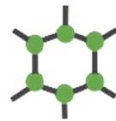


Binder-Free Battery Electrodes

Karlheinz Strobl^{1*}, Rune Wendelbo², Rahul Fotedar²,
Riju Singhal¹, and Mathieu Monville¹



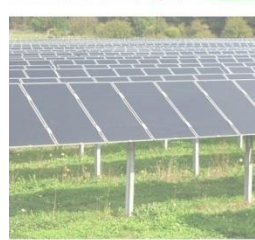
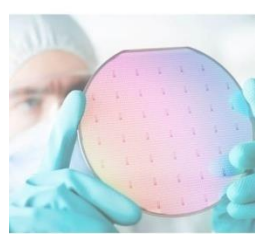
¹CVD Equipment Corporation, New York, USA



Graphene Batteries

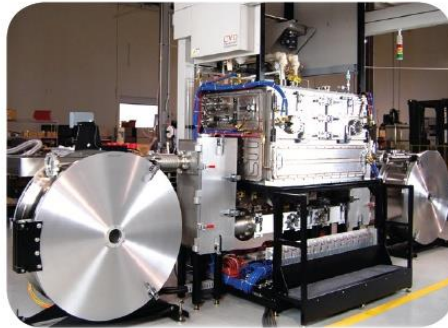
²Graphene Batteries AS, Oslo, Norway

* *V.P. of Business Development, CVD Equipment Corporation*



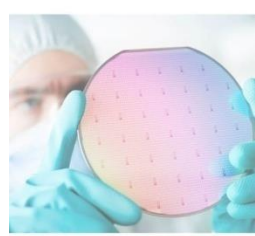
CVD Equipment Corporation

Designs and manufactures both **Standard** and **Custom** R&D, Pilot & Production **chemical vapor deposition** systems



Operates an Application Laboratory:

- Performs contract process development
- Develops processes and equipment for research materials
- Works with researchers to help accelerating the commercialization of nanomaterials



Commercialization of Nanomaterials

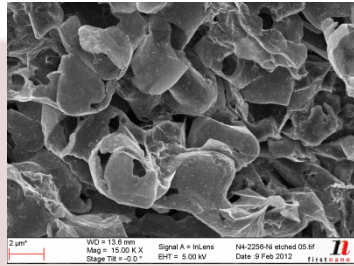


- Billions of \$\$\$ have been spent developing a range of nanomaterials
- A Nano to Macro transformation process allows manufacturing nano-enhanced Products with higher value propositions
- \$\$\$ can only be made at the Product level

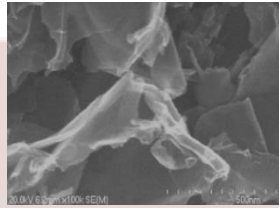
REQUIREMENTS TO DEVELOP NANO-ENABLED PRODUCTS:

- A large pool of starting nano raw materials (0D, 1D, 2D, 3D)
- A general purpose “Nano to Macro” material transformation method
- Ability to pre and post treat process materials to further tune end material properties
- Develop a scalable, low cost manufacturing process to produce nano-enabled macro sheets (roll-to-roll) with “cost effective” width and length
- Demonstrate value benefits for selected volume applications

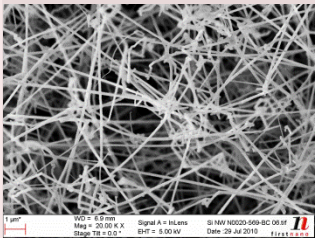
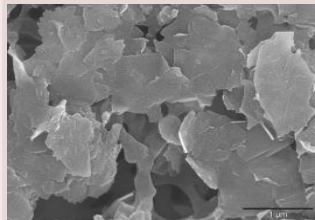
Novel Nano**to**Macro™ Manufacturing Platform



3D graphene, carbon-derived-carbons, hollow carbon structures, etc.

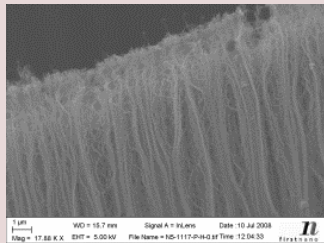


Nano platelets:
graphene
vermiculite,
clay
BN, MoS₂, ...

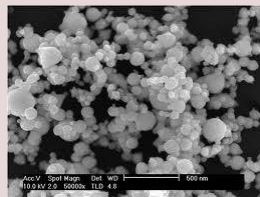


Nanowires:
Si, GaN, BN,
TiO₂...

Nanotubes:
VACNT, BN NT

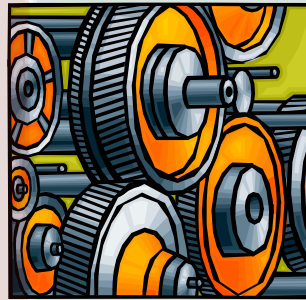


Nanoparticles:
LiFePO₄, ...



