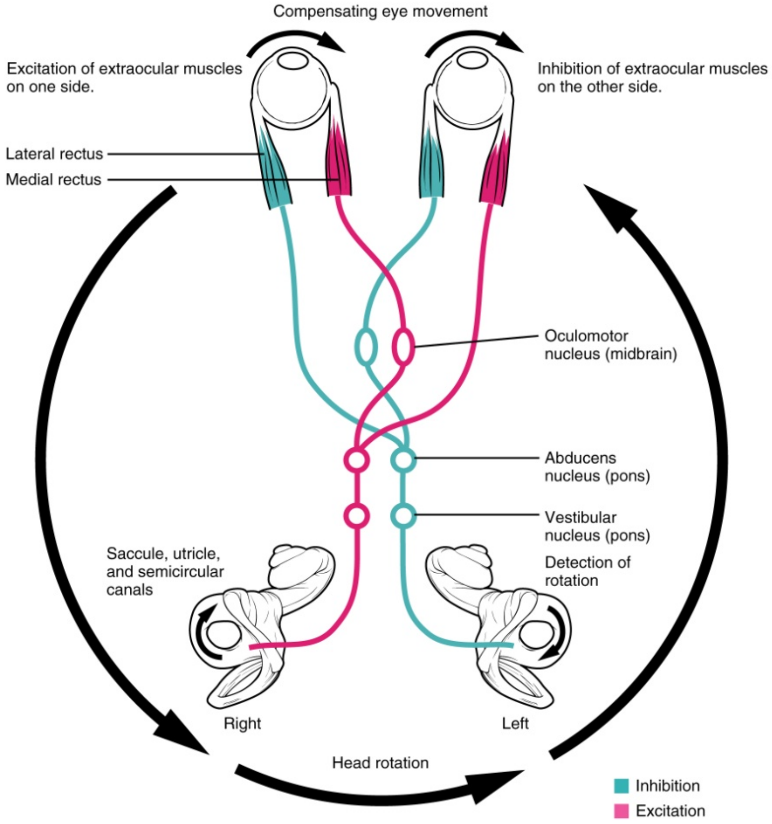


$40 billion market by 2020

Motion sickness problem:

78 % of women, 33 % of men for action games

“Real sick: The immersive experience of the virtual world is not for everyone” Science News 2017 March 18

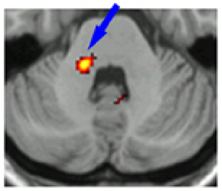


Cue conflict!

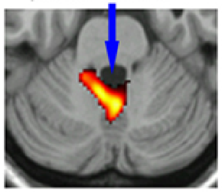
Visual and vestibular systems

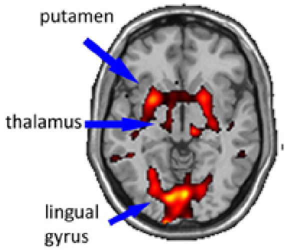
Connection between vision and balance

vestibular nuclei

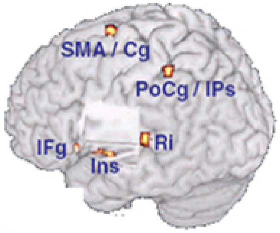


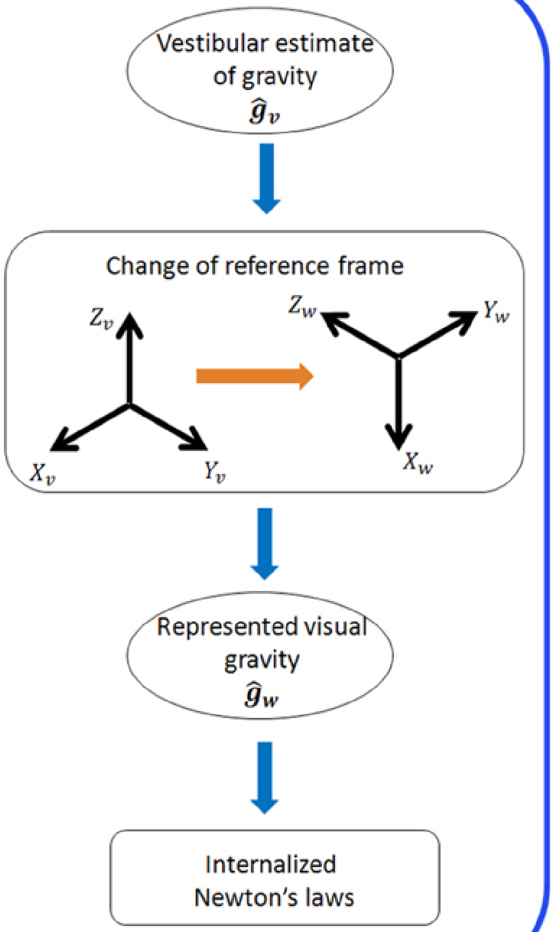
posterior vermis





vestibular network





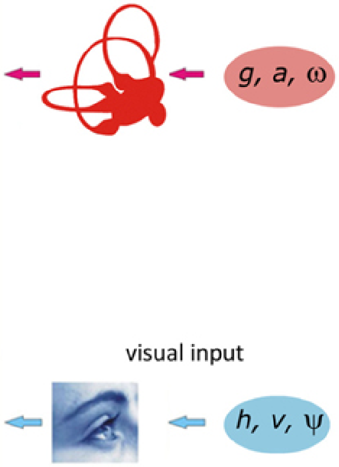
Vestibular estimate of gravity $\hat{g}_v$

Change of reference frame

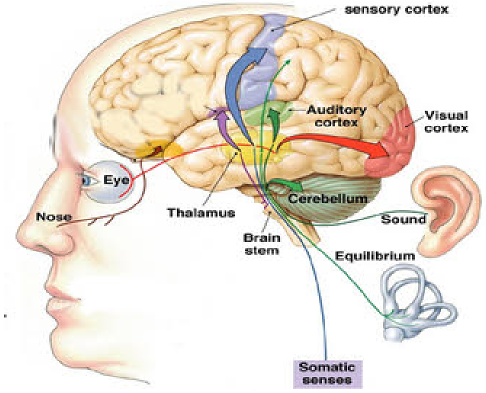
Represented visual gravity $\hat{g}_w$

Internalized Newton's laws

vestibular graviceptors



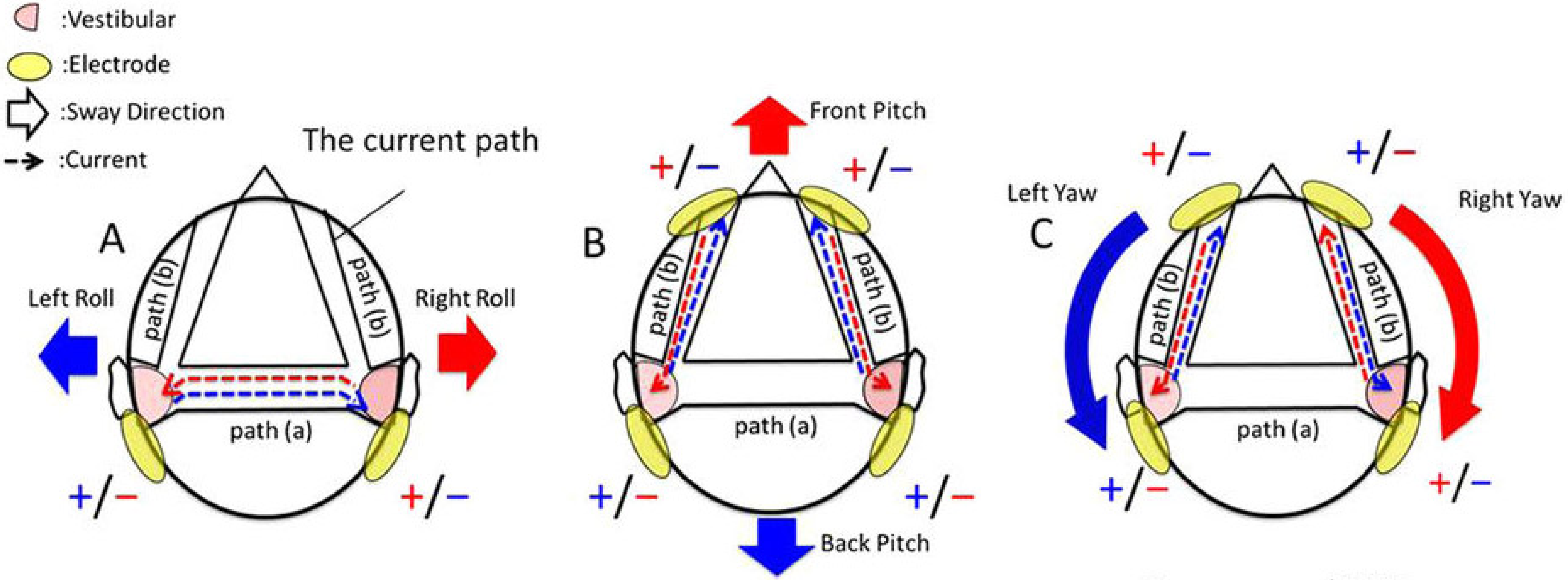
visual input



Need both systems in synch for motion and reflexes

Vestibular network

Based on electrical signals – external stimulation useful therapy



Conventional two-pole GVS

lateral directional stimulation
(LDS)

Conventional three-pole GVS
same directional
anteroposterior stimulation
(SDAS)

Our proposed GVS
opposite directional
anteroposterior stimulation
(ODAS)

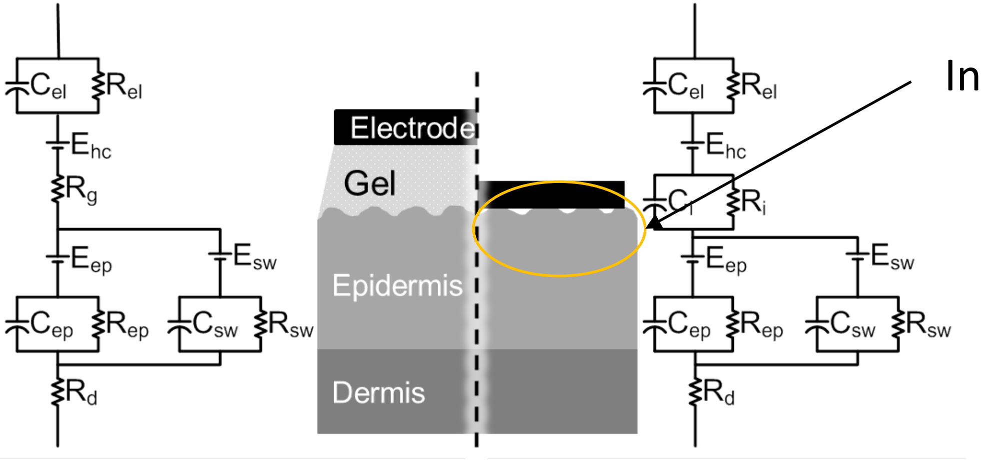
Aoyama et al. Sci. Rep. 2015, 5, 10168

Key for stimulation is good contact to the body

Stimulation of the vestibular network

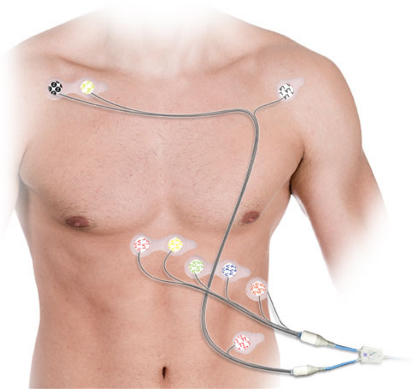
Standard electrodes use gel for contact

Dry electrodes

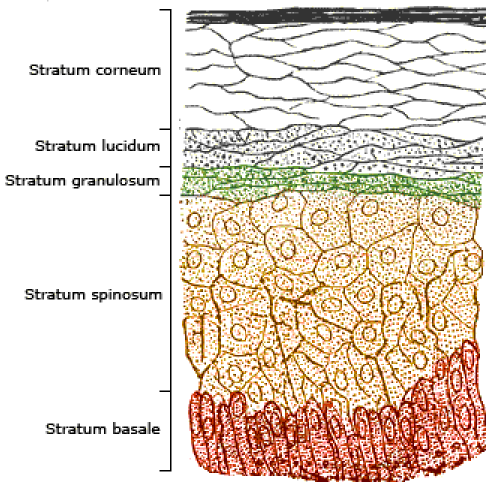


Interface important

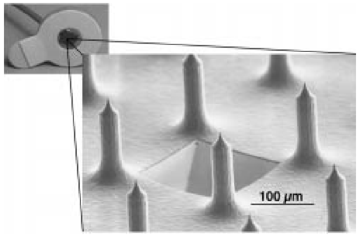
Meziane, *Physiol. Meas.*, 2013, **34,** R47



High resistance



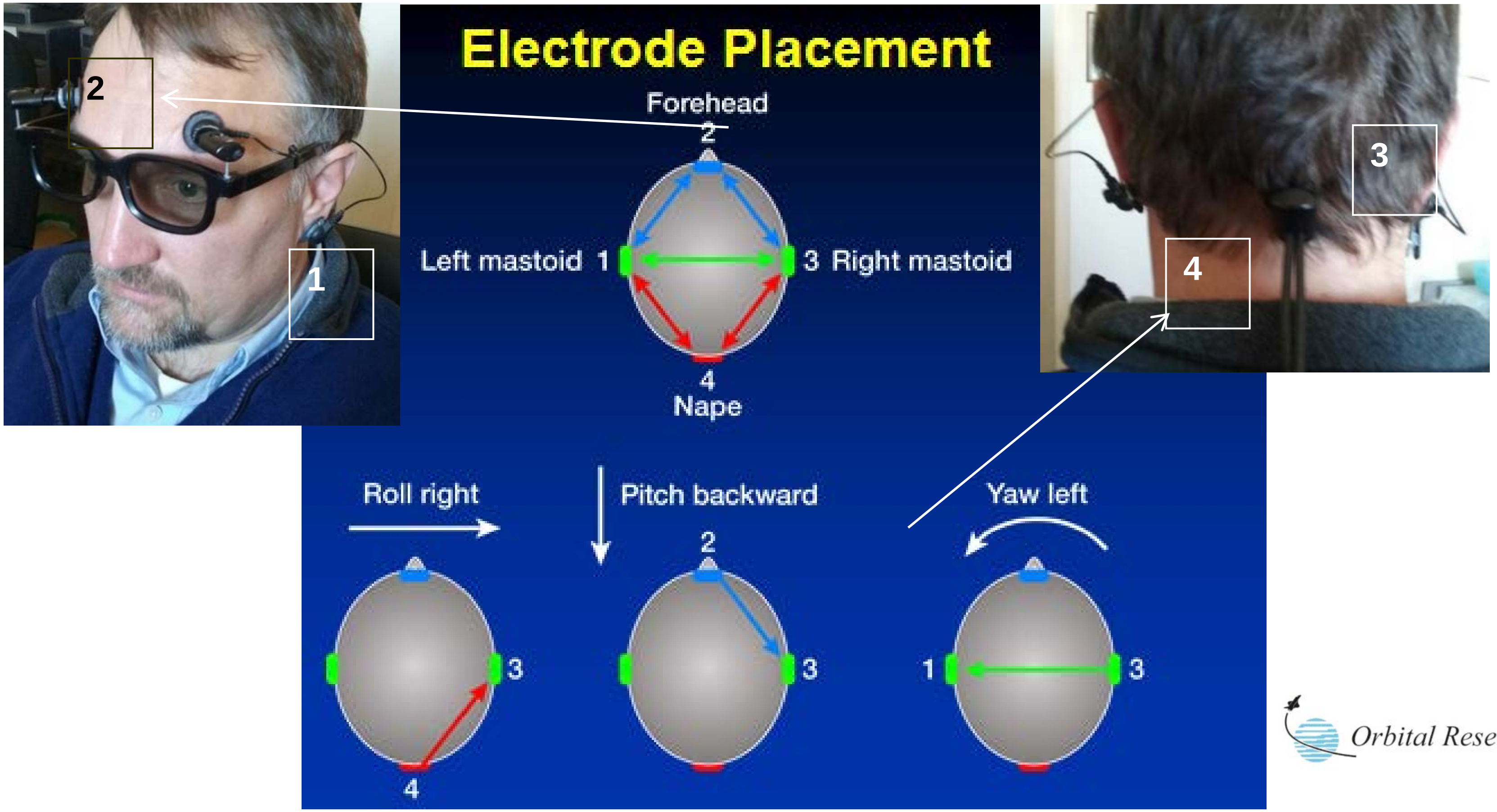
Standard Ag/AgCl electrodes for EKG



Disadvantage for gels: messy and undesired for VR

Proof of concept for dry electrodes

Galvanic vestibular stimulation and transcranial direct current stimulation



Orbital Research Inc.

