Global Climate and Energy Project (GCEP)

Project Goals:
1) 50% Energy Generation from Renewables
2) Greenhouse Gas Reduction
3) Stability of the National Electrical Grid

Program Sponsor – GCEP administered by Stanford University
Collaboration between UT-Austin and UT-Dallas

Project Approach – Develop Large Scale Energy Storage tied to the Grid
- Large Scale Energy Storage (UT-Austin)
- Revolutionary flywheel energy storage designs
- Nanotechnologies (UT-Dallas)
  – Game changing advances made possible by lighter, stronger materials

Hubless Flywheel Design
- For Both the Pendulum and Hubless Flywheel Designs:
  • High-strength nanostructured rotor materials permit higher performance
  • Performance boost is remarkable since energy stored is proportional with rotational speed squared
  • Superconducting nanomaterials greatly reduce bearing losses and improve motor/generator efficiency
Motivation for our GCEP Program on:

Low-Cost Flywheel Energy Storage for Mitigating the Variability of Renewable Power Generation

- Large scale energy storage is needed to improved stability, power quality, and reliability of the US electrical grid.
- Balancing power generation and electrical load consumption makes energy storage even more important as the US grid strives to handle increasing wind and solar resources.
Why Flywheel Technology is Part of the Solution

- Given that nearly all electricity in the world is produced from generators
  - And about 60% of the world’s power is used in motors

- It is clear that rotating machines, i.e. motors and generators, are part of the grid today

- Suggests that the revolutionary energy storage solution is a motor and generator combination with additional mass on the rotor for energy storage

- .....a flywheel battery
Low-Cost Flywheel Energy Storage for Mitigating the Variability of Renewable Power Generation

Program Flow and Tasks

UT-CEM
- Flywheel Design
  - Structural and Thermal Analysis
  - Rotordynamics
- Motor/Generator
  - Magnetics and Electrical Design
- BearingMagnetics and Electrical Design
- Control Design and Evaluation
- Bulk Material and Component Level Testing

UT-Dallas
- Advanced Materials Development
  - Development of Advanced Multi-functional Materials
  - Develop and Evaluate Mechanical, Magnetic, Electrical, and Superconducting Properties

Revolutionary Flywheel Design that drastically reduces the cost of utility-scale flywheels specifically for the benefit of wind and solar power generation.
Biscrolling Nanofiber Sheets and Functional Guests into Yarns for ENERGY Applications

- Our new technology enables the spinning of “unspinable” powders and nanofibers into weavable, sewable, and knottable multifunctional yarns.

- These weavable yarns can contain 97 wt % of generic micro- or nano-powders that remain highly functional.

- Demonstrated fabrication of superconducting yarns, high performance Li-ion battery electrode yarns, catalytic fuel cell yarns, and graphene yarns.
Strong, Transparent Carbon Nanotube Sheets are the Host

We spin strong MWNT sheets at up to 30 m/min from nanotube forests (over the 20 m/min for wool spinning). One cm length of 300 μm high forest converts to a 10 meter long sheet.

The self-supporting MWNT sheets initially form as a highly anisotropic aerogel that can be densified into strong sheets that are as thin as 50 nm. The areal density is ~3 μg/cm².

No fundamental limit on sheet width or length.

The measured gravimetric strength of orthogonally oriented sheet arrays exceeds that of the highest strength steel sheet.

Supported mm size droplets (left) are 50,000X more massive that the directly supporting sheet area.
Biscrolling provides multifunctional yarns containing up to 97 wt % of “unspinnable” powders or nanofibers

*Approach A:* Deposit guest on the spinning wedge during twist-based spinning from forest.

*Approach A:* Deposit guest on preformed sheet and then insert twist.
Fermat or Double Archimedean Scrolls Result for Symmetric Twist Insertion (depending upon end support)

**Fermat for forest spinning**

**Double Archimedean for rigid support spinning**

80% Ti@MWNT$_{2.0}$ wet spun between rigid supports

MWNT spun from forest

MWNT dry spun between rigid supports

Dry spun dry paint/MWNT
Guest Deposition on Only One Edge of Sheet Results in Sheath-Core Structure With Guest in Either Core or Sheath

G-H: TiO$_2$@MWNT$_{2,1}$ guest deposited on 15% of sheet width by patterned filtration on MWNT sheets and asymmetrically twisted in liquid.