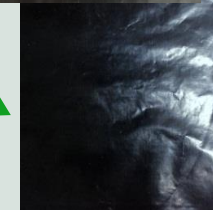
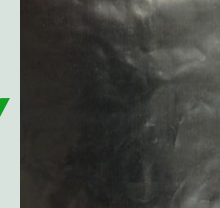
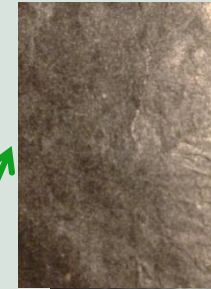
Raw nanomaterial
manufacturing process

Nano**to**Macro™ Manufacturing Platform



Sheet manufacturing process

- Larger range of nano-enabled macroscopic material formulations
- Economical manufacturing process no high-temperature step
- Universal process for a wide range of nano materials



OPTIMIZABLE FOR:

- thickness
- surface density
- density
- electrical conductivity
- thermal conductivity
- surface area
- capacitance
- fire retardant
- high temperature durability
- UV-FIR absorption
- mechanical interlocking
- shock absorption
- compression resistance
- strength, etc.

Novel Nano**to**Macro™ Manufacturing Platform

“The paper route applied at the nanoscale”:

What are the technical advantages of papermaking?



*Well-known
vacuum-filtration
method*



*Louis-Nicolas Robert's
1st papermaking machine*

Batch processing

Roll-to-roll engineering

*Integration of additives or
additional processing steps*

In-line manufacturing capable

*Easy-to-tailor to the required specificity
of the end product*

Recyclability / greener processing

Scalability



Today's industrial scale papermaking machine

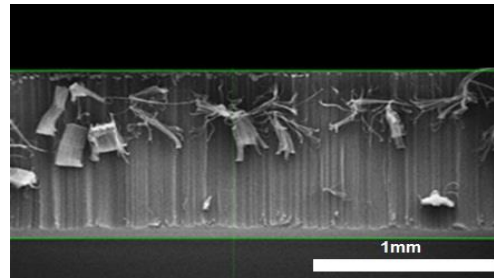
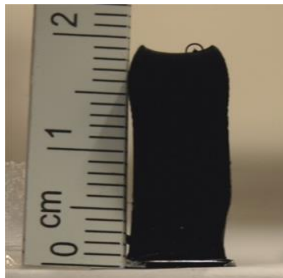


Nanocarbons can be both “Active Materials” and “Binder Materials” for Batteries and Supercapacitors

The aim of the carbon community is to create functional materials, having enhanced properties, using less materials with simpler and more environmental-friendly processes.

Our vision (binderless nano enabled sheets)

mm-long MWCNTs/SWCNTs can be utilized to form **3D mechanical and electrical nets** *binding* any other active material (carbon or non-carbon) together without the need for polymers



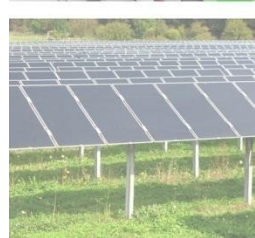
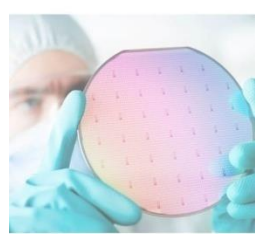
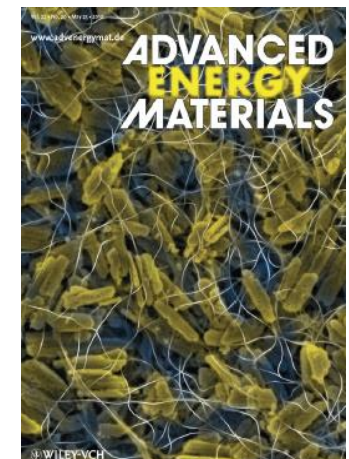
VAMWCNTs, removed from growth substrate



