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Nanophase Electrode Materials for Fast Rate Li-based Energy Storage Devices

Presentation at:

DOE Peer Review Meeting

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Program Overview

- **Goals**
  - Develop low cost & non-toxic nanostructured anodes with fast rate capability for Li-based energy storage devices
  - Fabricate prototype asymmetric cells with fast rate capabilities and long cycle life
- **Phase II Start date: July 2003**
- **Accomplished So Far**
  - Synthesized nanostructured WO_2 powders and performed detailed electrochemical and structural characterization
  - Synthesized and characterized nanostructured W_3O powders

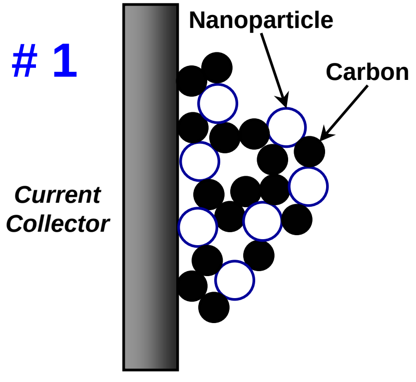
Overview Continued

- Fabricated and characterized prototype (2" X 2") asymmetric hybrid cells utilizing nano – WO_2 and macro-WO_2 anodes

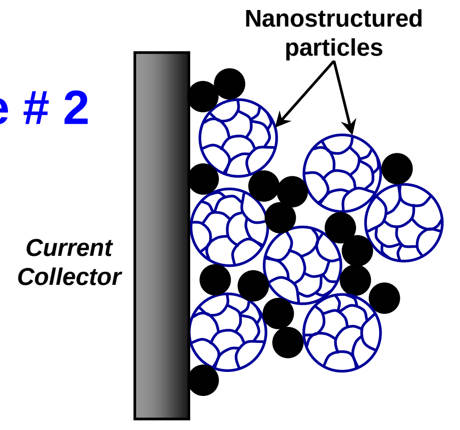
- **Future Milestone**
  - Improve 1st cycle efficiency of nano – WO_2 anodes

Current Density Increases with Decrease in Diffusion Distance

Structure # 1



Structure # 2



Rate of Li diffusion in electrode particles $= \dfrac{\alpha D_{Li}}{kTd^{m}}$

m = 3 (volume diffusion)

= 4 (grain boundary diffusion)

Current = $i = \dfrac{nFD_{Li}A(C_B - C_E)}{\delta}$

$$i = \phi\left(\frac{1}{d} - \gamma d^{m-1}\right)$$

Other Possible Advantages

- **Improved cycle life**
  - Better utilization of material
- **Can exhibit both faradaic and non-faradaic capacity**
  - Higher retention capacity
- **Can enable new materials**
  - Small D_{Li}
  - Large volume change as Li^+ cycle in and out

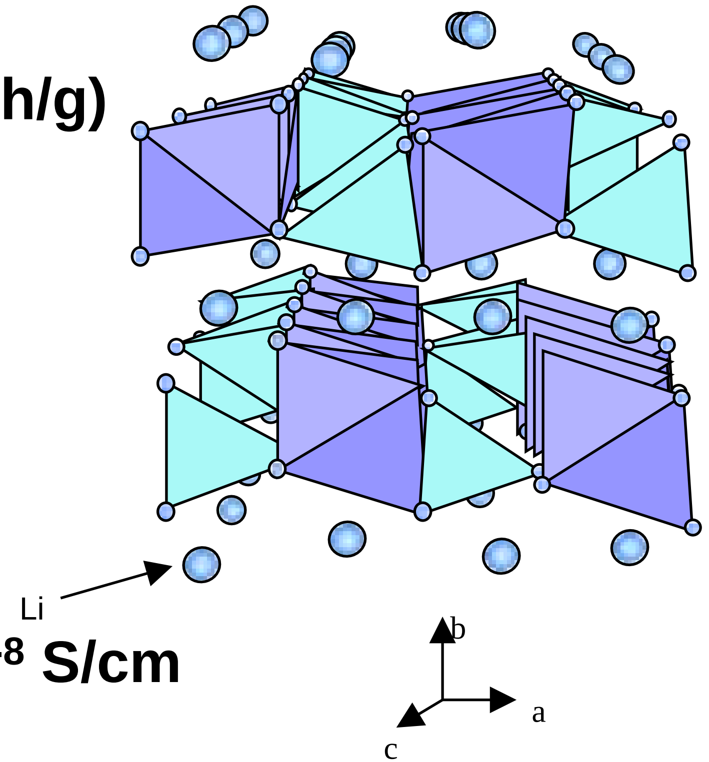
Nanophase Electrode Materials

- **Nanostructured $LiFePO_4$/C Composite Cathode**
  - **Structure # 1**

- **Nanostructured WO_2 Anode**
  - **Structure # 2**

$LiFePO_4$ Cathodes

- Highly Stable (safe, with low fade) and non-toxic
- Good specific capacity (~ 170 mAh/g)
- Flat voltage profile
- Cost effective
- Low D_{Li} : ~ 10^{-13} cm^2/sec
- Poor electronic conductivity: ~ 10^{-8} S/cm
- Approach
  - Nano – $LiFePO_4$/C composite powder



