Exceptional service in the national interest

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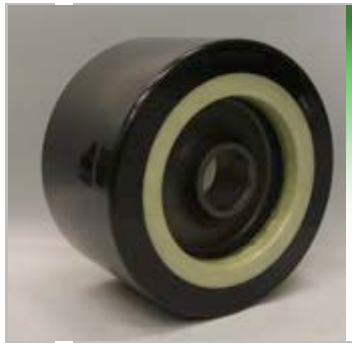
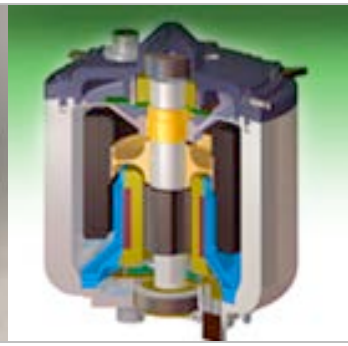

Nanofillers for Improved Flywheel Materials

September 2015

Timothy J. Boyle, Timothy N. Lambert, Nelson S. Bell, William Miller, Mark Ehlen

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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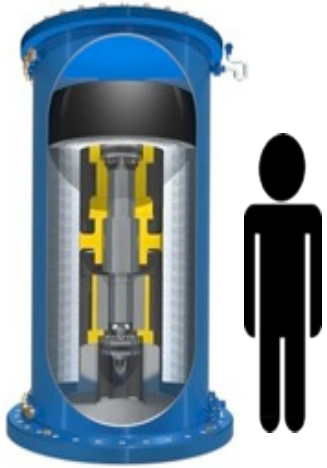
Project: Improved Flywheel Materials

Problem: Flywheels used to level the AC grid need to spin faster, which requires stronger rims. Focused on the material (C-fiber, glass fiber, resin) properties of composite flywheels.

No major changes to basic design, processing parameters, and/or cost can be incurred.



Goal: improve the overall strength of composite flywheel materials, so they can spin faster. Incorporate Sandia generated nano-filled materials into a commercial flywheel product and identify if there has been an improvement in the flywheel's performance

Approach: explore utility of nanomaterials in strengthening composite flywheel rims to improve performance. Low load levels (>5%) of nanoparticle fillers have led to dramatic property changes. Team with Cobham to produce Powerthru's existing commercial flywheel

Energy is stored in the rotor as kinetic energy, or more specifically, rotational energy:

$$E_k = \tfrac{1}{2} \cdot I \cdot \omega^2$$

ω = angular velocity, I = moment of inertia of the mass about the center of rotation

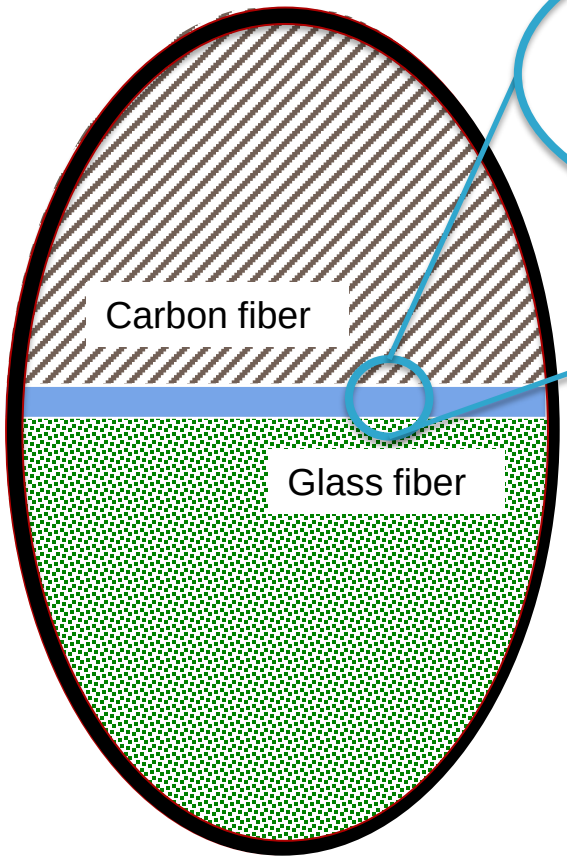
The amount of energy that can be stored is dependent on:

$$s_t = \rho \cdot r^2 \cdot \omega^2$$

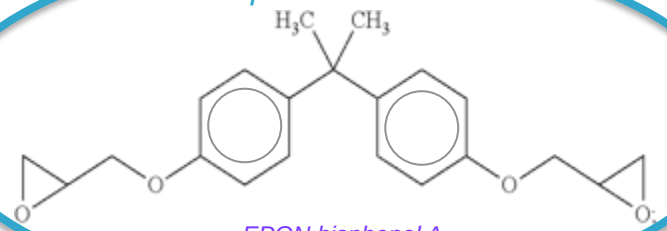
s_t = tensile stress on the rim, ρ = density, r is the radius, ω is the angular velocity of the cylinder.

Energy Storage Impact: The economics of flywheel-based energy storage can potentially be improved by a factor of 3 or more. The increased storage/supply is necessary to meet expected future complications expected as alternative energies (i.e., solar, wind, etc.) are introduced.

Approach to improve the composite flywheel materials properties.

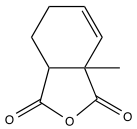


An example of an EPON resin

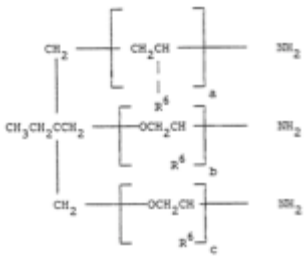


EPON bisphenol A

LS81k



Poly(oxypropylene) triamine



An activator or crosslinker required to polymerize

Ceramic and Graphene Nanofillers

+ Fillers are a simple cost-effective method to alter resin properties.
+ Meso-sized fillers require high loads (> 60%) due to small surface area.
+ Nanomaterials are 2 D fillers with all surface area; added at low levels.
+ Surface functionality of the nanofiller can interact with the reactive epoxide group of resin.
+ Reactivity can be tailored by surfactant on the nanomaterial
+ Previous results indicate that wires and planes have biggest impact at lowest load level.

Loading (wt %):	4	$Al_2Si_2O_5(OH)_4$:	*23%*	*storage, 113% flexural strength,*
	3	Al_2O_3:	*75%*	*tensile strength,*
	2	SiO_2:	*3%*	*hardness, 57% impact, 65 % flex, 88 % tensile strength,*
	2	ZrP:	*52%*	*Young's Modulus, 14% tensile strength 6 %, fracture toughness,*
	0.4% CNT-2%	ZrP:	*41%*	*Young's Modulus, 55% tensile strength.*

Overall Objectives: Defining functionalized nanoparticle fillers effects on the 'state-of-the-art' working flywheel system.

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Team determined approach and tasks assigned based on expertise

- Composite System
- Resin/Epoxy System
- Ceramic Nanomaterials
- Surface Characterization

TiO_2 /graphene nanomaterials

Optimized Functionalized Nanofiller /Epoxy Characterization

Sample Production Evaluation

Test Specimen Functionalized Nanofiller Characterization

TA filed

FY15 Flywheel Production

+ Increasing transverse strength is the pressing issue.

**** Incorporation of suggested nanomaterials or resins will represent verification of our approach***

Benefits to all involved are anticipated for the Carleton/Cobham, PowerThru, and Sandia collaboration (including OE and Zyvex).

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Albuquerque, New Mexico

Sandia
- Lab scale idea implemented
- Product viability stepping-stone for larger grid-based flywheel systems
- New interactions
- Another happy customer

Westminster, Maryland

Carleton/Cobham
- Develops a process for winding nano-loaded materials
- New job potential as C/C may assume overseas manufacturing

OE/DOE
- Lab to industry (tech transfer) of scientific study of nanofillers to improve flywheels.
- Manufacturing testing of nanofillers on processing variables
- Tech Transfer: TRL 1 to ~7
- Improved flywheels increase reliable electricity for grid
- 'Green' storage of electricity
- New US jobs

Livonia, Michigan

PowerThru
- Comparative analysis of flywheel produced w/ different resin system
- Improved flywheels
- Improved commercial and defense related UPS product

