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Nanostructured Materials for Lithium-Based Energy Storage

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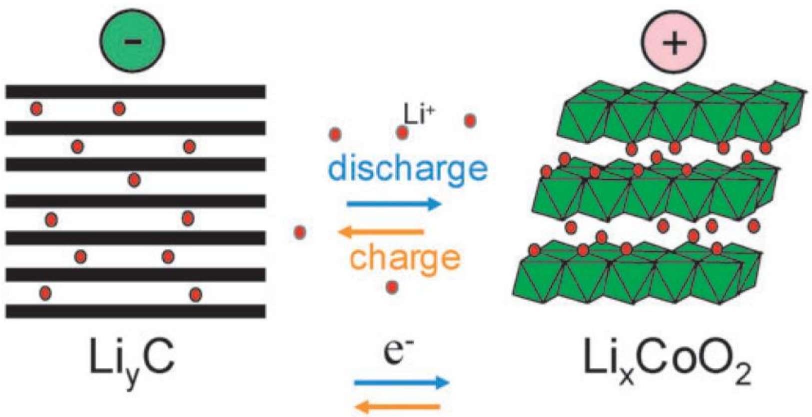
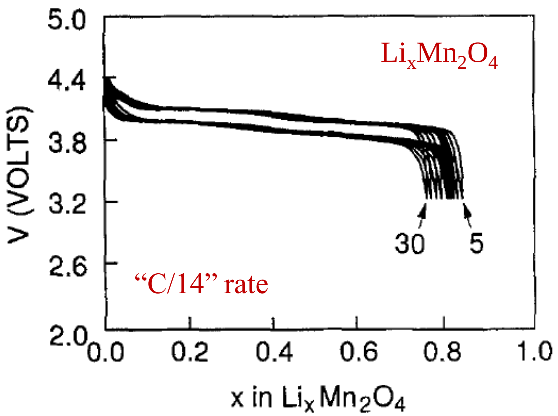
Lithium-Ion Batteries — Overview

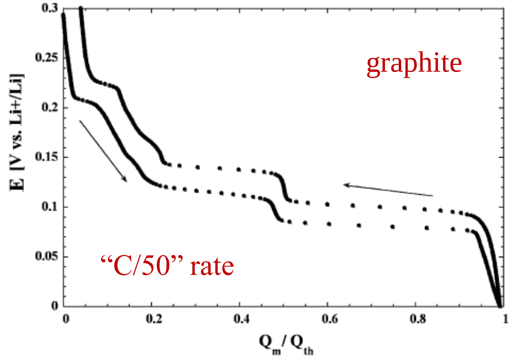


M. R. Palacín, *Chemical Society Reviews* **38**: 2565 (2009)

Typical galvanostatic voltage profiles



J. M. Tarascon et al., *J. Electrochemical Society* **138**: 2859 (1991)



Y. Reynier et al., *J. Power Sources* **19-121**: 850 (2003)

electrode	voltage (V)	capacity (mAh/g)
Li_xCoO_2	3.7	140
$Li_xMn_2O_4$	4	120
graphite LiC_6	0.1	370

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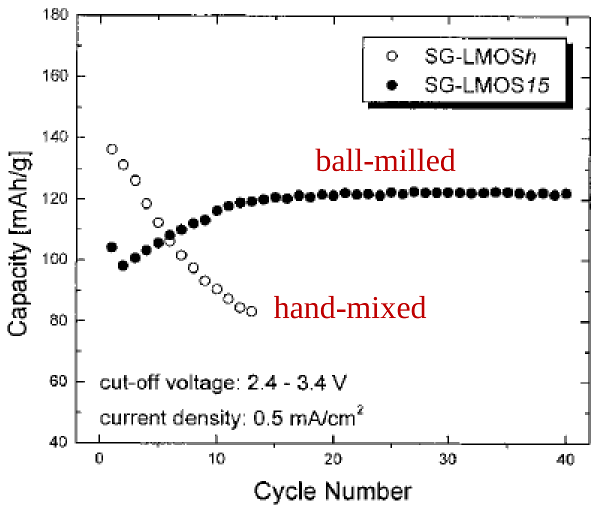
Nanodomain Structure – Cathode Materials

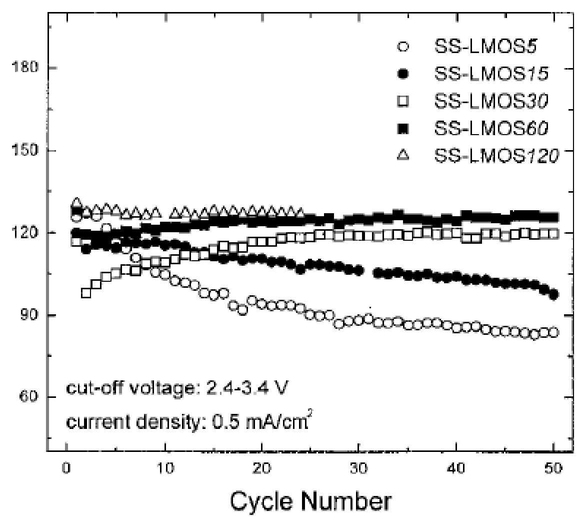
$Li_xMn_2O_4$ with nanoscale grains

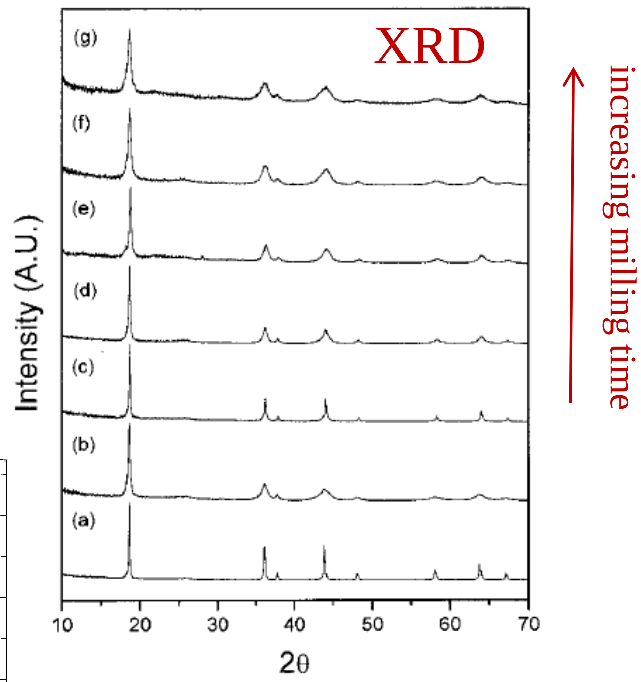
- mechanical milling after synthesis results in better cycling for the low-voltage range ($1 < x < 2$)
- improvement attributed to nano-sized grains, decreased anisotropic deformation, increased lattice strain from defects

sol-gel synthesis



solid-state synthesis



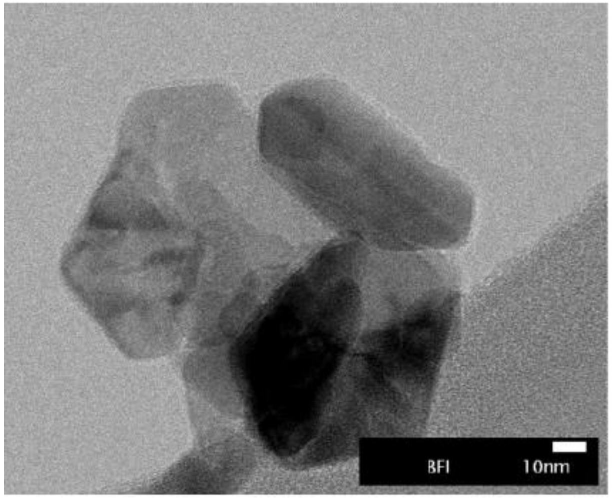


S. Kang, J. Goodenough, and L. Rabenberg, *Chem. Mater.* **13**: 1758 (2001)

Nanoscale Particles – Cathode Materials

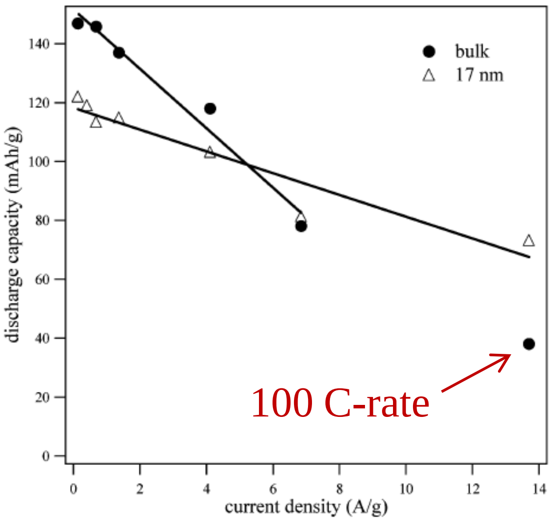
Nanoparticulate $LiCoO_2$

- size-controlled synthesis with hydrothermal reaction
- vary reaction time and temperature and reactant concentration
- average particle size 9–32 nm