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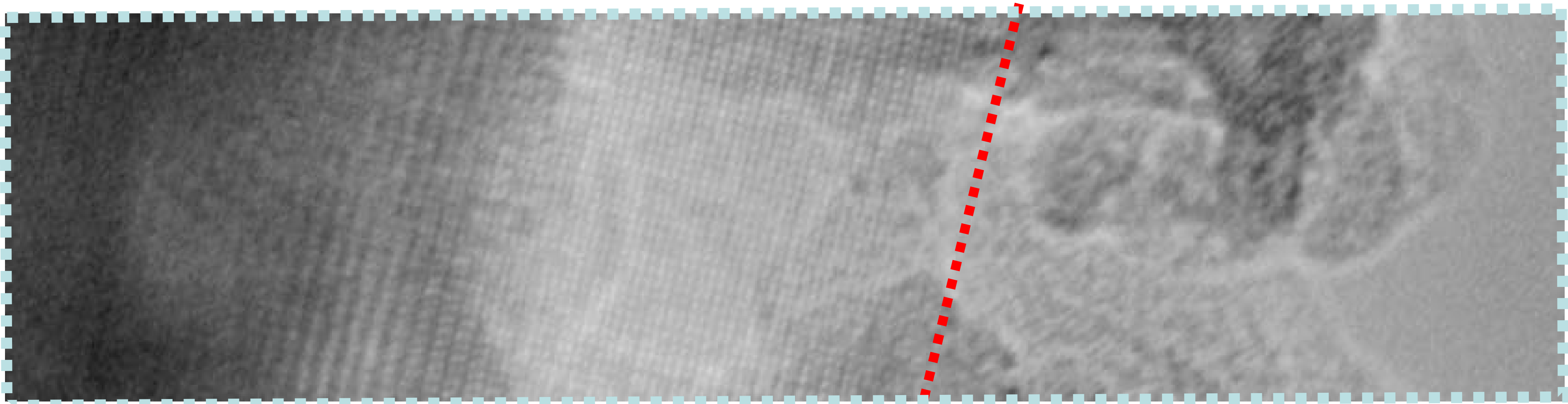
$LiFePO_4$/C Composite

- **Synthesized using a vapor phase process**

Crystalline

Amorphous carbon



Particle thickness increases

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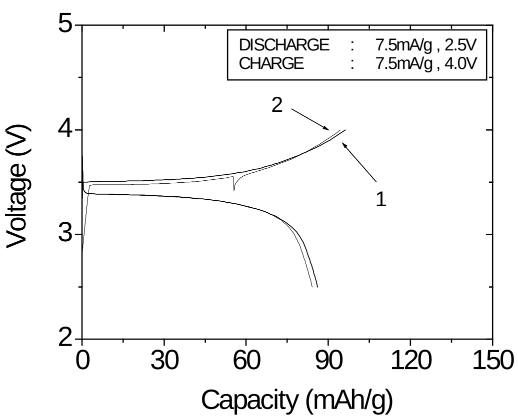
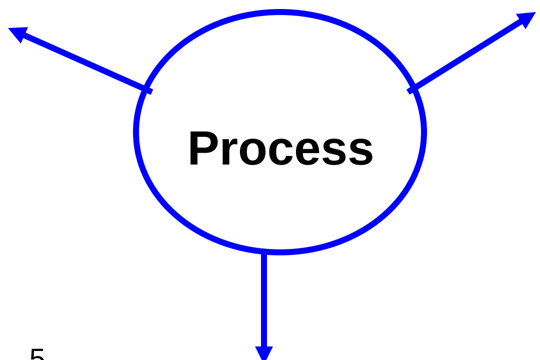
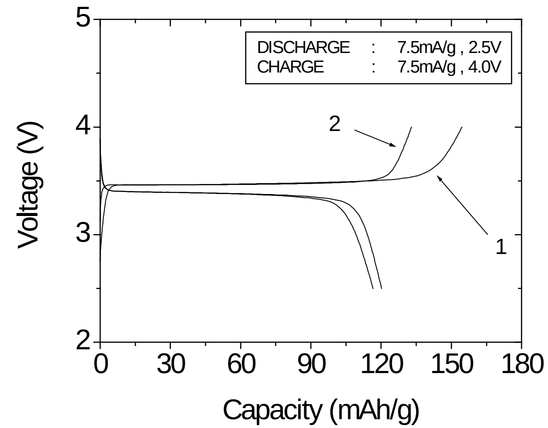
A New Synthesis Process for $LiFePO_4$/C Composite Powder