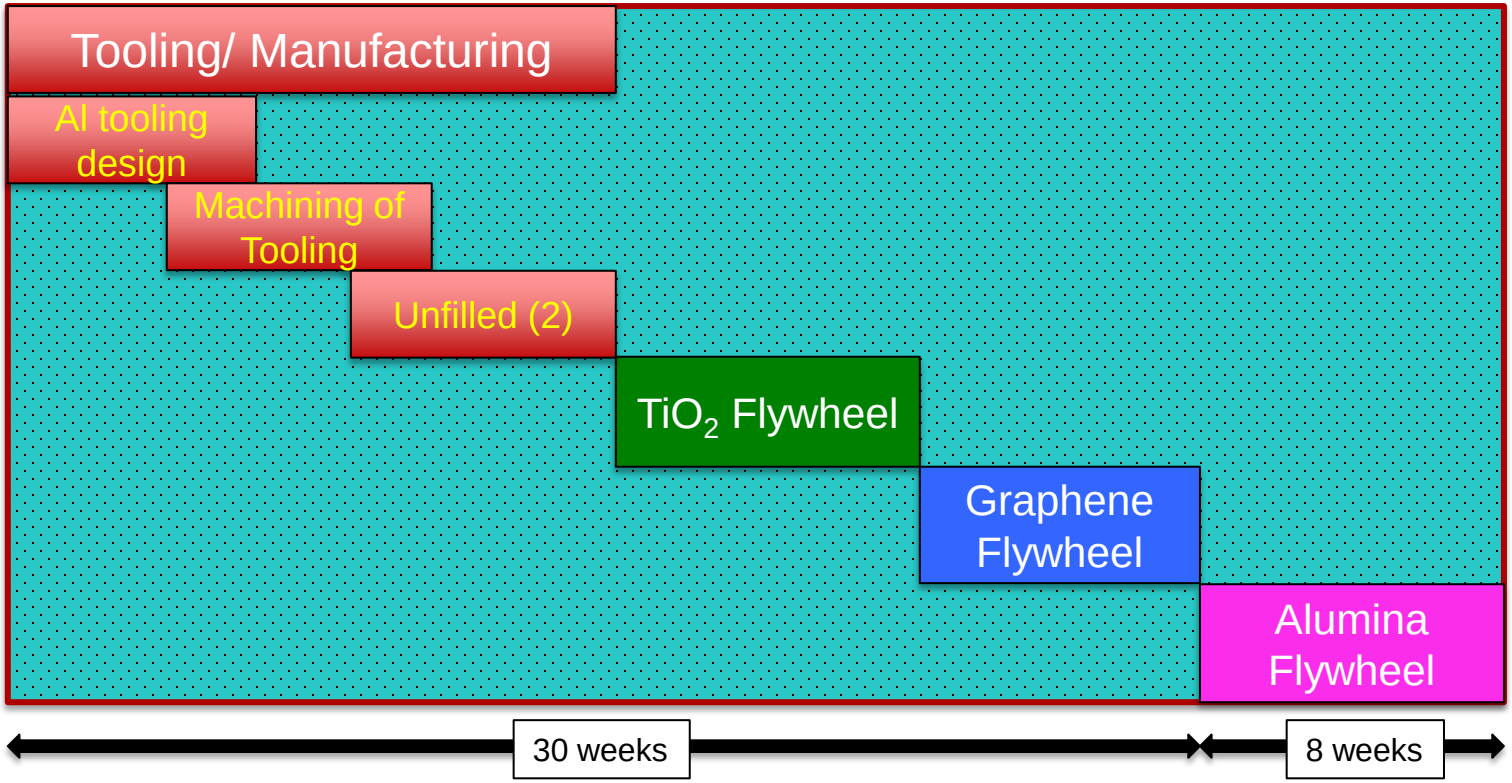
Columbus, Ohio

Zyvex
- New customer base
- Novel nanofillers (not CNT)
- New composite materials

3-way NDA in place

- *Selected C/C due to experience with Beacon processes.*
- *PowerThru selected due to smaller sized flywheels.*

Timeline for flywheel production determined and initiated.



