Development of Advanced Electrode Materials for Rechargeable Space Rated Li-Ion Batteries

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Nano-Engineered Materials For Rapid Rechargeable Space Rated Advanced Li-Ion Batteries

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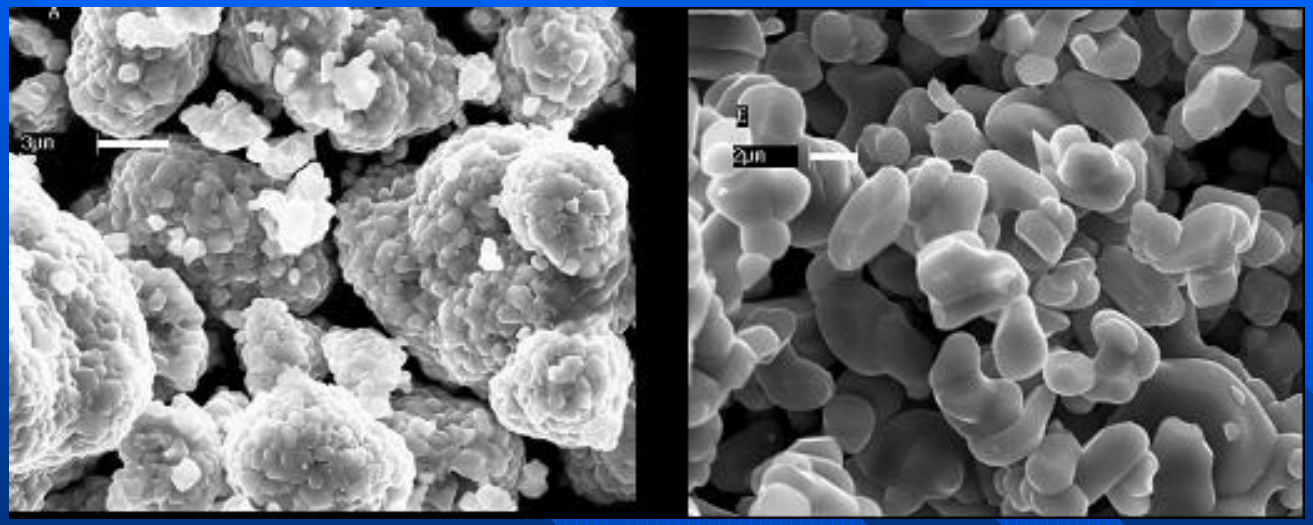
SBIR Phase II

Electrode Materials

Ultra Small particle size material for high power



SEM photographs of two cathode materials, the material on the left is easily milled to smaller primary particles, the particle size of the material on the right is not easily reduced.

Nanoparticle Electrode Process

- Issues:
  - Particle agglomeration
  - Loss of nanoproperty
- Solution:
  - Nanoengineered electrode
  - Preserve nanostructure
- Advantage:
  - *Safe & low impedance*

NANO Technology

- Li-ion Cells:
  - NanoEngineered Electrodes
    - » Anode (Fe_3O_4 & $Li_4T_5O_{12}$)
    - » Cathode (NAT7050, $LiCoPO_4$)
  - Electrode Manufacturing Methods
    - » Electrodeposition: AAO template assisted Copper nanorod / Fe_3O_4
    - » Slurry based: Carbon nanotube (CNT) deposition / anode/Cathode
    - » Combination of Slurry Based Coating and Electrodeposition Processes
  - Physical & electrochemical Characterization
- Milestone & Goals
- Summary

Electrodeposition

Electrochemical Anodization of Al

↓

AAO membrane with nanochannels

↓

Electrochemical synthesis of Cu nanorod arrays

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Nanostructured Cu electrodes

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Electrodeposition of Fe_3O_4

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Anodes for Li-ion battery

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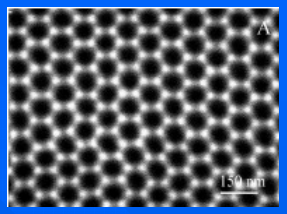
Characterization