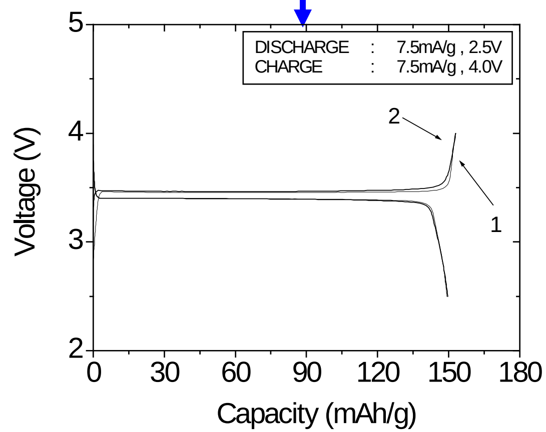


Parameters Z





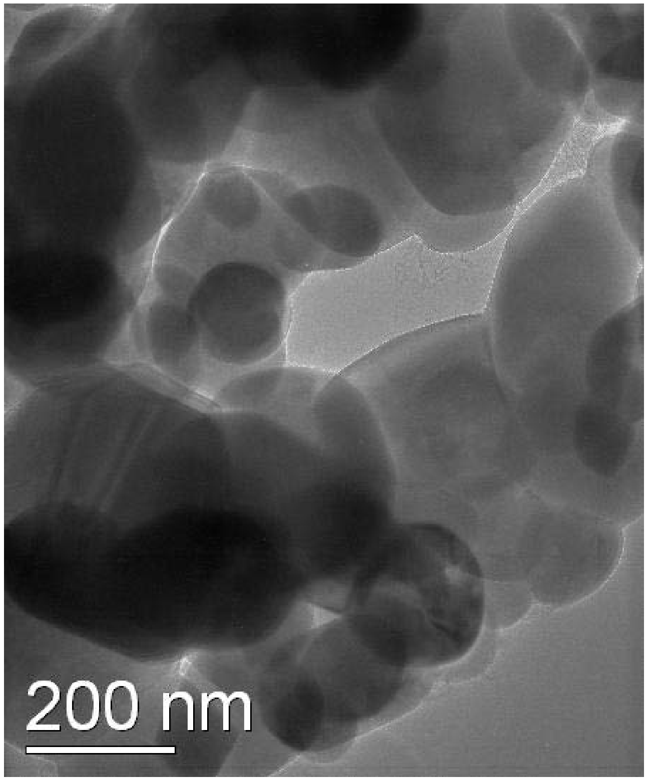
Parameters X

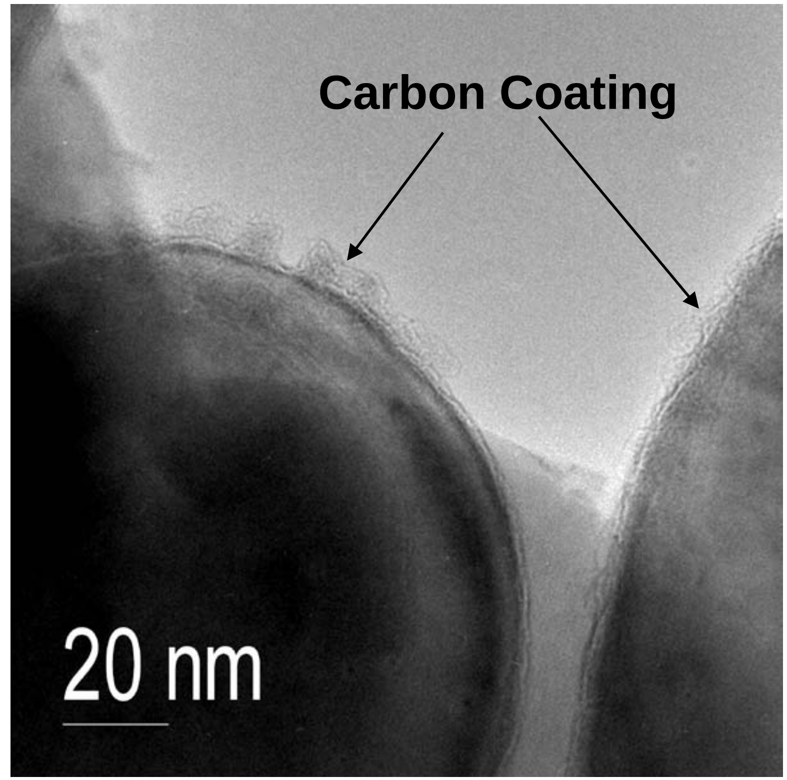


Parameters Y

- **Phase pure powders**

Carbon-coated $LiFePO_4$ Particles





- **Spherical single crystalline primary particles: size varies between 30 nm and 300 nm**
- **Surface area: 22 – 25 m^2/g**
- **Tap density: 0.7 – 0.9 g/cm^3**

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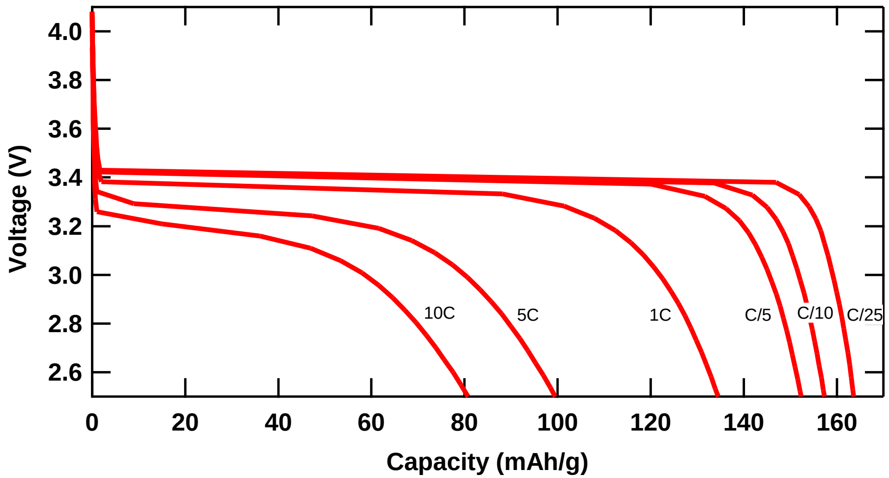
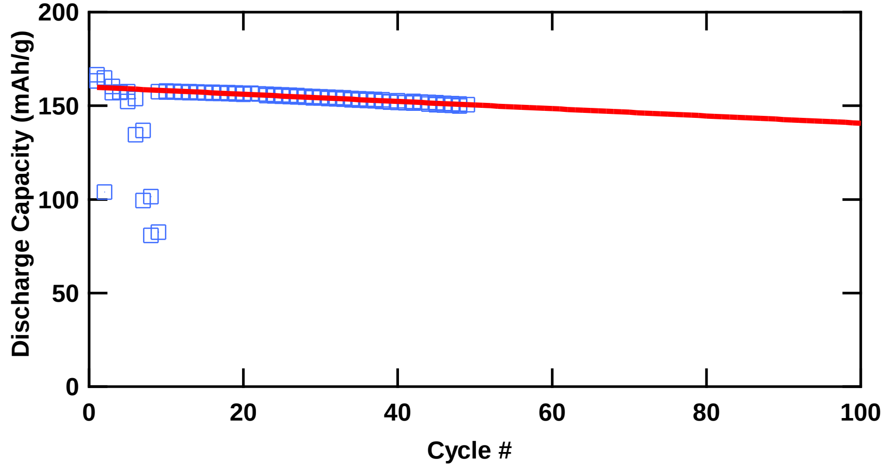
Excellent Rate Performance