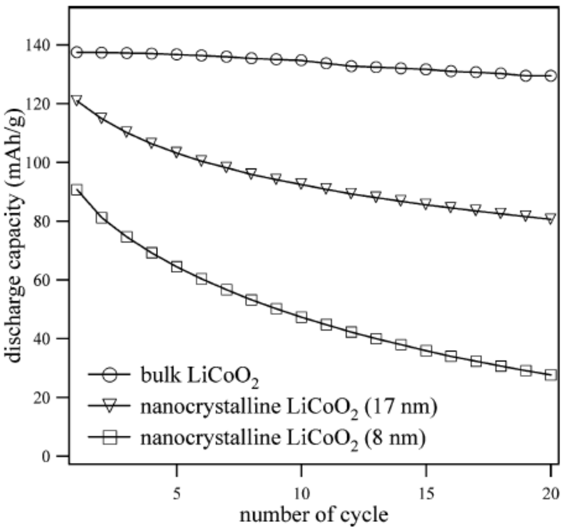


TEM

17-nm particles



nano: better rate capability



poorer cycling attributed to increased surface area

M. Okubo et al., *J. Am. Chem. Soc.* **129**: 7444 (2007)

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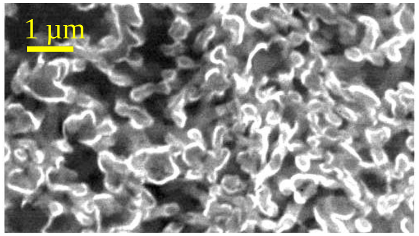
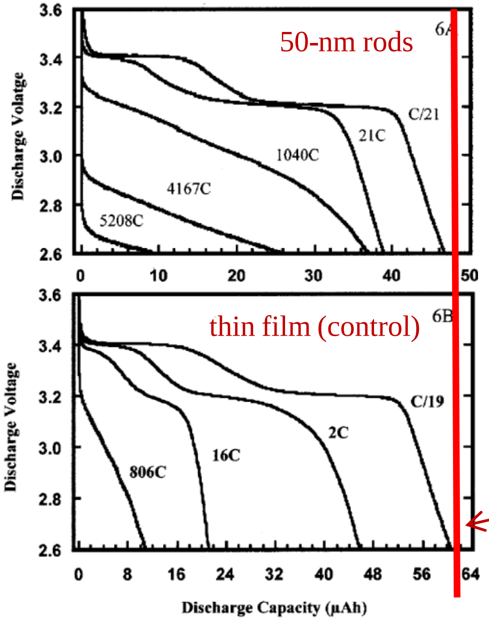
Nanoscale Particles – Cathode Materials

$Li_xV_2O_5$ nanostructures

templated nanorods



top-view SEM

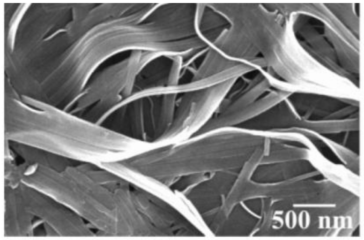


C. Patrissi and C. Martin, *J. Electrochemical Society* **148**: A1247 (2001)

nanorods demonstrate higher rate capability than thin-film control sample

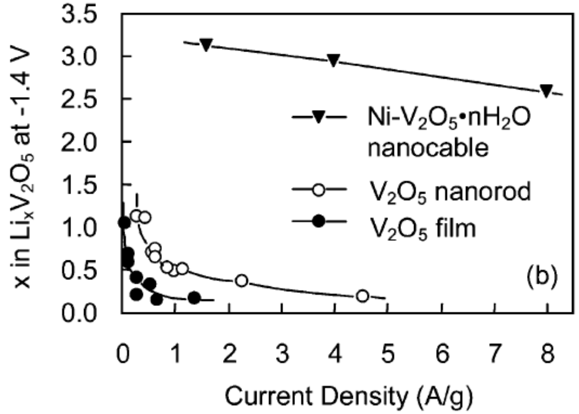
theoretical capacity for LiV_2O_5

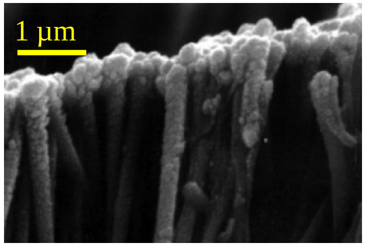
"nanobelts"



S. Shi et al., *Crystal Growth & Design* **7**: 1893 (2007)

"nanocables"





K. Takahashi et al., *J. Phys. Chem. B* **109**: 48 (2005)

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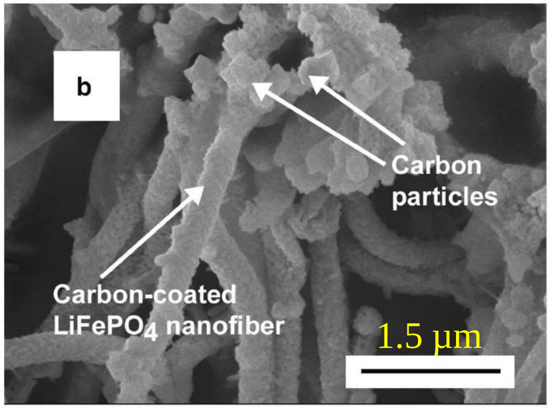
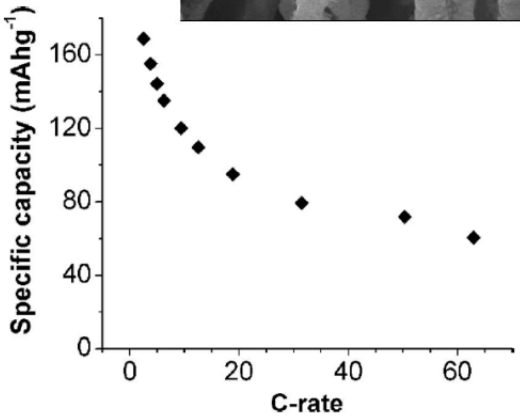
Nanocomposites – Cathode Materials

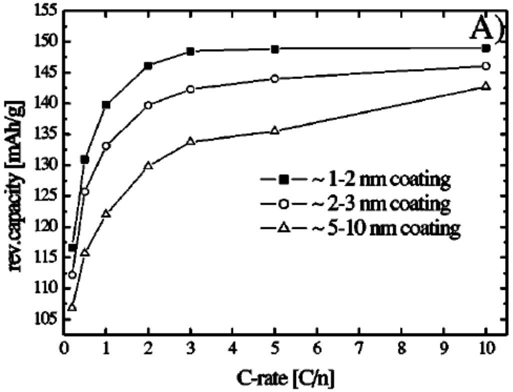
$LiFePO_4$-carbon nanocomposites

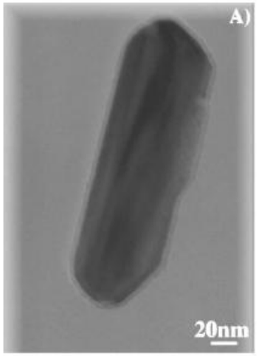
- $LiFePO_4$ is a popular alternative cathode, intended for electric vehicle applications (safer voltage, lower cost than $LiCoO_2$)
- low electronic conductivity
- particles or nanofibers coated with carbon during synthesis
- nanocomposite with carbon → high cycling rates, reach near the theoretical capacity of 170 mAh/g