It works but…

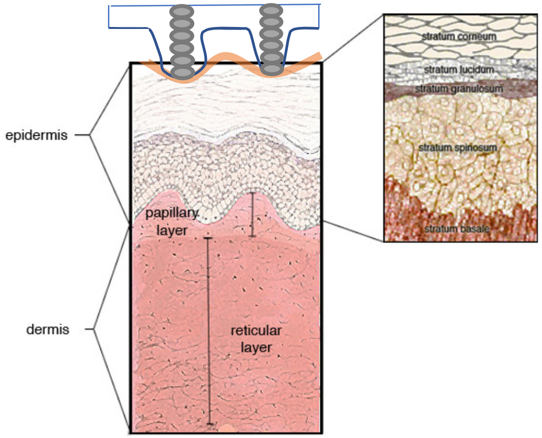
Painful after about 15 min

Ag/AgCl coating leaves tattoo

Problems with design

Injection molded carbon black filled ABS and then coated with Ag/AgCl

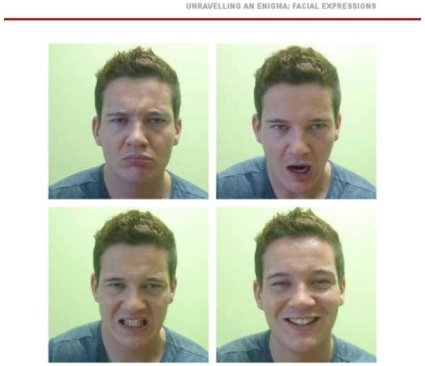
Bumps on surface compress dead skin to improve conductivity



Rigid electrode compressed on skin

Skin moisture + current reduces AgCl

Ag / Ag oxide particles form in dead skin

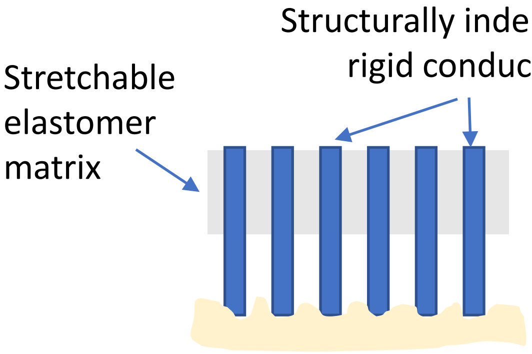


Facial expressions during VR use will lead to pinching of skin from rigid electrode

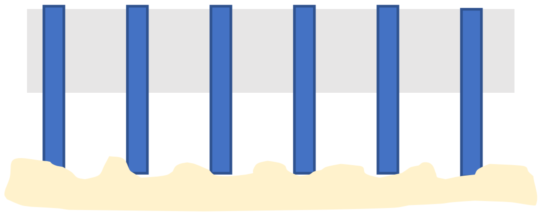
Best shape is dependent on:

- Skin hydration
- Age
- Race
- Gender

Ideal design?



Compressed into skin



Electrodes remain in place but skin around can stretch

- How to manufacture?
  - All electrode pieces are independent
  - Ideal shape is dependent on person

- Problem –acceptable cost for electrodes (Samsung) is only ~ $2/ea

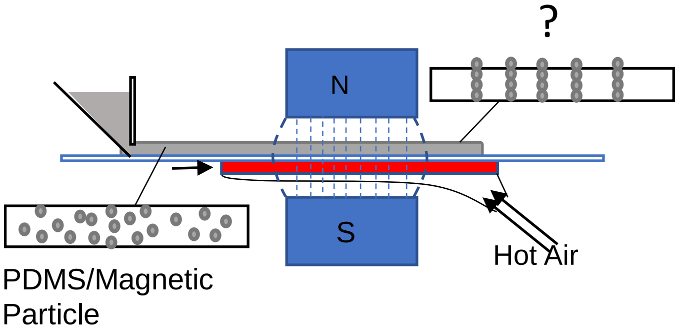
- Are there alternative manufacturing methods to obtain the same structure at lower costs?

Alternative disruptive manufacturing?

MACHINE DIRECTION

20 m line at University of Akron

Concept: sufficient magnetic strength to modulate surface of composite



Alignment of particles?

Ni525B

constrained

Increasing B

Fe_2O_3

3%

5%

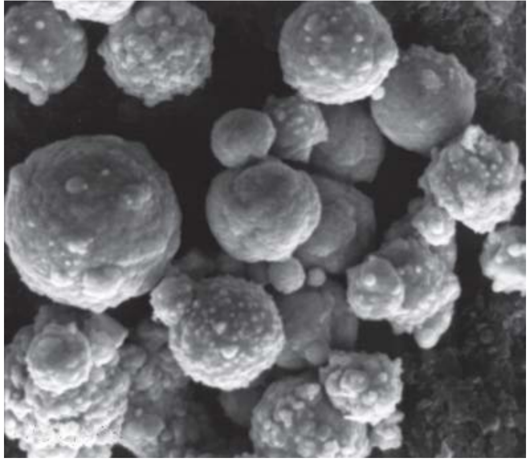
4:1 PDMS:particle (w:w)

Considering manufacture in materials selection

<u>Requirements:</u>

- Magnetic particles for alignment
- Electrical conductivity through material
- Skin-like stretching between electronic pillars

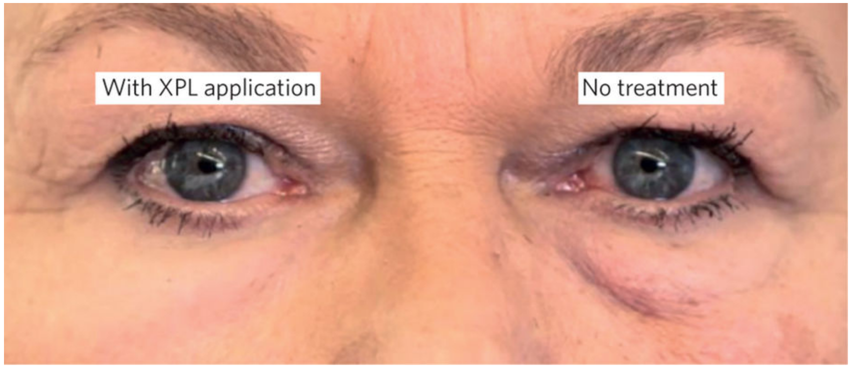
Ni@Ag particles for PV adhesives (Novamet)



Commercial low cost particles (35-45 μm)

+

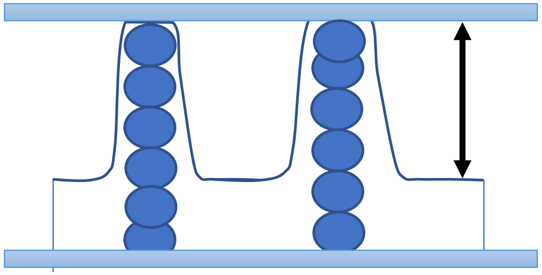
Soft siloxanes used for wrinkle treatment



Nat. Mater. **2016**, 15, 911-918

Easy to 'match' mechanical properties of skin

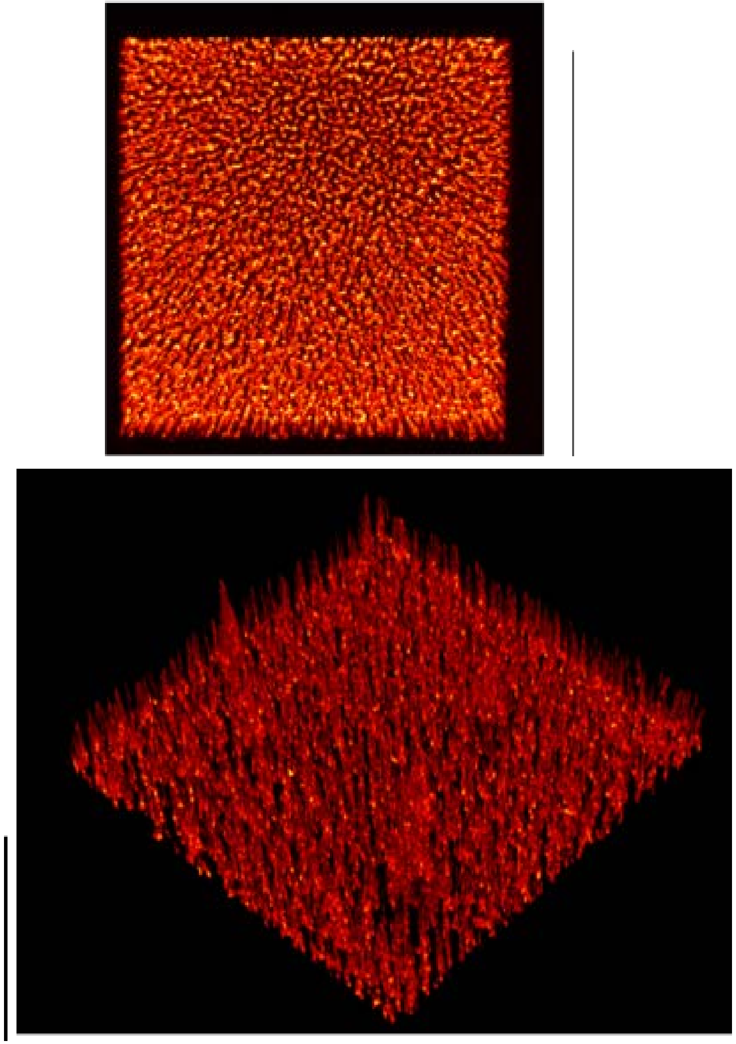
Target structure:

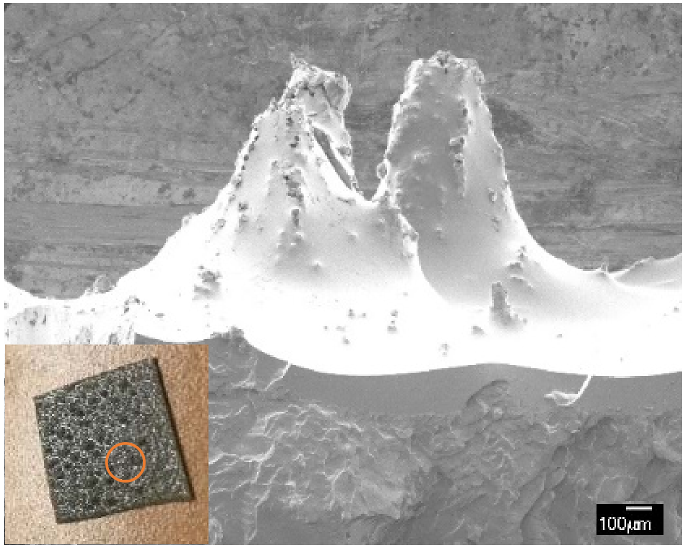


Magnetic field induced surface structures

Controlled surface morphology

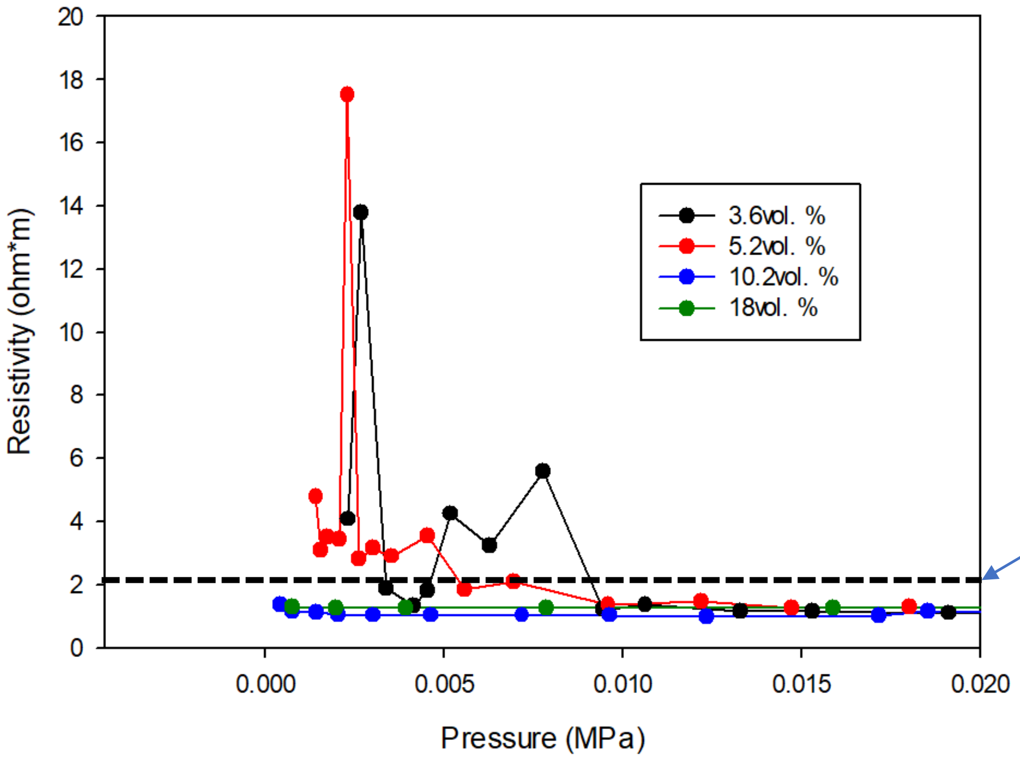
Increasing field strength





Can align between 2 permanent magnets

Conductivity through thickness



Injection molded electrode

Stable conductivity at ~ 10 vol % Ni@Ag particles
(well below percolation threshold)

Able to match initial prototype performance

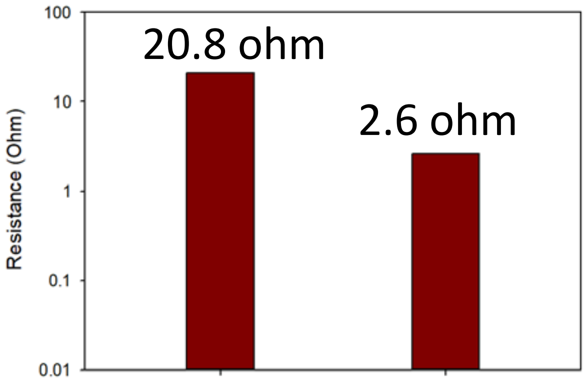
Decreasing the Ag requirement

Ni@Ag particles exhibit nanofeatures
Potential for reduced melting point?