Guest location in the sheath places photocatalyst in the region where light is available for such applications as self-cleaning textiles and Graetzel solar cells.
Biscrolled carbon nanotube yarns containing mostly other multifunctional guest can be plied, woven, sewn, and knotted like guest-free yarn.

90% colloidal-SiO$_2$@MWNT$_{3,0}$

85% TiO$_2$@MWNT in Kevlar textile
Could Biscrolled Yarn Textiles Be Washed?

*The following experiment was conducted to crudely mimic the destructive power of extreme washing cycles.*

- A 6 cm long biscrolled yarn was tethered by one end in a 200 ml beaker of hot (80°C), soapy water (1 wt % sodium dodecyl sulfate) that was continuously stirred at ~1100 rpm for 3 hours.

- The biscrolled yarn contained **93 wt % of filtration-deposited TiO₂ particles**.

- **Less than 2% weight loss occurred.**

- SEM images taken before and after this wash suggest an unchanged yarn structure.
Our Generic Methods For Making Biscrolled Yarns

**GUEST DEPOSITION**

*Dry State:*
- PECVD, e-beam evaporation,
- CVD, electrostatic painting

*Wet State:*
- filtration, electroplating *electrophoresis*, reaction of solution, crystallization

**BISCROLLING**

*Dry State or Wet State*

*Twist, False Twist, or Liquid Densification*

Precursor to Biscrolled Yarn is Spinning Wedge From Forest or *Sheet Ribbon*

Example of Biscrolling from Spinning Wedge:

Deposit Guest onto the Wedge or Forest
AEROSOL APPROACH CAN CONTINUOUSLY PRODUCE BISCROLLED YARNS BY GUEST DEPOSITION AND TWIST INSERTION IN AIR

Schematic of continuous biscrolling

MWNT forest

SWNTs Spray

Spinning wedge

Pictures illustrate process for aerosol made by $\text{TiCl}_4 + 2 \text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4 \text{HCl}$
TEMPLATING: Conformal coating of MWNTs in MWNT sheets (and optional removal of MWNT cores) leads to new hosts.

11 cm long Si$_3$N$_4$ nanotube sheet obtained by templating a MWNT sheet.
Biscrolled Superconducting MgB$_2$

Superconducting bi-scrolled yarn was made by *filtration-based deposition* of Mg/B powder over two MWNT sheets, and covering the Mg/B layer with a third MWNT sheet. **The annealed (750° C, 30 min.) biscrolled yarn was 97 to 98 wt % MgB$_2$.**

$T_c$ (38 K) is close to the expected 39 K.

Eliminates the 30 odd drawn-down steps of powder-in-tube methods.
Biscrolling Provides Metal-Free Catalytic Oxygen Fuel Cell Electrodes that are Flexible & Weavable

- The onset potential for oxygen reduction by NₓMWNT@MWNT shifts by ca. +0.3 V with respect to that for MWNT@MWNT.
- The same shift was observed for the precursor bilayer sheet stack, indicating that biscrolling is not interfering with catalysis.
- Optimization can therefore focus on pyridinic/quaternary nitrogen ratio and N content.
- The ability to confine catalysts Without decreasing activity is generically important.

Catalytic oxygen reduction by CV (5 mV/s) was in a 0.5 M aqueous H₂SO₄ that was saturated with O₂ by air bubbling. The counter electrode was Pt mesh. The Nₓ-MWNTs were synthesized by a floating catalyst CVD method (Chem. Commun. 23, 2335 (2000)).
NEW APPROACH:

FUEL CELLS Using N-doped CNT as Yarn Host

CNT Sheet

0.9 V% NH₃/He plasma

N-doped CNT Sheet

Twist insertion

N-doped CNT yarn
Yarns of 100% \( N_x \)MWNTs Provide MUCH HIGHER Capacitances than Undoped CNT yarns

Cross section of a N-doped yarn.
Biscrolled yarn LiFePO$_4$ cathode and biscrolled yarn Si anode for flexible Li-ion batteries

Both electrodes can be a woven sheet

Both electrodes can be a single yarn, so each battery is a two-ply yarn (like for our CNT supercapacitors).