C. R. Sides et al., *Electrochem. Solid-State Lett.* **8**: A484 (2005)



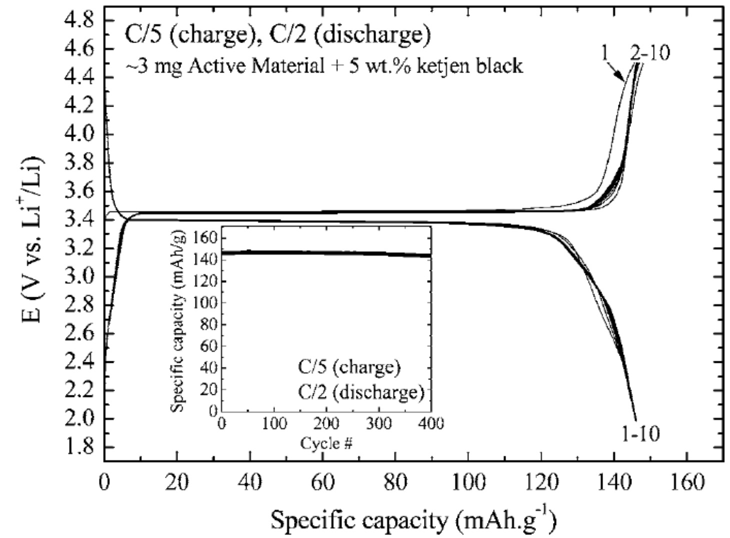


R. Dominko et al., *J. Electrochem. Soc.* **152**: A607 (2005)

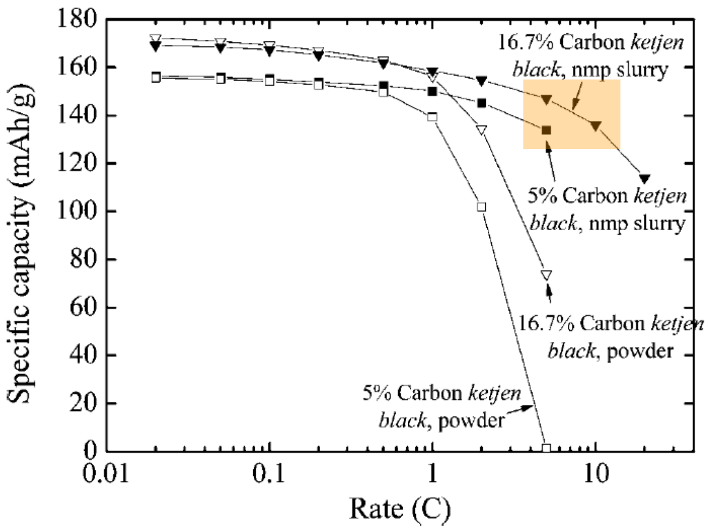
Nanoscale Particles – Cathode Materials

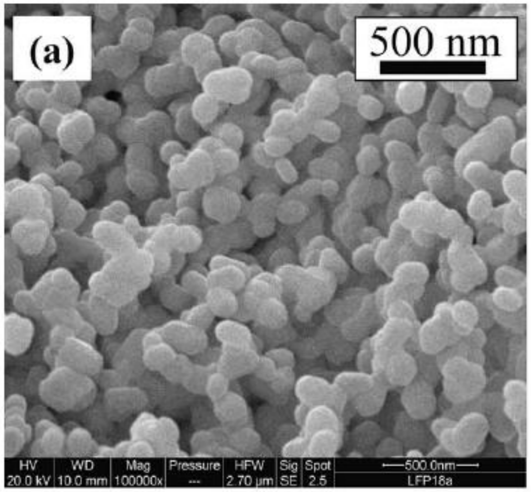
Carbon-free $LiFePO_4$ nanoparticles

- low-temperature precipitation synthesis yields particles 100–200 nm
- nanoscale particles do not require carbon coating (short diffusion distances for electrons and Li^+)
- charge-discharge with low hysteresis for > 400 cycles
- 10C rate also demonstrated
- narrow particle-size distribution → uniform current distribution?



charge-discharge curves





C. Delacourt et al., *Electrochem. Solid-State Lett.* **9**: A352 (2006)

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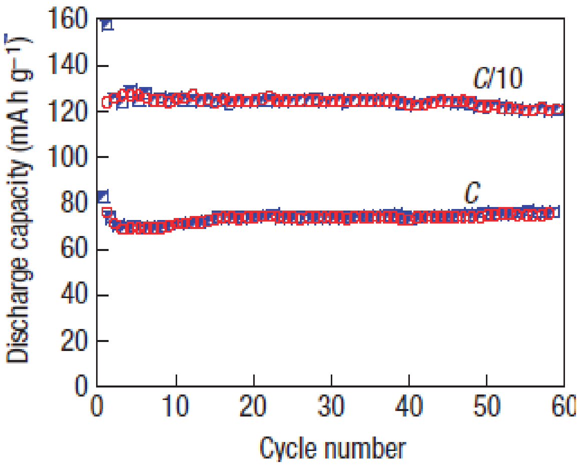
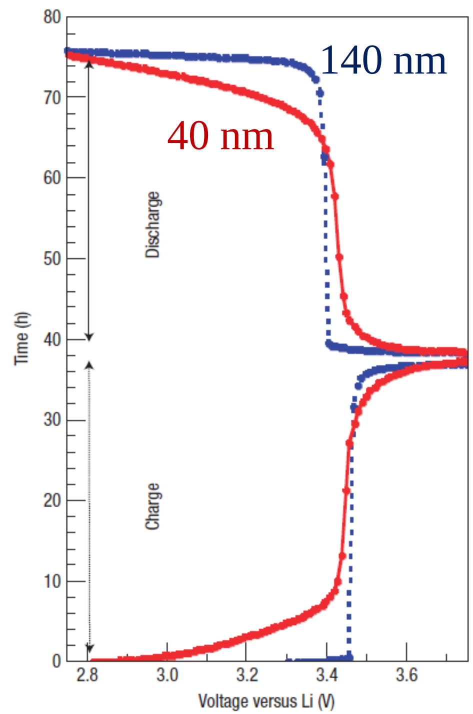
Nanoscale Particles – Cathode Materials

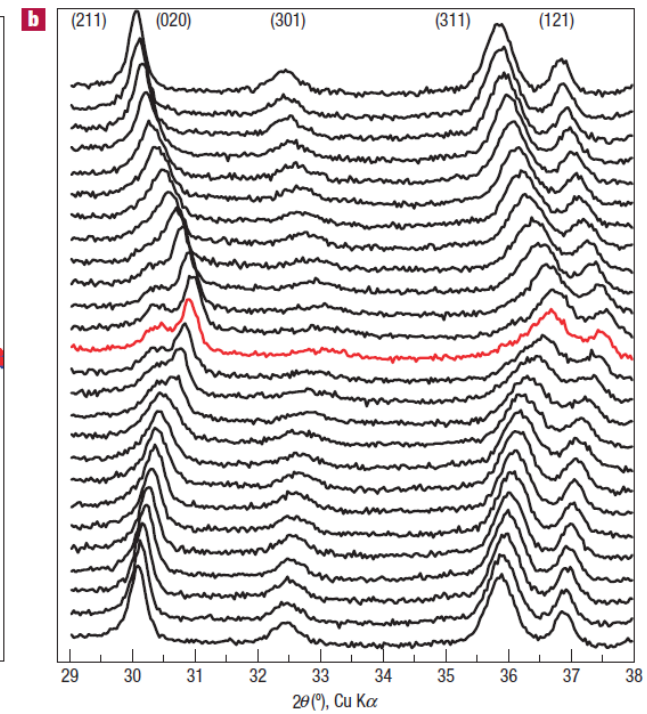
$LiFePO_4$: nanoscale effects

- reduction of particle size to 40 nm
- stable cycling
- single-phase behavior observed: sloping voltage profile and gradual shift of lattice parameters
- effect of particle size, synthesis conditions, or both?





cycle at C/40



XRD for 40-nm particles

P. Gibot et al., *Nature Materials* **7**: 741 (2008)

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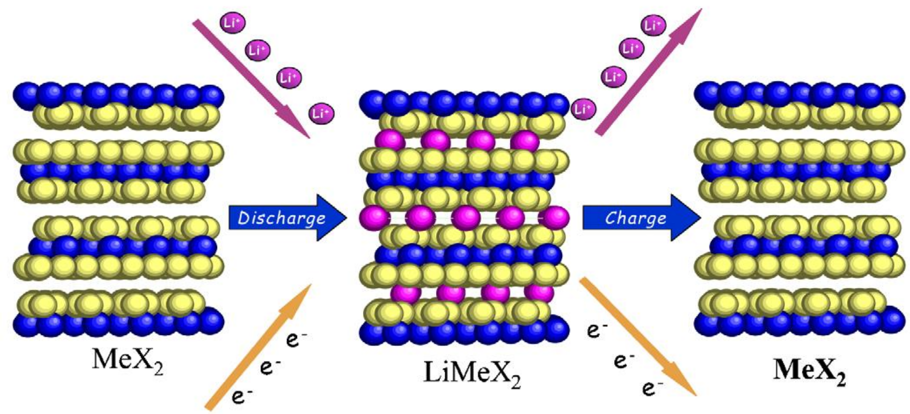
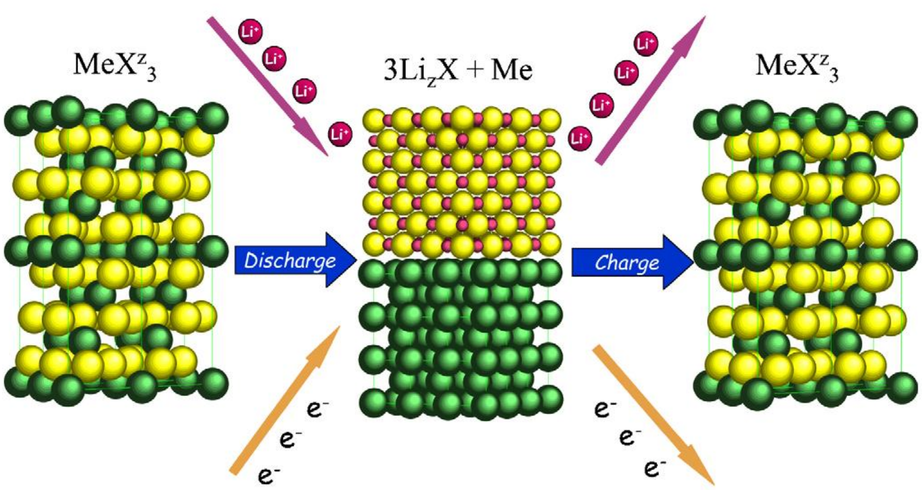
Nano-Enabled "Conversion" Reactions