↓

Optimized structure

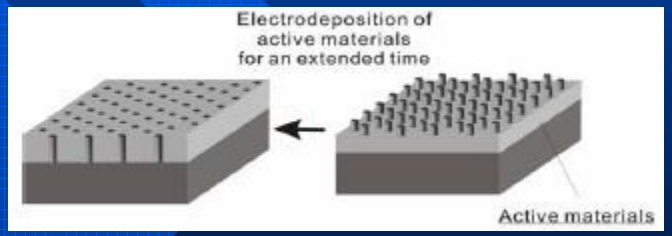
↓

Device



AAO Template

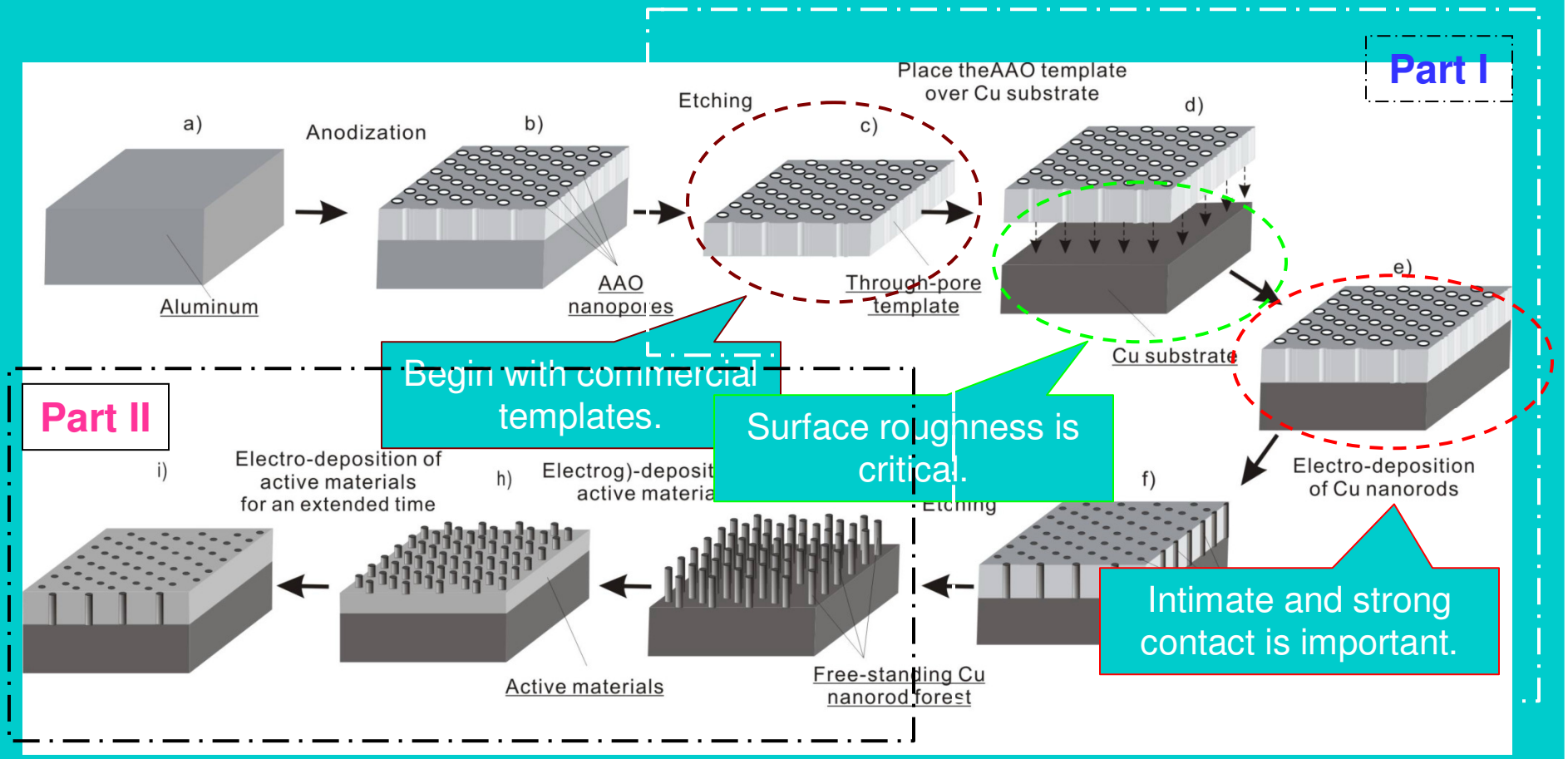
Cu-nanoRod



Electrodeposited Fe_3O_4

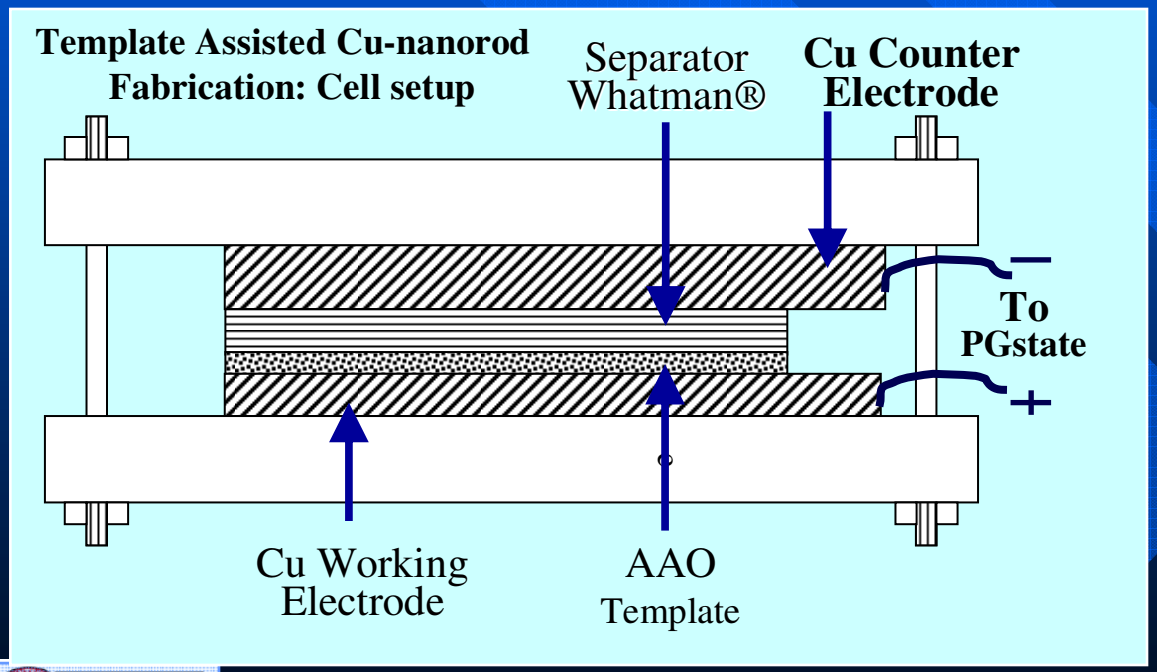
AAO Template

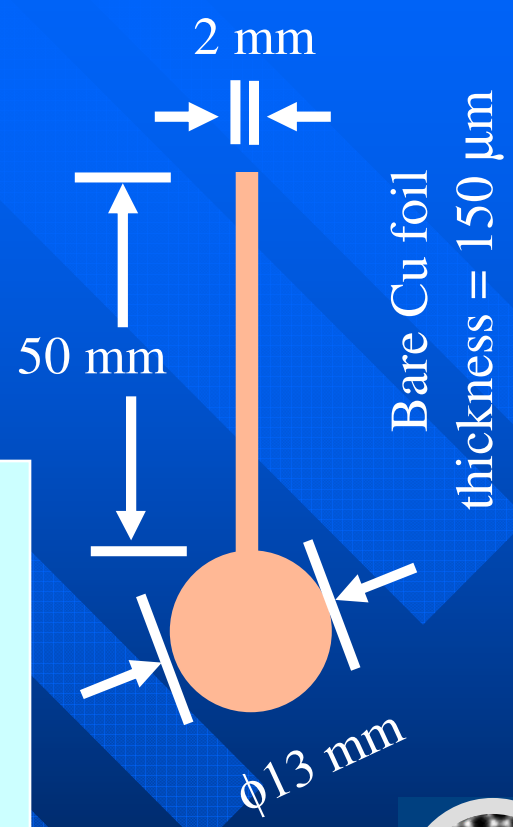
- Commercial
- Homemade

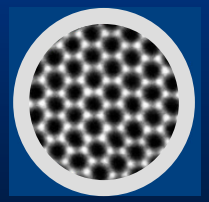


Nanoarchitectured Copper Current collector

1) Mechanical Polishing
2) Ultrasonic Cleaning
3) Template assisted Cu-Nanorod growth by electrodeposition
4) Fe_3O_4 deposition
   i) Electrodeposition*
   ii) Ultrasonic spray coating
   iii) Sol gel process



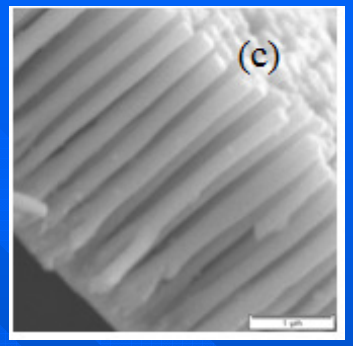


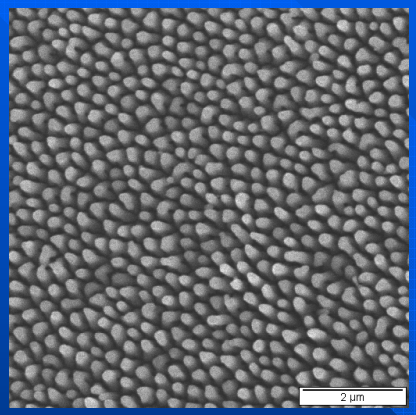


AAO Template

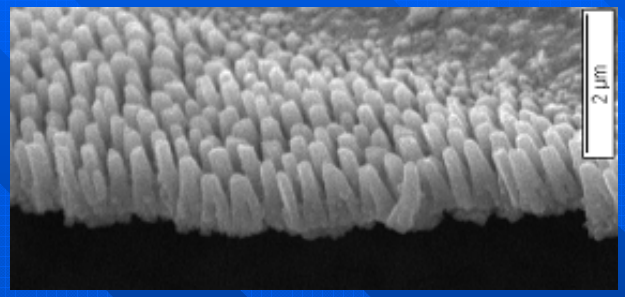
Cu-Nanorod Fabrication Electrodepositions

- Electrolyte: 100 g/L $CuSO_4 \cdot 5H_2O$, 20 g/L $(NH_4)_2SO_4$, 80 mL/L Diethylenetriamine (DETA).
- Separator: Whatman® Grade 41 diam. 4.25 cm.
- Template: Anodized aluminum oxide (AAO)





Top View



Cu-nanorod on Cu-foil (0.5 mil)

- Electrochemical depositions: 1.2 – 1.5 VDC @ 25°C for 15-20 mins. Cu-nanorod length of 3-µm was achieved for 5 min electrodeposition time period
- AAO Template removal: Etched in 1M NaOH solution at 80°C

Fe_3O_4 Electrodeposition

Electrodeposition:

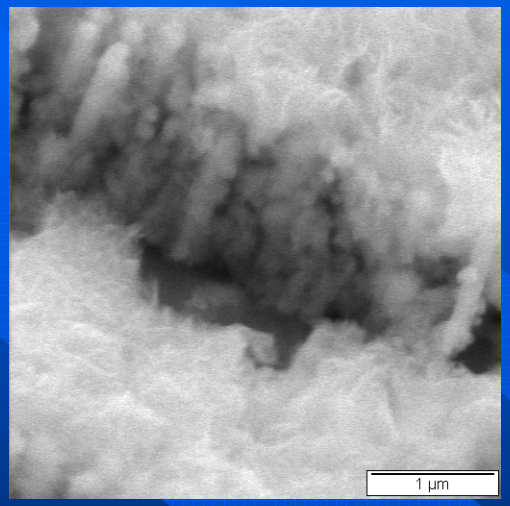
Solution consists of 2M NaOH, 0.09M $Fe_2(SO_4)_3.5H_2O$ [iron sulfate pentahydrate] complexed with 0.1M tri-ethanol-amine (TEA). The magnetite coating was produced under stirring at a constant current density of 5mA/cm^2 at 50°C. Copper plain surface and / or copper Nanopillars acted as the working electrode. The electrodeposition was carried out at several deposition times.

Physical Characterization: XRD, SEM, TEM, EDEX

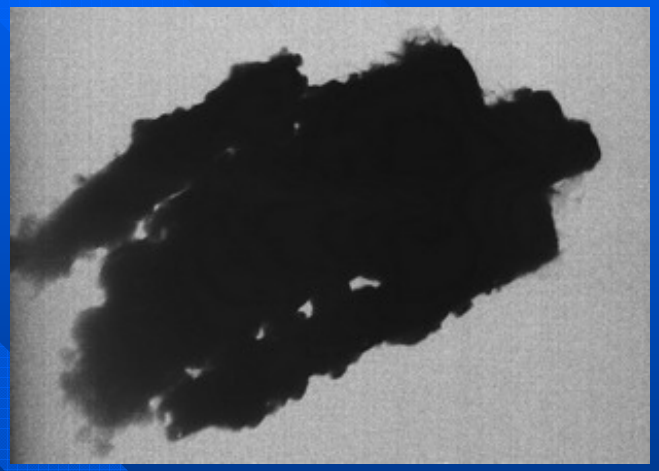
Electrochemical characterization: Half and Full coin & pouch cells.