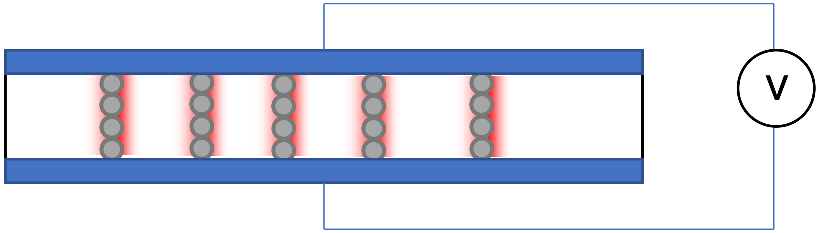
PDMS/Ni@Ag5.3vol%

As cured

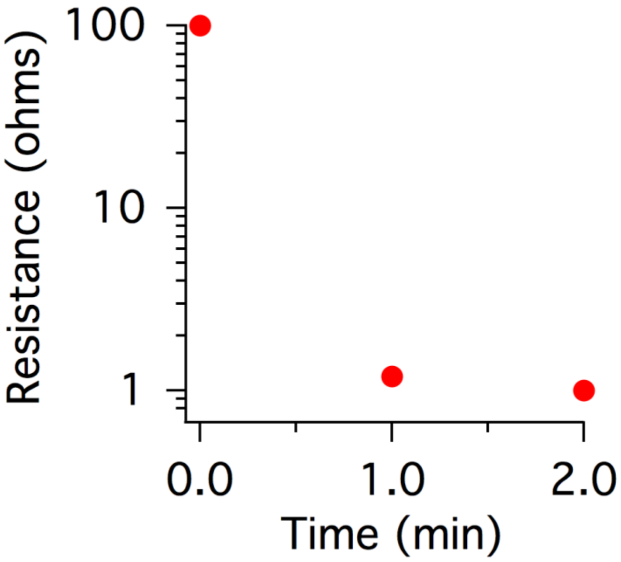
230°C for 2h



Heat generated: $Q=I^2Rt$



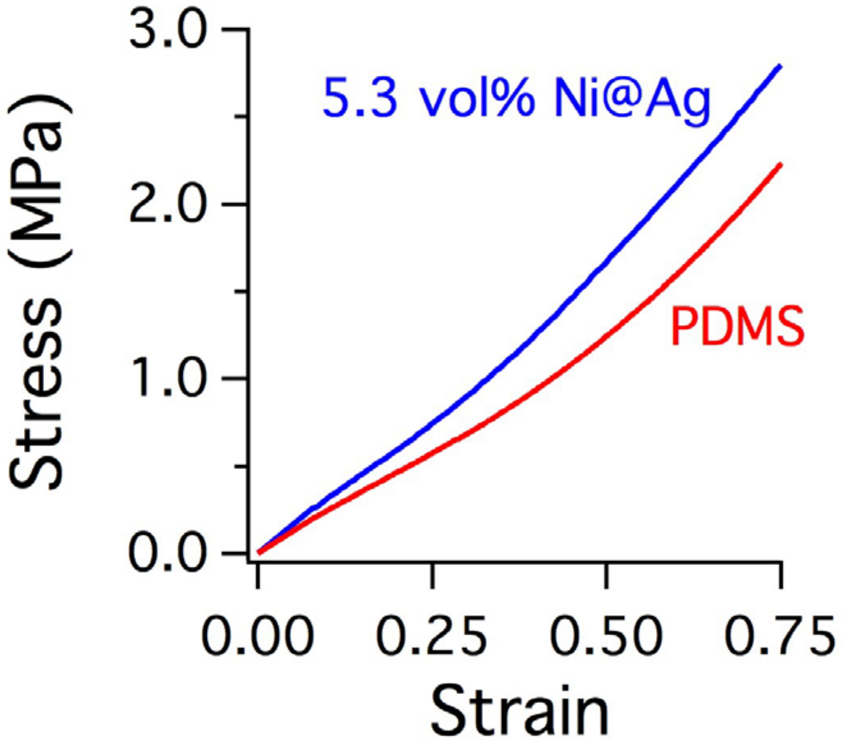
Aligned with 1.8 vol % Ni@Ag



No embrittlement

2 orders of magnitude decrease in resistance with quick current heating
Potential for decreased Ag utilization while maintaining performance

Flexible electrodes from R2R processing



Limited impact of Ni@Ag on mechanical properties of PDMS at modest strain

Resistance decreases on stretching (3.5 → 2.6 ohm) as thickness decreases (1.44 → 1.22 mm)

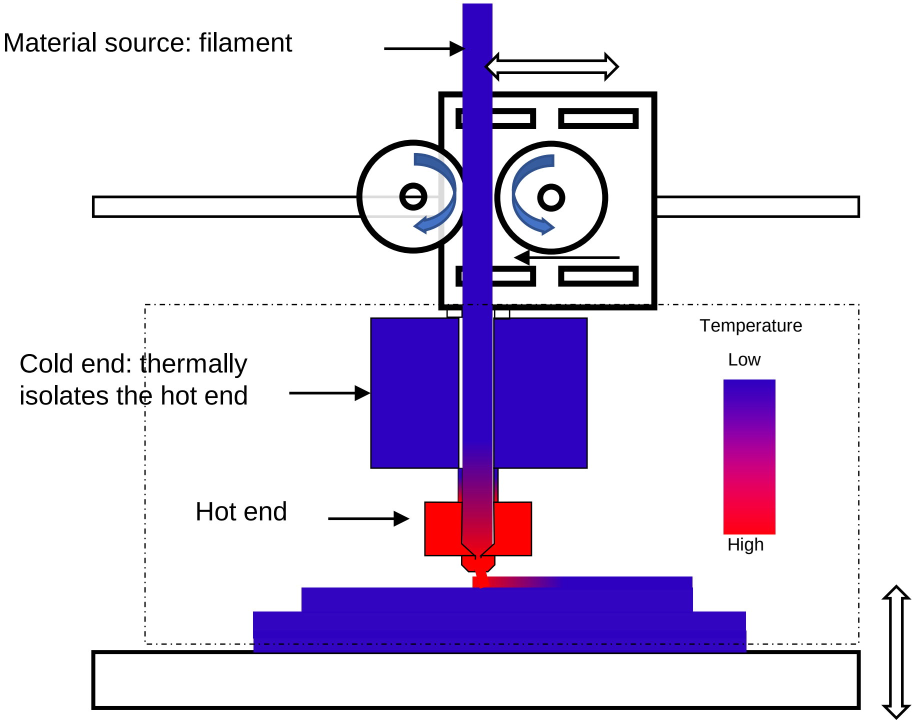
Summary

- Roll-to-roll with magnetic field can produce textured surfaces
  - Texture is controlled by field strength and particle loading
- Resistance of well aligned particles similar to injection molded hard design
- Electrodes can be modestly stretched without significant loss of conductivity
- Performance of these electrodes exceeds that of current state of the art
  - Stretchability provides comfort during use
  - Low pressure threshold for conductivity less than required to ensure contact during operation
  - Simple continuous process using commercially available materials to generate complex structures
- Key remaining challenge: integration of electrode

3 vignettes on scalability considerations

- Stretchable dry electrodes
    - Problem: Motion sickness during virtual reality (VR) use
    - Requirements: Tunable areas and surface structures for contact with skin
- 3D printing
    - Problem: Trade-off between mechanical properties and dimensional accuracy
    - Requirements: Use commercial materials and compatible with existing 3D printers
- Room temperature sodium sulfur batteries
    - Problem: Polysulfide shuttling degrades lifetime
    - Requirements: low cost precursors and highly reproducible

3D printing of polymers



Fused Filament Fabrication (FFF)

Fused Deposition Modeling (FDM) - Stratasys

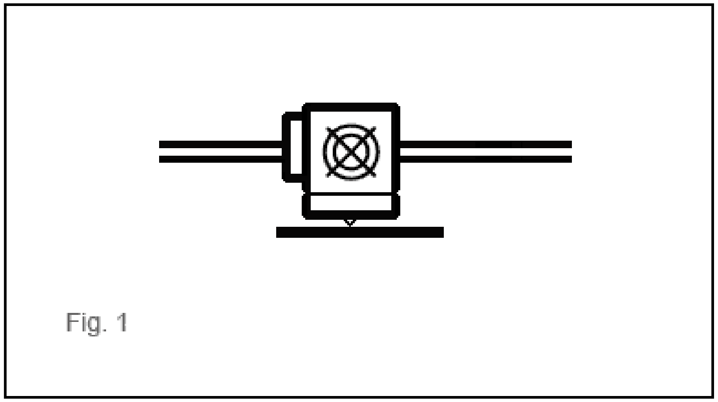
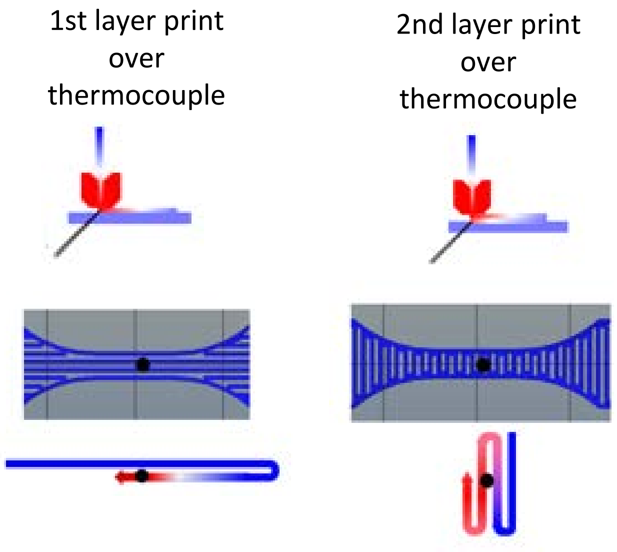


Fig. 1

Advantage:
- Cost-efficient: consume thermoplastic filaments
- Inexpensive machine: as low as $300
- Many potential polymer options:
  - ABS / PLA most common
  - Nylon / PC / PET / PPSF
  - PEEK /Ultem 9085

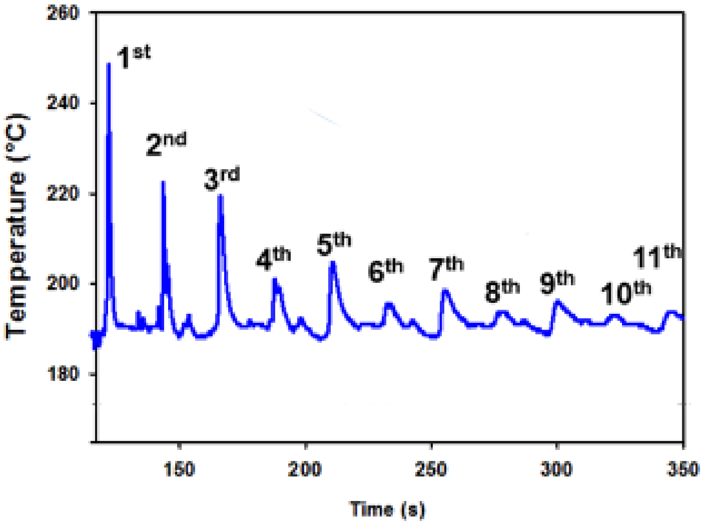
DuPont: Hytrel®, Zytel®, and Surlyn®

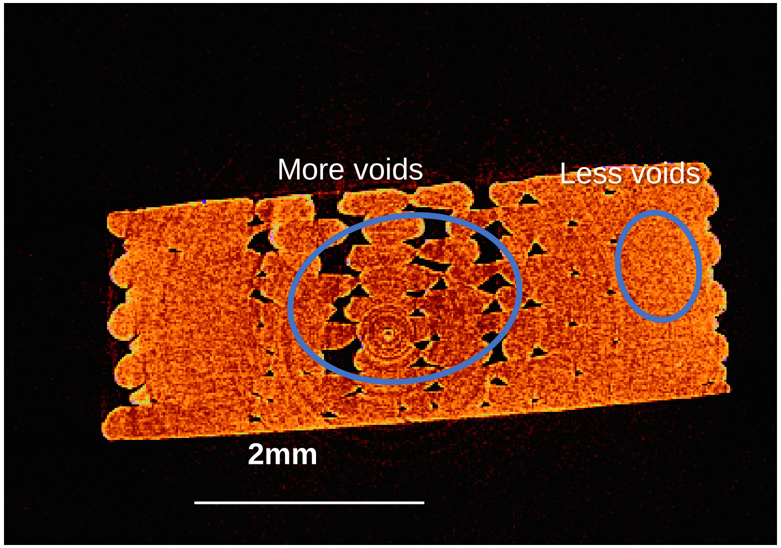
Challenges of 3D printing by FFF



1st layer print over thermocouple

2nd layer print over thermocouple



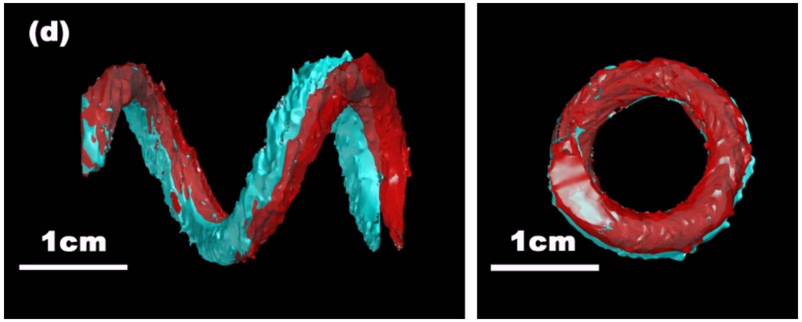


Spaciotemporal thermal history for the part

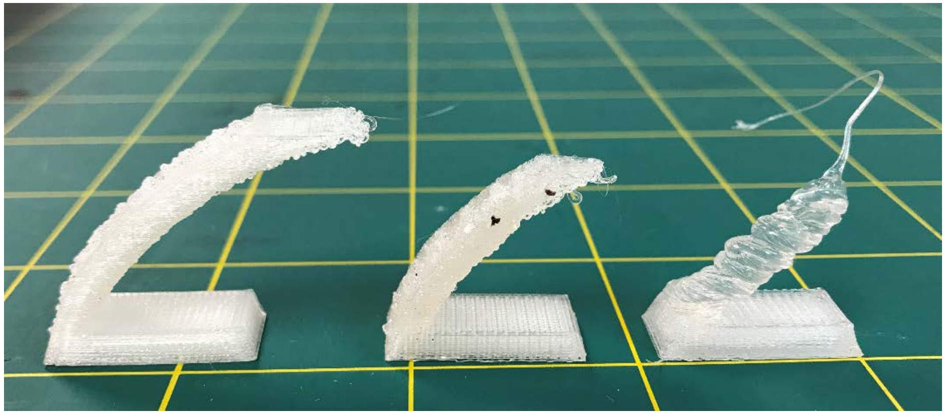
Too low of temperature = voids

Challenges of FFF

Dimensional accuracy



Part overlay



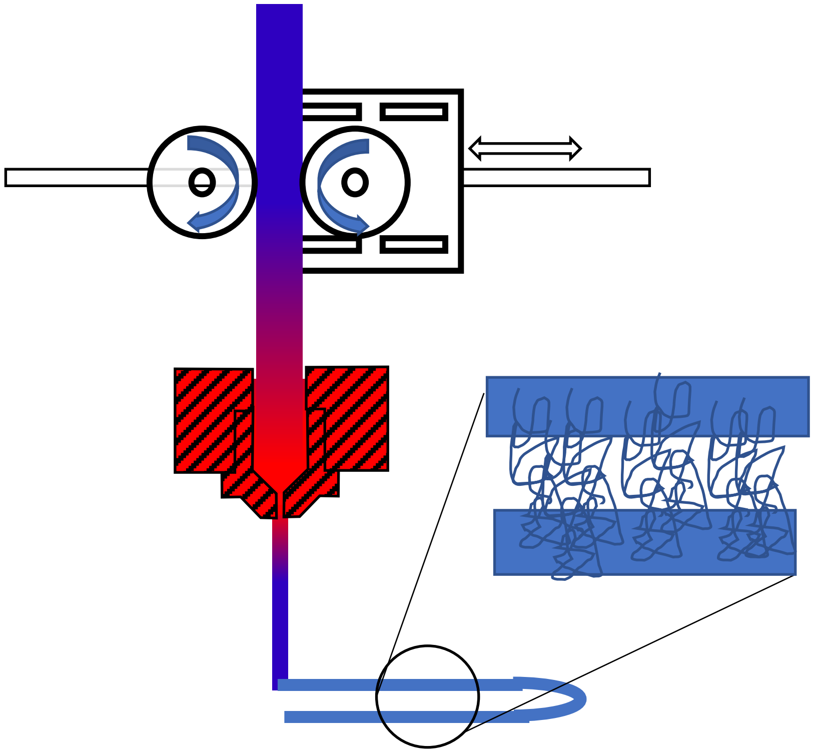
Too high of temperature and part shape is incorrect

Intrinsic process trade-off between mechanical properties and dimensional accuracy

Flow and high temperature desired for eliminating voids

Rapid solidification desired to maintain shape

Hypothetical "ideal" behavior



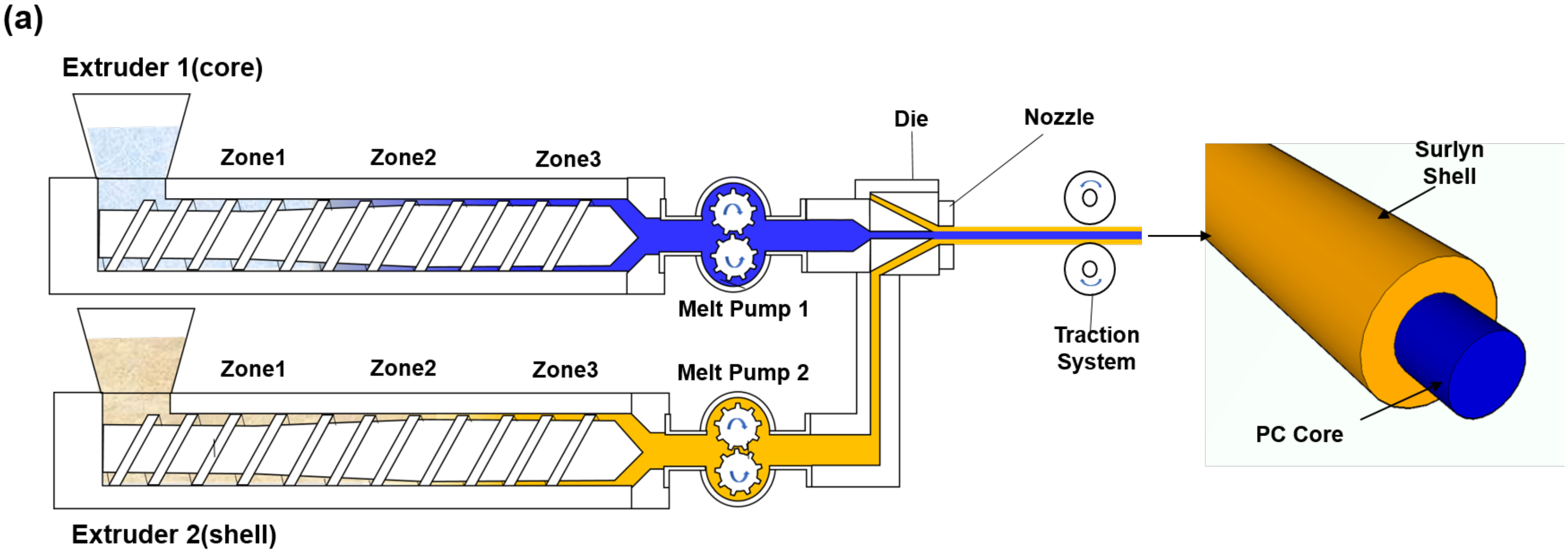
Unimpeded flow across interface for interfacial strength
(slow solidification at interface)

Bulk of polymer solidifies rapidly to maintain shape

Combination of properties challenging to achieve

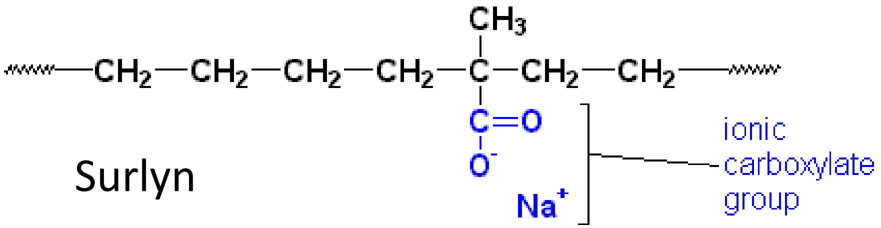
Is there a route to engineer such behavior for 3D printing?