Intercalation

- Li-ion inserted into vacancies between layers
- crystal structure maintained
- when discharged, typically 1 Li^+ per metal atom
- AKA "single-phase", "non-stoichiometric", "solid solution"



Conversion

- major structural changes
- discharge leads to mixture of metallic particles with lithium compounds
- anodes: oxides, sulfides, phosphides, nitrides
- cathodes: fluorides
- >1 Li^+ per metal atom → capacity > 600 mAh/g
- electrically insulating → slow kinetics
- nanocomposites and nanodomains enable good reversibility and kinetics (shorter path lengths for ion and electron transport)

G. Amatucci and N. Pereira, *J. Fluorine Chemistry* **128**: 243 (2007)

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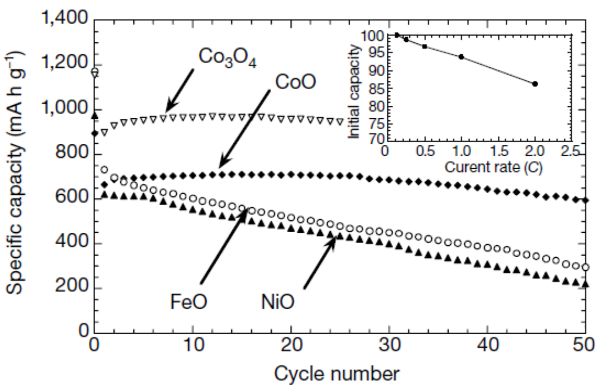
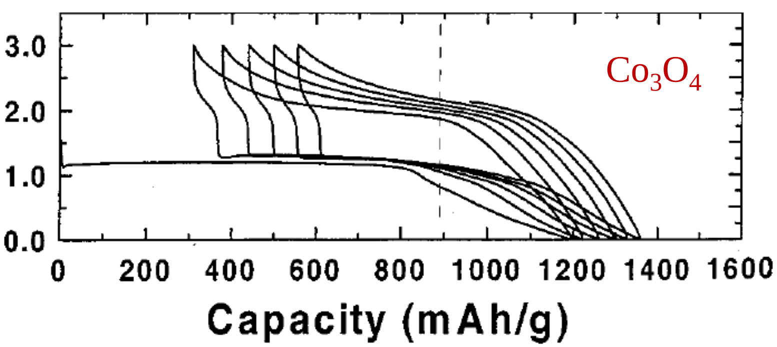
Nano-Enabled Conversion Reactions

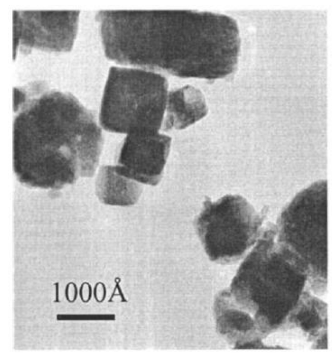


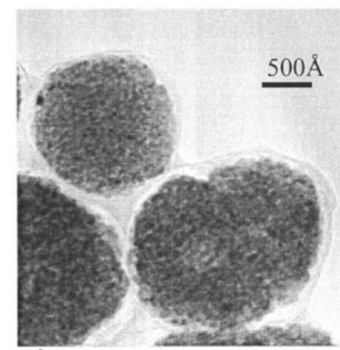
P. Poizot et al., *Nature* **407**: 496 (2000) ← cited 910 times

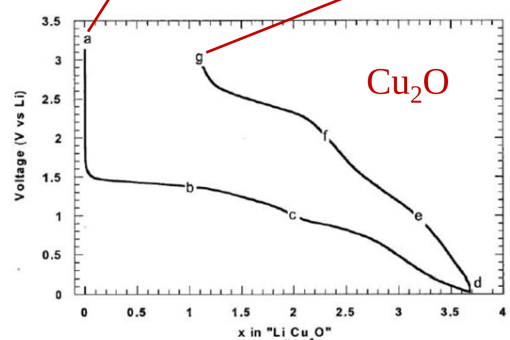
- example reaction: $Co_3O_4 + 8Li^+ + 8e^- \leftrightarrow 3Co + 4Li_2O$
- particles are 100–200 nm in diameter
- product of first discharge is metal nanograins (1-5 nm) in a Li_2O matrix, i.e. "amorphization"
- upon cycling, nanograin/amorphous structure is preserved
- capacity is > 2x capacity of graphite



D. Larcher et al., *J. Electrochemical Society* **149**: A234 (2002)







nanograins visible after one cycle (also confirmed with XRD)

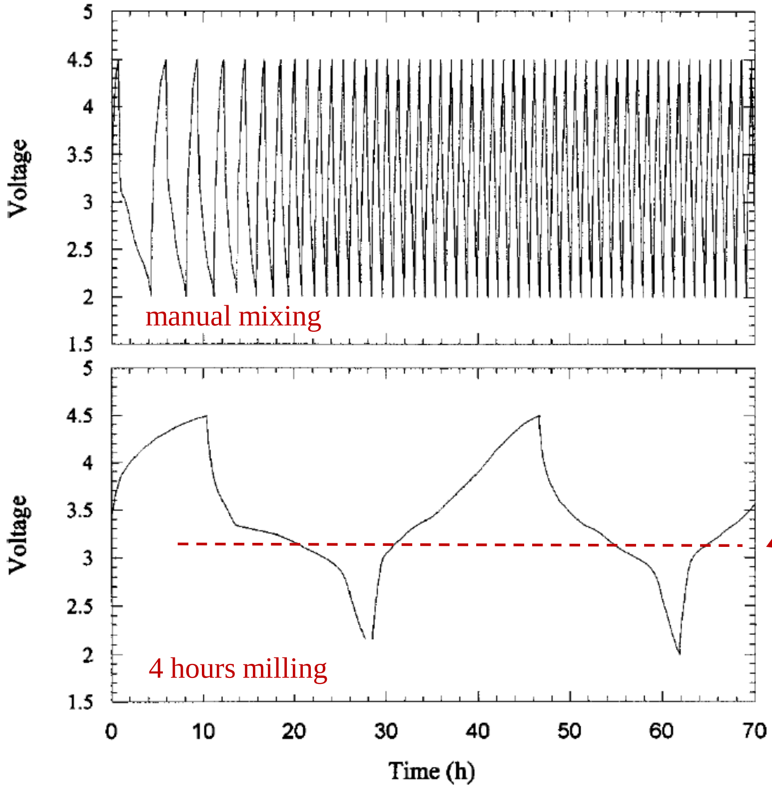
S. Grugeon et al., *J. Electrochemical Society* **148**: A285 (2001)

Conversion Reactions – Cathodes

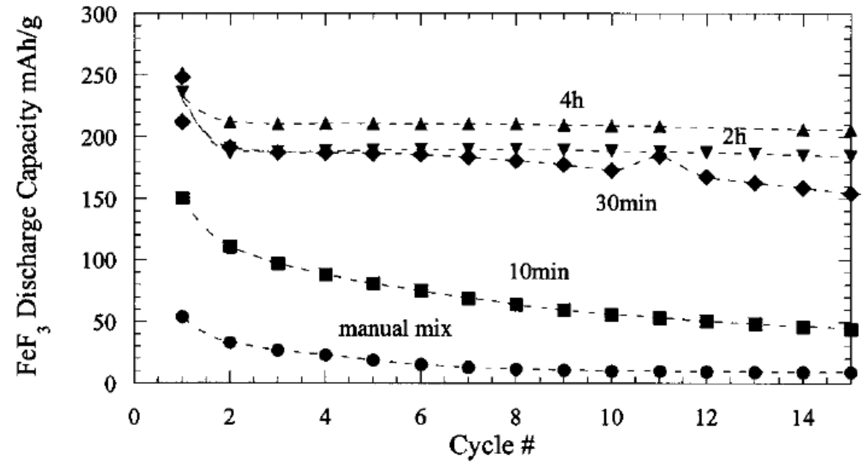
Fluoride/Carbon nanocomposites

- higher-voltage conversion reactions:, FeF_3, CrF_3, BiF_3, CuF_2
- high-energy mechanical milling with carbon creates nanocomposite, enables cycling and high capacity