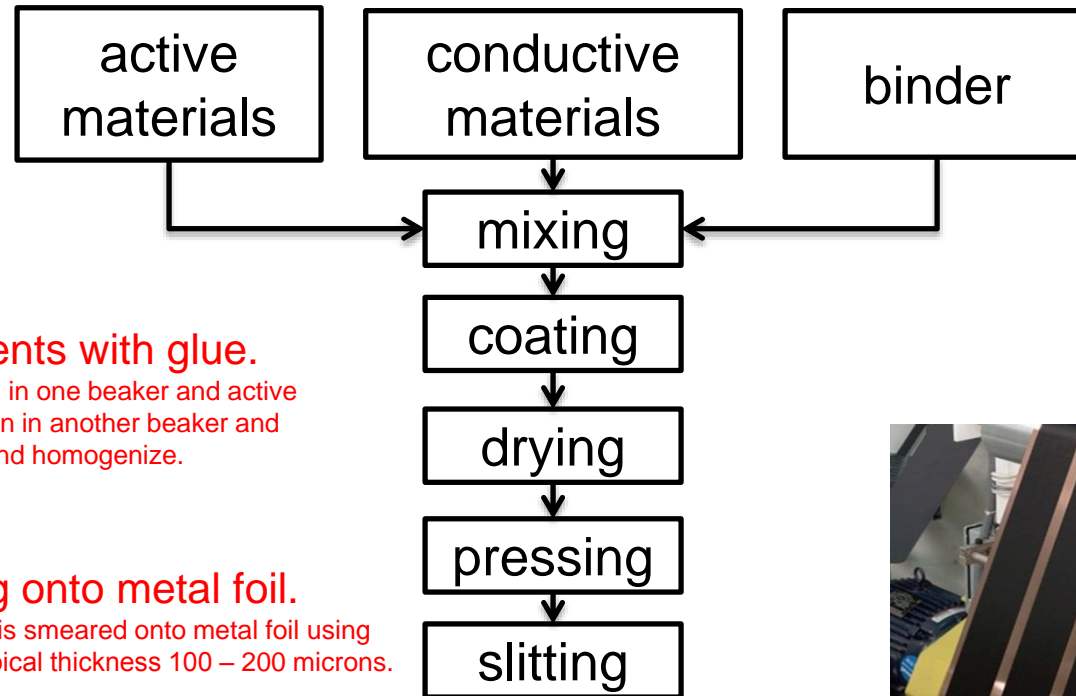
The “paper” platform route utilizing mm-long CNT’s as 3D net enables the manufacture of many multifunctional nano-enabled materials.

Related concepts: NREL

- C. Ban, Z. Wu, L.Chen, Y. Yan, A.C. Dillon
Adv. Mater. 2010, 22, E145–E149
- US 2011/0070495 A1
- US 2011/0111279 A1



Traditional Battery Electrode Manufacturing



Step 1.

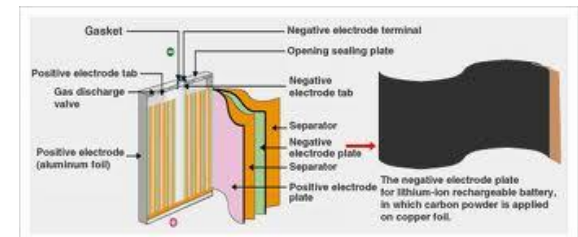
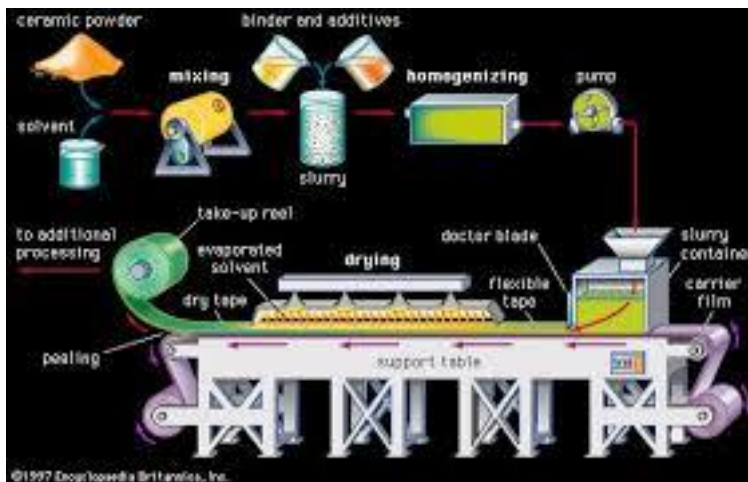
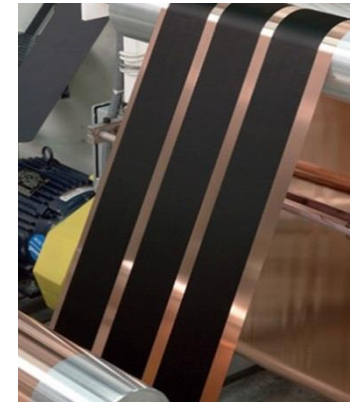
Mix ingredients with glue.

Make glue solution in one beaker and active material and carbon in another beaker and then mix the two and homogenize.

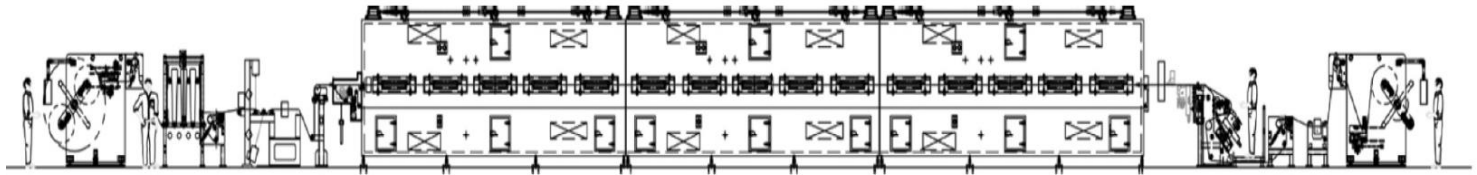
Step 2.