NanoEngineered Anode Electrodeposited Fe_3O_4

Photo Image



SEM

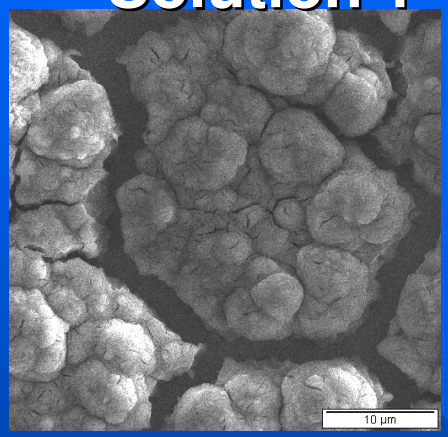


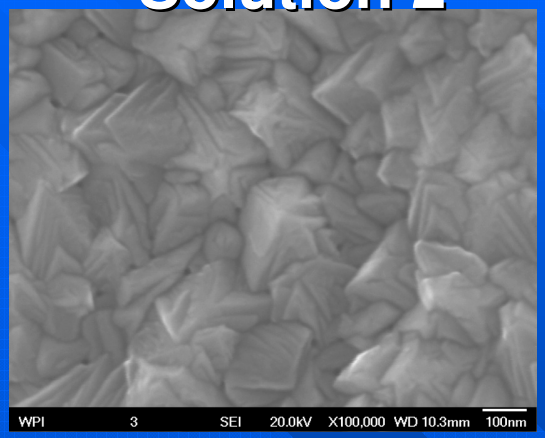
TEM

Fe_3O_4 surface morphology

-1.25 V for 120 s @ 50 ^{0}C

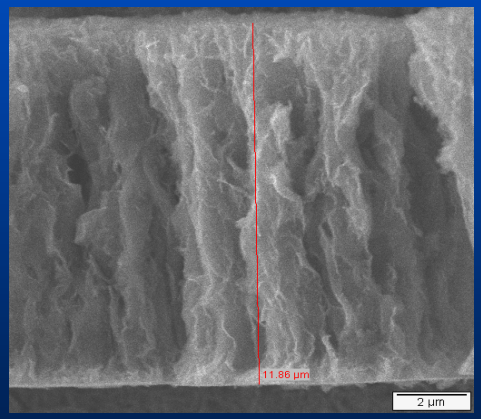
Solution 1 **Solution 2**

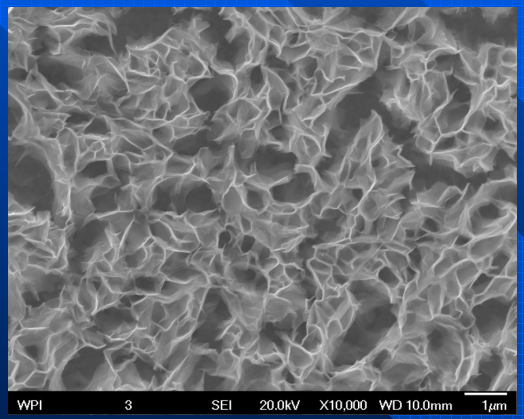


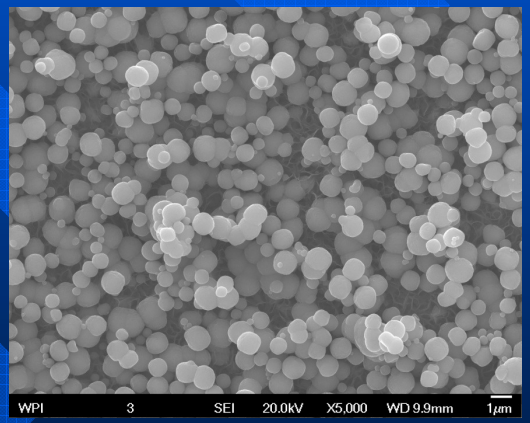


Electrodeposition
Various conditions

- Electrolyte solution
- Temperature
- Potentiostatic
- Galvanostatic



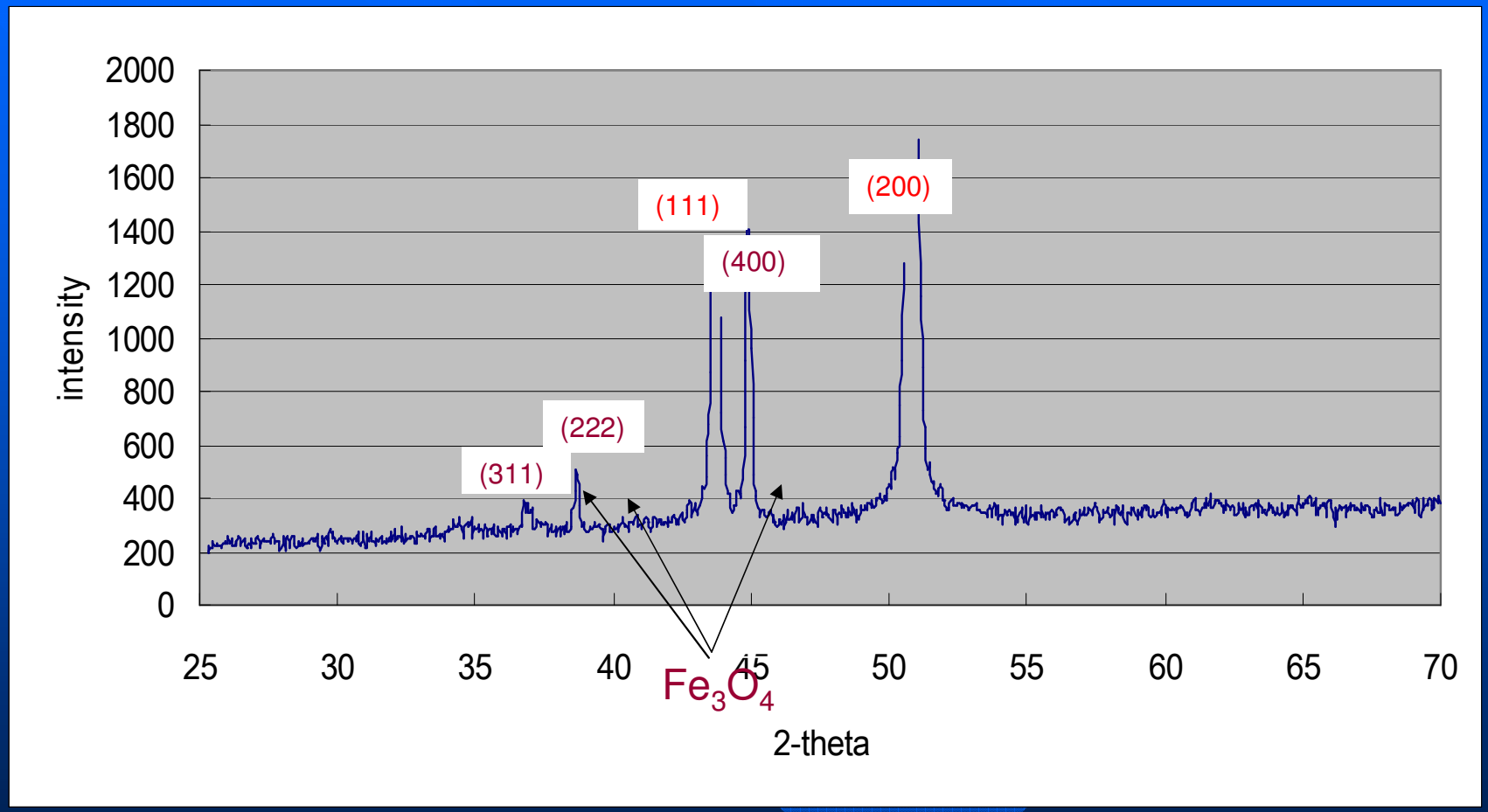




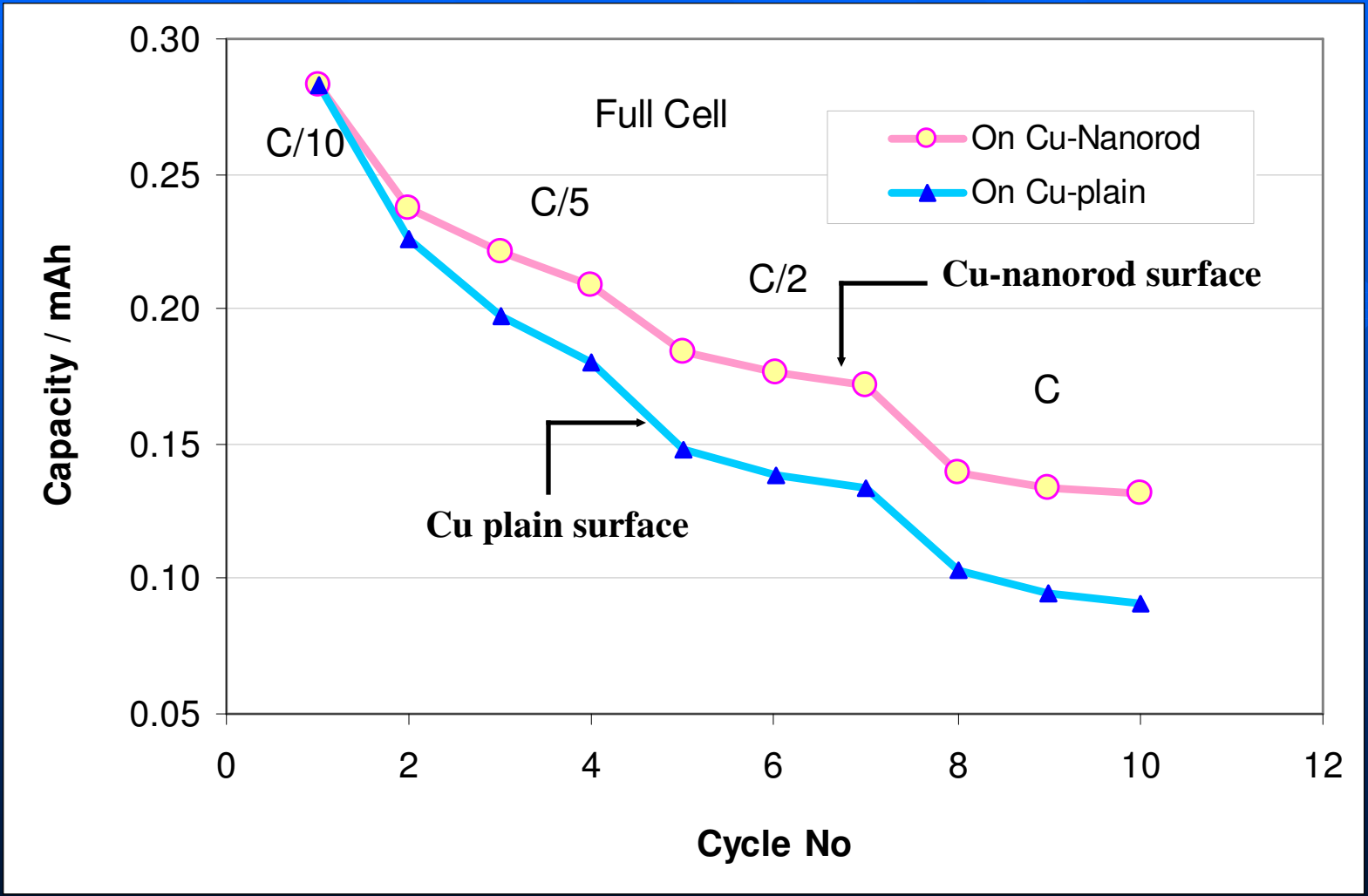
Solution 1 **Solution 2** **Solution 2**

2 mA/cm^2 for 500 s @ 50 ^{0}C **2 mA/cm^2 for 500 s @ 80 ^{0}C**

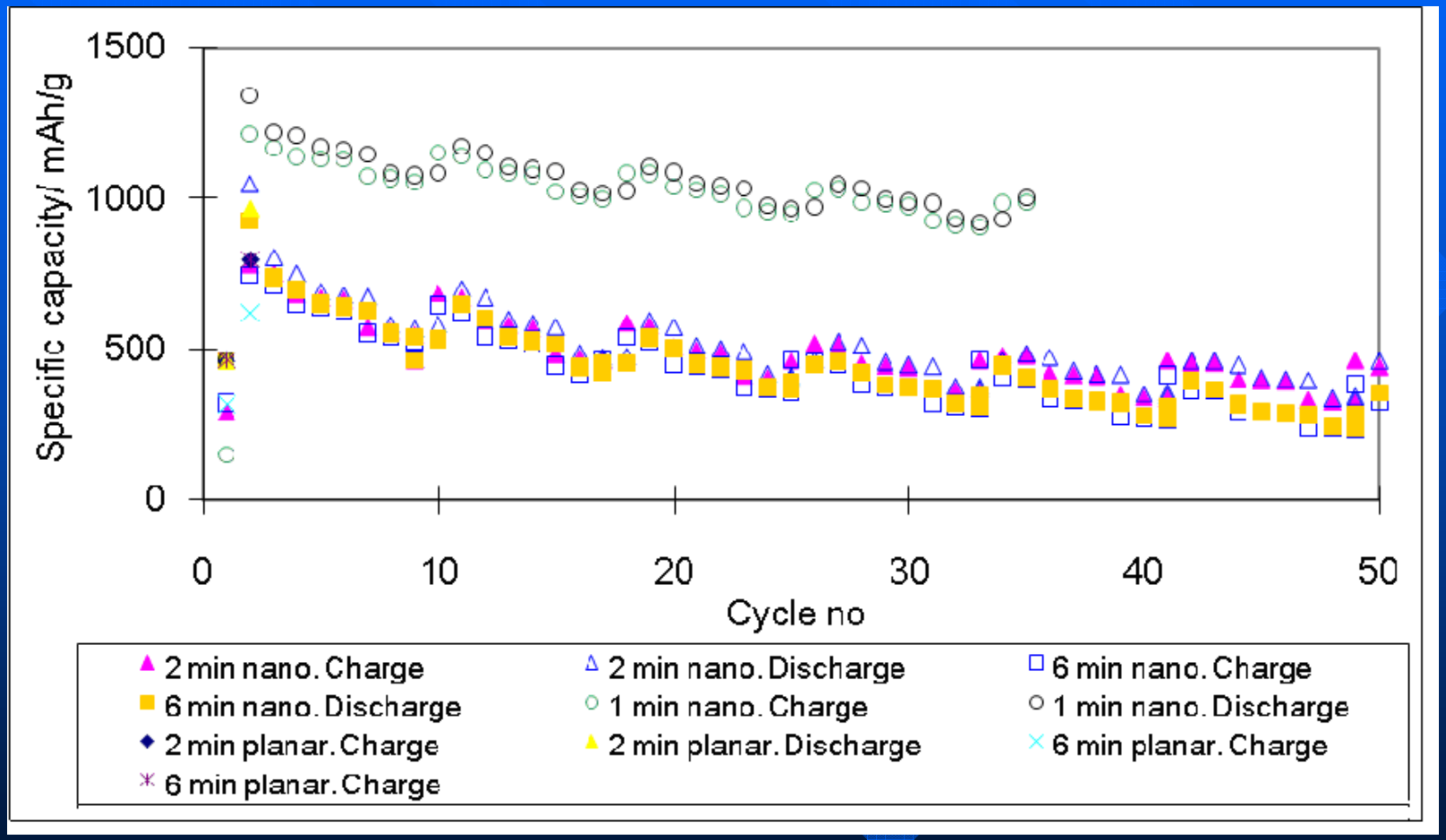
XRD pattern of the Fe_3O_4-Cu nanorod sample.