FeF_3/carbon composite: cycling



~3-volt cycling



F. Badway et al.,
J. Electrochemical Society
150: A1209 (2003)

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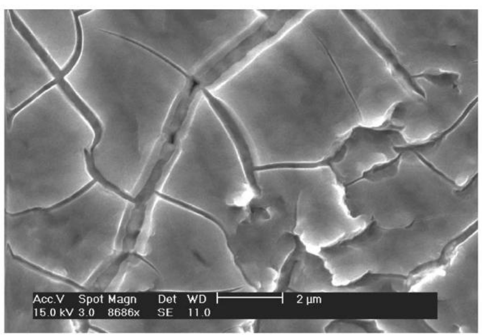
Lithium Alloys as Anodes

Lithium alloys

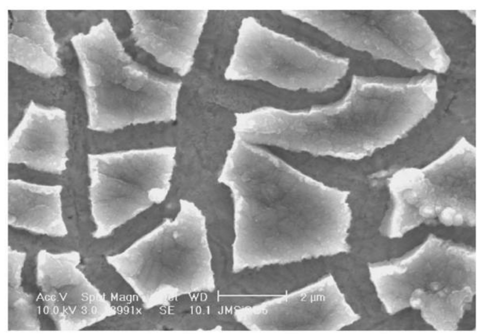
- low potential (< 1 V vs. Li/Li^+)
- high gravimetric and volumetric capacity
- similar to conversion reactions: large structural changes
- volume changes > 300% (Si) upon alloying with lithium
- alloying/de-alloying cycle causes fracture in bulk metals

alloy	capacity (mAh/g)	capacity (mAh/cm^3)
$Li_{22}Si_5$	4200	10000
$Li_{15}Si_4$	3580	8300
$Li_{22}Sn_5$	990	7200
LiAl	990	2700
$Li_{22}Pb_5$	570	6500

amorphous silicon thin film



after one cycle



after 30 cycles

compare to graphite at 372 mAh/g, 1000 mAh/cm^3

J. P. Maranchi et al., *J. Electrochemical Society* **153**: A1246 (2006)

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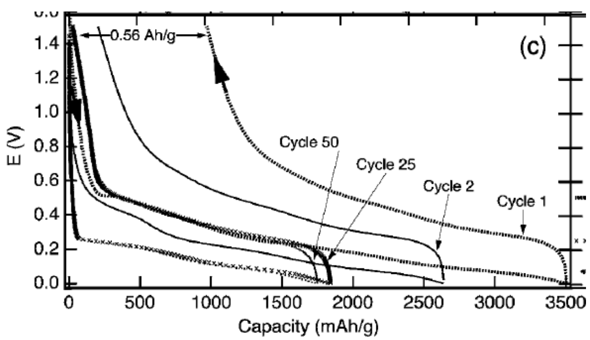
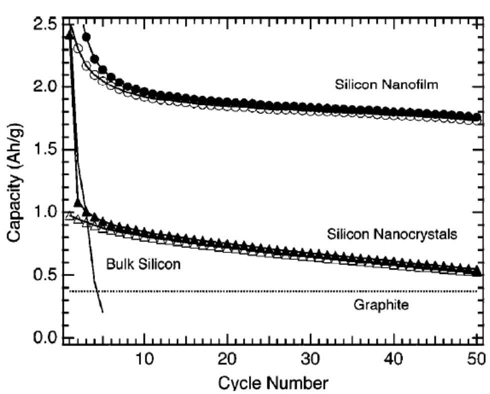
Lithium Alloys as Anodes

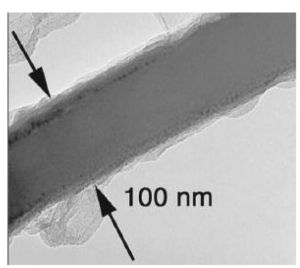
Lithium-Silicon Alloys

- most widely studied lithium alloy: theoretical capacity of $Li_{22}Si_5$ is 4200 mAh/g (10x higher than graphite)
- review article (162 refs) on lithium-silicon anodes: U. Kasavajjula et al., *J. Power Sources* **163**: 1003 (2007)

evaporated amorphous silicon nanofilm

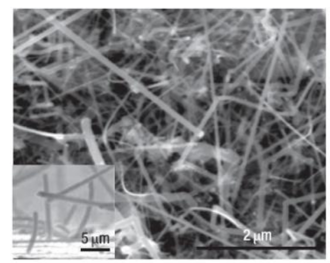


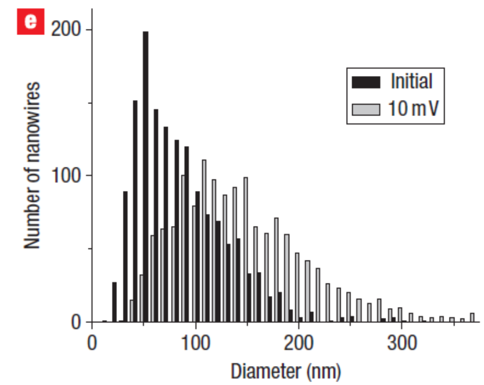


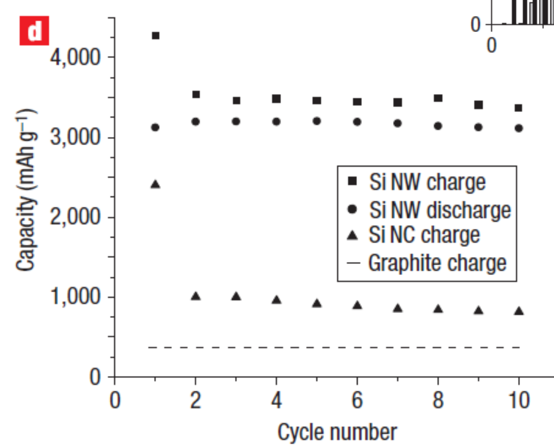


J. Graetz et al., *Electrochem. Solid-State Letters* **6**: A194 (2003)

silicon nanowires from vapor-liquid-solid growth







C. Chan et al., *Nature Nanotechnology* **3**: 31 (2008)

cited 143 times

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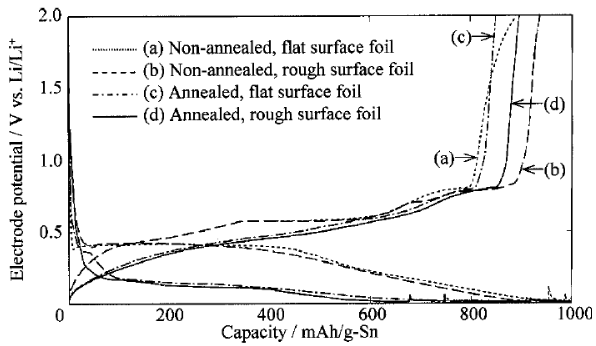
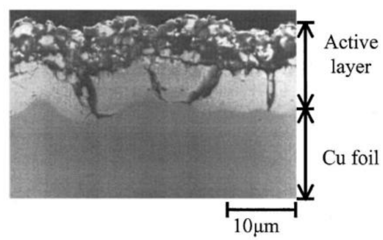
Lithium Alloys as Anodes

Lithium-Tin Alloys

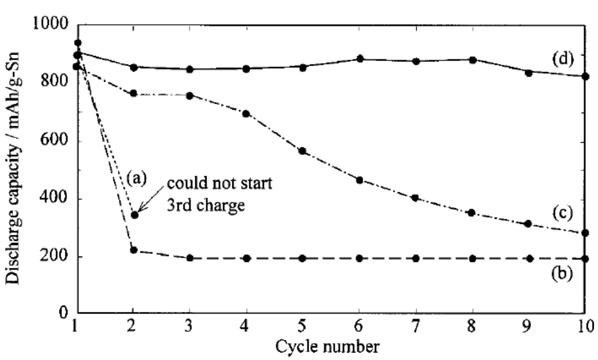
- theoretical capacity of $Li_{22}Sn_5$ is 990 mAh/g

electrodeposited tin film (micro-scale)



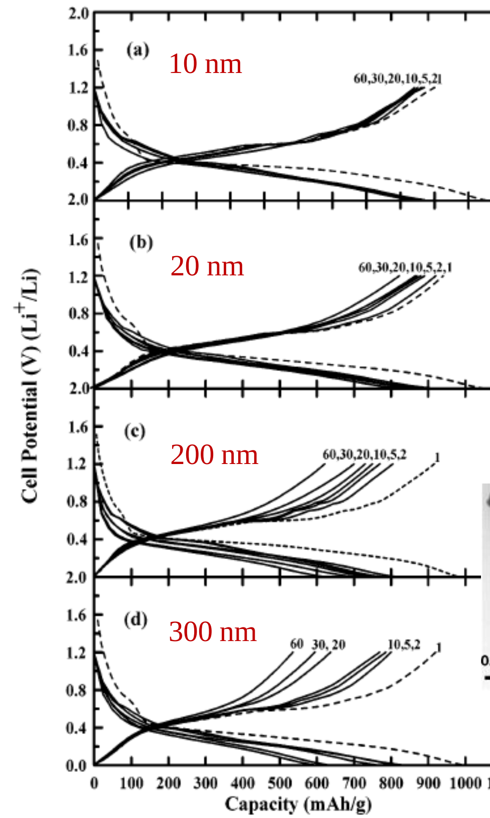


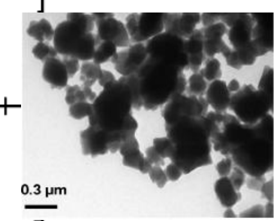
structural deformation evident after one cycle