- **Good cyclability (with a fade rate of 0.13%/cycle)**

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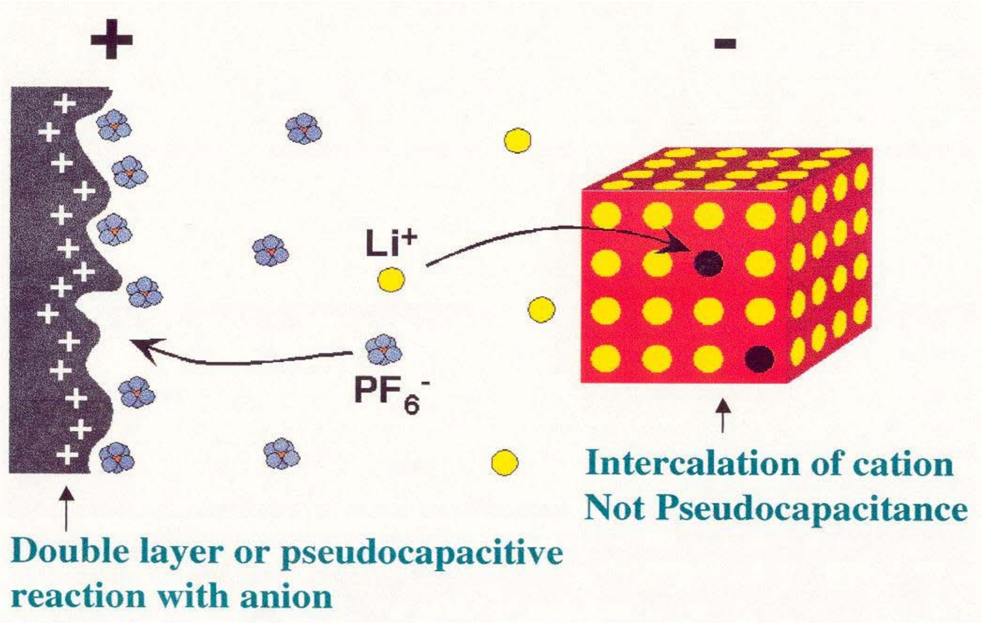
Concept of An Asymmetric Hybrid Cell



Courtesy Telcordia Technologies

A thin, flexible, highly manufacturable and non-aqueous plastic laminar device

Reference: Amatucci et al., *Journal of The Electrochemical Society*, **148** (8), A930 (2001)

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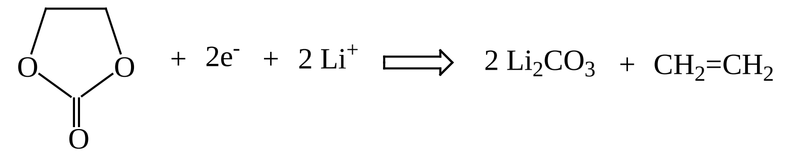
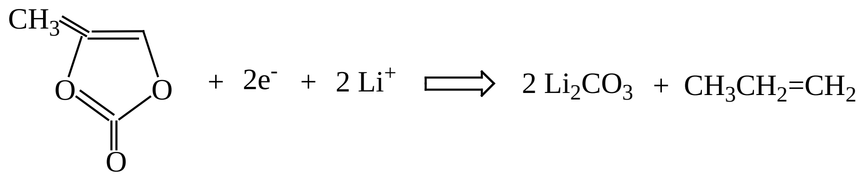
High Potential Nanostructured Anodes

- **Minimal SEI formation**
  - **1.5 V vs Li^+/Li for $Li_4Ti_5O_{12}$**
  - **~ 0.75V vs Li^+/Li for WO_2**
- **High stability of $Li_4Ti_5O_{12}$**
  - **No volume change**
  - **Excellent cyclability**
- **High safety at fast charge rates**
  - **No Li plating problem**



EC



PC

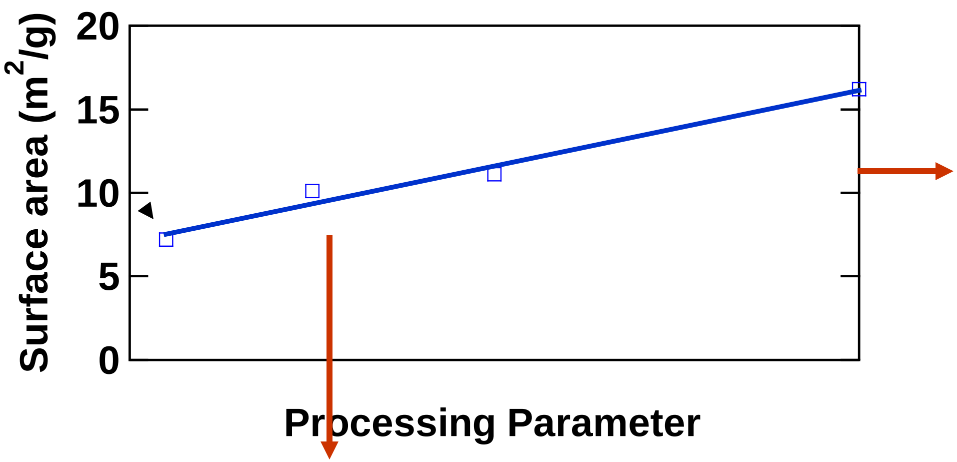
Reference: D. Peramunage, K. M. Abraham, J. Electro. Chem. Soc., 145 (8) 2615 (1998).