16 weeks to produce the first unfilled flywheel (includes)

- Manufacturing aluminum tooling to wind rim parts
- Time for machining filament wound rim parts
- Manufacturing time for aluminum tooling to press hub into rim

8 weeks to produce the TiO_2 filled flywheel (all processes)
7 weeks to produce each Graphene flywheel (all processes)
8 weeks to produce the Al_2O_3 filled flywheel (all processes)

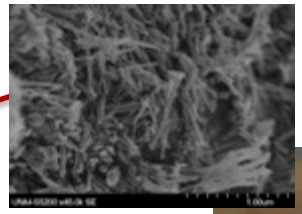
Baseline and nanofiller flywheel processing underway

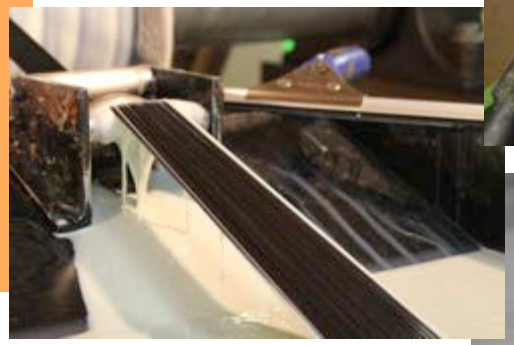
Overall FY15 Goals:

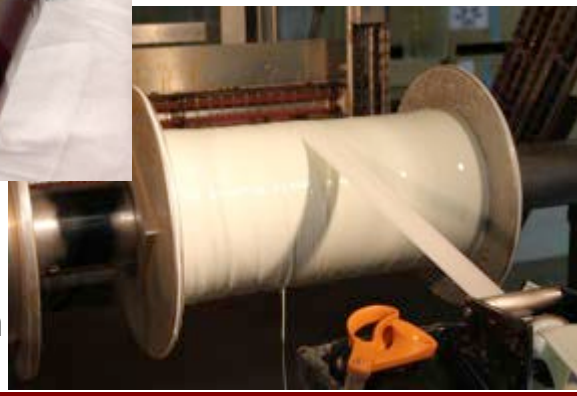
+ Produce two EPON A flywheels
  (1) no nano fillers
  (2) resin filled 5% TiO_2 nanowires

+ Produce two EPON B flywheels
  (1) no nano fillers
  (2) resin filled 5% graphene

+ Test 4 Flywheels for breakdown properties







Project Challenges:

- Production of LS TiO_2 NW (**Sandia**).
- Uniform dispersion of the nanomaterials in resin (**Zyvex**).
- **Cobham** relies on a subcontractor to machine and press the flywheel assembly.
- **Powerthru**'s commercial flywheel is produced overseas and are only provided a finished product; not privy to their outsourced vendor's proprietary fabrication details, therefore Cobham had to develop their own fabrication process.

Sandia's Project Status:

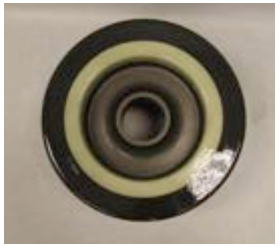
+ synthesized/procured all necessary NM for winding.

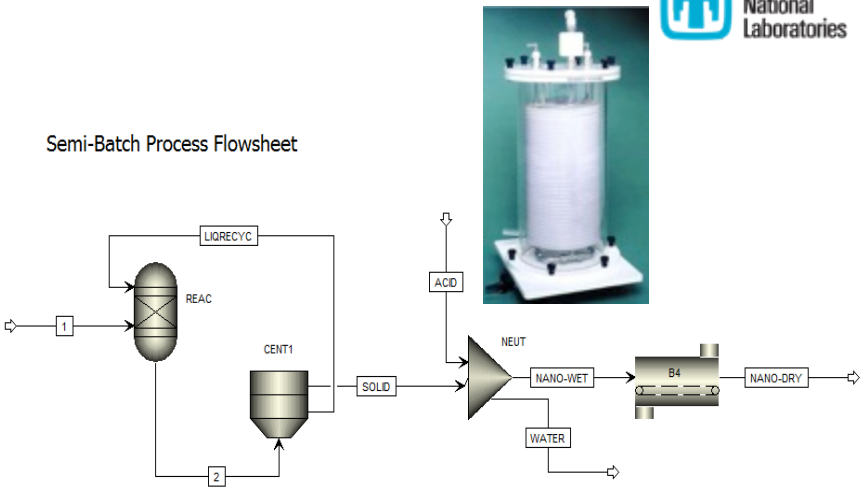
+ established a contract with Zyvex to commercially disperse Sandia produced nano-fillers in epoxy resins for Cobham's use