Full Coin Cell
NanoEngineered vs. Plain surface



Half Coin Cell Cycling Test
Li Vs. NanoEngineered Fe_3O_4



Scaleup

Challenges

- Issues:
  - Larger Electrode dimensional area
  - Commercial AAO Template is not available for such sizes
  - Homemade AAO are very expensive
- Solution:
  - Multilayer (CNT) based coating
  - Electrodeposition + slurry based hybrid deposition

NanoEngineered Electrode Manufacturing

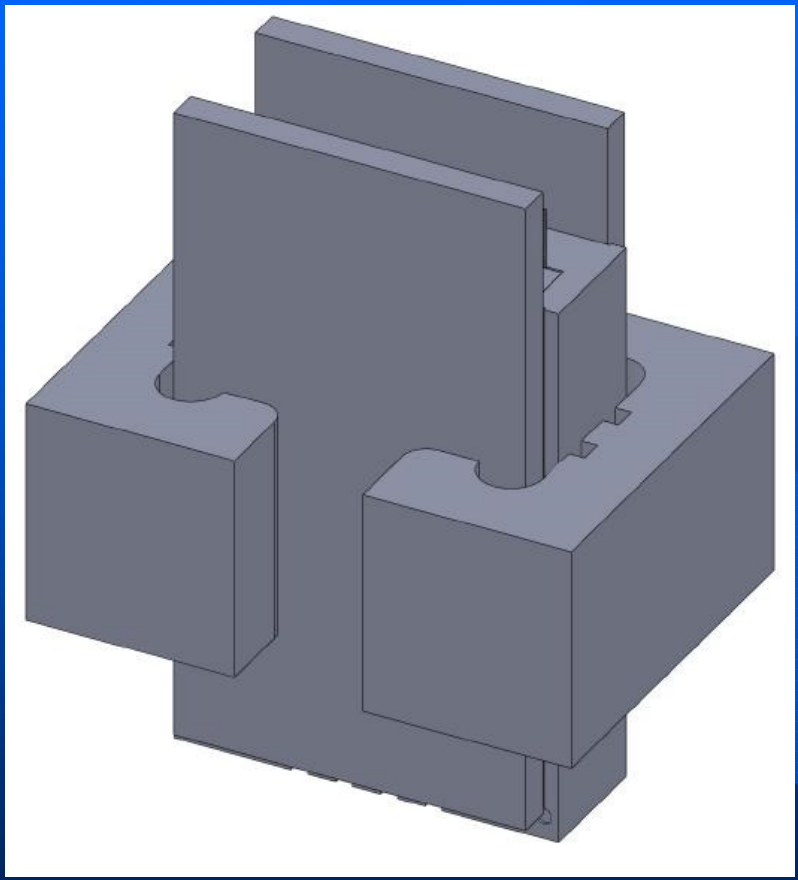
Electrodeposition

Multilayer coating

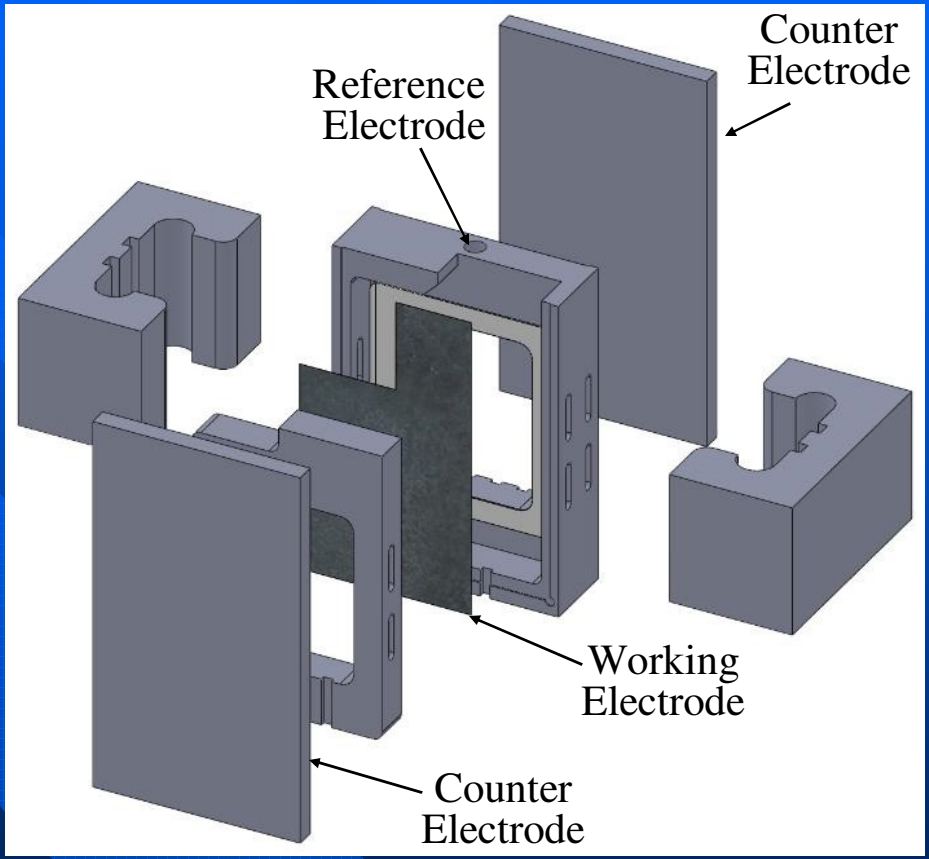
Composite Hybrid Nanoelectrode

NanoEngineered Electrode

Test Fixture

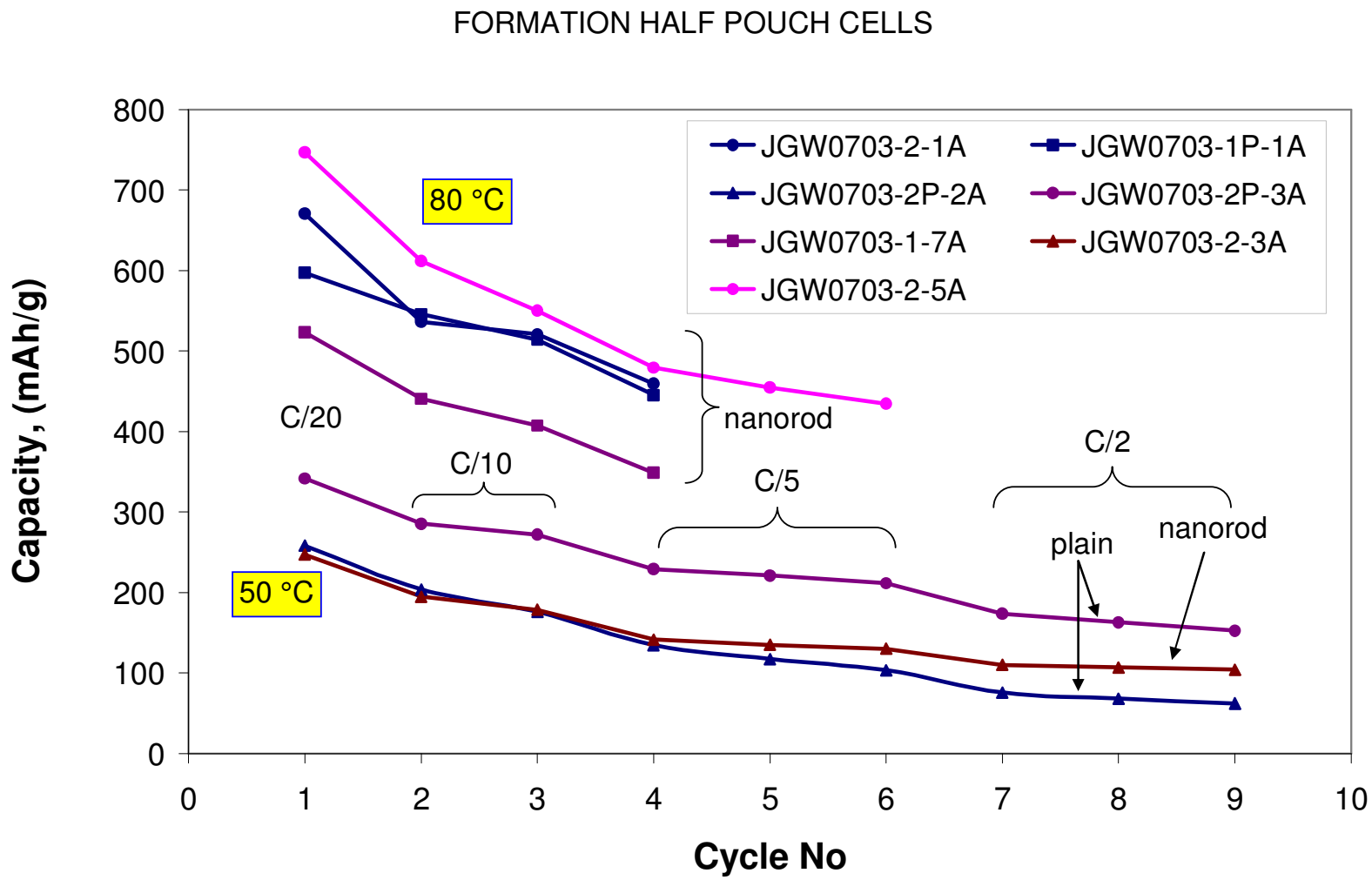


In working condition



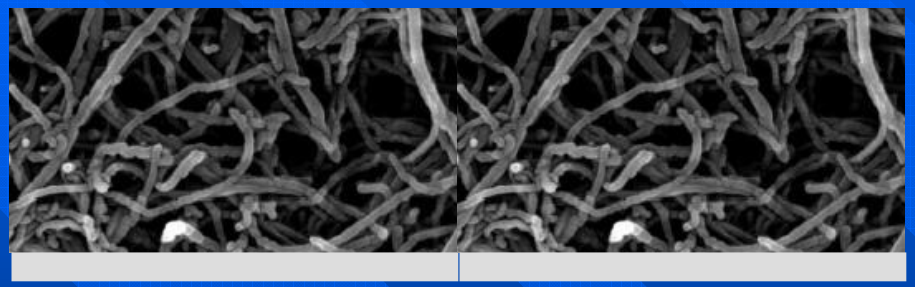
Exploded view

Pouch Half Cells (Li vs. Fe_3O_4)