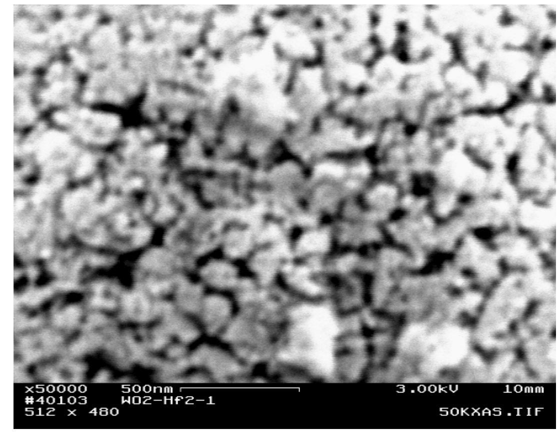
Why Nanostructured WO_2- based Anodes

- **Poor retention capacity (~60 mAh/g) of coarse WO_2**
  - **J. J. Auborn and Y. L. Barberio, *J. Electrochem. Soc*., vol 134, 638 (1987)**
- **Faster rate capabilities**
  - **Higher Li-ion diffusion rates**
- **May offer both faradaic and non-faradaic capacity**
  - **Larger amount of surface sites**
- **High intercalation voltage**
  - **~ 0.75 V vs SHE**

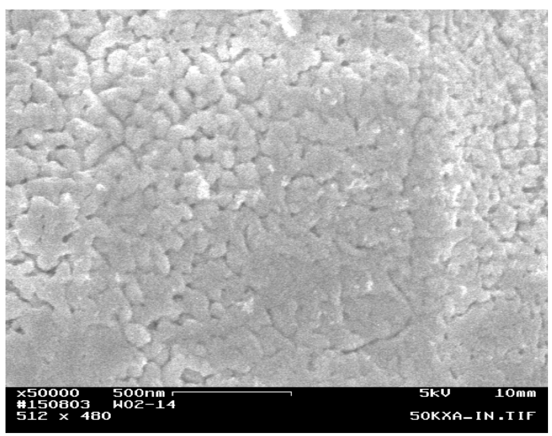
Nanostructured WO_2 Spheres

WO_2: potential anode material



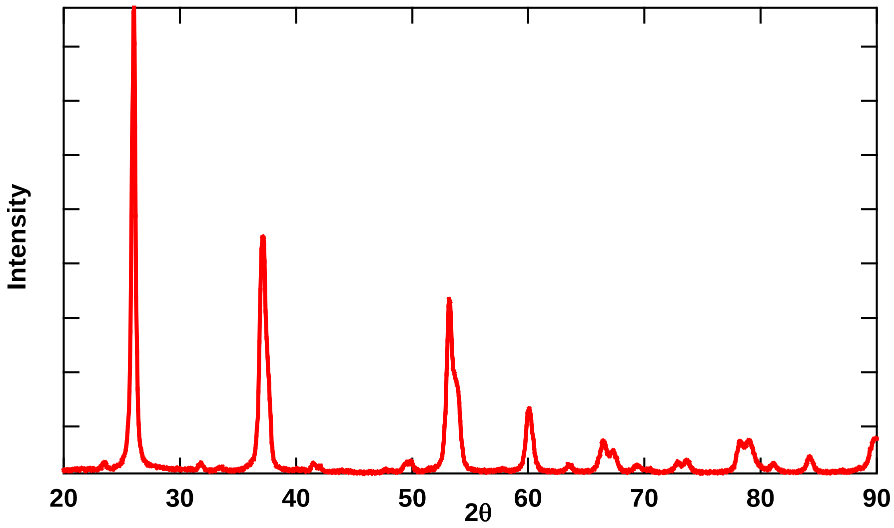


Avg. primary particle size:
~ 50 nm

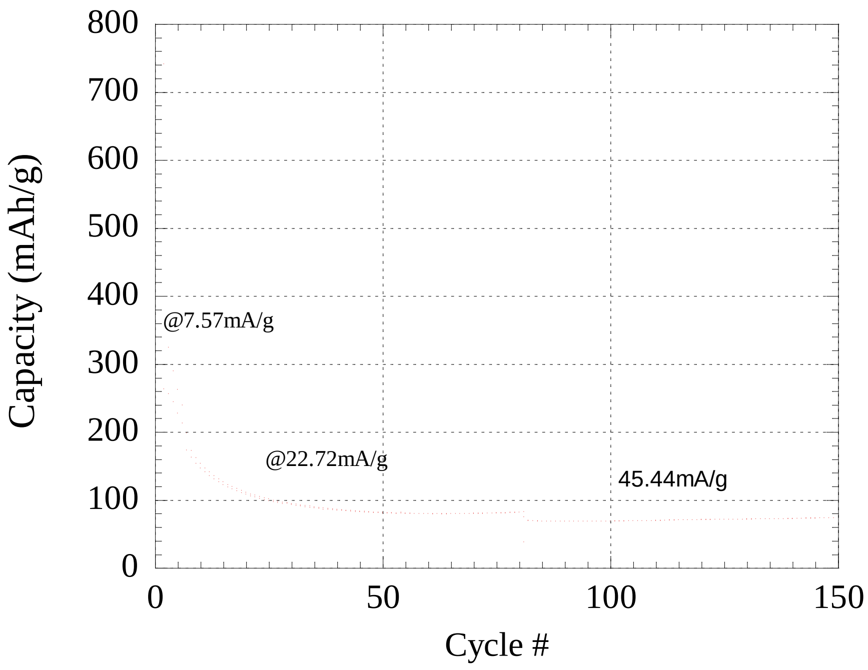


Avg. primary particle size:
~ 100 – 150 nm

WO_2: potential anode material (contd..)