+ supplied Cobham with Sandia's existing inventory of Hysol EA9396 epoxy - commercially unavailable at this time (Henkel isn't manufacturing it)

+ supporting Cobham with engineering support on their technical issues

+ procured all of Powerthru's individual components (hubs and shafts) necessary to produce the flywheel





Initial Economic Analysis of TiO_2 Batch Process*

Cost of Pilot Plant Equipment: maximum of $106,000 USD startup cost
Rate of Production: 5 kg nanowires over 3 days (pre-functionalization)
Cost of Reactants : approx. $4,500
Sigma Aldrich Market for Titania Nanowires: $218.00 for 500 mg.

*neglects utility cost, cost of labor, V. Sheffy

+ finalizing a contract with Powerthru to 'qualify' the flywheels: degassing and balancing assembly; then low-high speed cyclic testing (27-52K rpm).

+ parallel materials testing at Sandia underway

+ started an economic impact study: TiO_2 large scale route evaluated.

Zyvex's Project Status:

Dispersed nanofillers (TiO_2 and graphene) in the supplied resins using 3 roll mill and high shear mixer and analyzed resulting composites.

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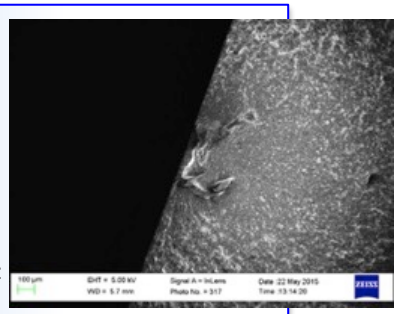
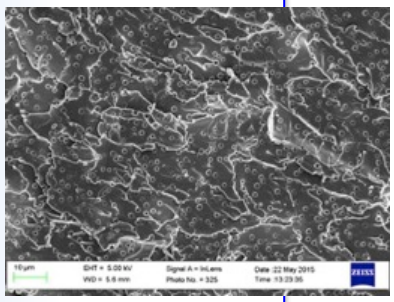
FAILURE ANALYSIS OF TIO_2 FILLER INVOLVEMENT

• THE INSPECTOR USED THE DEFINITIONS IN ASTM C1322: STANDARD PRACTICE FOR FRACTOGRAPHY AND CHARACTERIZATION OF FRACTURE ORIGINS IN ADVANCED CERAMICS, MIL-HDBK-790: FRACTROGRAPHY AND CHARACTERIZATION OF FRACTURE ORIGINS IN ADVANCED STRUCTURAL CERAMICS, AND NIST: FRACTOGRAPHY OF CERAMICS AND GLASSES.

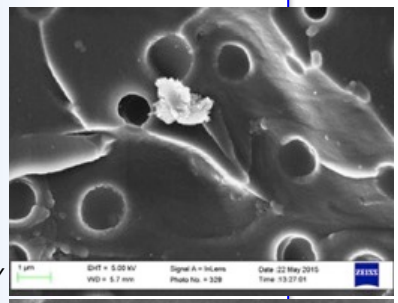


• THE CRACK FOLLOWS A FAIRLY TORTURED PATH ACROSS THE ENTIRE FRACTURE FACE BUT **THE TIO_2 PARTICLES, OR (VOIDS), DO NOT TO APPEAR HAVE PARTICIPATED IN SLOWING THE CRACK**. THE CAUSE FOR THIS CONCLUSION IS THAT THE FRACTURE FEATURES TYPICALLY GO THROUGH THE CAVITIES INSTEAD OF AROUND THEM, AND THERE IS LITTLE TO NO EVIDENCE OF STRAIN BEING BUILT UP AROUND THE CAVITIES.