Structured multicomponent filament



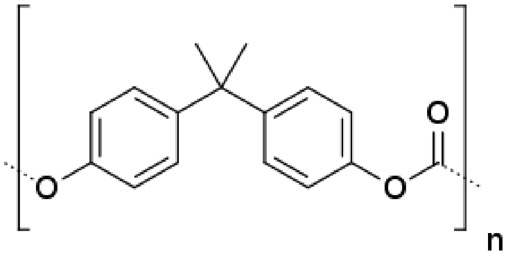
Co-extrude filaments designed based on the flow and thermal properties

Core = high strength and mechanically robust to maintain structure
Shell = tough and easy to flow at high temperatures to minimize the voids

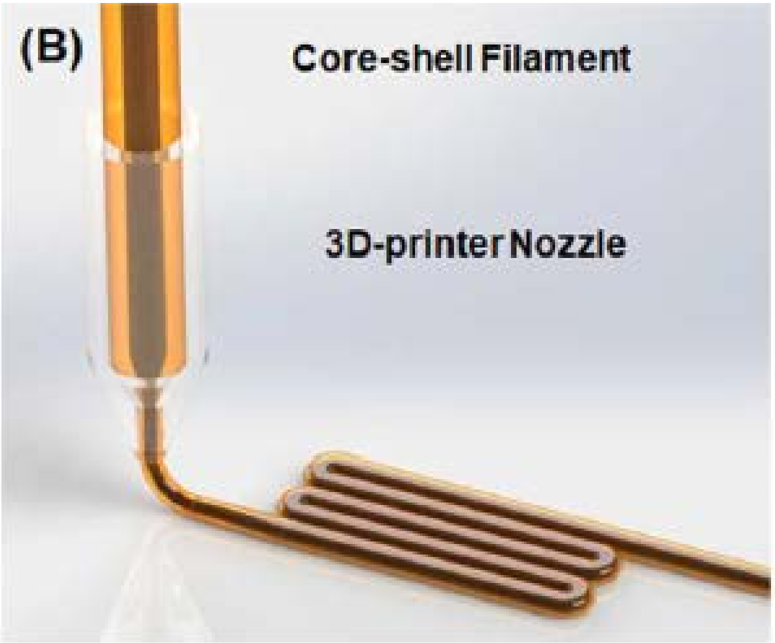


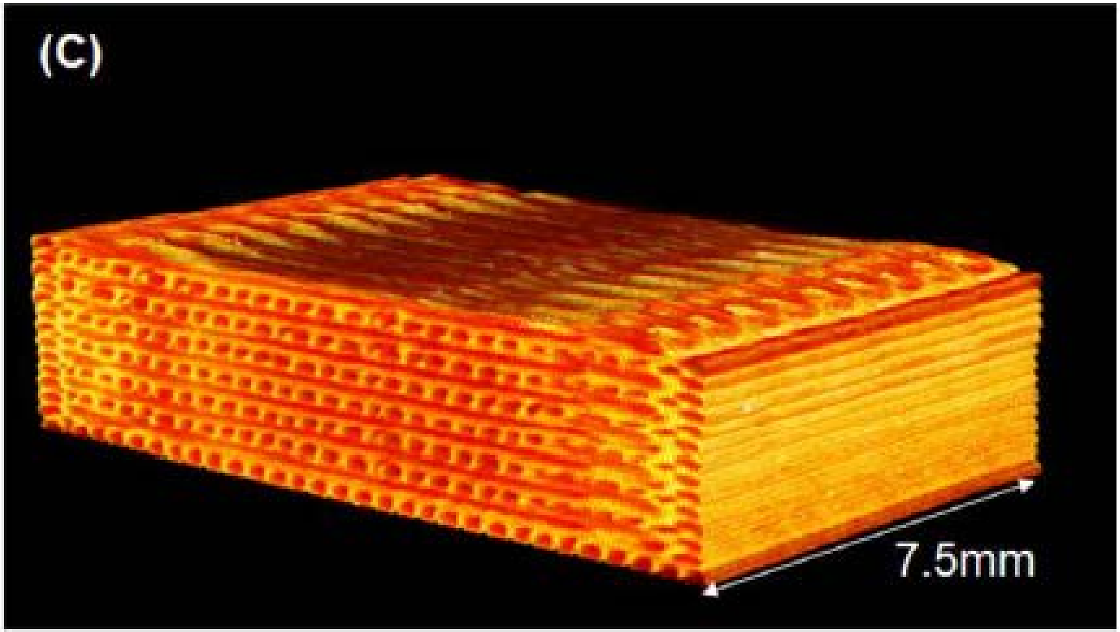
Surlyn

PC



Printing core-shell filament





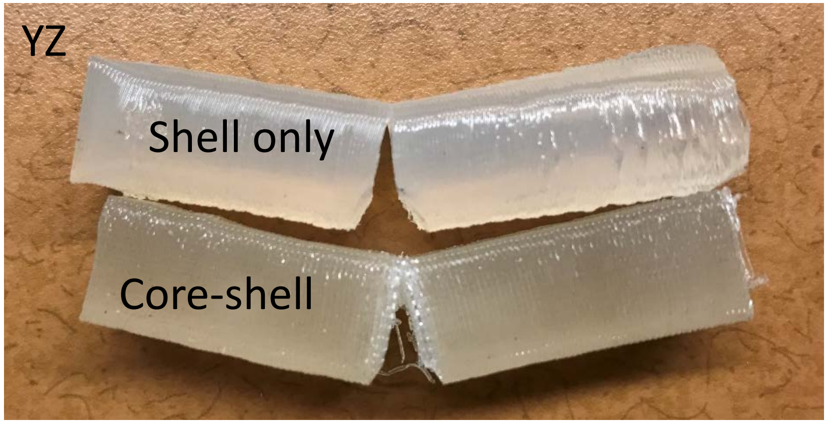
Electron density difference allows structure to be observed with x-ray tomography

Note: no voids are observable with μCT

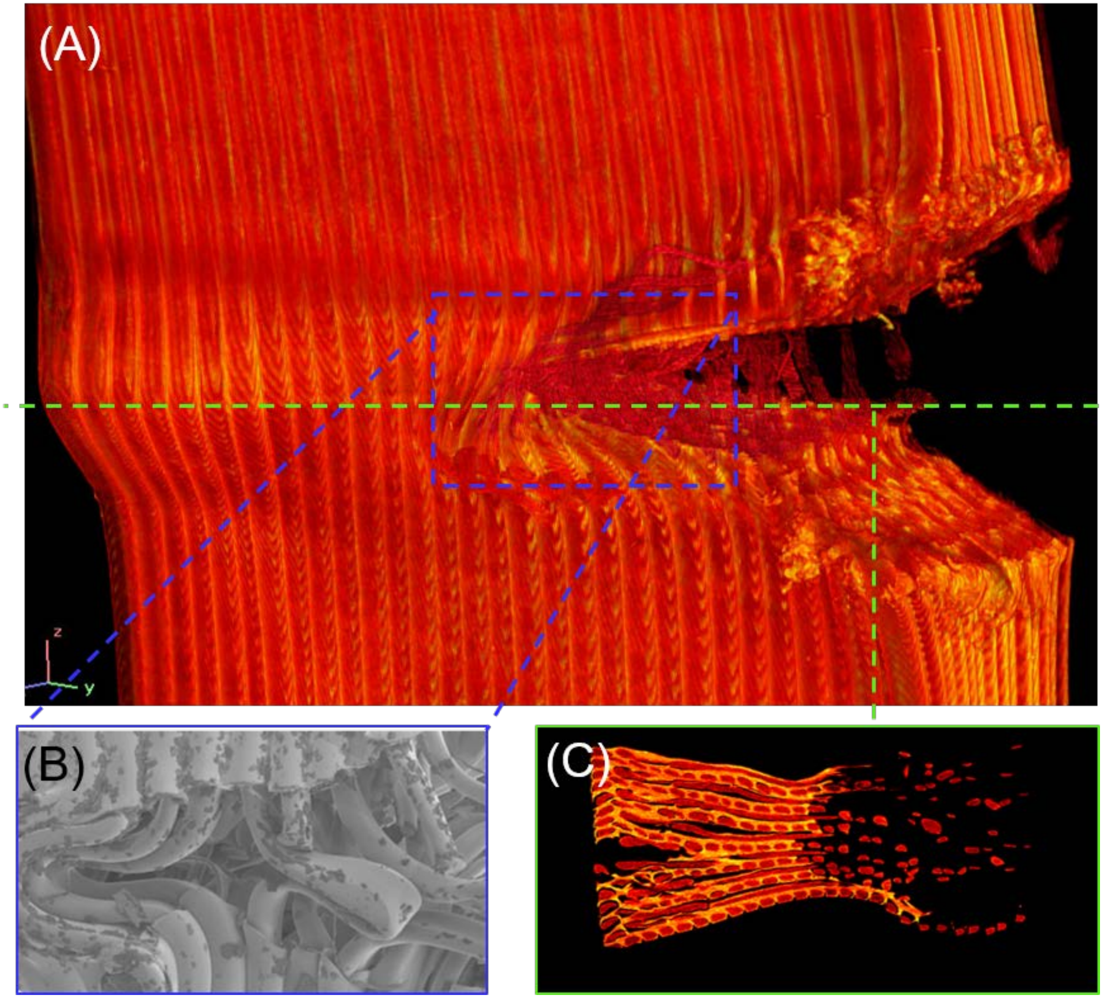
(Printed at optimized conditions for the pure PC)

Impact properties – Bane of 3D printing

Orientation effects on Izod impact



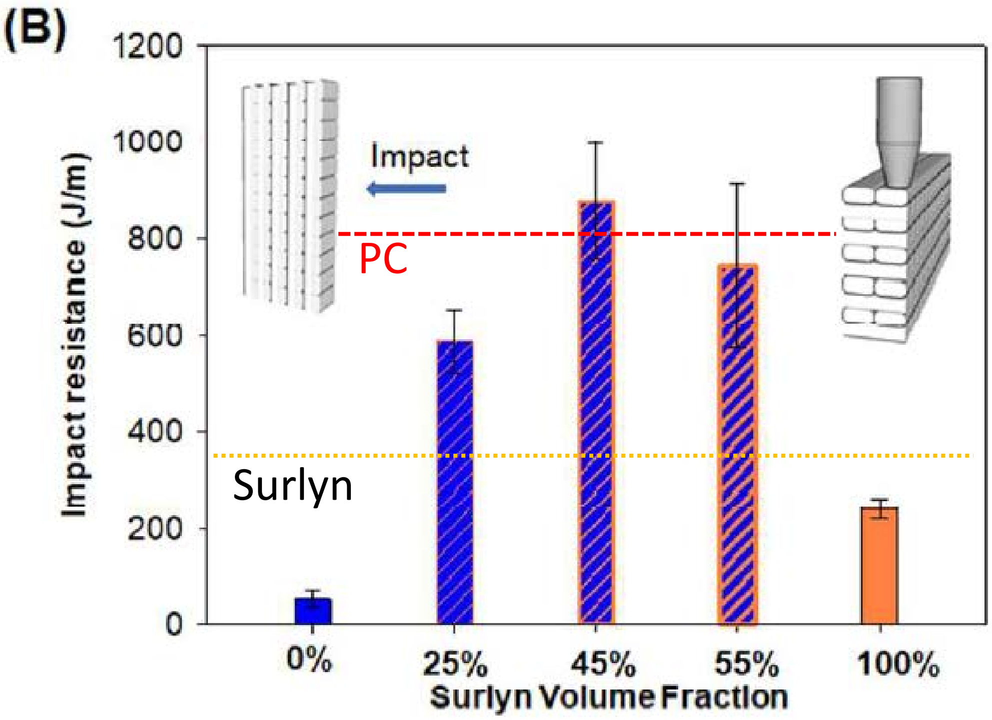
Examination of crack tip

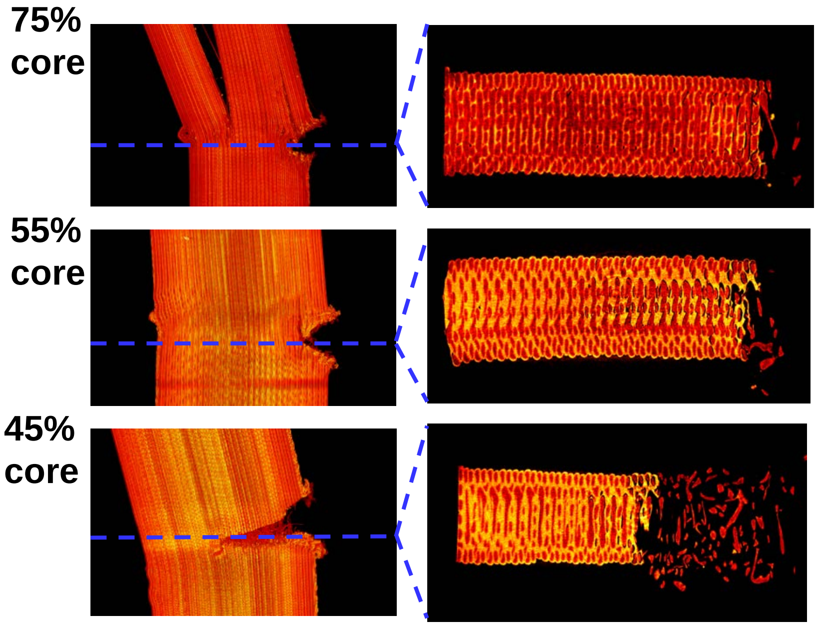


Buckling of core and delamination of shell as energy dissipation for high impact 3D printed parts?