Calendering onto metal foil.

Slurry from step 1 is smeared onto metal foil using "doctor blade". Typical thickness 100 – 200 microns. Then let dry.



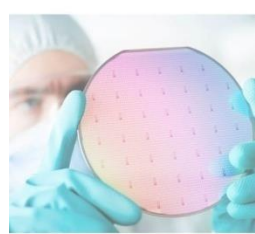
Problems of Polymeric Binders in battery electrodes!



- Lithium Batteries Manufacturing typical used large amounts of
- toxic chemicals (NMP) to dissolve binders (70% of slurry)
- Requires special facilities (10-100 m tall chimney) to exhaust, dry and recover toxic solvent vapors:

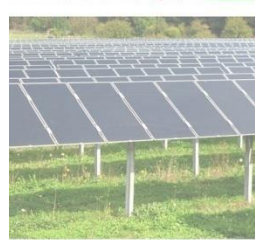
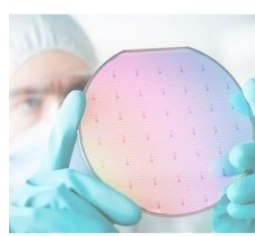


-> capital intensive and high operating cost



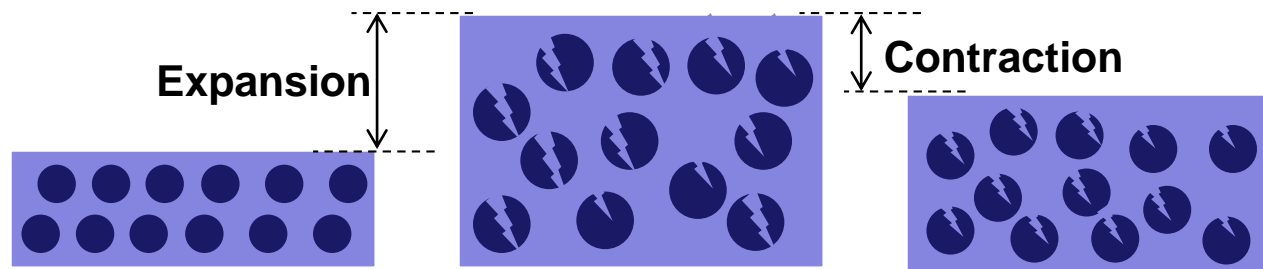
Polymeric Binders limit performance in battery electrodes!

- Reduce conductivity of electrodes
- Limits the practical usable thickness of electrode for given C rate
- Can swell over time and thereby limiting the battery life (especially with ionic liquids)
- Result in low lifetime (100 cycles) for higher capacity active materials that have large volume changes (Si, Sn, etc.)

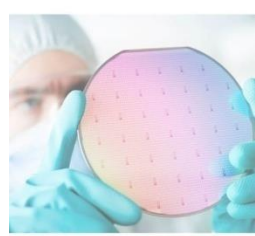


Li-Ion Batteries: Recent Developments

- Developments in this field were slow until recently when significant increase in cell capacity was demonstrated by inclusion of Si (and other entities capable of repeatedly alloying & de-alloying with Li)
- However, expansion-contraction makes particles disintegrate and lose electrical contact
- Further, expansion-contraction is not reversible resulting in a net volume change.
- **Therefore: binders which are used to hold electrode material in place are one potential area for improvement.**



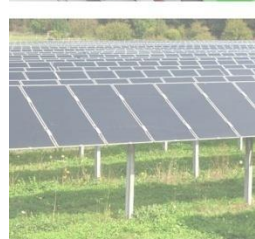
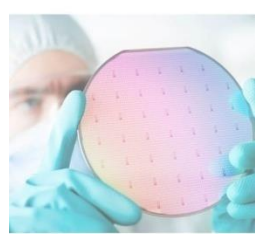
- **Partial Irreversible** Expansion-Contraction cycle
- => Particle disintegration