N. Tamura et al., *J. Electrochemical Society* **150**: A679 (2003)

monomer-capped tin nanoparticles





M. Noh et al., *Chemistry of Materials* **17**: 3320 (2005)

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Lithium Alloys as Anodes

$SnO_2 + 4Li^+ + 4Li^- \rightarrow Sn + 2Li_2O$

irreversible conversion

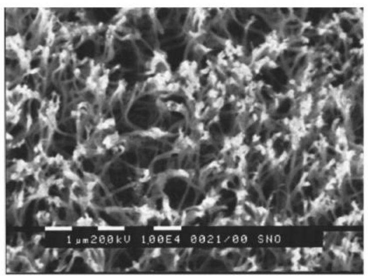
↑ inactive matrix

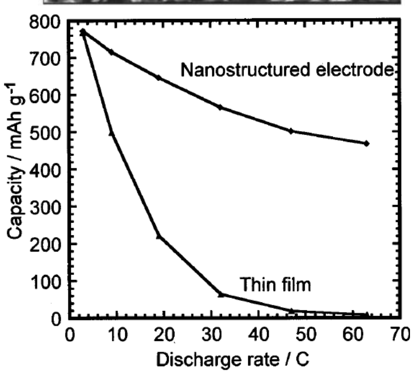
reversible alloying reaction

$Sn + xLi^+ + xLi^- \leftrightarrow Li_xSn$

780 mAh/g

"nanofibers" by template/sol-gel synthesis

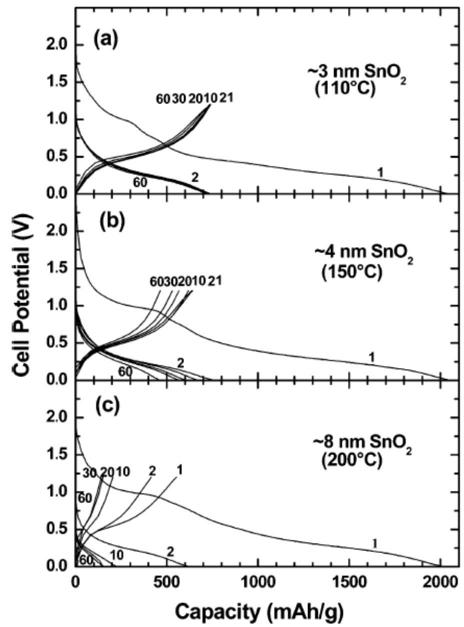




cycled 1300 times at 58C, >500 mAh/g

N. Li and C. R. Martin,
J. Electrochemical Society **148**: A164 (2001)

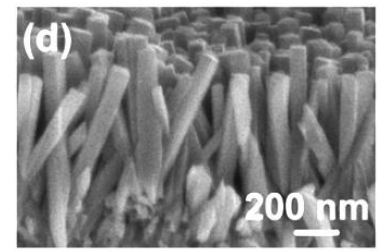
particle-size study,
hydrothermal synthesis

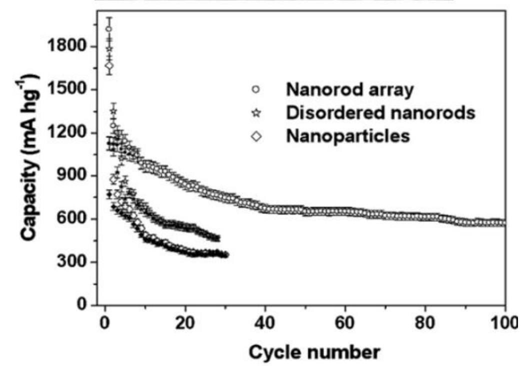


particle aggregation with larger particles

C. Kim et al., *Chemistry of Materials* **17**: 3297 (2005)

nanorod array,
template-free synthesis





J. Liu et al., *J. Materials Chemistry* **19**: 1859 (2009)

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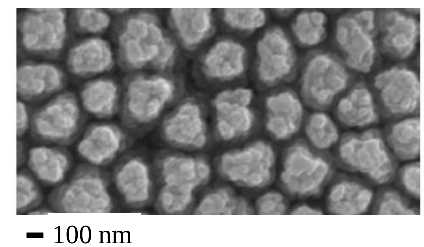
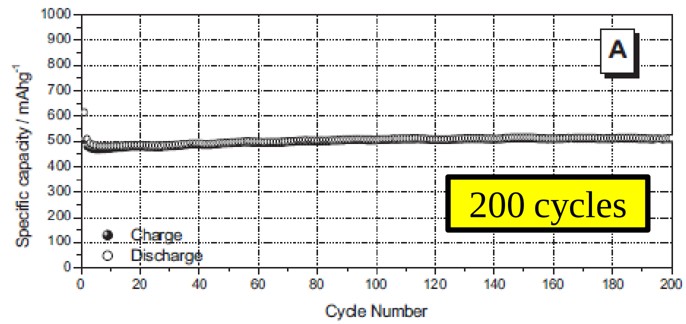
Nanostructured Electrode Architectures

Nanostructured current collectors (substrates)

- nanorod array of inactive conductor (e.g. Cu)
- active electrode material deposited onto nanorods
- good for active materials with low conductivity or large volume changes
- low specific capacity (volumetric and gravimetric)
- thin-film electrodes (potential for scaling up?)

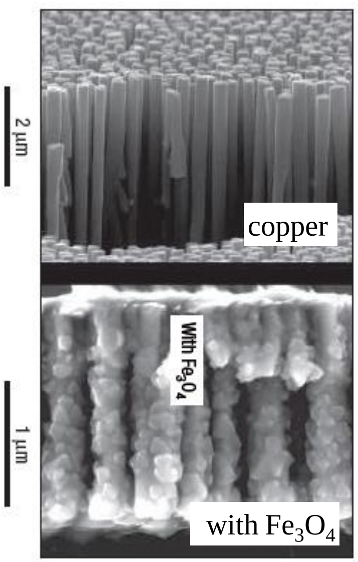
Ni_3Sn_4 electrodeposited on copper nanorods