Impact properties (IZOD)

XZ orientation print (edge on)



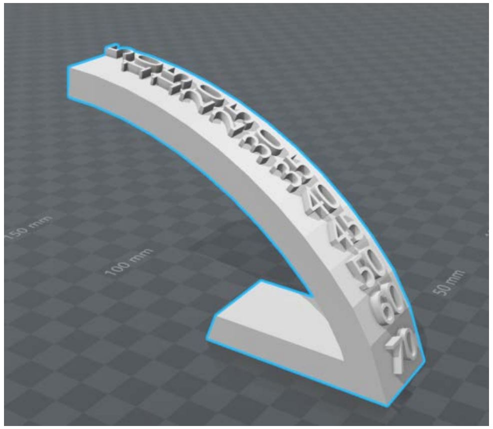


Impact strength can EXCEED individual components from injection molding: 807 J/m (PC) 362 J/m (Surlyn)

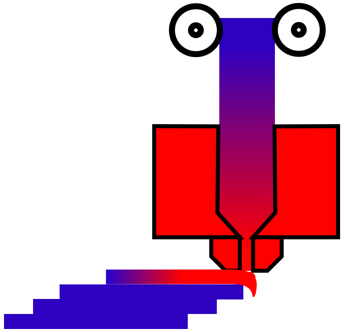
Failure mode is composition dependent

Printability of the filaments

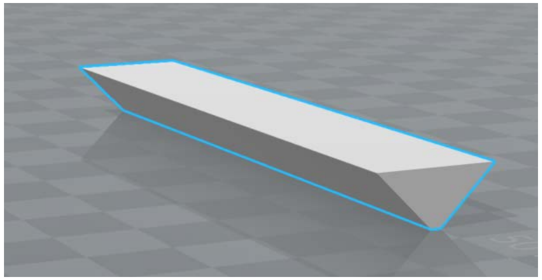
Overhang angle test

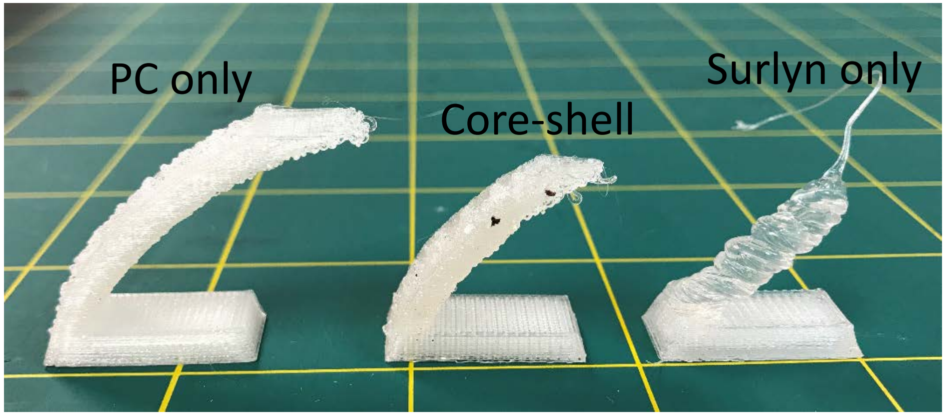


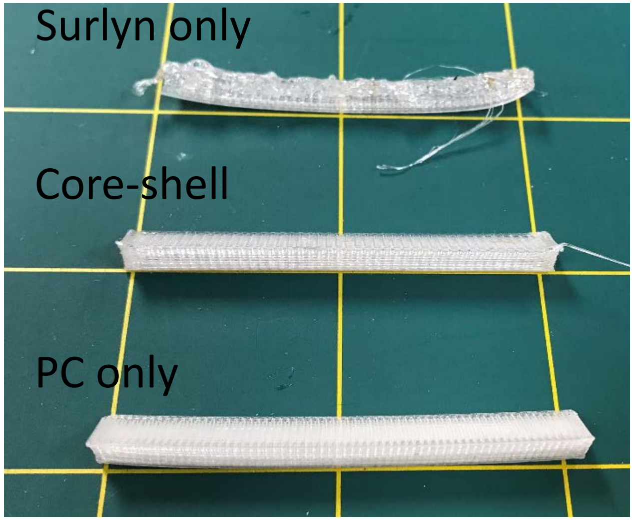
Melt dripping happens when solidification is slow



Warp of sample

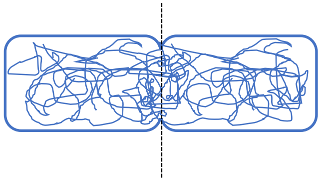


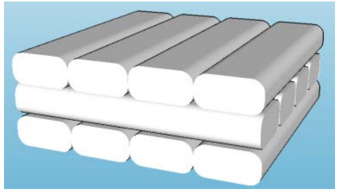


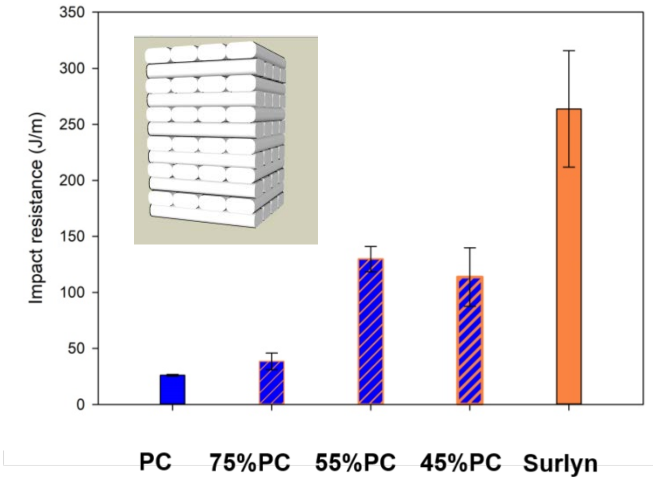


Mechanism of Impact Resistance Improveme

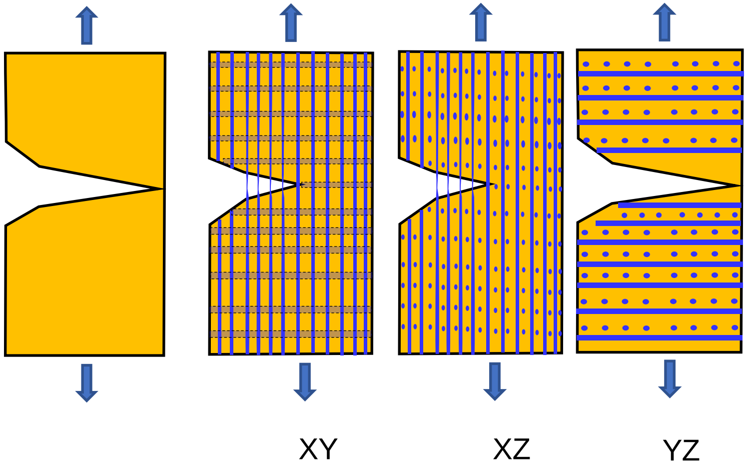
Shell: Enhanced Interface Strength







Core: Fiber Reinforcement



Inhibition of crack formation by core reinforcement

Summary

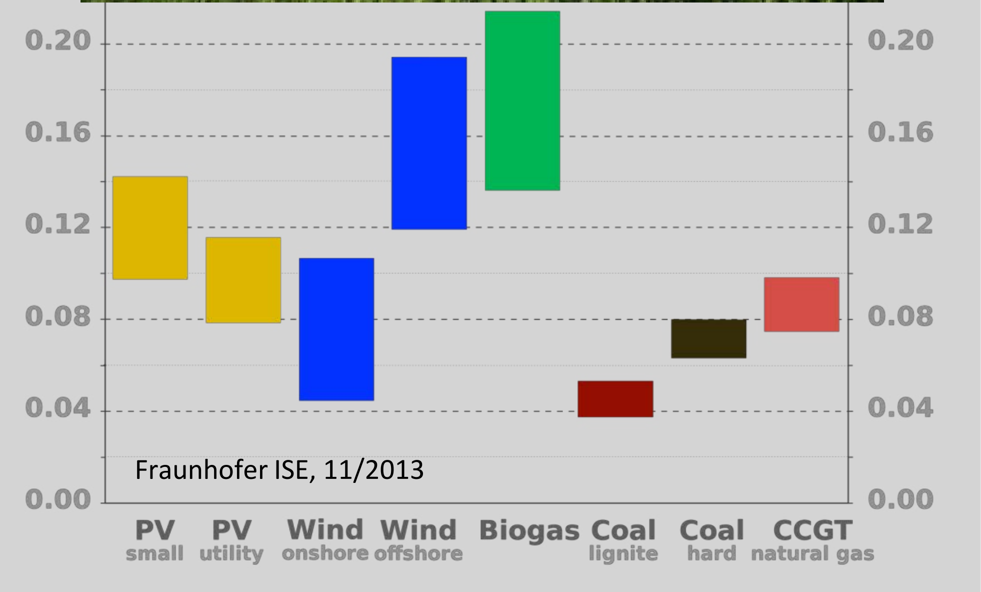
- Identification of fundamental trade-off between dimensional accuracy and mechanical properties
- Core-shell structured filaments can overcome trade-off
- Commercial polymers can be combined to generate materials with impact properties that exceed the individual components
- Structural characterization provides insights into synergies in impact properties
- Structured filaments produced by coextrusion using commercial polymers for minimizing the barriers to commercialization

3 vignettes on scalability considerations

- Stretchable dry electrodes
  - Problem: Motion sickness during virtual reality (VR) use
  - Requirements: Tunable areas and surface structures for contact with skin
- 3D printing
  - Problem: Trade-off between mechanical properties and dimensional accuracy
  - Requirements: Use commercial materials and compatible with existing 3D printers
- Room temperature sodium sulfur batteries
  - Problem: Polysulfide shuttling degrades lifetime
  - Requirements: low cost precursors and highly reproducible

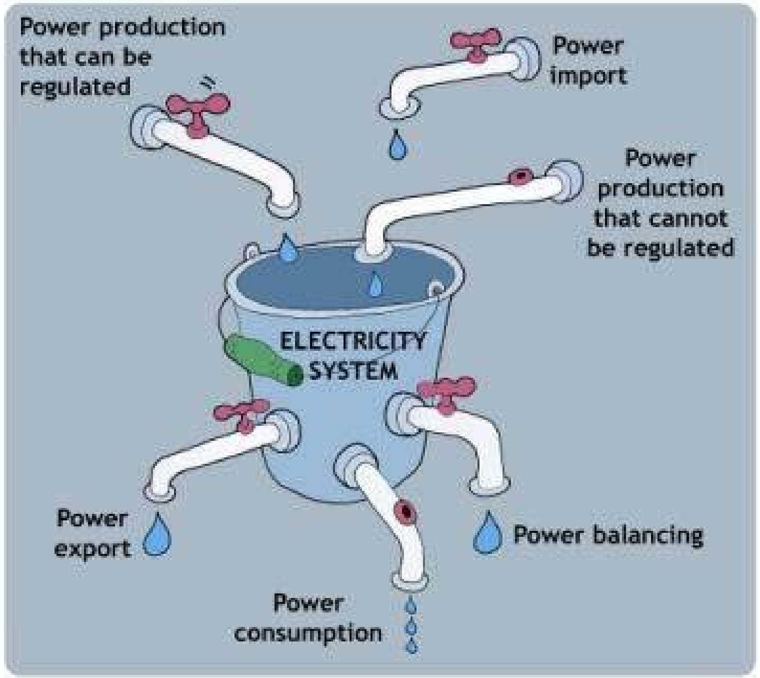
Challenge: Competitive sustainable energy

Solar and wind power



Fraunhofer ISE, 11/2013

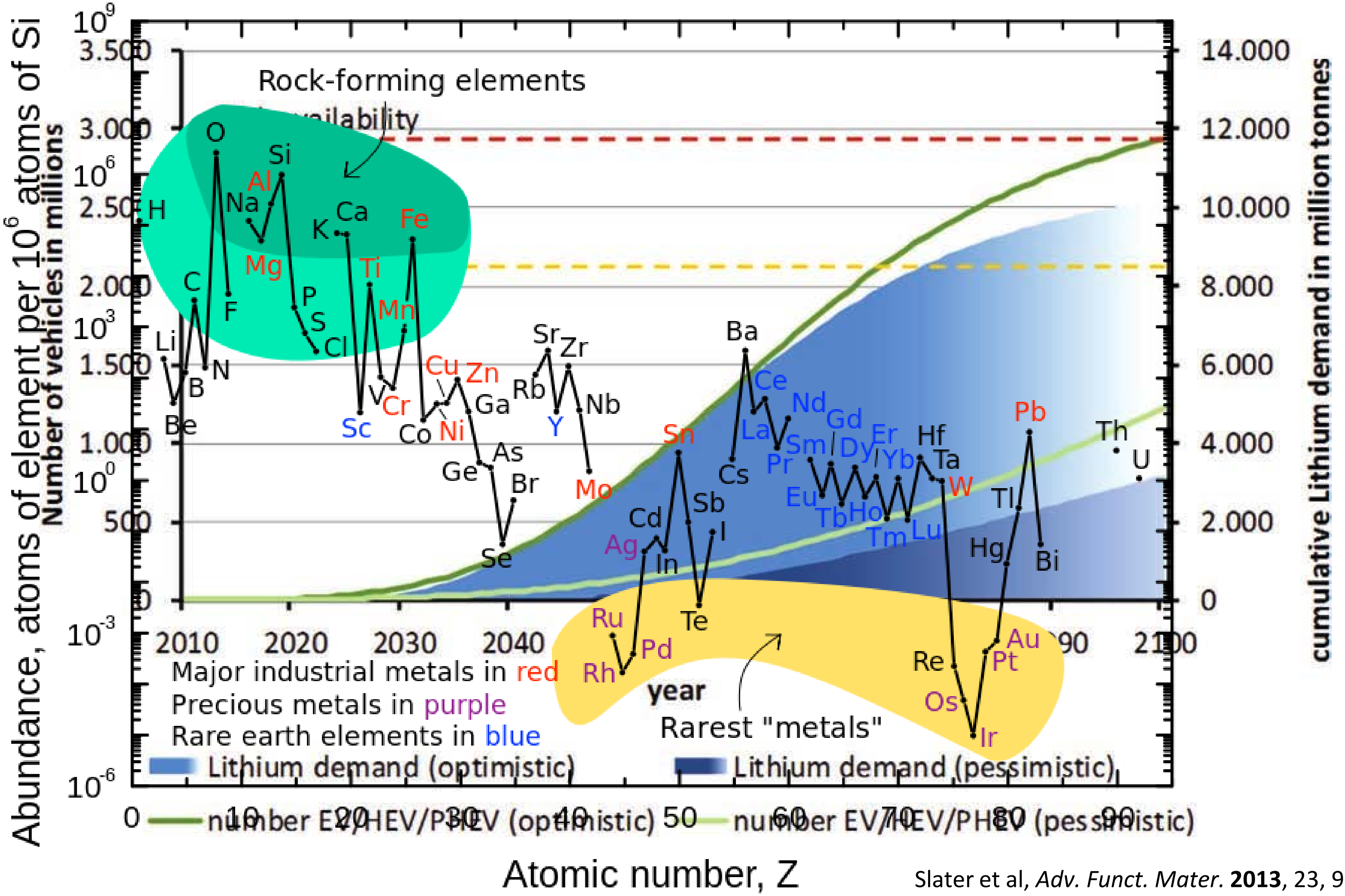
Intermittent power: require integrated storage and generation