Pure WO_2 phase



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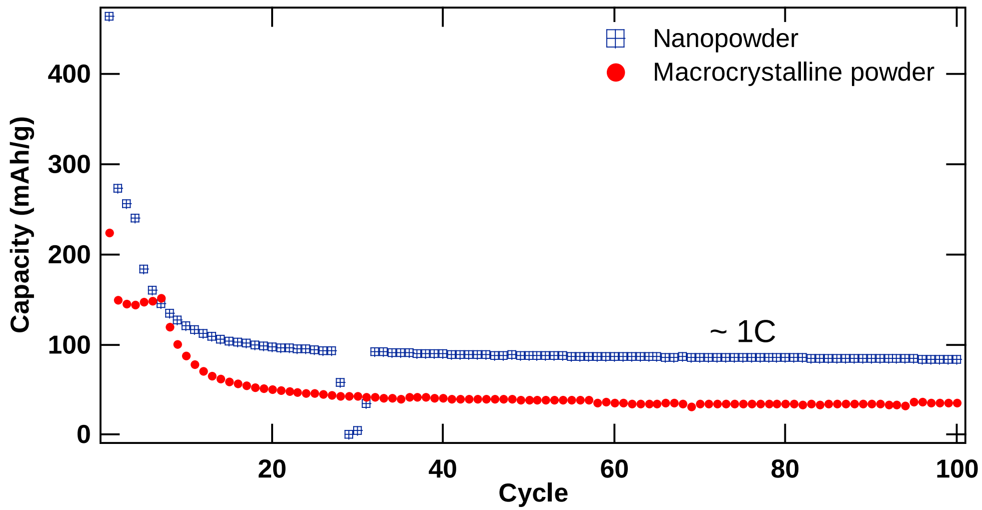
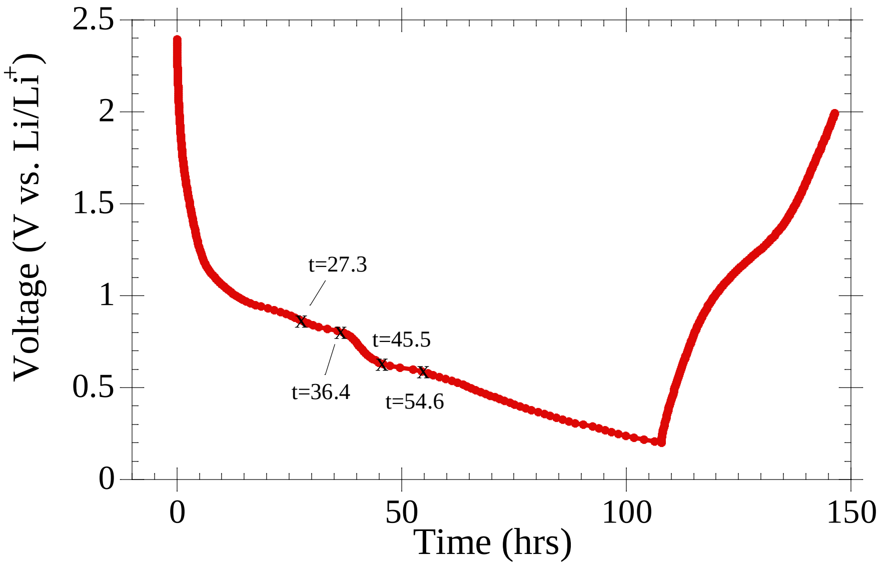
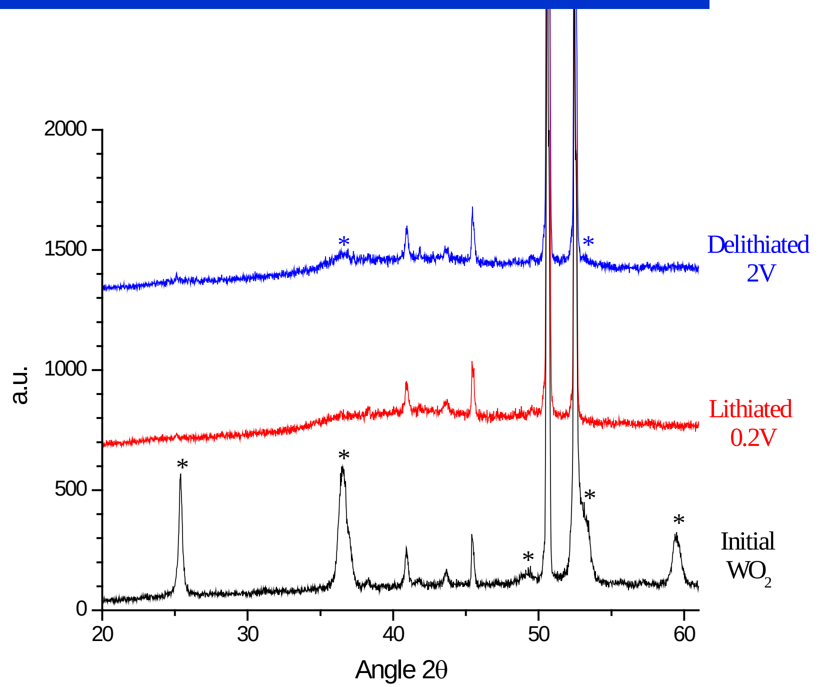
Superior Rate Performance of Nano-WO_2



(discharge voltage range: 2.0 – 0.5V)