CNT Based NanoEngineered Electrode Manufacturing

Mass production



Issues

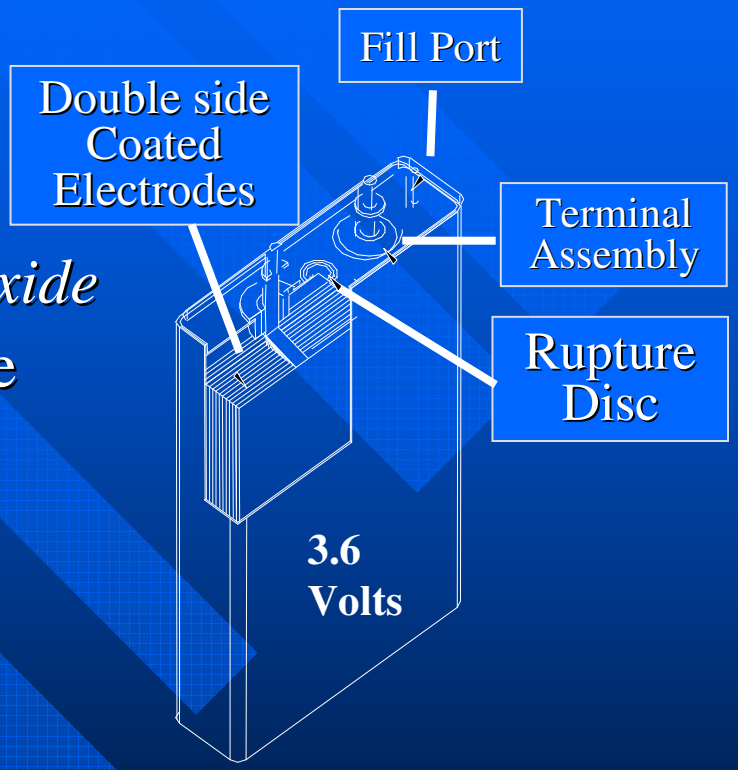
- CNT Dispersion
- Fe_3O_4 is difficult to coat using slurry based coating due to its magnetic property

NCP-type Baseline Li-ion Cells

YTP Li-Ion Prismatic Cell

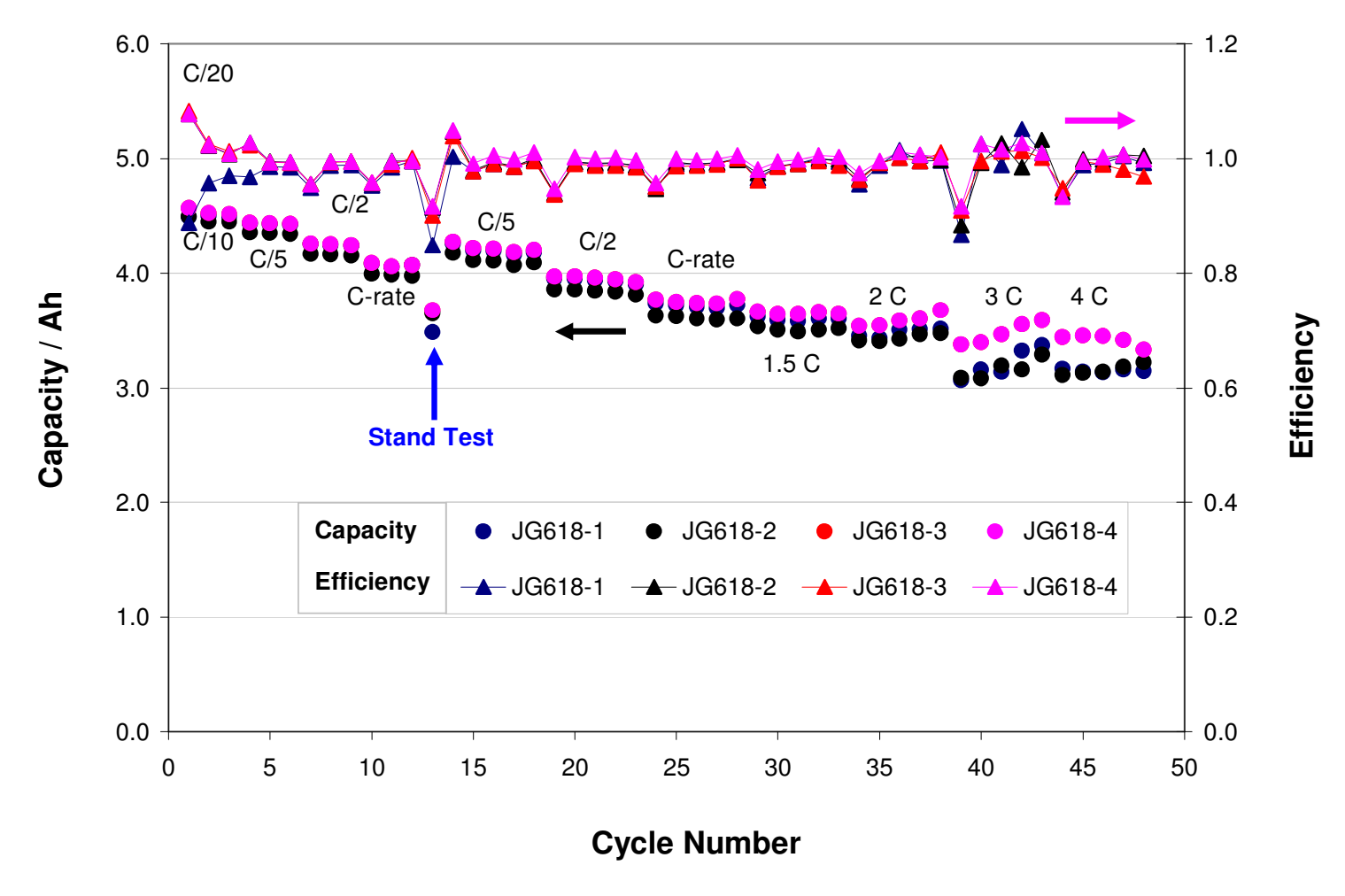
$Li_4Ti_5O_{12}$ vs. $LiNi_{0.8}Co_{0.2}O_2$

- Internal Components
  - » Intercalation Anode and Cathode
  - » *Active Material -- Mixed Metal Oxide*
  - » Organic Solvent Based Electrolyte
- Construction
  - » Hermetically Sealed SS Case
  - » Cell Stack Insulated from Case
  - » Glass-to-Metal Seal Terminals
- Safety Features
  - » Burst Disc in Cover



NTP 4Ah Li-ion cells

$Li_4Ti_5O_{12}$ vs. $LiNi_{0.8}Co_{0.2}O_2$



Summary

- Cu-nanorod (200nm diameter) forest of 4μm length was grown on copper surface using template assisted electrochemical deposition method;
- Nanoengineered Fe_3O_4 anodes were electrodeposited at different deposition times and characterized. It required 30 seconds to fill up the gaps between the copper nanorod forest;
- Pouch and coin cells were fabricated in half (*vs.* lithium) and full cell (*vs.* $LiNi_{0.8}Co_{0.2}O_2$) configurations and cycled at different current densities;
- SEM images taken from the cycled electrodes suggest that the nanoengineered electrodes were stable and they were not disintegrated even after aggressive cycling tests;
- Full coin cell showed better rate capability for the cells made from nanoengineered Fe_3O_4 anode compared to that made from Fe_3O_4 deposited on plain copper surface;
- Scaling up the nanoengineered based Li-ion cells are being carried out.
- NTP type Li-ion baseline cells were manufactured using Titanate and lithium nickel cobalt oxide and cycled.

thanks to

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Dr. Joe DiCarlo
Frank Puglia
Bill Moscaritolo
Dick Fallon

Advanced Battery Materials For Rechargeable Advanced Space Rated Advanced Li-Ion Batteries

Dr. Ratnakumar Bugga, JPL, NASA
Dr. Joe Gnanaraj, Yardney
Dr. Maggie Gulbinska, Yardney

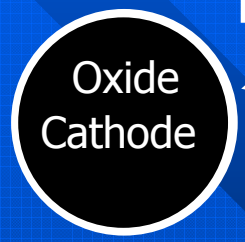
The goal of Phase I of this project was to develop

1) Cathode (HighCapacity ~ 300 mAh/g)

$Li[Ni_xLi_{1/3-2x/3}Mn_{2/3-x/3}]O_2$

Doping: divalent cation (Ca, Zn)

In situ $LiCoPO_4$ coating



$LiMPO_4$ (M=Fe, Mn, Ni, Co etc)

2) Silicon based Anode (Si = 4199 mAh/g)

(MxOy ~ 1000 mAh/g)