Wind and large PV can be competitive with coal / natural gas

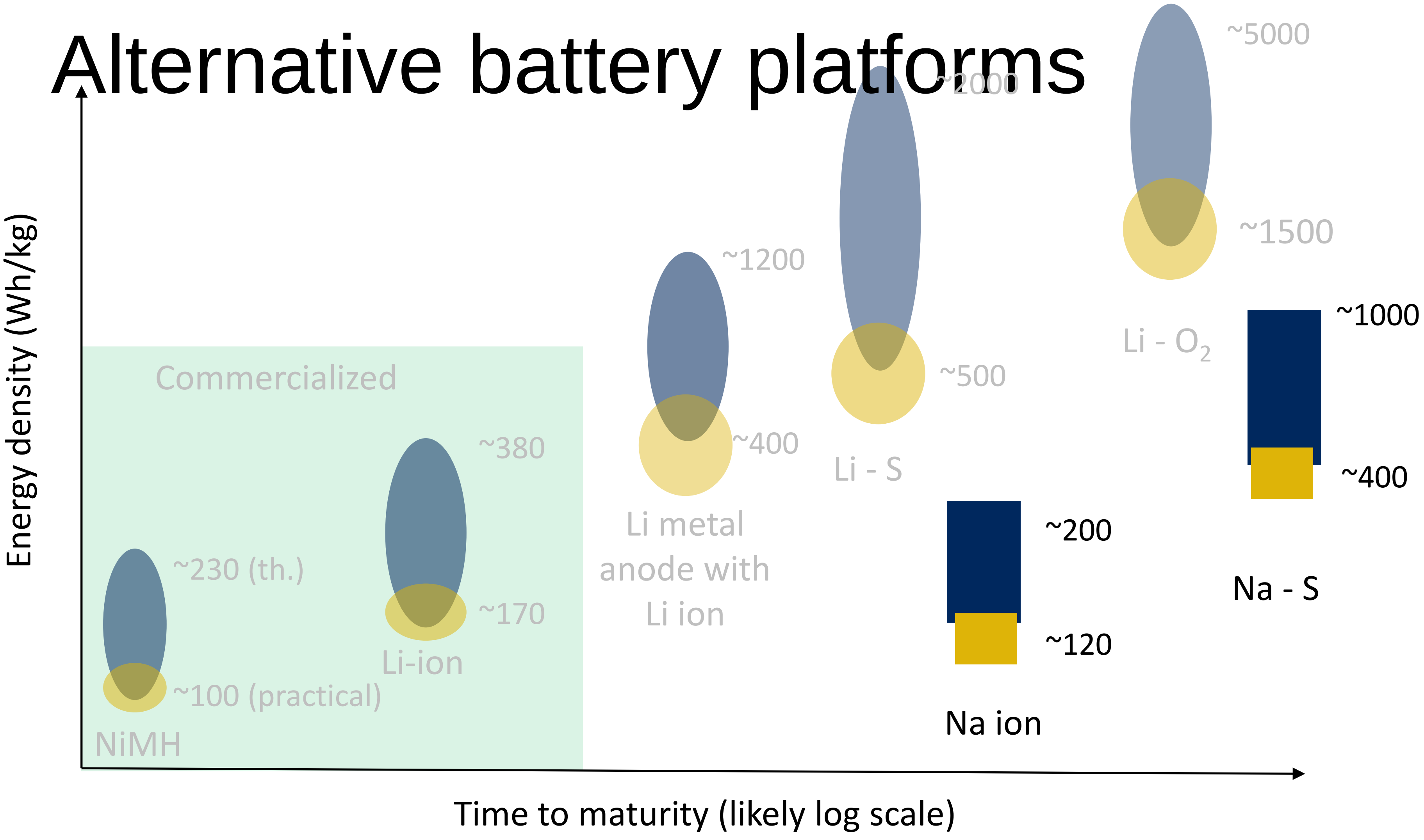
Cost is major consideration

Potential Li issue



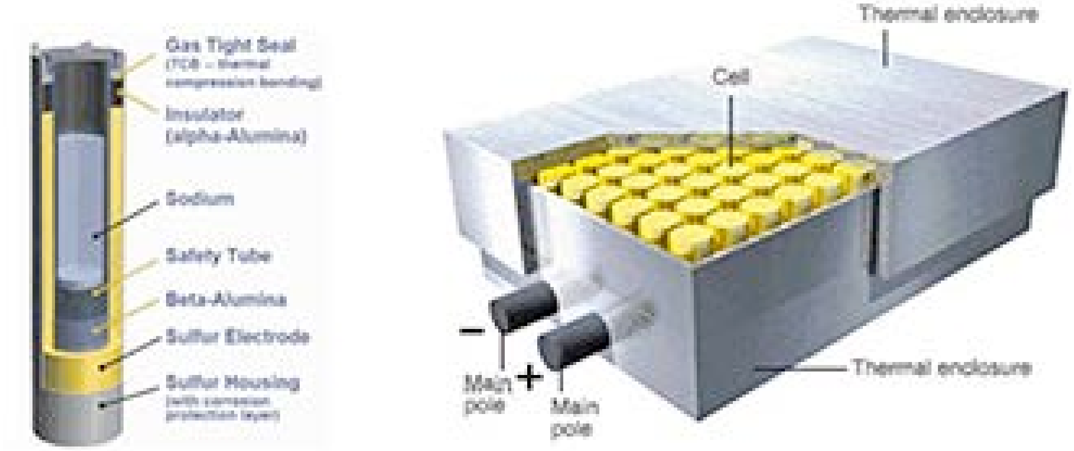
Slater et al, *Adv. Funct. Mater.* **2013**, 23, 947.

Alternative battery platforms



Big jump in performance if use solid Li metal anode

High temperature Na - S



Sodium-Sulfur (NaS) Batteries

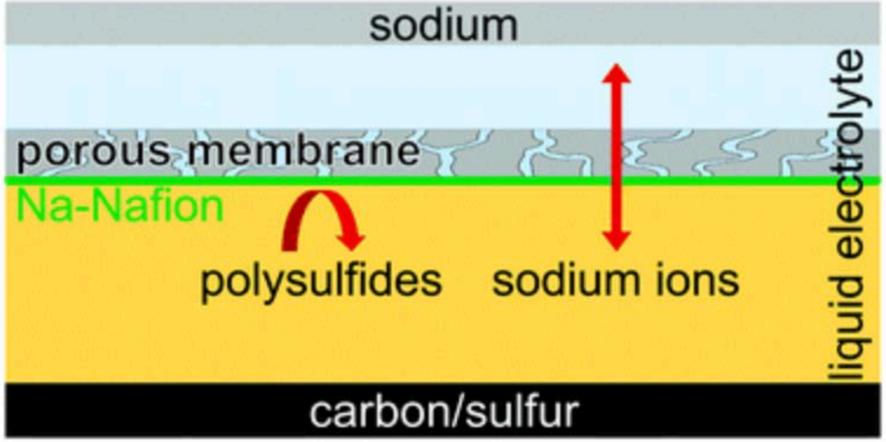
Uses inorganic solid electrolyte to require high temperature operation
Manufactured by NGK for stationary energy storage since 2002
90 % efficiency for lifetime

Major fire issues on Sept 21, 2011 – stopped production

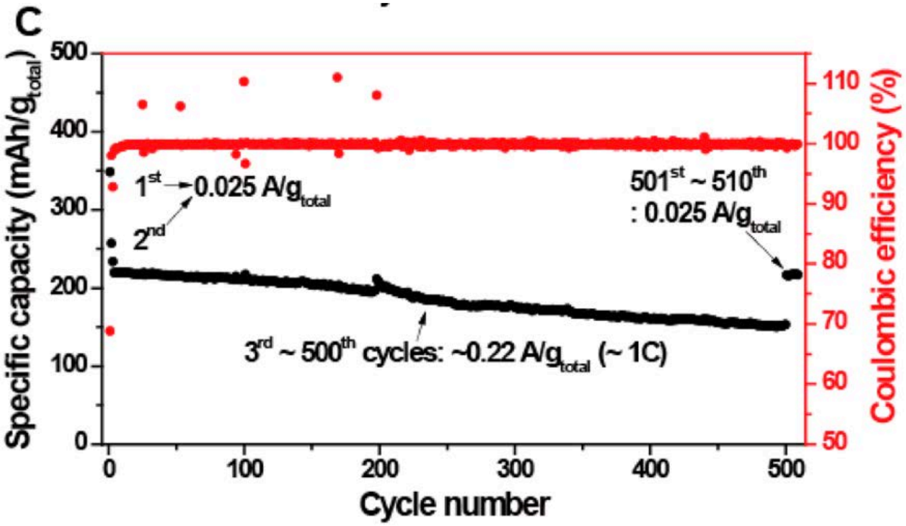
Corrosion at high temperature appears to be safety fault

Room temperature Na-S battery

Anode



Cathode



S. Kaskel, *Chem. Comm.*, **2014**, 50,3208-3210

$$2\mathrm{Na} + n\mathrm{S} \rightarrow \mathrm{Na_2S}_n(5 \geq n \geq 2) \rightarrow \mathrm{Na_2S}_n(4 > n \geq 2)$$

(Discharge process)

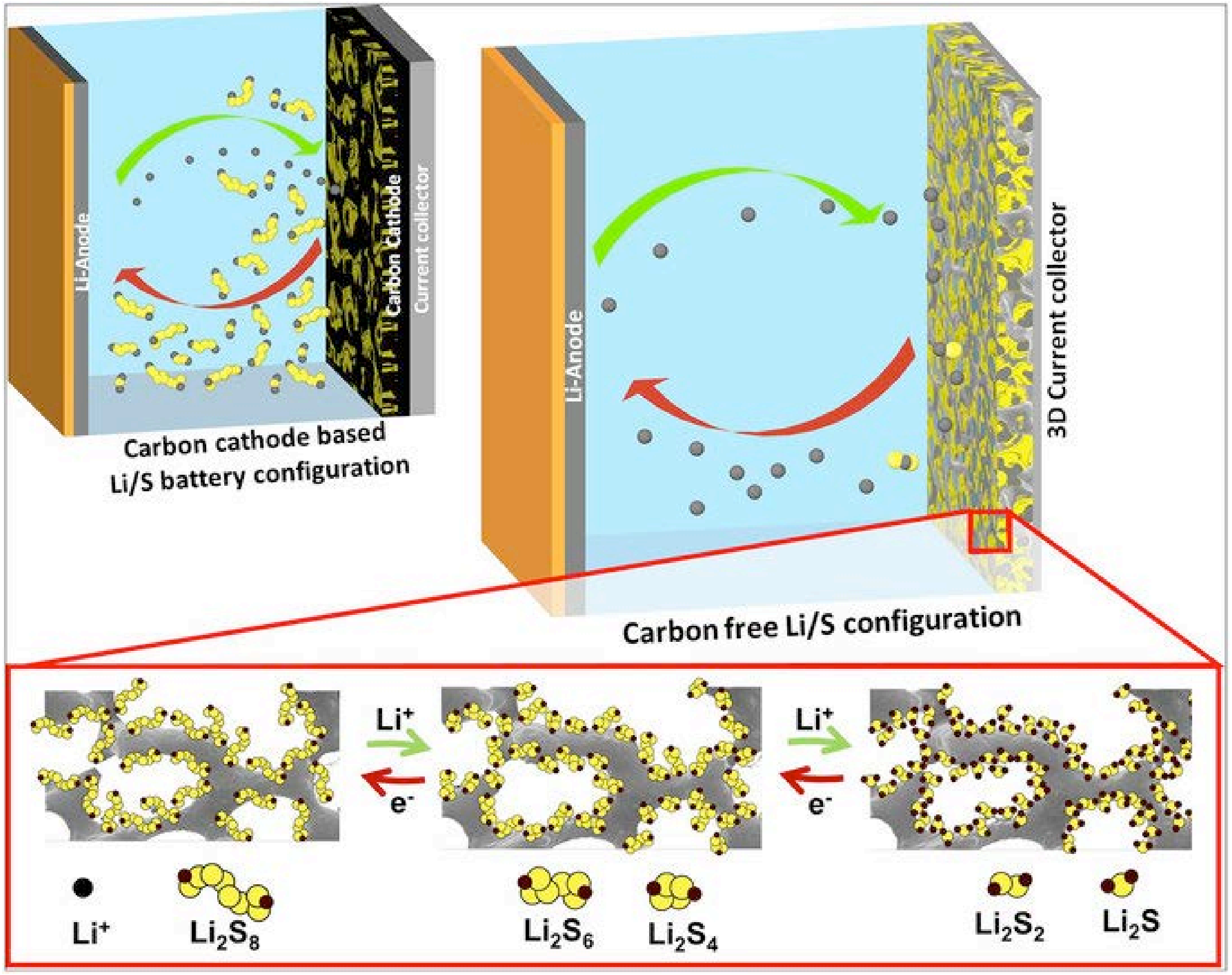
$$2\mathrm{Na_2S}_n(4 > n \geq 2) \rightarrow 2\mathrm{Na} + n\mathrm{S} + \mathrm{Na_2S}_n(5 > n \geq 3)$$

(Charge process)

Theoretical capacity:
628 mAh/g for Na_2S_2
discharge product

Issues: low conductivity of S, polysulfide shuttling, reversibility

Porous conductors for Li-S

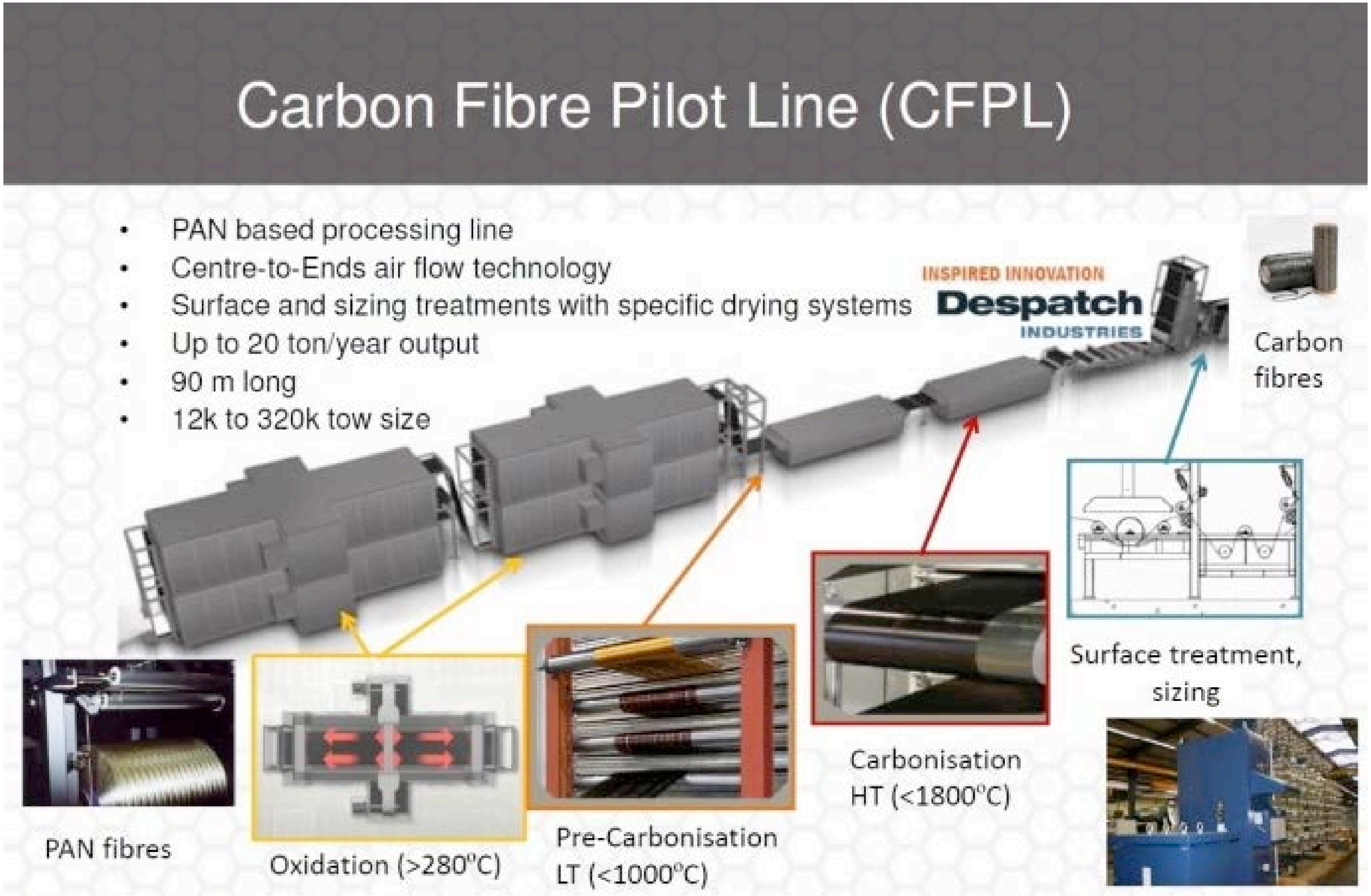


ALM Reddy, *Scientific Reports* **2015**, 5, 8763

Performance depends on pore size and pore chemistry

Desire high porosity doped carbon with 30-40 nm pores, but need to make this scalable and low cost

Scalable synthesis of carbon fibers



Carbon Fibre Pilot Line (CFPL)

- PAN based processing line
- Centre-to-Ends air flow technology
- Surface and sizing treatments with specific drying systems
- Up to 20 ton/year output
- 90 m long
- 12k to 320k tow size

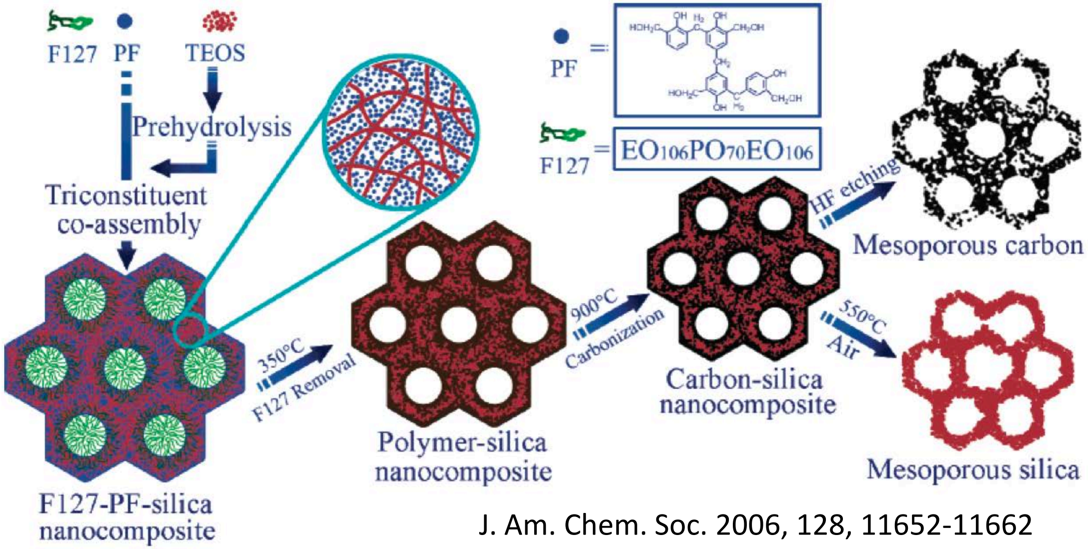
(Despatch industries)