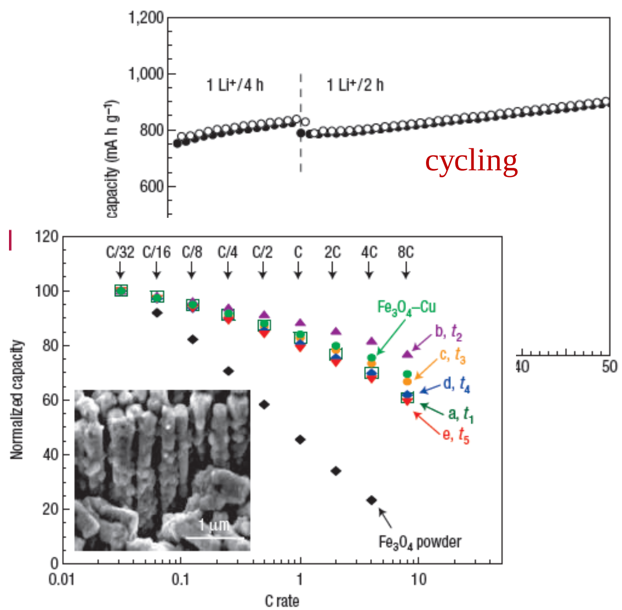




J. Hassoun et al., *Advanced Materials* **19**: 1632 (2007)

Fe_3O_4 electrodeposited on copper nanorods



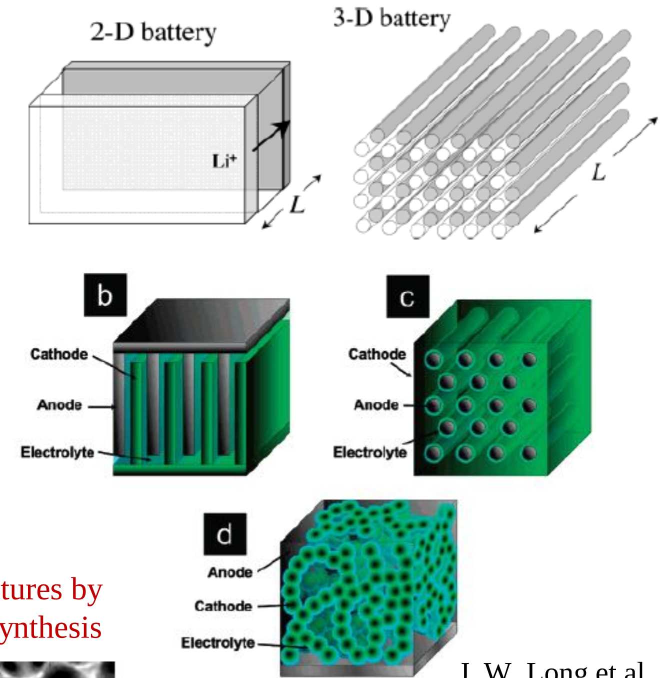


P. L. Taberna et al.,
Nature Materials **5**: 567 (2006)

Nanostructured Electrode Architectures

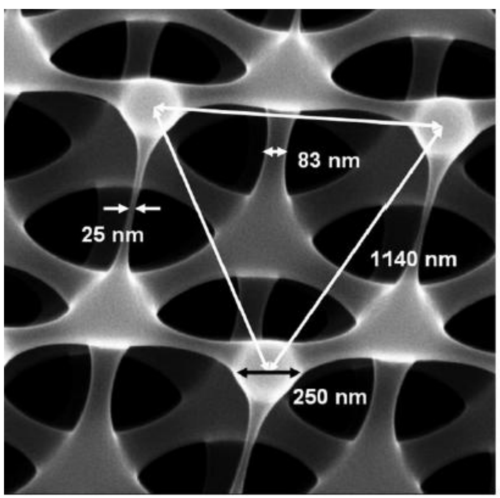
Three-dimensional microbatteries

- alternative to conventional, sandwich-type architecture
- increase energy density while maintaining short ion-transport distances (i.e. no sacrifice in power density)
- size increase in any dimension increases power output, capacity, and energy content
- few systems experimentally demonstrated



J. W. Long et al., *Chemical Reviews* **104**: 4463 (2004)

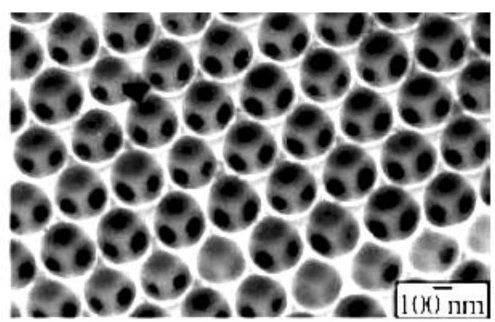
3D carbon structures by interference lithography



Sandia/UNM collaboration

D. B. Burckel et al., *Small* **5**: 2792 (2009)

3D carbon structures by template/sol-gel synthesis



K. T. Lee et al., *Adv. Funct. Mat.* **15**: 547 (2005)

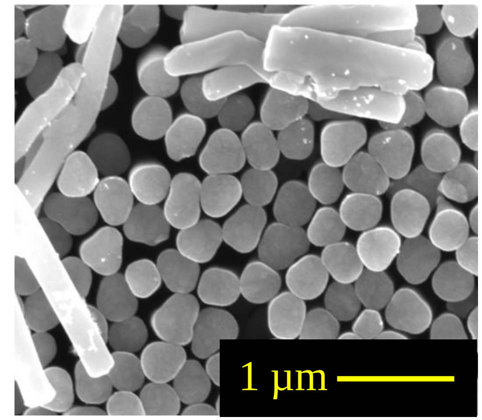
Research at CINT

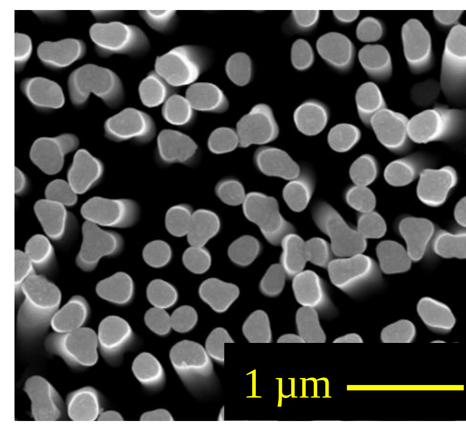
Nanostructured Electrode Architectures

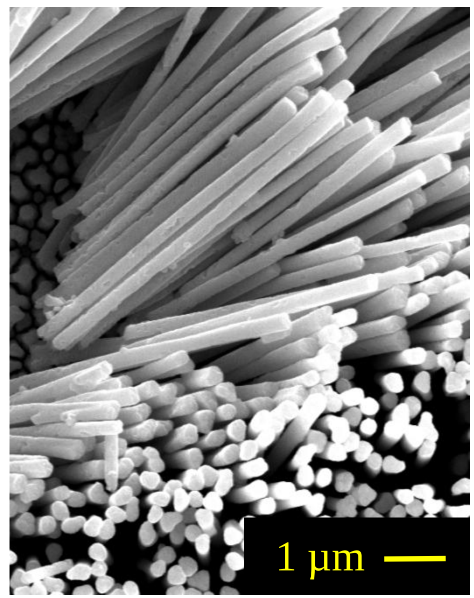
Electrodeposited nanostructures

- various electrodeposited nanostructures as current collectors (copper, nickel)
- electrodeposited, nanostructured active materials (e.g. Aluminum nanostructures for lithium alloying)
- nanorods: effect of diameter, length, packing density, ordered array vs. randomly oriented

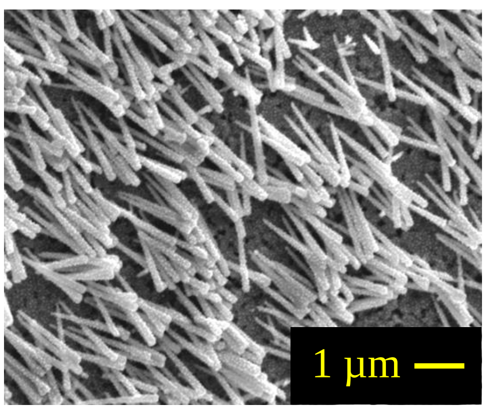
Copper nanorods by electrodeposition into anodic aluminum oxide (template removed)







Copper nanorods by electrodeposition into polycarbonate template (template removed)



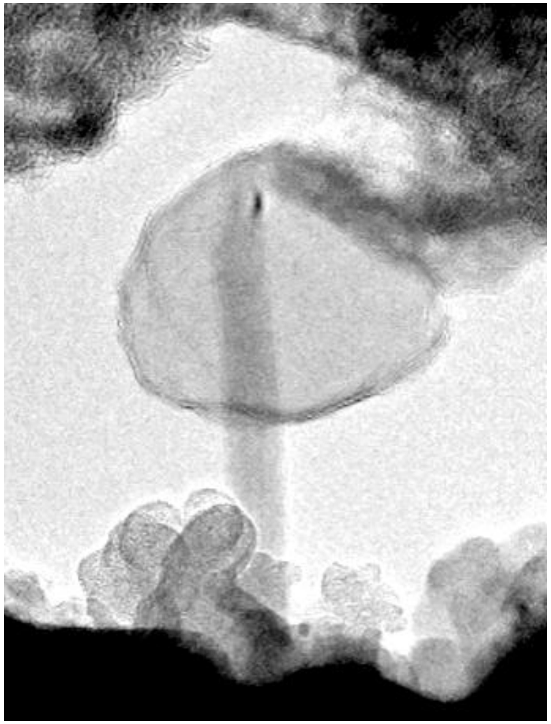
Dale Huber & Nick Hudak, Sandia/CINT

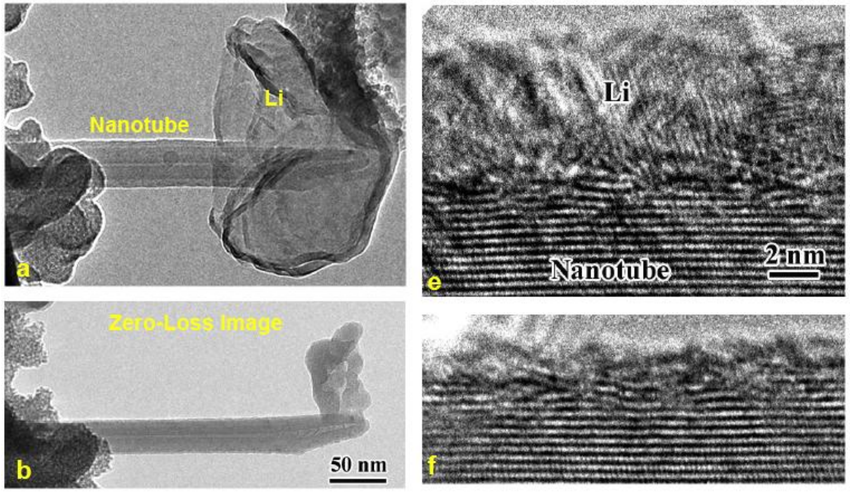
Research at CINT

in situ TEM Imaging of Nano-electrodes

Transmission-Electron Microscopy

- demonstrated solid-state uptake of lithium by multi-wall carbon nanotube (MWNT)
- nanomanipulators used to position nanoparticles/wires
- goal is to view *electrochemical* lithium reaction to study:
    - nanoscale materials (nanotubes/rods/wires)
    - nanoscale electrochemical processes, e.g. formation and evolution of solid-electrolyte-interphase (SEI)
- ionic liquid electrolyte (low vapor pressure) in TEM
- standard organic electrolytes in encapsulated cell in TEM