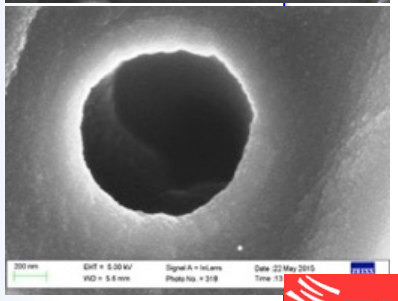
• **THE TIO_2 PARTICLES, OR(VOIDS) APPEAR TO WET WELL WITH THE MATRIX**

• **THE TIO_2 NANOWIRES SEEM TO ACT AS SEEDS FOR CREATION OF CAVITIES APPEARING ON THE SEM'S AS VOIDS.** THE MECHANISM OF FAILURE IS VERY SIMILAR TO NANOSIZE CORESHELL RUBBERS.



• BASED ON THE SEM'S THERE IS A POSSIBILITY OF LOWERING THE TG BECAUSE OF THE CAVITIES, HOWEVER THE CAVITIES MAY ALSO IMPART **SOME IMPROVEMENTS TO FRACTURE TOUGHNESS**.

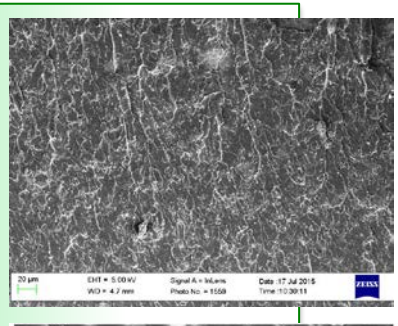
• **THE TIO_2 PARTICLES, OR (VOIDS), APPEAR TO BE VERY WELL DISPERSED** FROM THE UNIFORM DISTANCE OF THE CAVITIES FROM EACH OTHER.



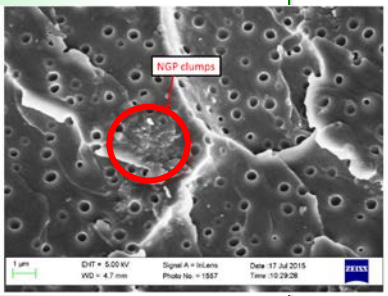
Failure Analysis of graphene Filler Involvement

Epon B at 7.48% Nanographene (NGP) was mixed with Activator A and cast into mold and cured.

‣Resin cast was broken into 2-3 mm long samples and dispersion was checked by SEM



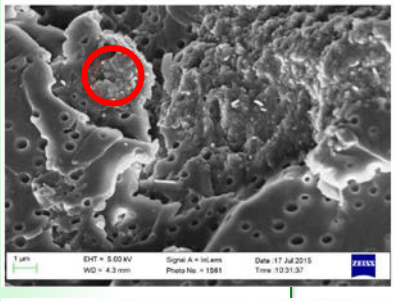
‣ Couple of spots had **clumps of NGP in agglomerated state** (see RED circles)



‣The **NGP seem to be embedded below the surface of the epoxy layer**

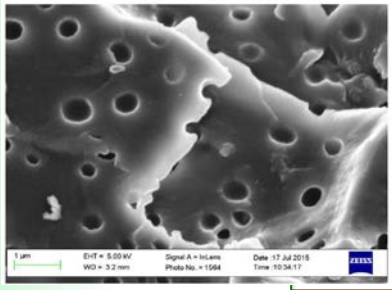
‣Voids (or second phase) in the SEM photos may have been induced by the **well-dispersed NGP**

‣Uniform distribution of the voids (or second phase) and their size is a clear indication of the uniform dispersion



‣**NGP seem to create second phase through voids; the voids (or second phase) would help in bifurcation of the propagating crack and possibly help in improving fracture toughness**.