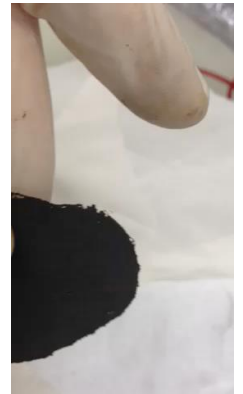
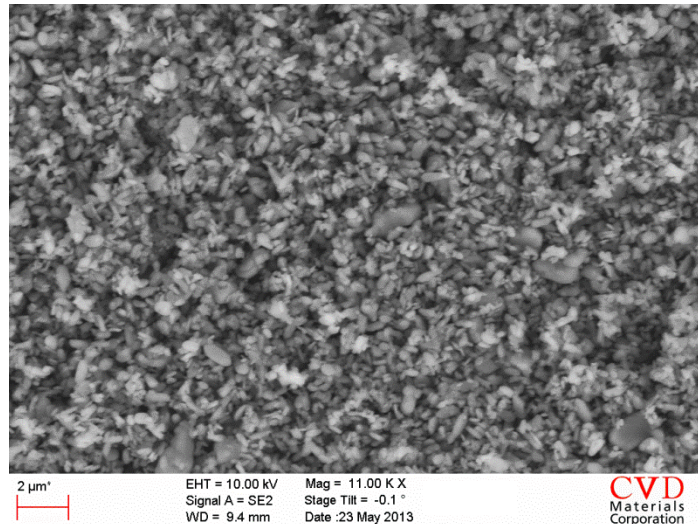
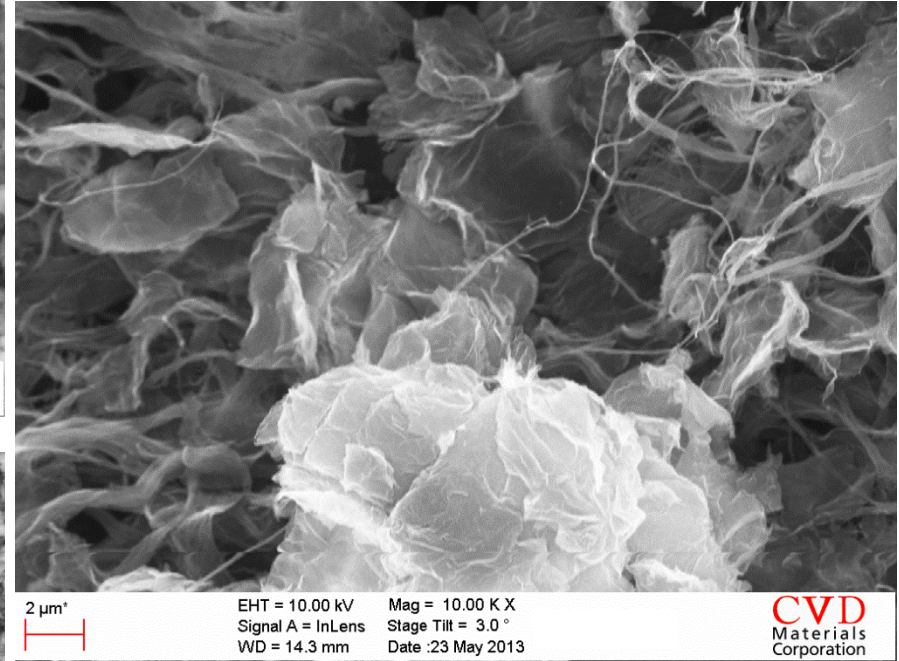
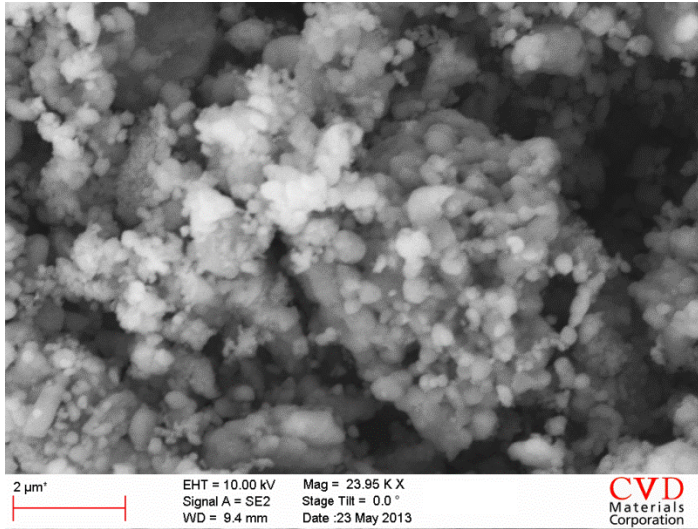
Li-Ion batteries: Need for new binder materials

- Binders used for batteries in portable devices should be thermally stable for temperatures which sometimes exceed 250 °C
- Fluorinated binders commonly used pose an environmental risk
- The most popular binder PVDF can excessively swell and requires volatile and toxic solvents (e.g. N-Methyl Pyrrolidone)
- Binders should preferably be electrically conducting so that the resulting electrode material has higher electrical conductivity

=> Millimeter long CNTs offer high strength, flexibility, porosity and high electrical conductivity, making them a suitable candidate for binder material