MxOy, M = Fe, Mn, Co, Ni,

e.g., Fe_3O_4, Co_3O_4

Cathode

Li_2MnO_3 Layer structured based cathode

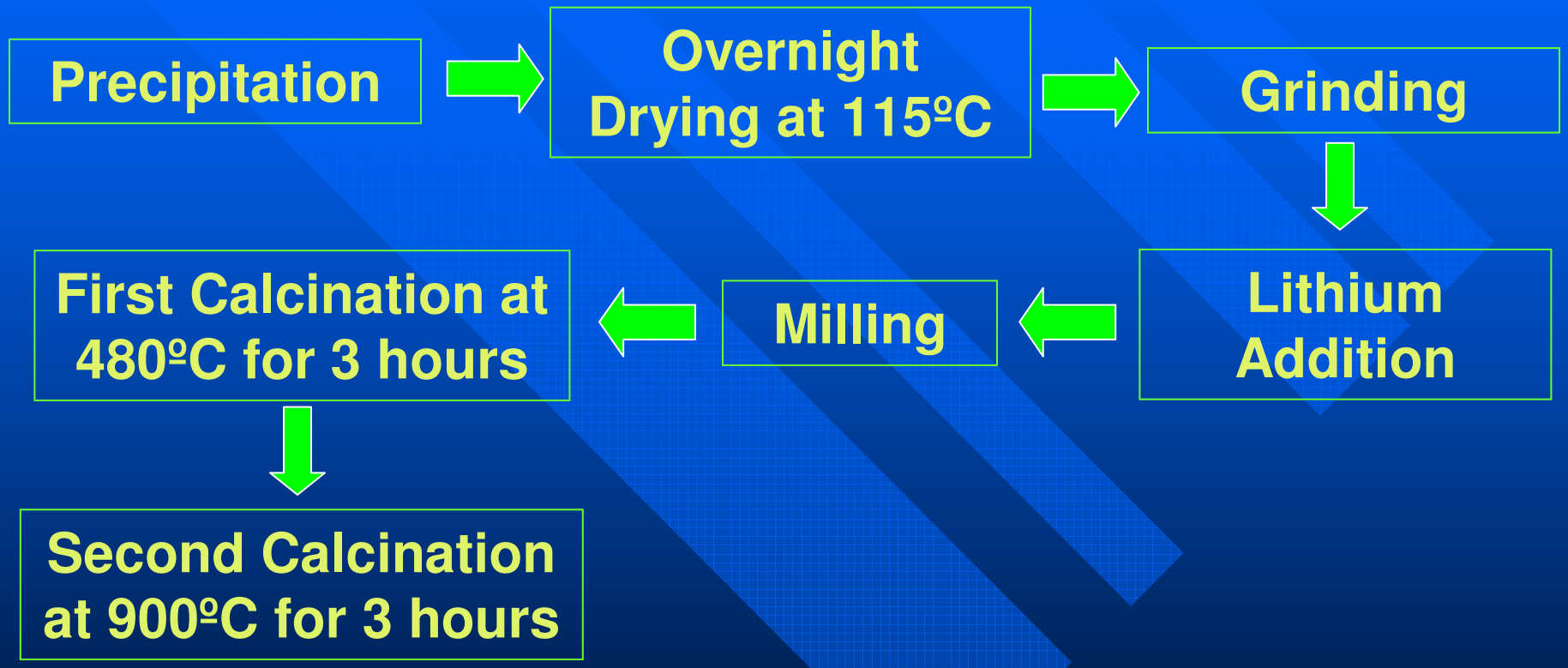
$LiNMO_2$

- Generation 0: $Li_{1.2}Mn_{0.4}Ni_{0.4}O_2$ - "Gen O"
- Generation 1: $Li_{1.3}Mn_{0.6}Ni_{0.1}O_2$ - "Gen 1"
- Generation 2: $Li_{1.3}Mn_{0.6}Ni_{0.08}Cu_{0.02}O_2$ - "Gen 2"
- Generation 3: $Li_{1.3}Mn_{0.6-x}N_xNi_{0.08}Cu_{0.02}O_2$ - "Gen 3"

N = Ca, Zn

$x = 0 < x < 0.1$

Complex Carbonate synthesis method

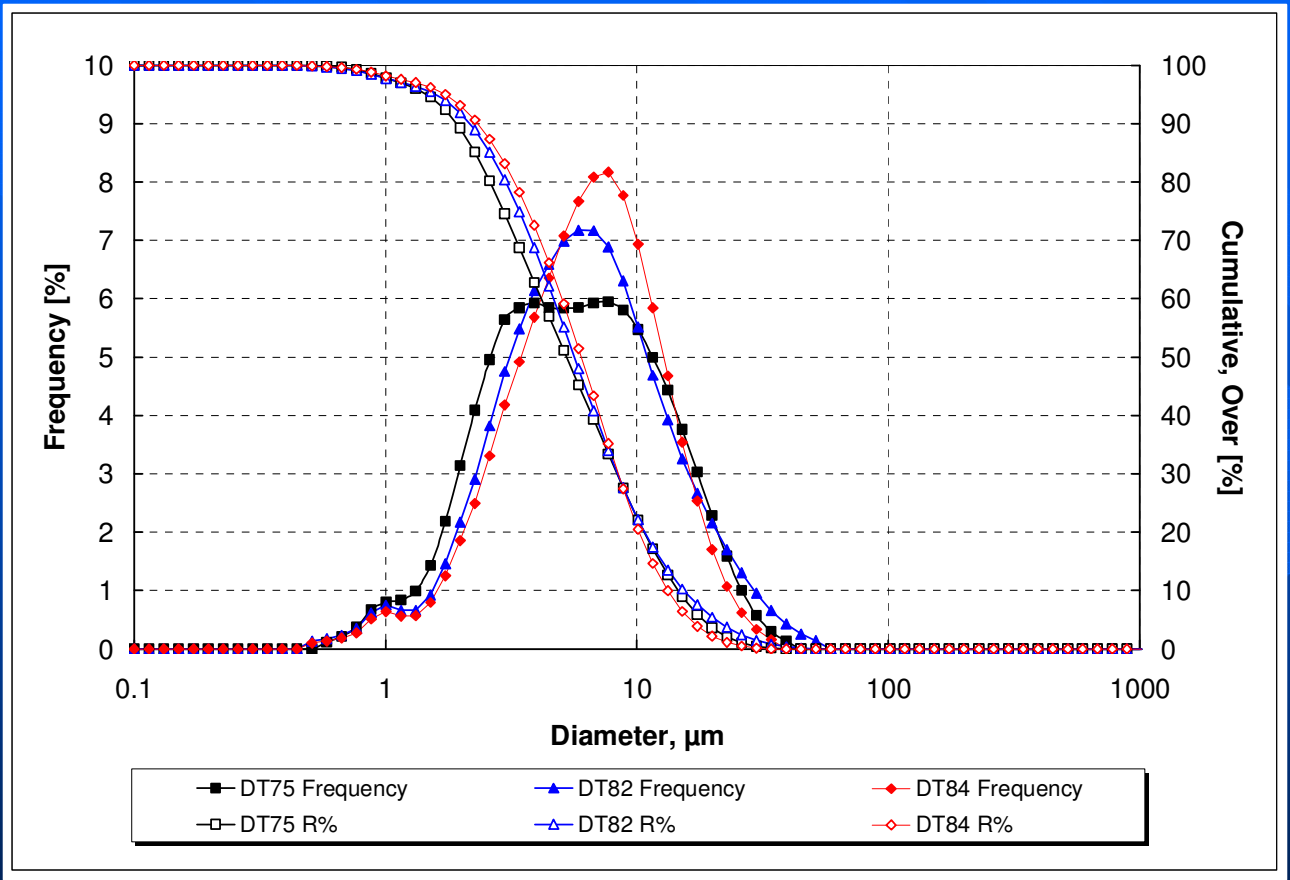


Elemental analyses results (DCP, EDX)

$Li_{1.2}Mn_{0.4}Ni_{0.4}O_2$

	Sample ID							
	DT75	**DT82**	**DT84**	**DT91**	**DT94**	**DT95**	**EN5**	**EN6**
	Bulk Analysis: DCP							
Li/(Mn+Ni)	0.98	1.17	1.07	1.68	1.41	1.19	1.78	1.70
Mn/Ni	0.95	5.62	5.92	1.25	0.58	1.34	1.38	1.29
	Surface Analysis: EDX							
Mn/Ni	0.93	5.68	6.04	1.25	N/A	N/A	N/A	1.51

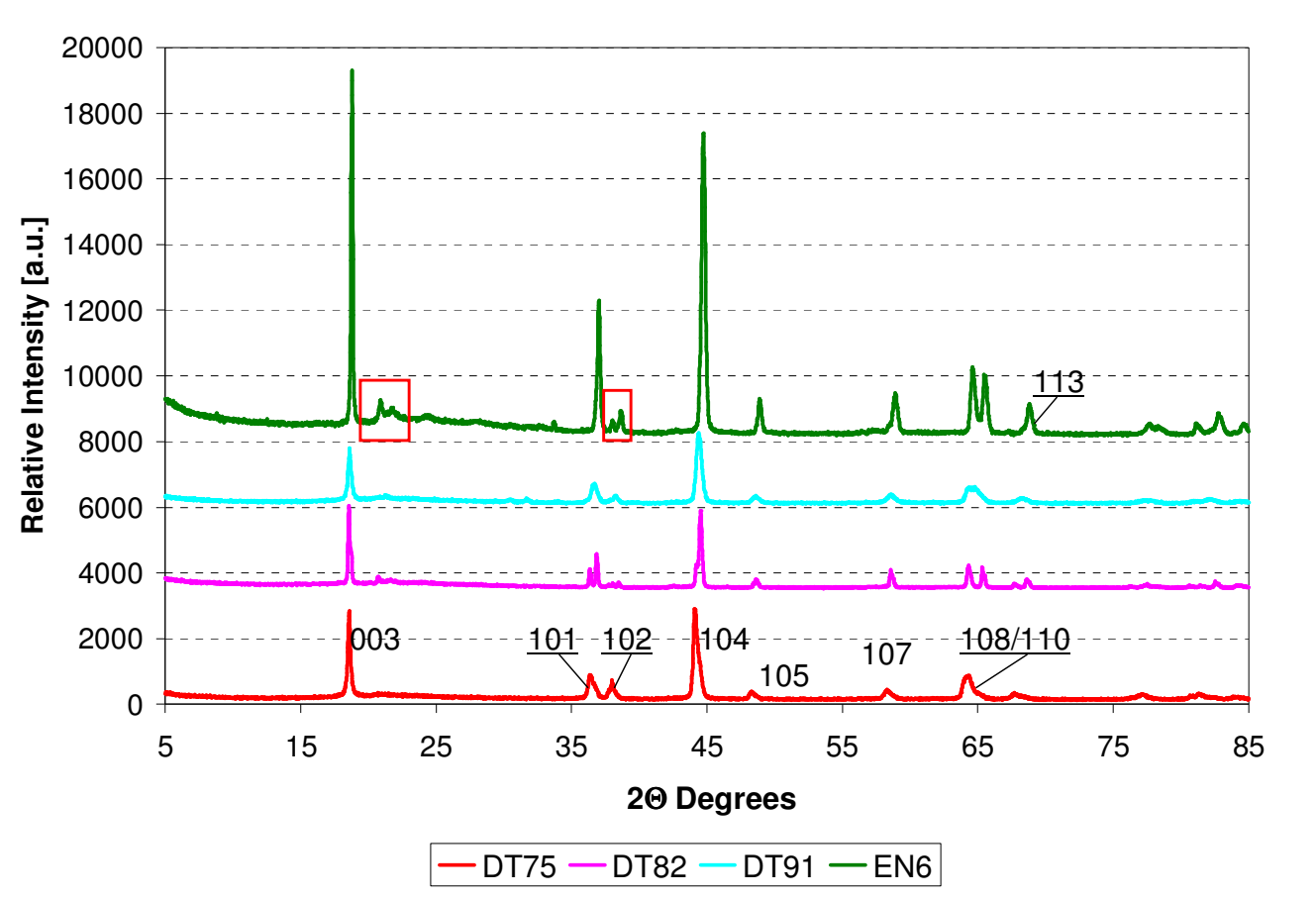
$Li_{1.2}Mn_{0.4}Ni_{0.4}O_2$
Particle size distribution



Laser Scattering Particle Size Distribution Analyzer LA-910 (Horiba , Ltd.).