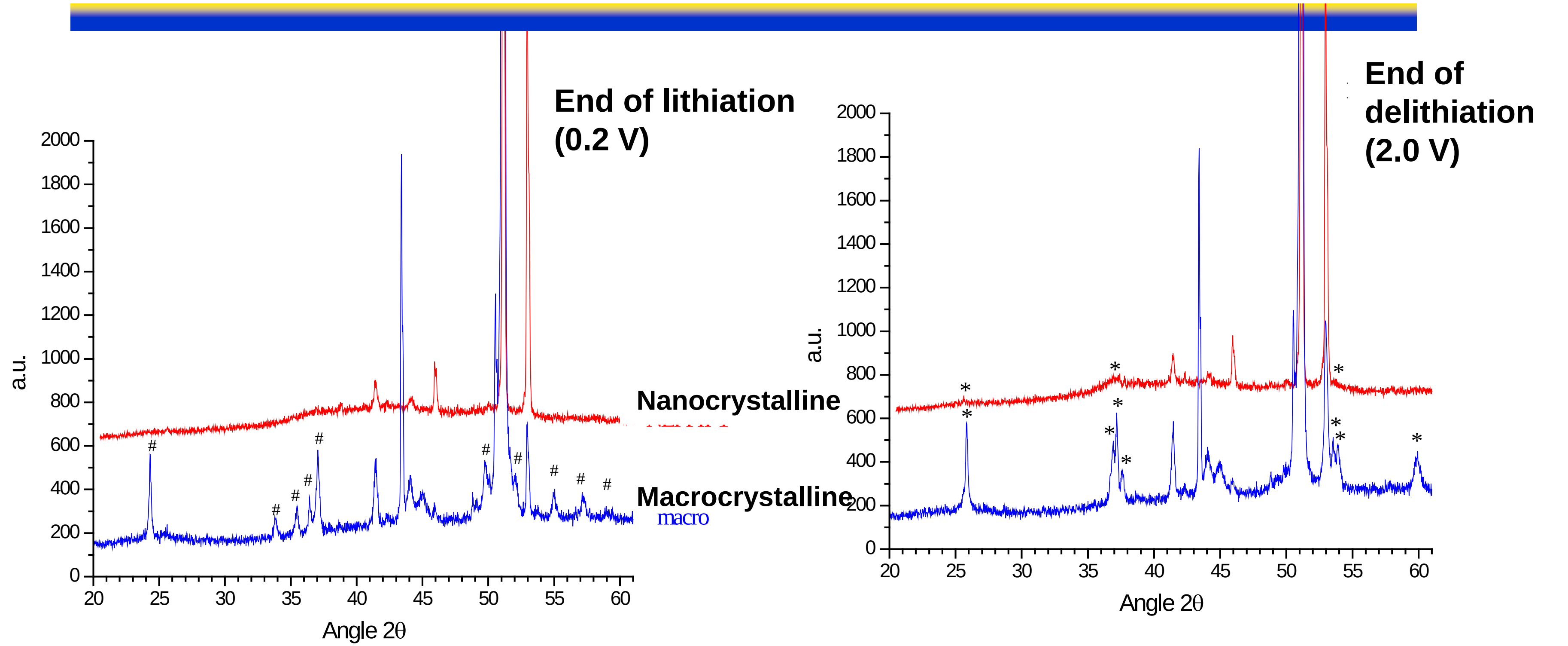
In-situ X-ray Diffraction





- **Amorphous-like structure at the end of lithiation (0.2 v)**
- **WO_2 type of structure at the end of delithiation (2.0 V)**

In-Situ XRD Contd…..



- **Macrocrystalline material remains crystalline during lithiation at slow discharge rates**
- **Reformation of WO_2 type structure upon delithiation for macrocrystalline material**