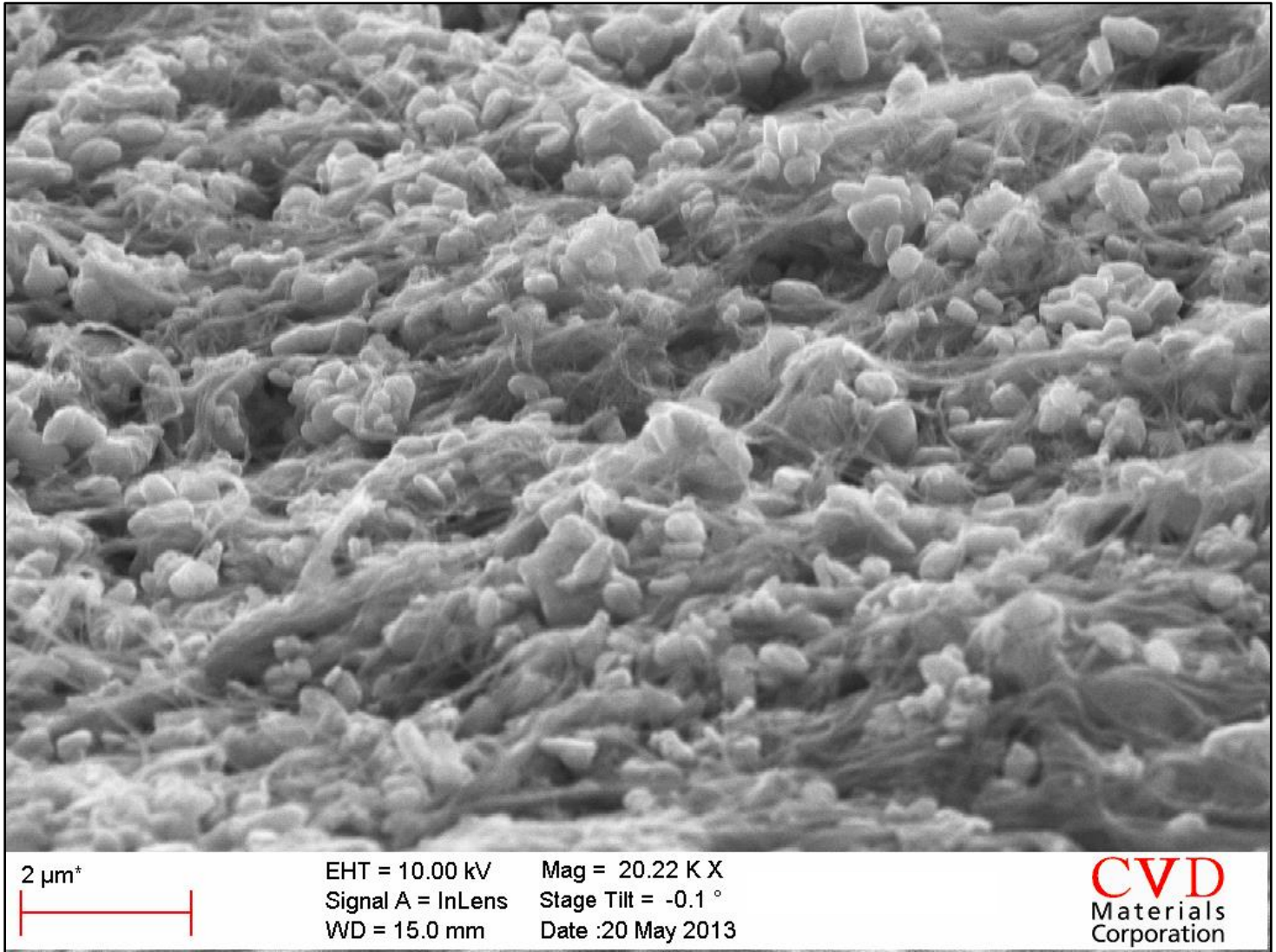
Converting different size LFP powder to “paper”-like sheets



mm-long CNTs trap active nano/micro material
in electrical and mechanically interconnected 3D net



Binder-Free Battery Electrodes



8% mm-long CNTs + 92% Lithium Iron Phosphate



Binder-Free electrodes bonded Binder-Free to metal foil



- **More active materials**
- **Better conductive network**
- **Tunable tortuosity**
- **No polymeric binder**
- **Thicker electrodes possible**
- **Flexible electrode possible**
- **New type of current collector possible**

Binder-free bonding of
Binder-free electrodes to
Current conductor

Working Towards

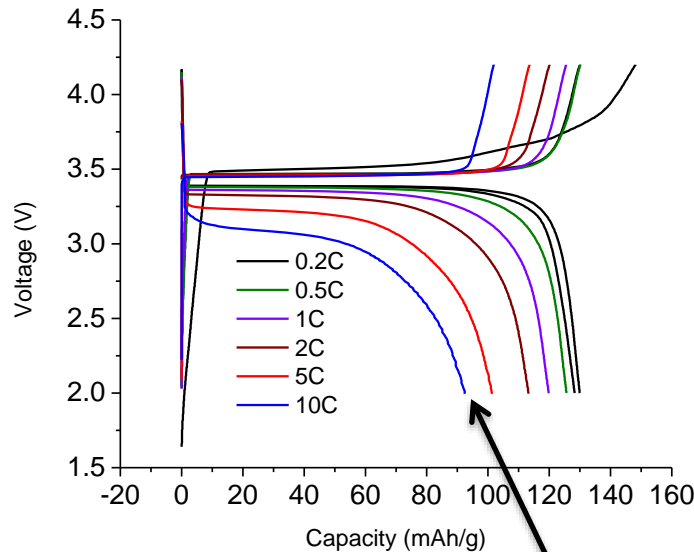
- 1) binder-free technology
- 2) thicker electrodes
- 3) longer life
- 3) higher energy densities
- 4) Higher power capacity devices