$Li_{1.2}Mn_{0.4}Ni_{0.4}O_2$

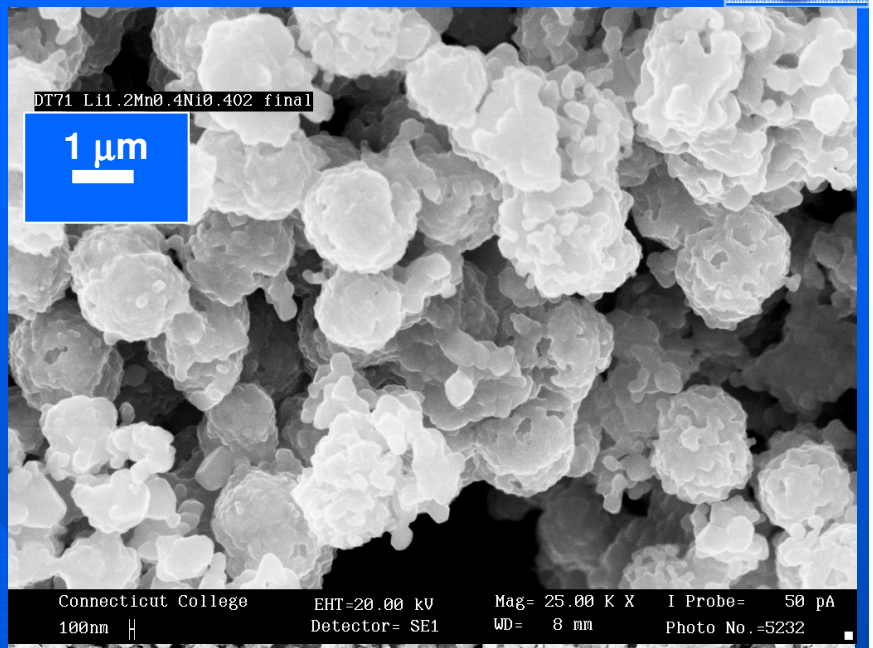
XRD patterns of the layered cathode materials

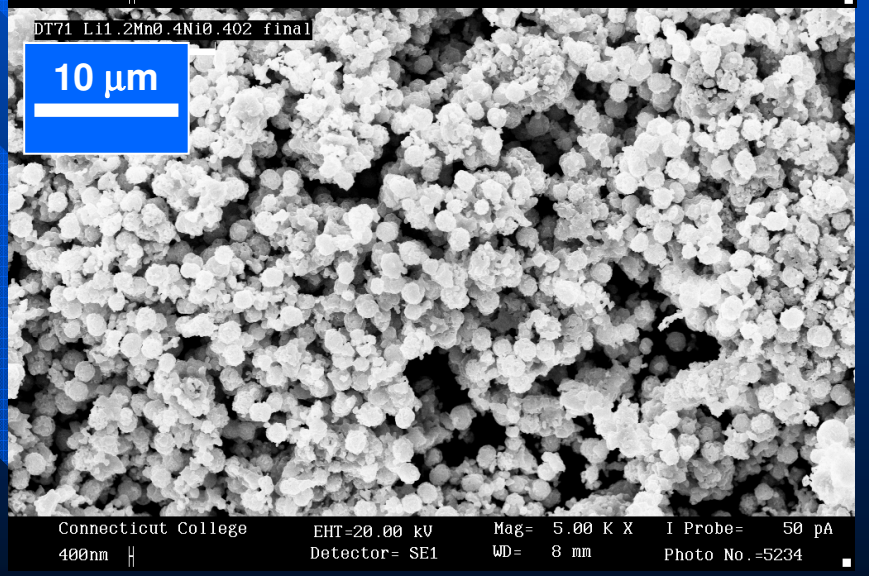


$Li_{1.2}Mn_{0.4}Ni_{0.4}O_2$

- *Desired morphology and Mn/Ni ratio*
- *Particles size distribution is about 1-2 μm and uniform Some agglomeration of the particles may be present*