SUPERCAPACITOR OF ELECTROLYTE-SEPARATED HELICALLY-WOUNDED CNT FIBERS

TWO CNT FIBER SUPERCAPACITORS WOVEN INTO FABRIC (*Nature*, 2003)

**PROBLEMS PROVIDE OPPORTUNITIES**

- LiFePO$_4$: Rate and capacity are high (170 mAh/g, theoretical) but low electronic conductivity means ~30 wt % of electrode is carbon/binder/Al foil.
- Si has a theoretical capacity of 4200 mAh/g, but cycle life is poor even at much lower capacities, because of up to 400% volume change.
- Electrodes and batteries are rigid, and unsuitable for deployment in clothing, as conformal sheet layers, or for structural reinforcement.
The Affect of Additives on Increasing Weight of LiFePO$_4$ Cathodes

<table>
<thead>
<tr>
<th>OPTIMIZED USUAL CATHODES</th>
<th>OUR BISCROLLED CATHODES</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Active material</strong></td>
<td><strong>LiFePO$_4$</strong></td>
</tr>
<tr>
<td>PVdF</td>
<td>75-80 % wt.</td>
</tr>
<tr>
<td>LiFePO$_4$</td>
<td>90-98 % wt.</td>
</tr>
<tr>
<td><strong>Binder</strong></td>
<td><strong>PVdF</strong></td>
</tr>
<tr>
<td>5-10 % wt.</td>
<td></td>
</tr>
<tr>
<td><strong>Conductive carbon</strong></td>
<td><strong>C black</strong></td>
</tr>
<tr>
<td>5-15 % wt.</td>
<td></td>
</tr>
<tr>
<td><strong>Current collector</strong></td>
<td><strong>CNT sheet</strong></td>
</tr>
<tr>
<td>Al foil</td>
<td>extra 20 % wt.</td>
</tr>
<tr>
<td></td>
<td>10-2 % wt.</td>
</tr>
</tbody>
</table>

Maximum theoretical capacity of 170 mAh/g for LiFePO$_4$ becomes
- Achievable 136 mAh/g (based on total weight) for usual cathode
- Achievable >153 mA/g (based on total weight) for biscrolled cathode
Our Biscrolled Yarns Containing 95 wt % LiFePO$_4$ Remain Flexible Enough to be Woven and Knotted

Biscrolled yarn cathode in which 95 wt % LiFePO$_4$ is in helical corridors of 5 wt % MWNT host.

Connectivity between LiFePO$_4$ and MWNTs. Yarn knotted after use as battery cathode.
Initial Results as Li-Ion Battery Cathode are Promising

Biscrolled yarn (100 µm diameter) is 95% LiFePO$_4$@MWNT in an electrolyte of 1M LiPF$_6$ in a 1:2:3 by volume mixture of propylene carbonate, ethylene carbonate, and dimethylcarbonate. Li foil is anode.

Charge-discharge use constant charge rate (C/20) and variable charge rate (10C-C/3).

Based on total electrode weight:

- Charge storage capabilities of 115 mAh/g at C/3 rate
- 99 mAh/g at 1C rate

For comparison, the theoretical charge density of LiFePO$_4$ is 170 mAh/g.

- Energy storage density was 379 Wh/kg at 180 W/kg power and 180 Wh/kg at 4590 W/kg power.
Application Possibilities for Biscrolled Yarns (optionally plied, woven, knitted, braided, etc.)

- Superconducting cables
- High-energy-density, high-power-density flexible batteries and supercapacitors (electronic textiles)
- Vascular yarn structures for accessibly contained hydrogen-storage powder
- Woven textiles containing >50 wt% of bio- or chemo-protection agents for first-responder clothing
- Textile antennas
- Flexible woven textile electrodes for fuel cells and biofuel cells
- Heat storage textiles for clothing and other applications
- Flexible woven solar cell electrodes (electrochemical or solid state), where efficient charge separation is enabled by close proximity of excitons and collector
- Magnetic yarns for actuators and transformers
- Yarn containers for catalysts (like N-doped carbon nanotubes, which outperform Pt for O₂ electrodes)
- Thermal electrochemical and mechanical-electrical energy harvesting
- Self-repairing structures and artificial muscles
- Multifunctional structural textiles