C-rate testing of half cells

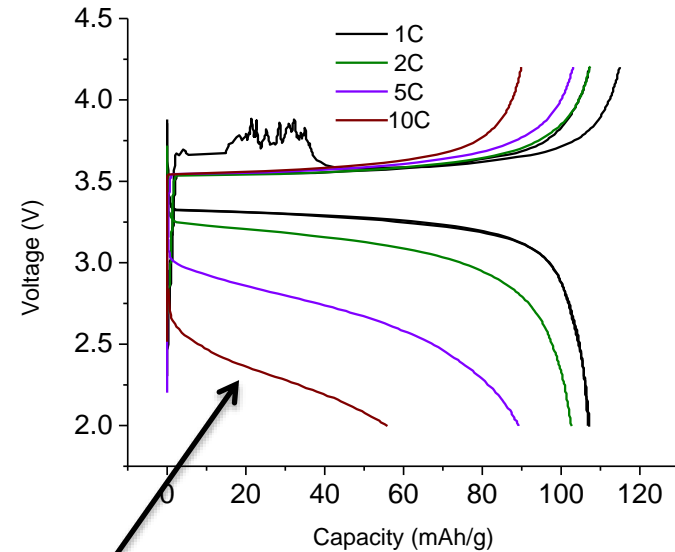


PRELIMINARY DATA



Binder-free electrode
LFP 92%, CNT 4%,
CB 2%, rGO 2%, 35mg/cm²

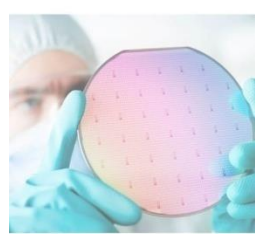
**Shows higher rate capability
for similar charge capacity**



Reference electrode (LFP)
80%, 10% CB, 10% binder),
5-6 mg/cm²

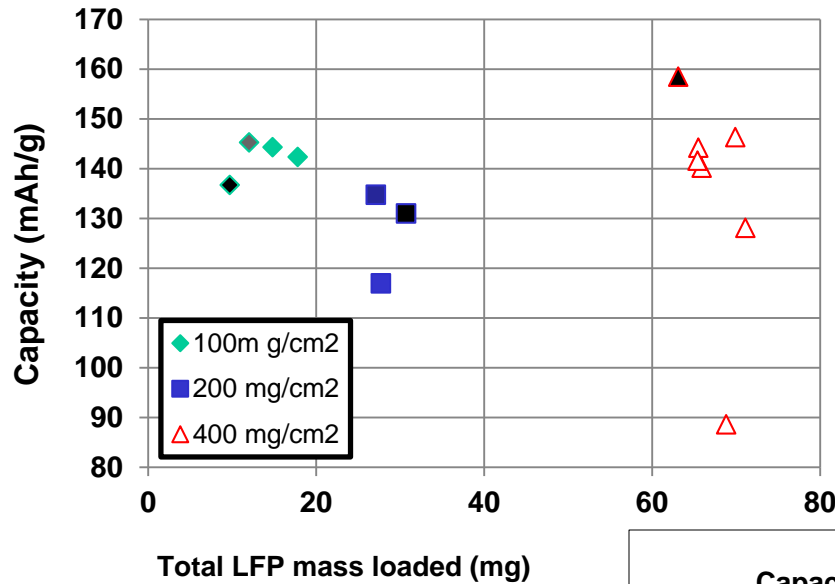
PRELIMINARY DATA

www.graphenebatteries.no



C-rate testing of half cells

Capacity vs. mass loading @ DC C/10



PRELIMINARY DATA

www.graphenebatteries.no

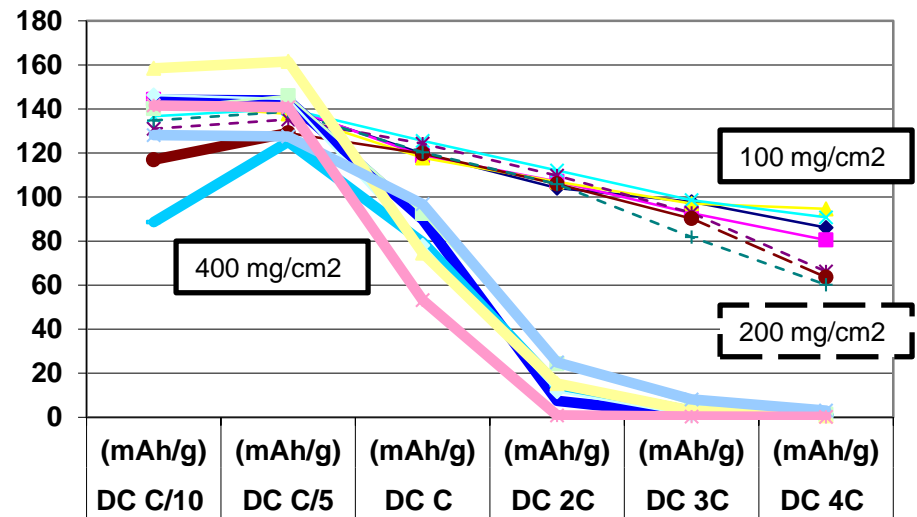
Process uniformity needs to be improved!