‣In epoxy resins, presence of second phase is known to improve fracture toughness through cavitation and shear banding



‣**Similar voids were seen previously when Epon A/TiO2 nanowires was cured with Activator A**

‣It is not clear if the **Activator A induces ation of voids (or second phase)**

zyvex technologies

Cobham's Project Status:

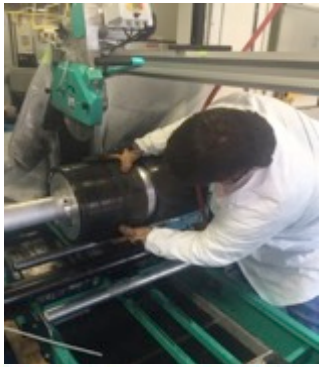
+ designed and produced an aluminum winding mandrel used for winding the flywheel rim parts.

+ wound the 'first article' rim parts. The parts have been inspected and are slightly 'out of tolerance'. Problem was resolved as the rim parts are press-fit together.

+ teamed with a machine shop to develop the process for machining the nominal rim parts to their final tolerances. Cobham also worked with the shop to design the press fixturing necessary for pressing the flywheel assembly together.

+ The baseline flywheels:
  a. blank for TiO_2 are finished
  b. blank for graphene were wound and pressed together but cracked
  c. filled TiO_2 is finished
  d. filled graphene is cracked.

+ Working to find another source for pit testing flywheels to destruction.



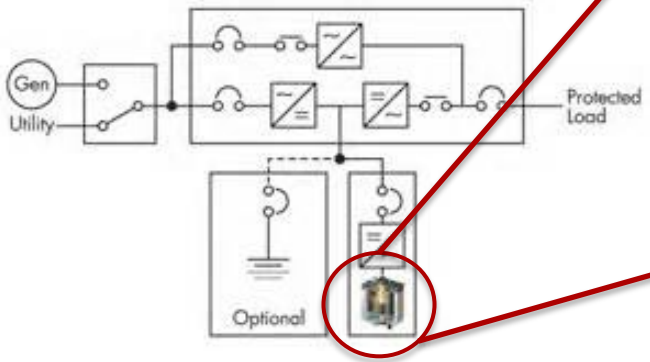
PowerThru's Project Status:

+ Inspected flywheels for initial evaluation/acceptance

+ initiated PO for baseline qualifications in place.

+ initiated discussion on different process for 'breakage' of flywheels.

+ alternative approaches for testing



Woburn, Ma

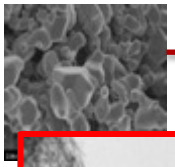
Barbour Stockwell, Inc.

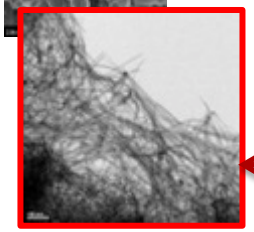
POWERTHRU™
Clean Flywheel Energy Storage