Large scale, continuous production of carbon fiber from PAN

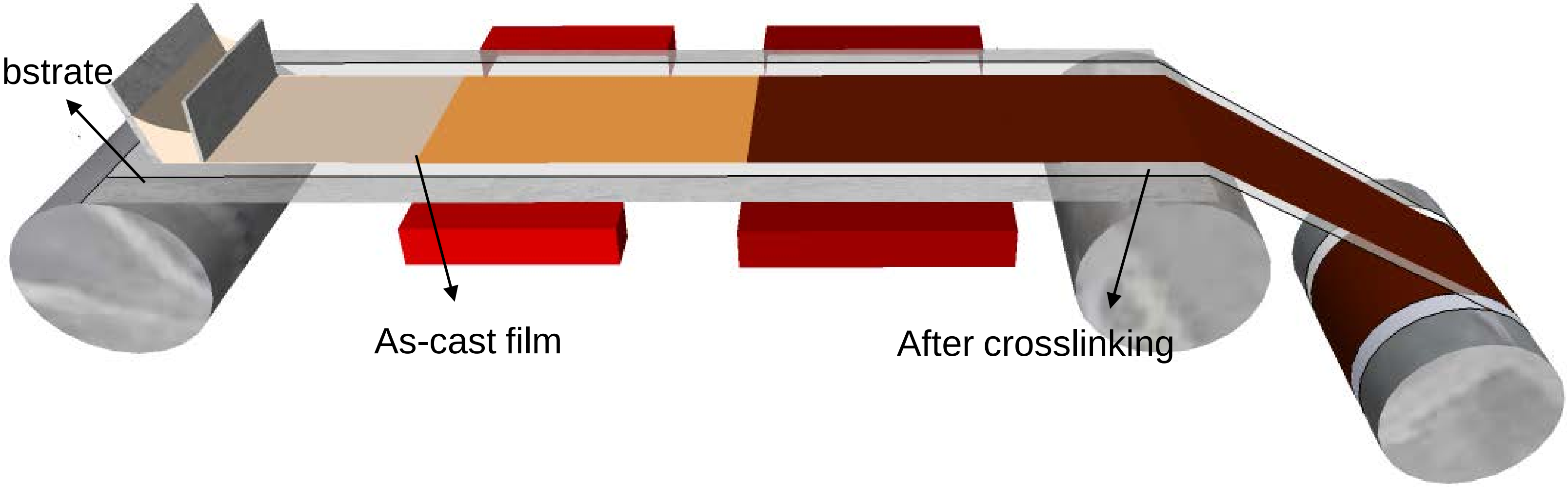
Roll-to-roll processing

Continuous production potential – proof of concept

R2R fabrication



J. Am. Chem. Soc. 2006, 128, 11652-11662



Doctor blade casting

Heating zone 1
solvent evaporation

Heating zone 2
Thermal annealing

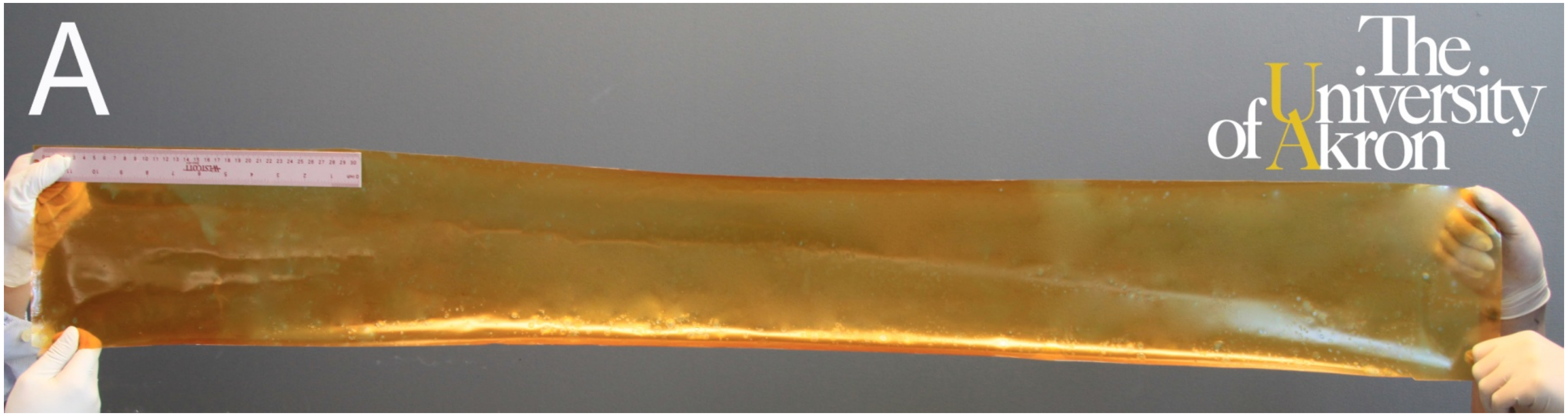
PET substrate

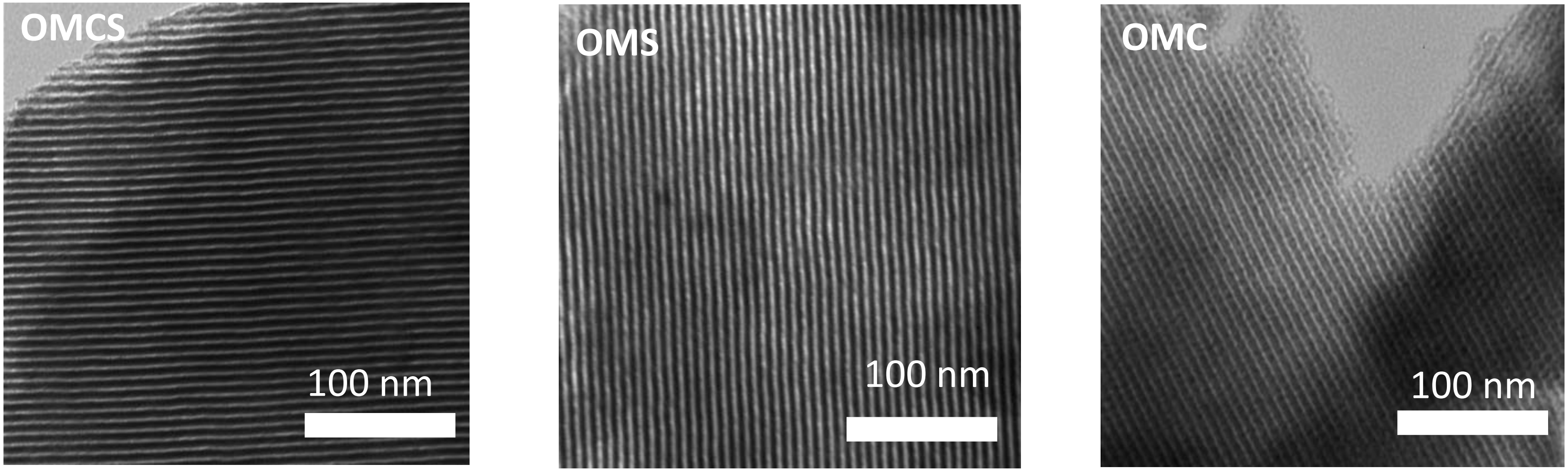
As-cast film

After crosslinking

Qiang, Vogt, et al. *ACS Appl. Mater. Interfaces* **2015**, 7, 4306-43010

Structure of materials





D-spacing: OMCS: 9.2 nm

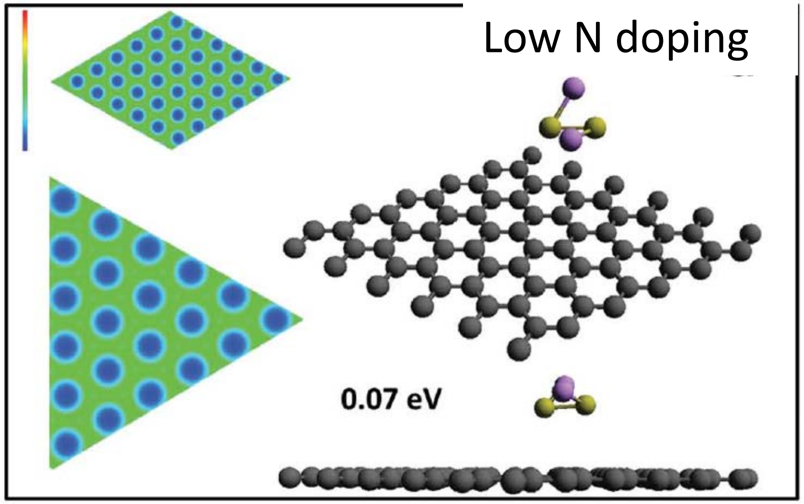
OMS: 9.7 nm

OMC: 10.1 nm

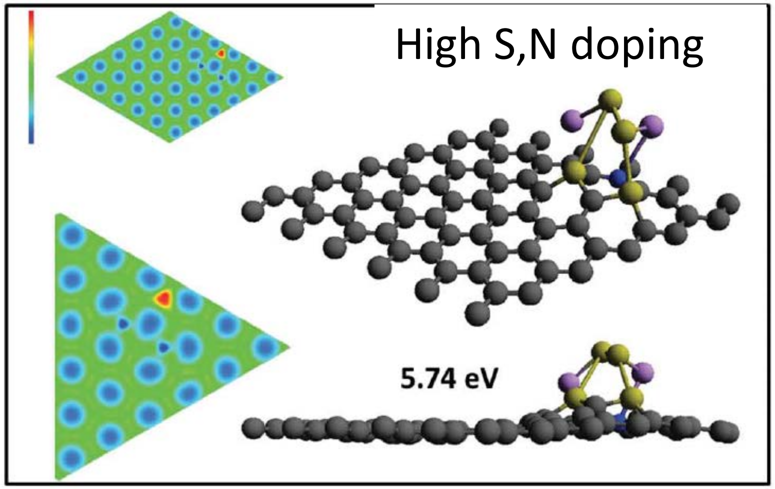
Qiang, Vogt, et al *ACS Appl. Mater. Interfaces* **2015**, 7, 4306-43010

Similar structure to small scale powders, but can make kg’s at a time

Surface chemistry effects

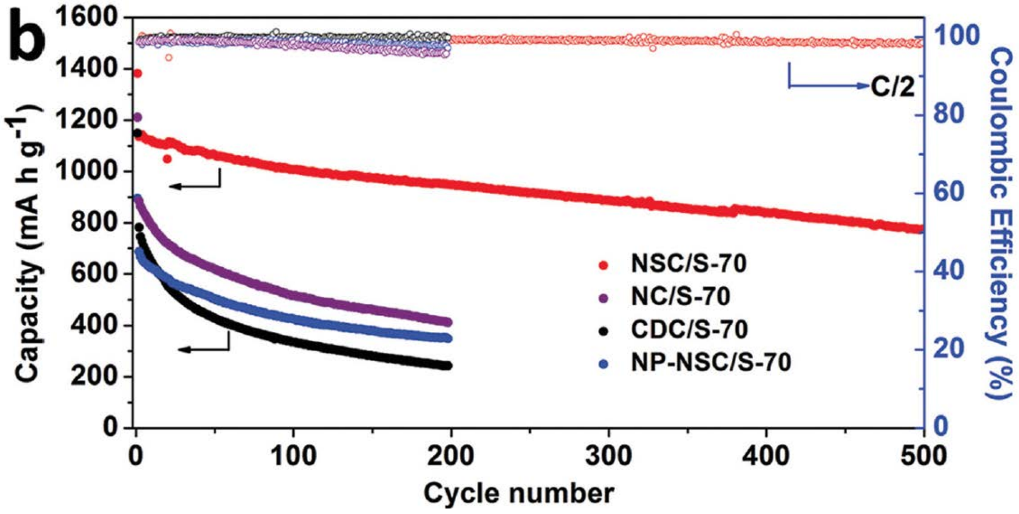


Low N doping



High S,N doping

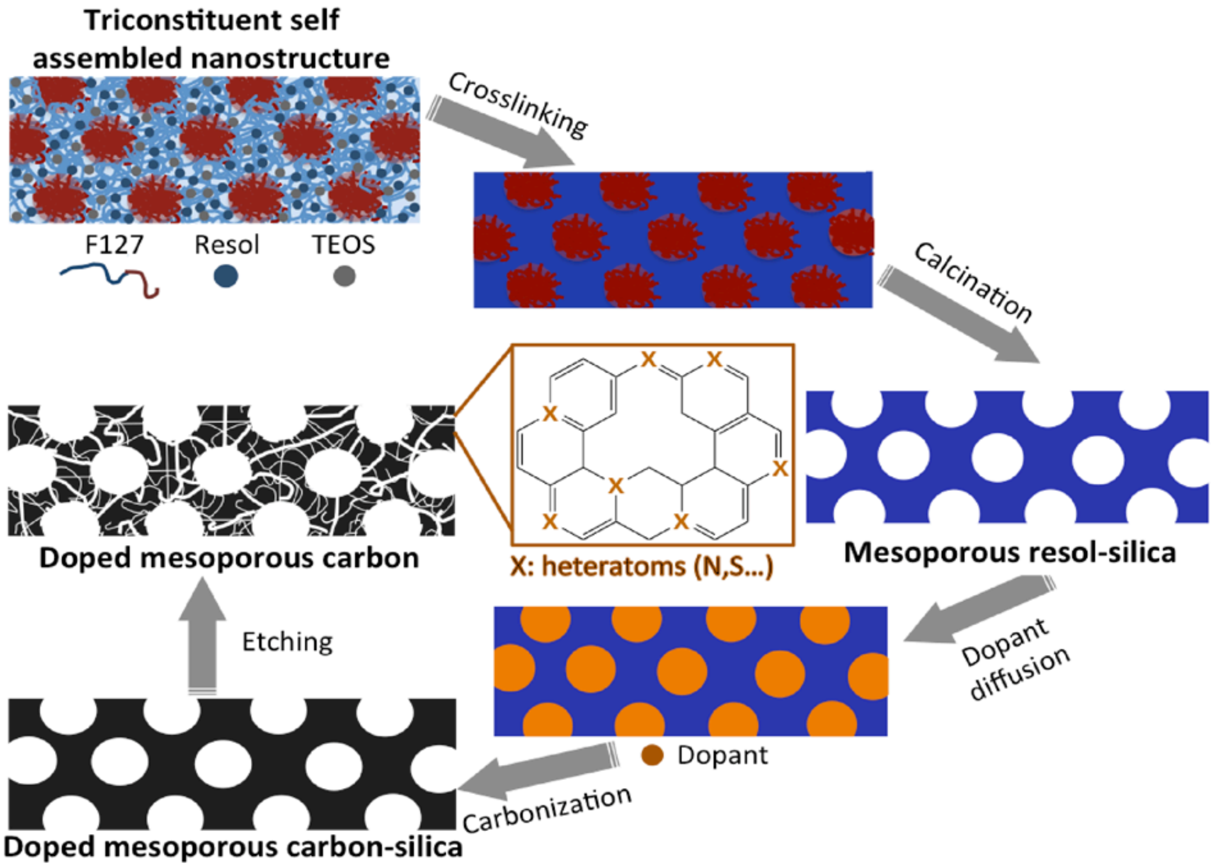
Codoping with S,N improves performance of Li-S batteries



Nazar *Adv. Mater.* **2015**, *27*, 6021–6028

How to efficiently fabricate large quantities of S,N doped carbons?