Jianyu Huang, Sandia/CINT

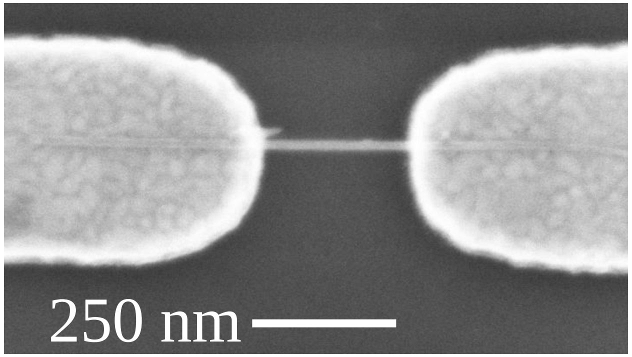
Sandia National Laboratories

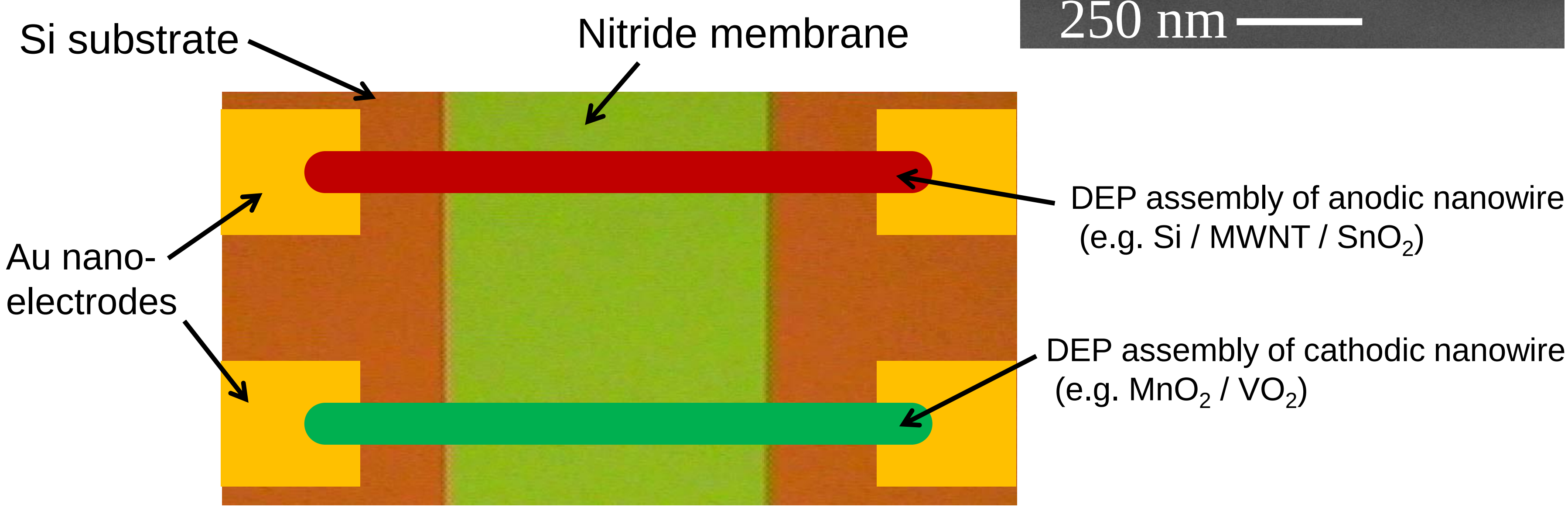
Research at CINT

Single Nanowire Lithium-Ion Electrodes

Single nanowires placed across electrodes using di-electrophoresis (DEP)

SEM of multi-walled carbon nanotube (MWNT) by DEP





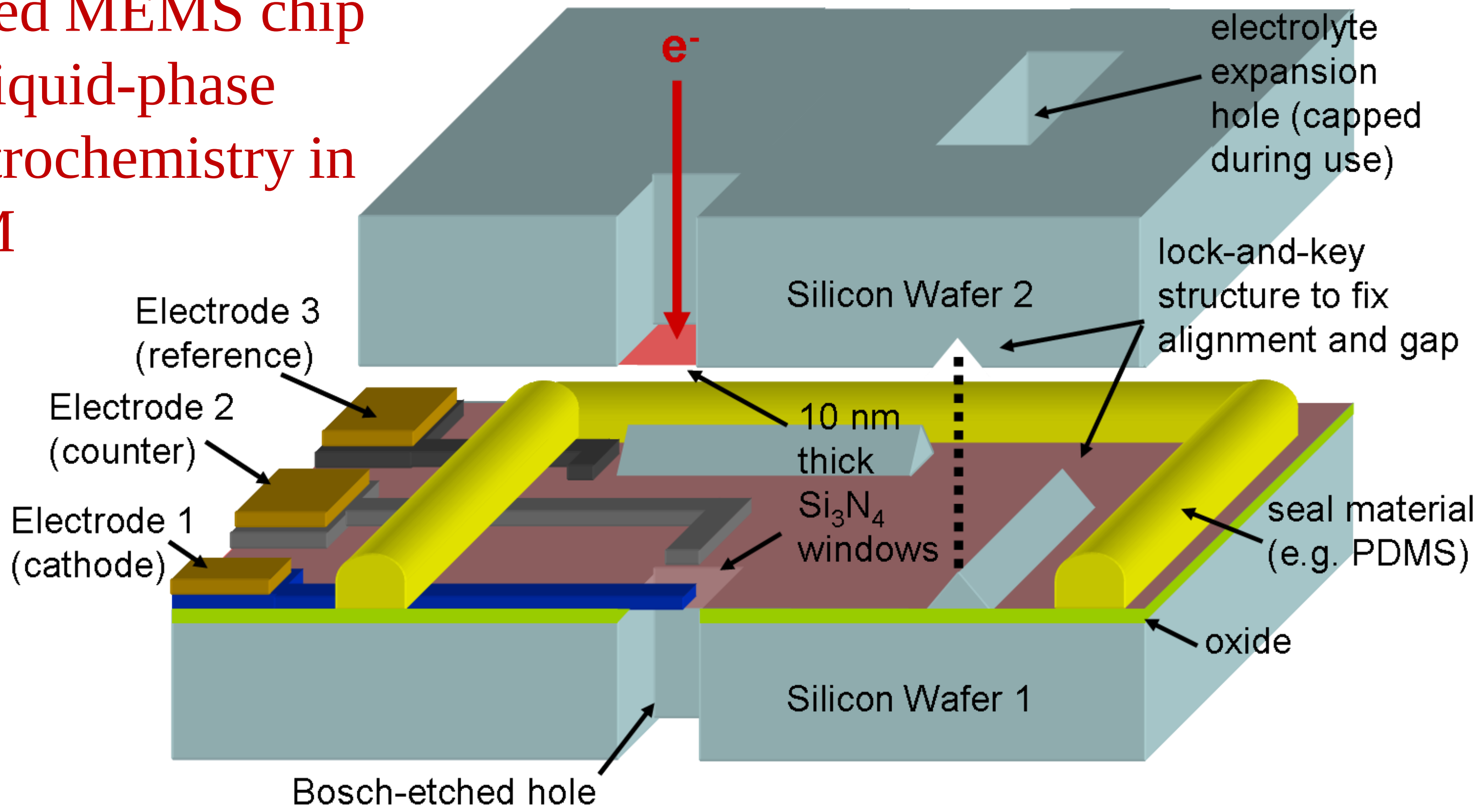
John Sullivan & Arunkumar Subramanian, Sandia/CINT

Sandia National Laboratories

Research at CINT

in situ TEM Battery Studies

Sealed MEMS chip for liquid-phase electrochemistry in TEM



John Sullivan & Mike Shaw, Sandia

Sandia National Laboratories

Summary

Nanostructured electrode materials for lithium-ion batteries

- improved cycle life, rate capability or power output compared to bulk materials
- increased surface area of nanoparticles may be detrimental to cycle life
- nanoscience enables the effective use of $LiFePO_4$, "conversion reaction" materials, and lithium alloys
- nanostructured electrode architectures for improved performance and novel three-dimensional batteries

Nanoscience for lithium batteries at CINT and Sandia

- electrodeposited nanostructures as current collectors or active materials
- in situ TEM observation of lithiation/de-lithiation in nanowires
- encapsulated electrochemical MEMS cell for use of liquid electrolytes in TEM