2010

Beacon

TRL 0





10M KOH

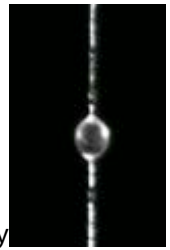
185 ºC

3d

7g prep

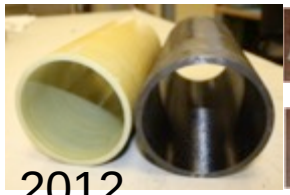
Fiber w/ microdroplet

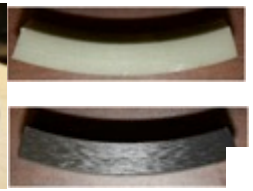
Microdroplet de-bonded by calipers



2011

AFRL

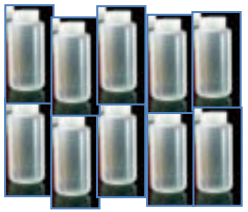




AFRL – 4" wind

2012

TRL 3



500 g prep

Cobham

Cobham/KCP – 4" wind

2013

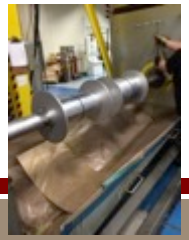
Cobham/PowerThru

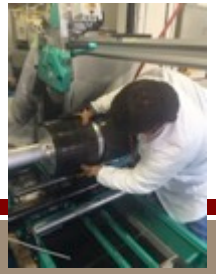
TRL 5

2014

Zyvex

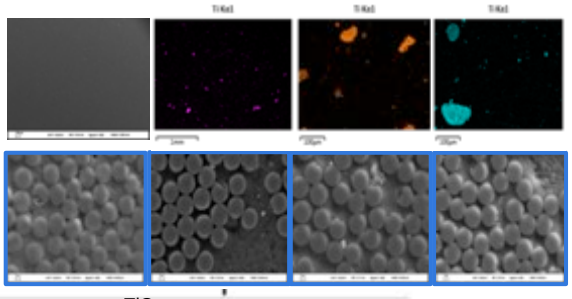
Cobham/PowerThru – 4 Flywheels

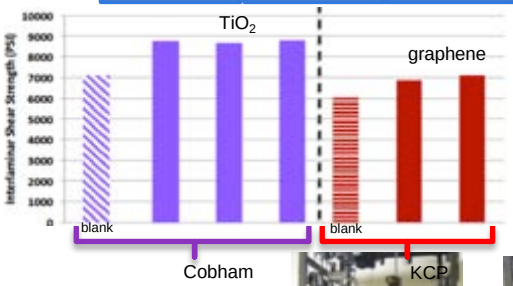


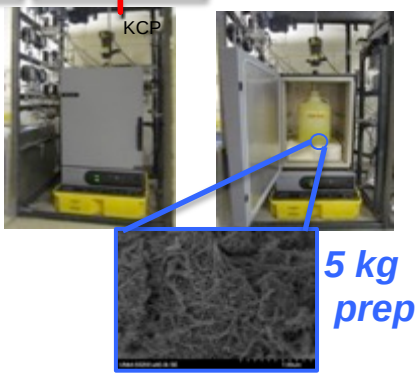


TRL 7/8

Cobham – 4" wind test







5 kg prep

Cobham/PowerThru

2015

High level financial impact evaluation will reveal:

Given the demonstrated laboratory (30%) and industrial (25%) coupon improvements spin rates of > 52,000 rpm with only small increases in costs of production and testing are anticipated.

$$E_k = \frac{1}{2} \cdot I \cdot \omega^2$$

- This high spin rate markedly increases the storable energy (based on flywheel spin rate) and throughput power (based on flywheel acceleration/deceleration).
- Improvements occurring on latest, smaller flywheel creates expanded if not new financial/economic market opportunities for kinetic-electric battery storage applications.

$/kWh

Financial/economic analysis will focus on:

- Estimating benefit-cost and other economic metrics of improved performance due to nanocomposite modified flywheel.
- Estimating DOE-consistent potential levelized cost of energy (LCOE) and comparing with other DOE/EPRI data based on power, energy, and cost characteristics.
- Identifying new or expandable markets in which these improved flywheels would be competitive.

Summary/Conclusions

Milestones:

+ Large scale of TiO_2 NP route has been established

+ Investigation into large scale processing has been initiated.

+ Cobham overcame scheduling issues due to lack of expertise in the machine shop.

+ Manufactured the tooling to machine the rim parts, as well as designing and making the press process tooling was achieved.

+ The assembly of the four flywheels was achieved. Cracking due to cure cycle of Epon B being resolved.

+ Evaluation by PowerThru (balancing) underway (est'd Oct finished).

+ New testing site for breakdown of flywheel (Barbour Stockwell, Inc)

Future Tasks: Milestones for FY 16

- Test breakdown properties of operating flywheels
  + contract with PowerThru
  + transfer of flywheels.
  + testing of breakdown properties (Barbour Stockwell, Inc.)

- Overcome cracking issue and assemble final two flywheels

- Analysis of results and determine if additional work on nanofillers is going to improve overall spin speed.

- Financial impact evaluation based on breakdown analysis.

- Analyze 'spare' flywheels for in-lab evaluation.

- Al_2O_3 planar material incorporation into flywheel

- Analyze results of C-fiber resin interaction using dog-bone test and optimize.

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Energy Storage Program Manager – Dr. Imre Gyuk

Contact Information

Timothy J. Boyle
Sandia National Laboratories
Advanced Materials Laboratory
1001 University Boulevard, SE
Albuquerque, New Mexico 87106

tjboyle@Sandia.gov Ph:(505)272-7625