Thicker electrodes possible.

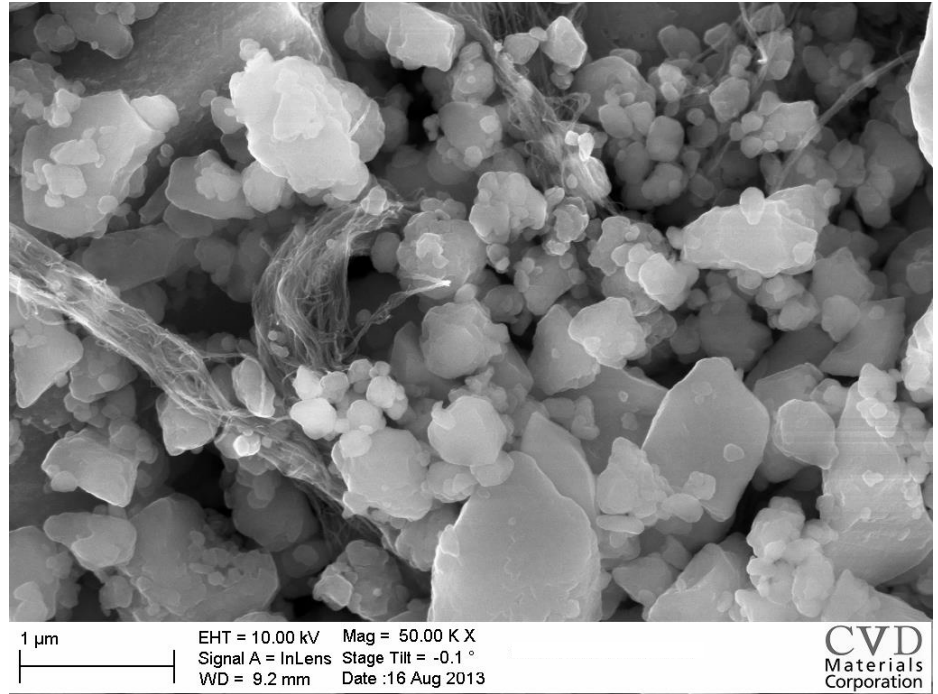
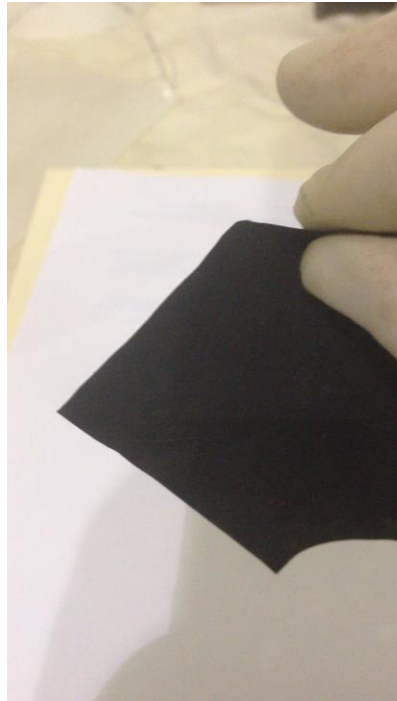
Thicker electrode need more vertically aligned pores to increase electrolyte Transport.

Delamination between Current conductor and Binder-less Electrodes under investigation, mixed data at 200 cycles.

Capacity vs. C/x rate for different mass loading groups



Binder-Free Si-sheets with mm long CNTs



**mm-long CNTs trap active Nano sized Si powder
in electrical and mechanically interconnected 3D net**

www.graphenebatteries.no

Summary:

- **CVD** Equipment Corporation continues to expand capabilities in
 - Equipment design
 - Process development
 - Material applications
- **CVD** Application Laboratory supports custom process and material development opportunities to advance the state of the art.
- We now leverage a growing range of nanomaterials developed in-house and manufactured by others.
- Our low cost, **Nano to Macro™** sheet manufacturing process is highly flexible and can manufacture many different types of multifunctional materials.
- **Binder-free battery electrodes are possible and are under further investigation!**

Thank You!

What material / application problems can we help solve for you today?

www.cvdequipment.com

www.cvdmaterialscorporation.com