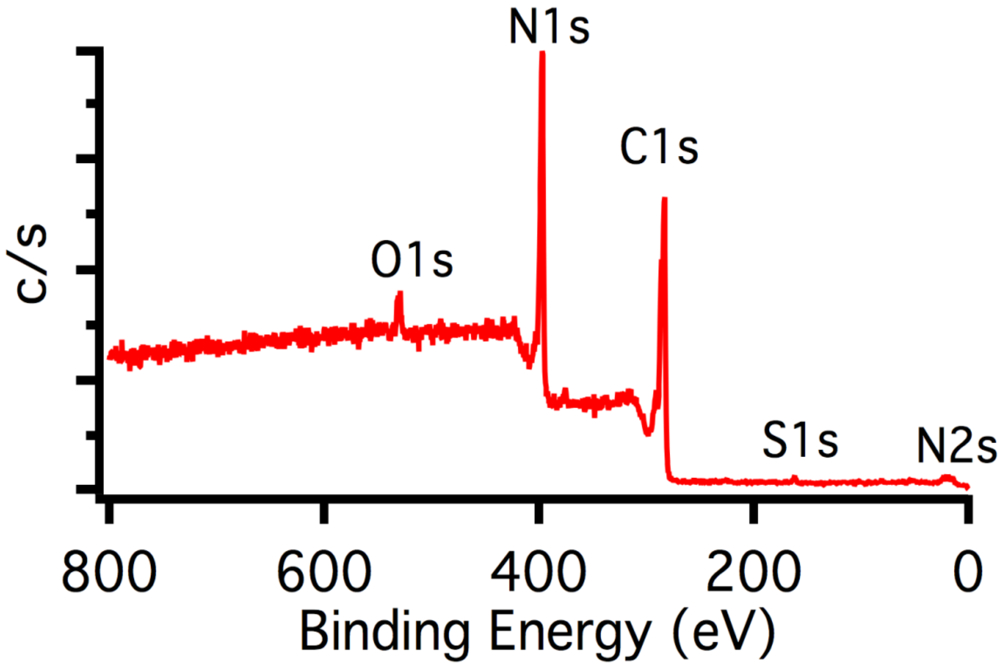
Scalable co-doping

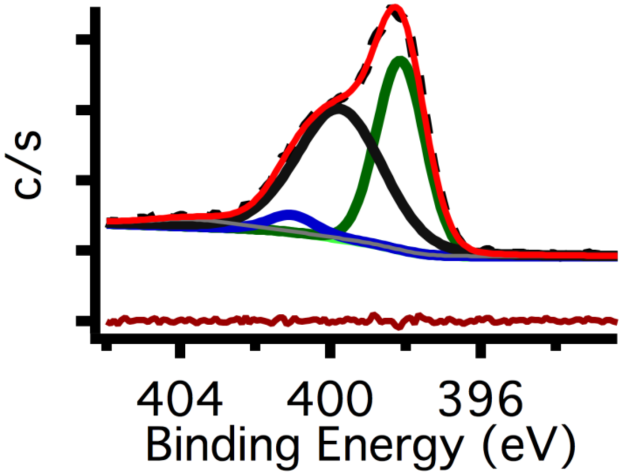


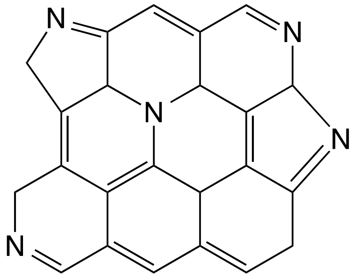
Use both melamine and benzyl disulfide as dopants

Codoping from XPS

Fill pores with melamine and benzyl disulfide for N-and S-doping during carbonization







● Pyrrolic: 53%

● Pyridinic: 40%

● Graphitic: 6%

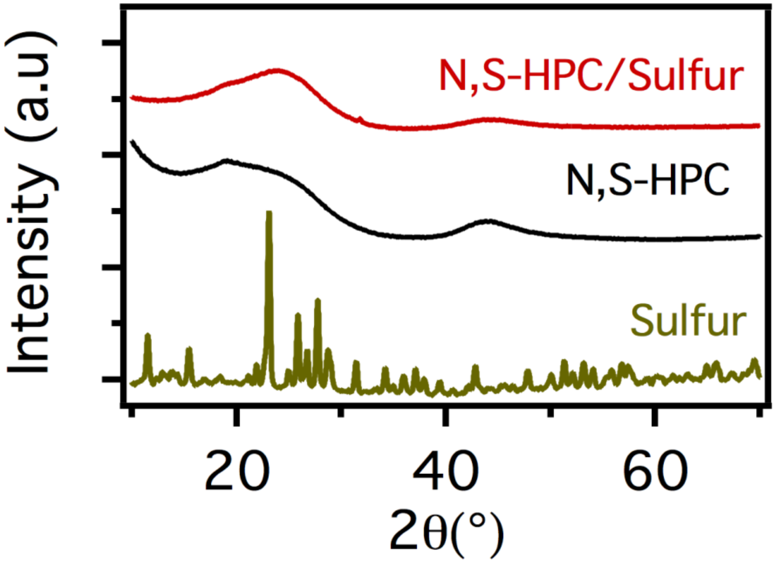
After carbonization, 39.1 at% N and 0.9 at% S in the carbon framework

N displaces S from sites during carbonization

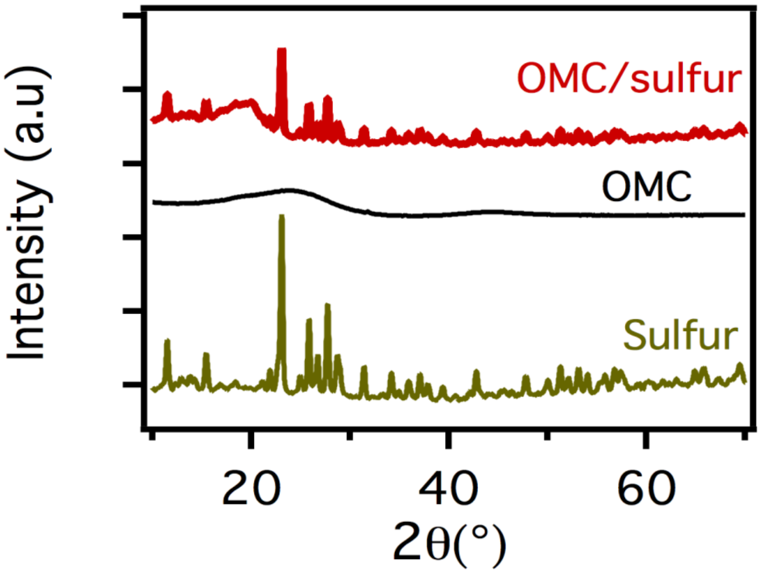
Doping stops sulfur crystallization

X-ray diffraction studies

Doped carbon



Undoped carbon

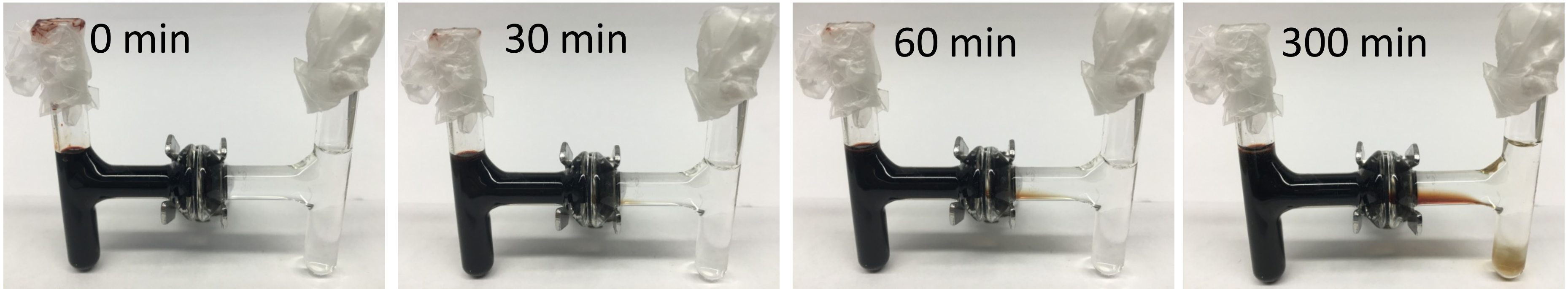


Inhibition of crystallization of S within the doped mesopores
Suggests strong binding of S to the S,N doped carbon

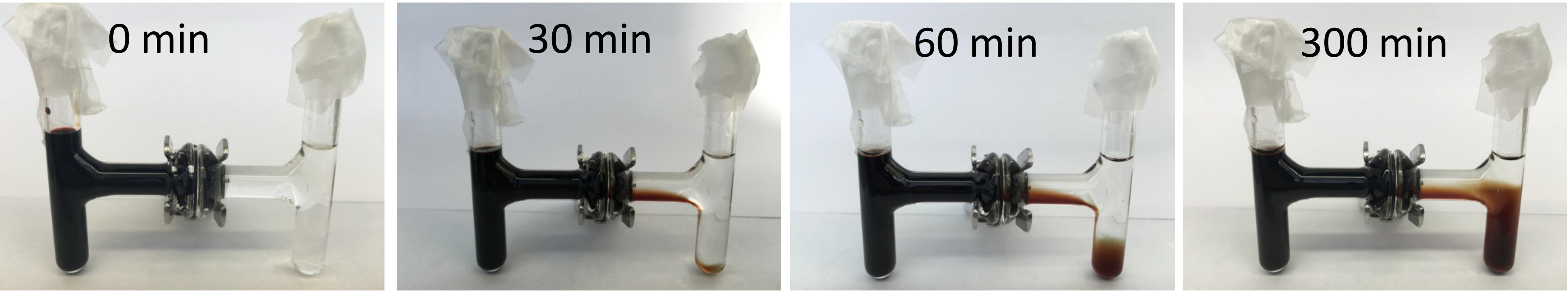
Promising to avoid shuttling of the polysulfides

Diffusion inhibition

N,S-HPC



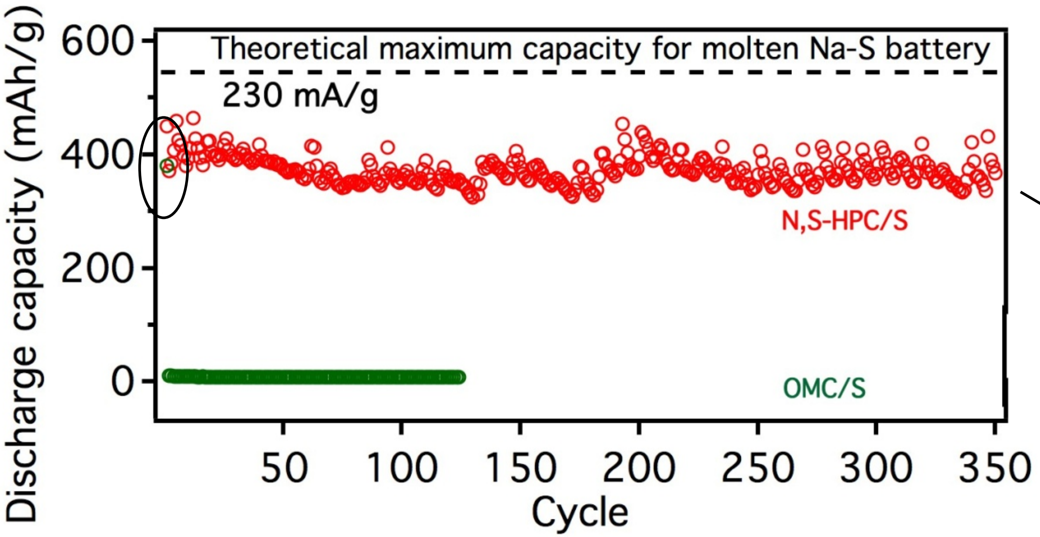
OMC

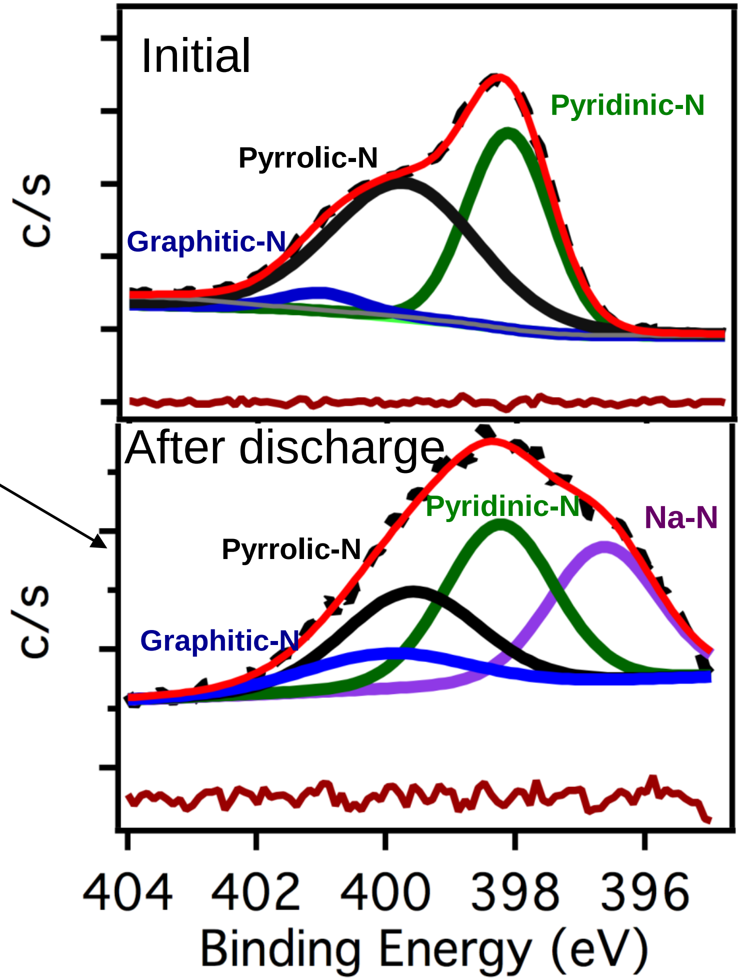


H-cell filled with polysulfides – separated by packing of porous carbon

Impact on Na-S battery performance

Rapid capacity fade without doping





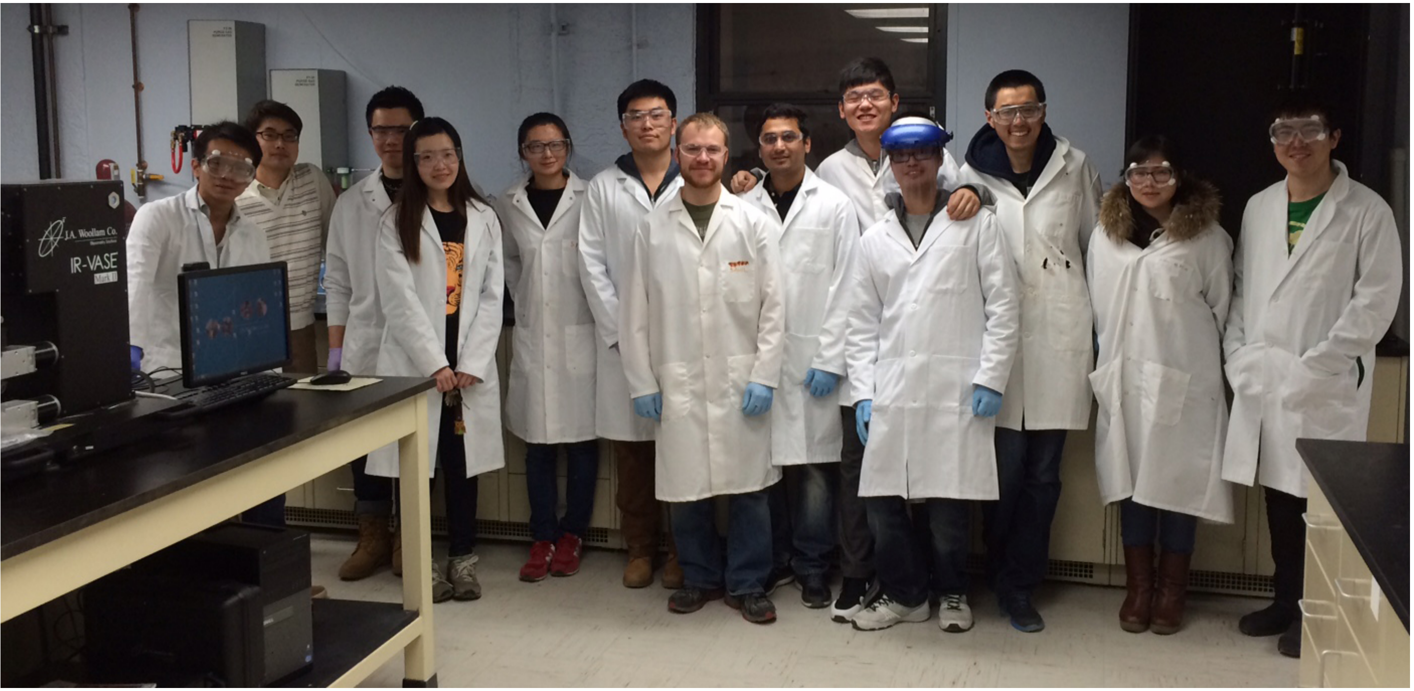
Initial capacity is almost identical for doped and undoped carbon electrodes

Tremendous improvement in the stability with the doped carbon

Summary

- Roll to roll processsing effective for fabrication of ordered mesoporous materials
- Mesoporous polymer precursor enables high doping levels in carbon
- High N doping inhibits sulfide shuttling in Na-S batteries
- Excellent performance stability for Na-S battery using co-doped mesoporous carbon

Acknowledgments



Collaborators

Y. Zhu
N. Zacharia
M. Soucek
K. Cavicchi
M. Becker
R.A. Weiss
J. Zhang
D. Simmons

M. Cakmak (Purdue)
T. Epps (Delaware)
M. Fukuto (BNL)
D. Nielsen (ASU)
C. Soles (NIST)
M. Tyagi (NIST)
C. White (NIST)
K. Yager (BNL)

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Durable Module Materials Consortium

KALION, INC.

ACS PRF