Element	*Sigma [%]*	*Atomic [%]*
Mn	1.02	48.67
Ni	1.61	51.33
Total		100.00



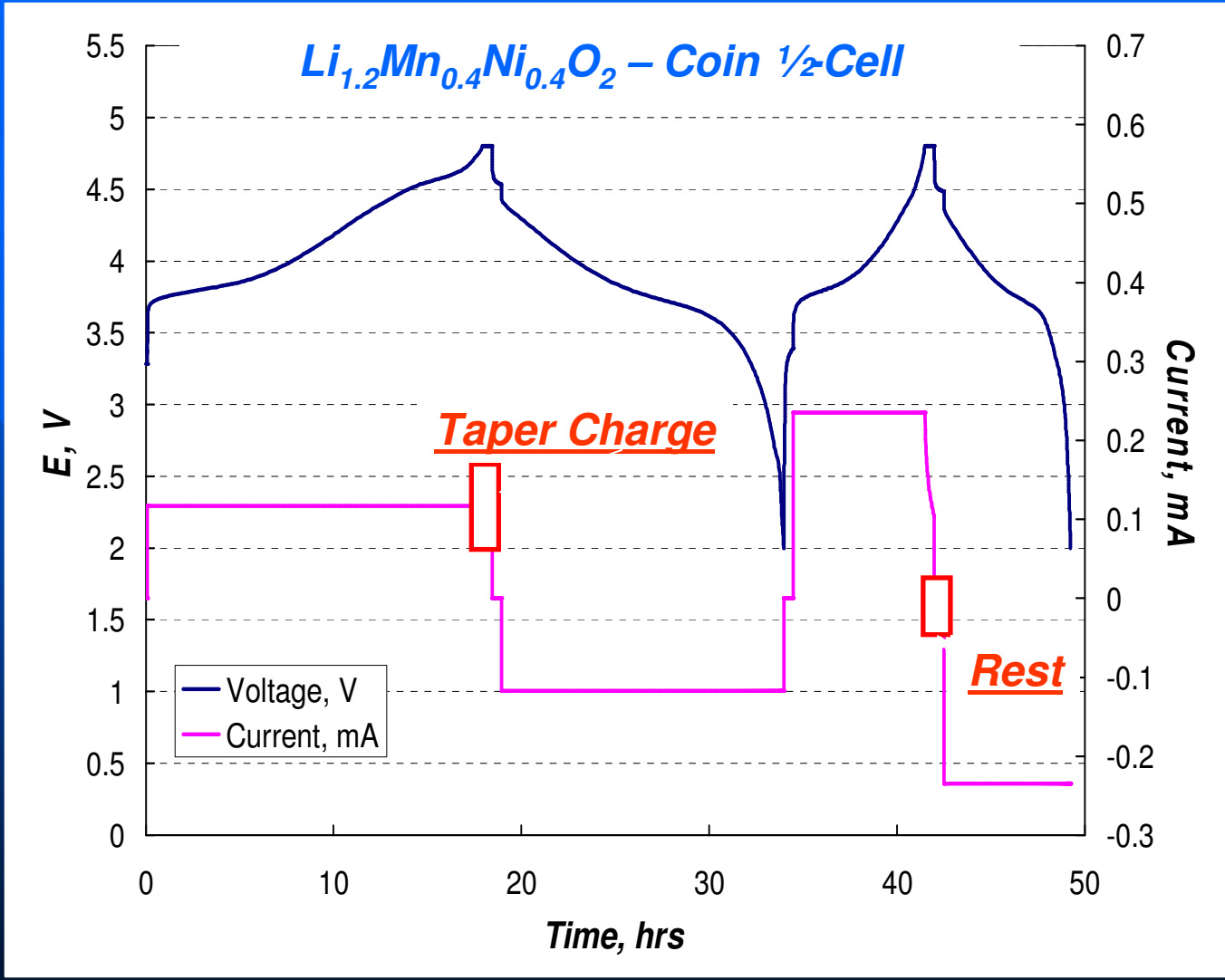


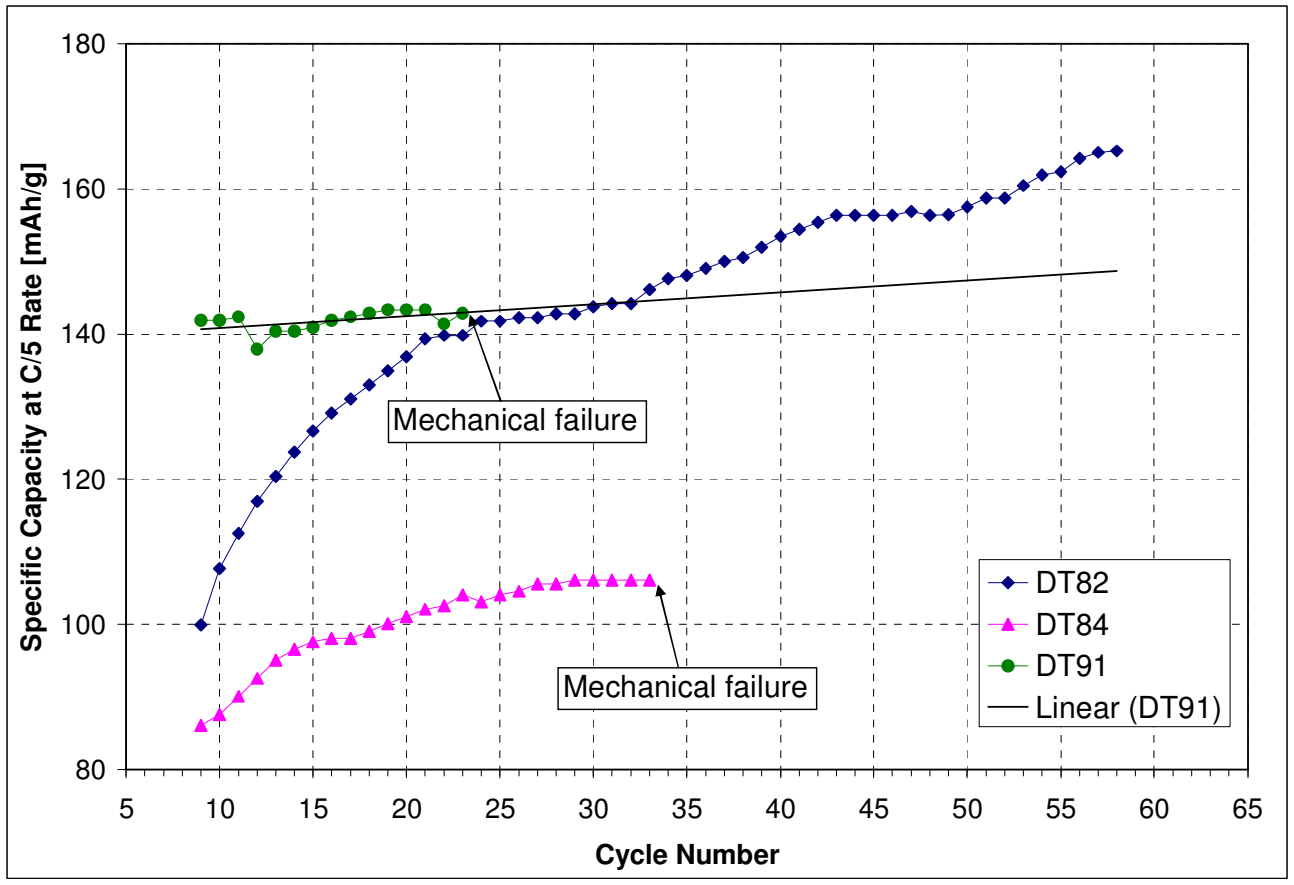
$Li_{1.2}Mn_{0.4}Ni_{0.4}O_2$

- *First two cycles*
- *Coin ½-cell*
- *4.0V - 2.0V*
- *C/20*
- *0.09 mA/cm²*

- *C/10*
- *0.19 mA/cm²*

1st charge = 235 mAh/g
Irreversible = 18%
Reversible = 193 mAh/g





Extended coin ½-cell testing of the layered cathode materials

Silicon and Co_3O_4 composite

Mechanochemical Dry Process

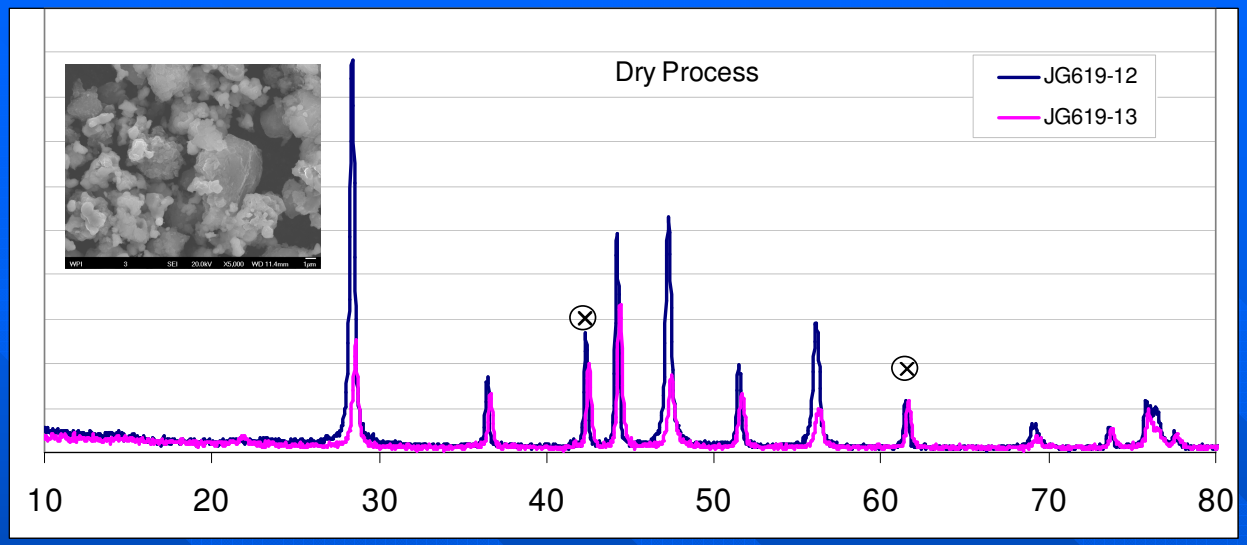
Scheme	Composition	Process	Calcination Temp
1	Silicon + oxide	Ball mill	RT
2	Silicon + oxide + super P	Ball mill + high power shaker milling	RT
3	Silicon + Toluene	High power milling	700 °C
4	Silicon + oxide + Glucose + Toluene	High power milling	700 °C
5	Silicon + oxide + glucose + Toluene	High power milling	900 °C

Silicon and Co_3O_4 composite

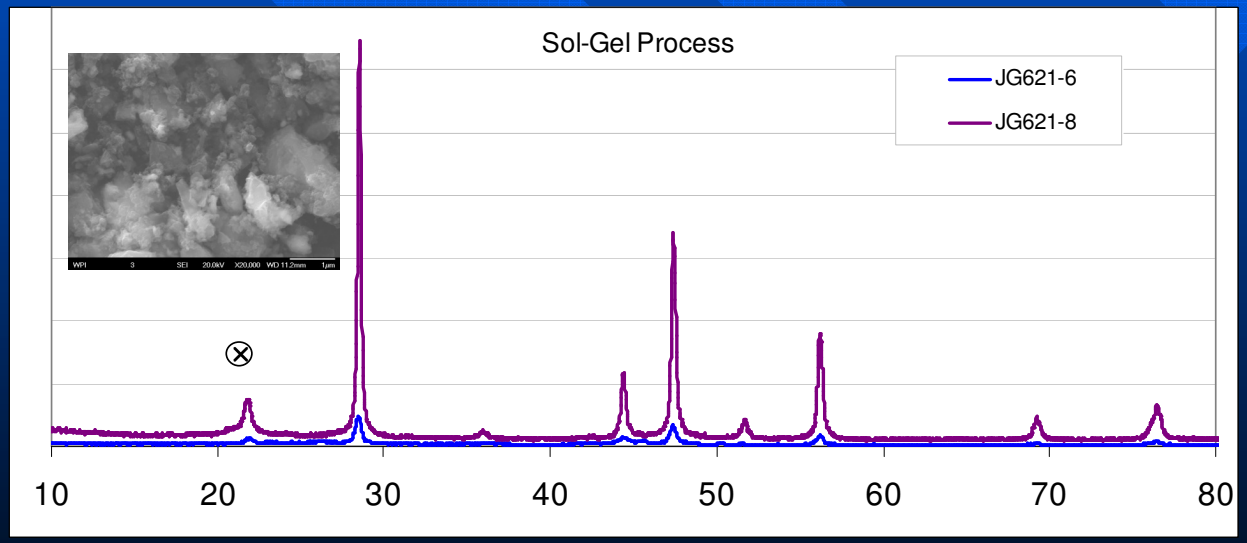
Sol-Gel Process

Composition:	Silicon + Cobalt acetate
Chelating agent:	Maleic acid
The pH value:	6.5-7.0
Calcination Temp:	800 to 900°C
Atmosphere:	argon / nitrogen

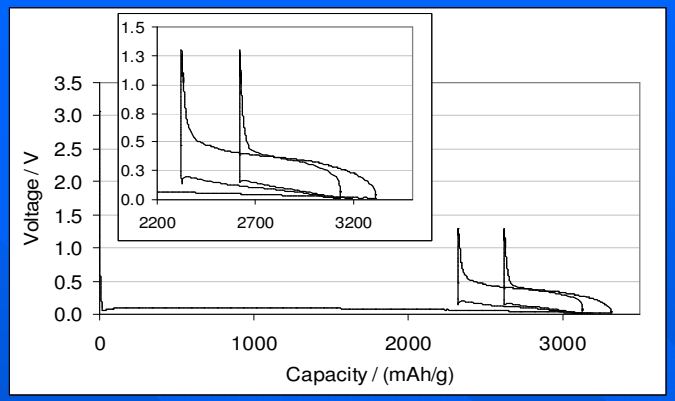
Silicon and Co_3O_4 composite



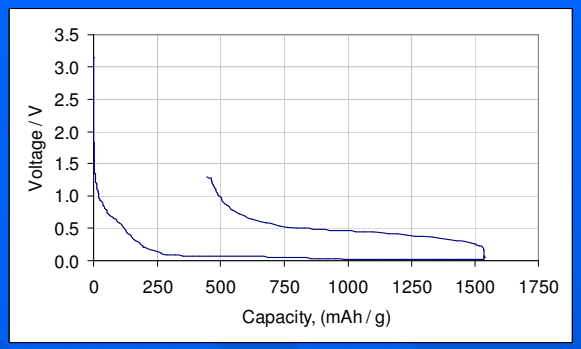
XRD pattern of silicon and Co_3O_4 composite synthesized from dry mix process.



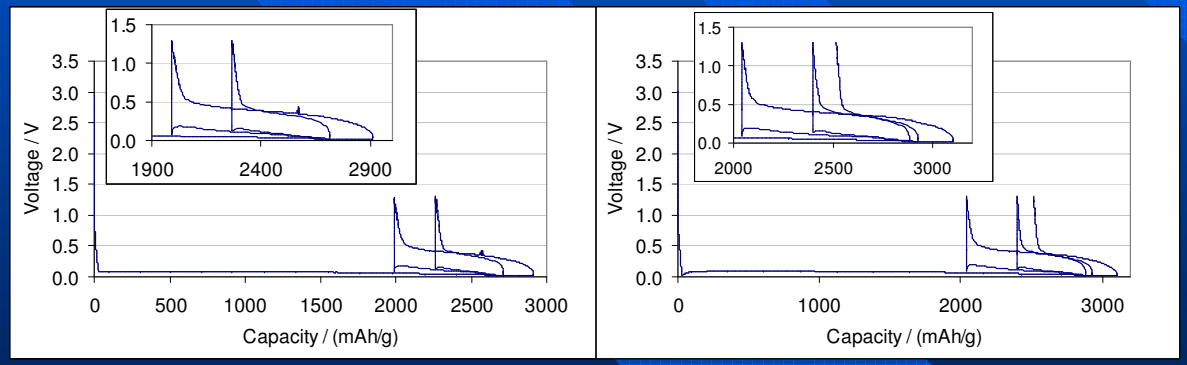
XRD pattern of Co_3O_4-coated silicon synthesized by sol-gel process.



Pristine silicon anode half coin cells: voltage vs. specific capacity. Inset shows expanded scale.



Pouch half cell: Co3O4 coated silicon anode prepared by sol-gel method.



Silicon anode prepared by a) Scheme 3, and b) Scheme 4, + 5% Fe3O4. Insets show expanded scale.

summary

•Silicon-based composite anode materials were synthesized successfully. Silicon composite material was coated and/or mixed with layer of 3d transition metal oxide element (MxOy, M = Fe, Mn, Co, Ni), were manufactured using dry process mechanochemical, ball milling and sol-gel processes. A wide verity of 3d transition metal oxides with high capacity Fe3O4 (magnetite) and Co3O4 are of great interest due their high capacity ~ 1000 mAh/g (*vs.* Li/Li+). Silicon and transition metal oxide were mixed at different proportions, milled and heat treated at high temperatures.

•Layered structured Li_2MnO_3 based cathode materials were synthesized at low (480 °C) calcination and high (900 °C) calcination temperatures for 3 h. The cathode material particles synthesized using mixed hydroxide and/or complex carbonate methods were spherical in shape and 2 micron in diameter.

•As-synthesized electrode materials were characterized by X-ray powder diffraction (XRD) for structure determination, Scanning Electron Microscopy (SEM) for morphology studies, particle size analyses, and the Brunauer Emmett Teller surface area measurements.

•The manufactured electrode (both anode and cathode) materials were characterized in coin/pouch cells in standard electrolyte solutions. The voltage profile of silicon and transition metal oxide based anode indicates that 90% of the capacity (1000 mAh/g) obtained are at the lithium-silicon alloying potential (<500 mV vs Li/Li+). The synthesized cathode materials were cycled between 3 and 4.8 V which gave specific capacity >230 mAh/g.

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Thank you

Questions ?