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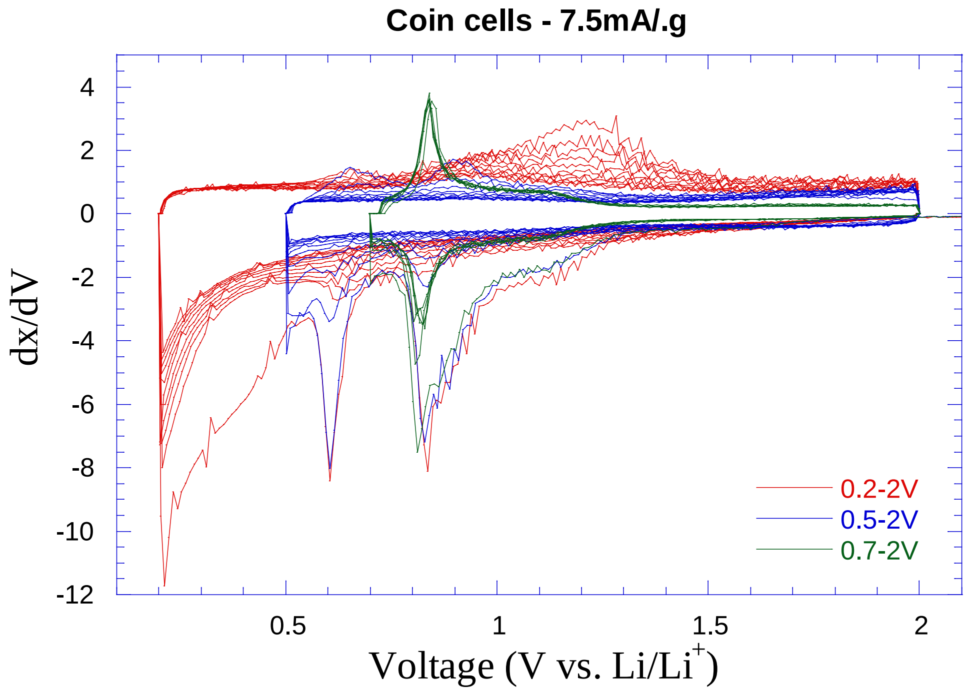
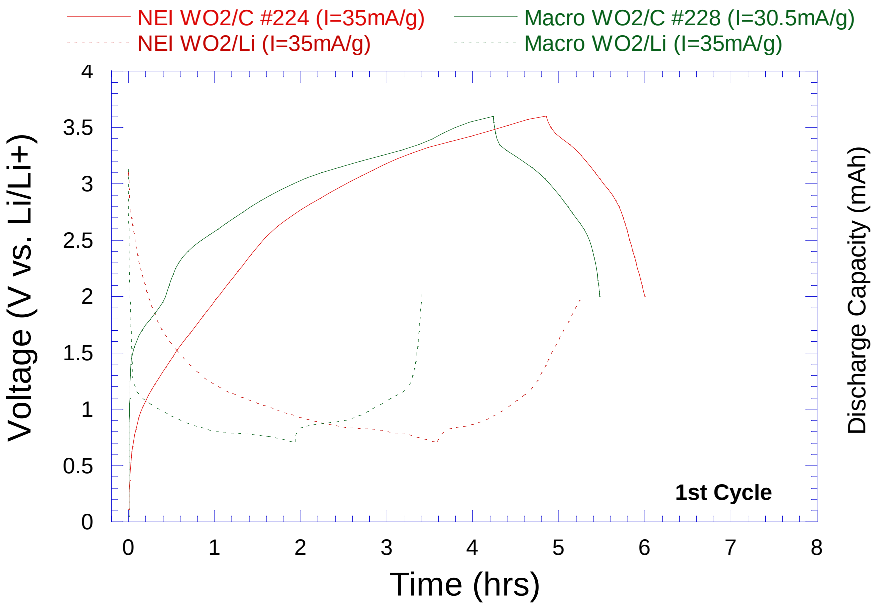
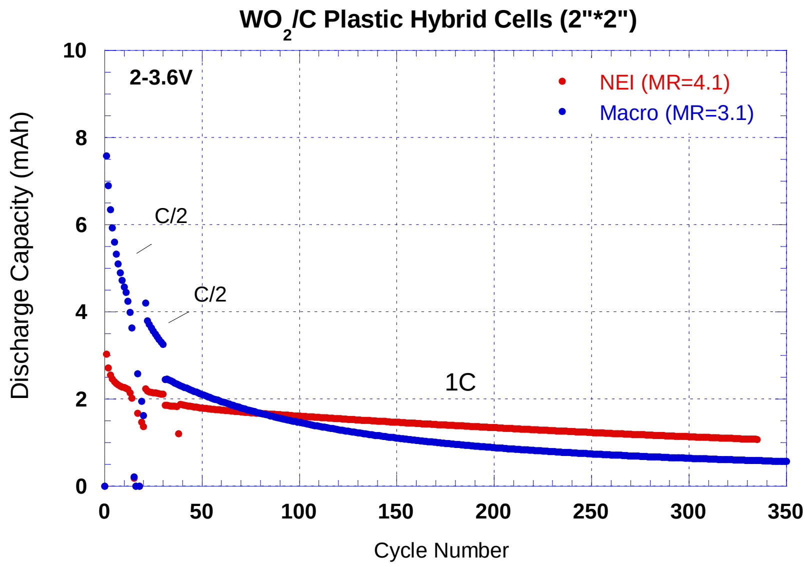
Nano-WO_2 Crystallinity and Discharge Voltage Range



- **nano – WO_2 remains crystalline over 0.7 – 2 .0V range**

Prototype Hybrid Cells





- Better cyclability with nano – WO_2
- Average voltage of prototype cells: > 3.0 V

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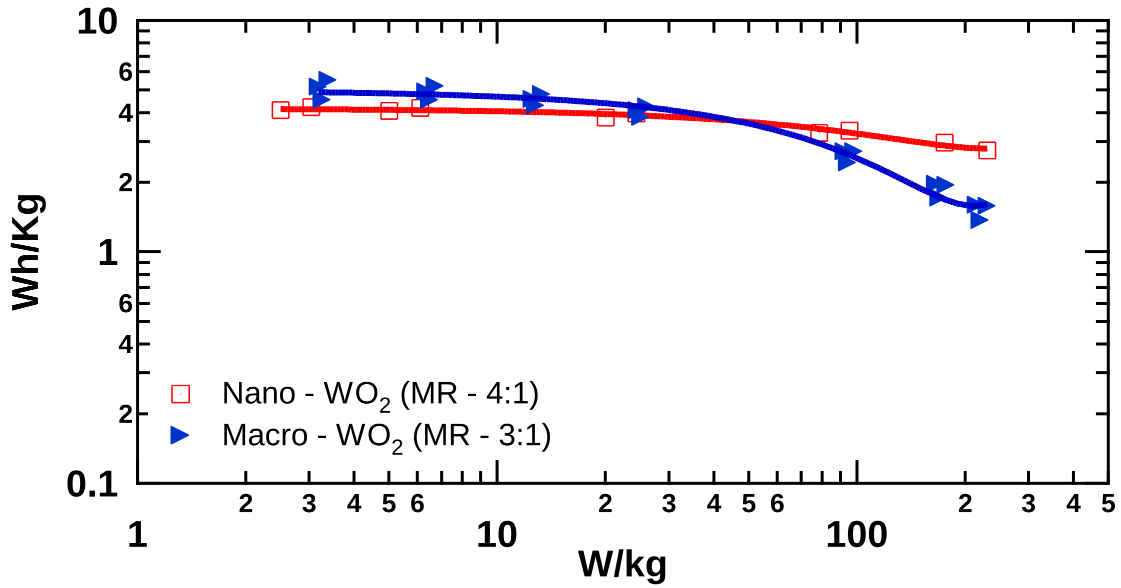
Rate Performance of WO_2/C Cells



- **Good rate performance of nano – WO_2/C cells**
- **Poor 1st cycle efficiency**

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Summary

- Nanomaterials offer tremendous potential in improving the properties (e.g., rate capability, capacity fade) of Li-based energy storage devices
- Composition, microstructure and feature size are important
- Scalable and cost effective processes are the keys to successful market entry
- Reducing crystallite size of WO_2 anodes improves their rate capability

Acknowledgments

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