Metal Oxide Nanoparticles for Improved Electrochromic and Lithium-Ion Battery Technologies

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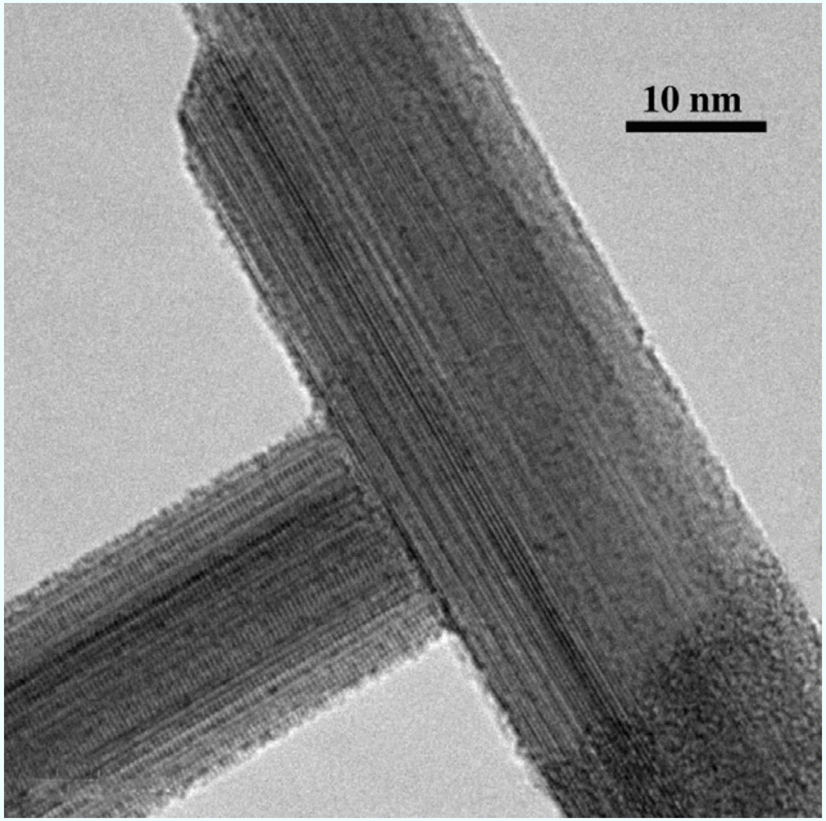
Supported by: NREL's Laboratory Directed Research and Development Program

Metal-oxide Nanorods and Particles



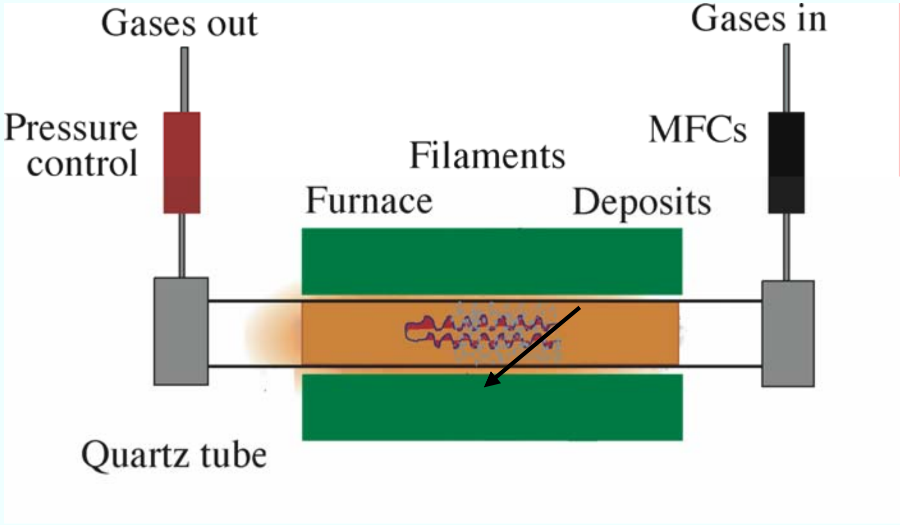
Crystalline WO_3 Nanorods

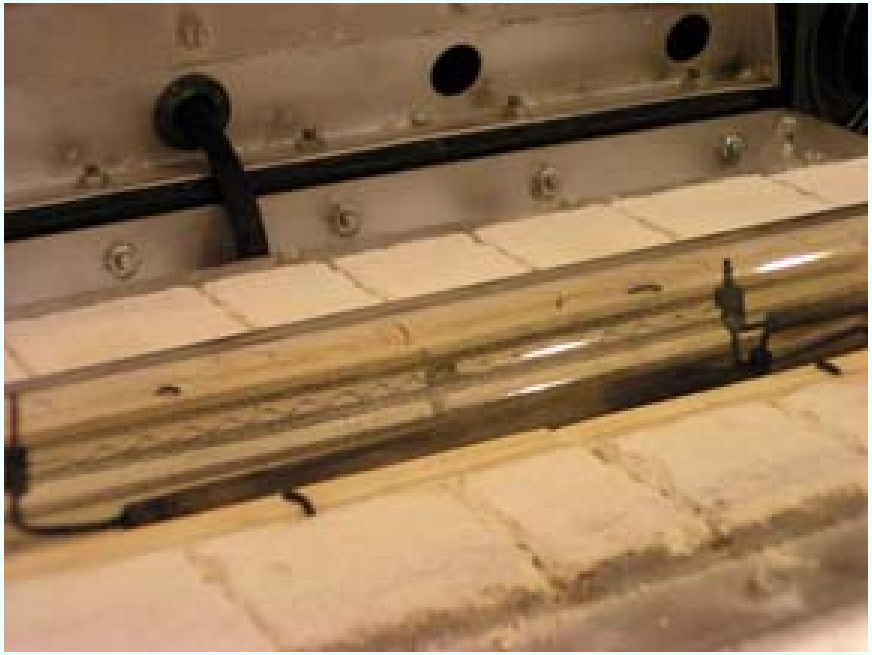
- Metal-oxides have a host of applications including electrochromic (EC) windows and high-energy-density Li^+ ion batteries.
- Both rely on Li^+ and H^+ insertion.
- Kinetics of the insertion reaction is limited by solid-state diffusion of the ions.
- Time constant determined by diffusion coefficient (crystal structure) and length of diffusion path (microstructure).

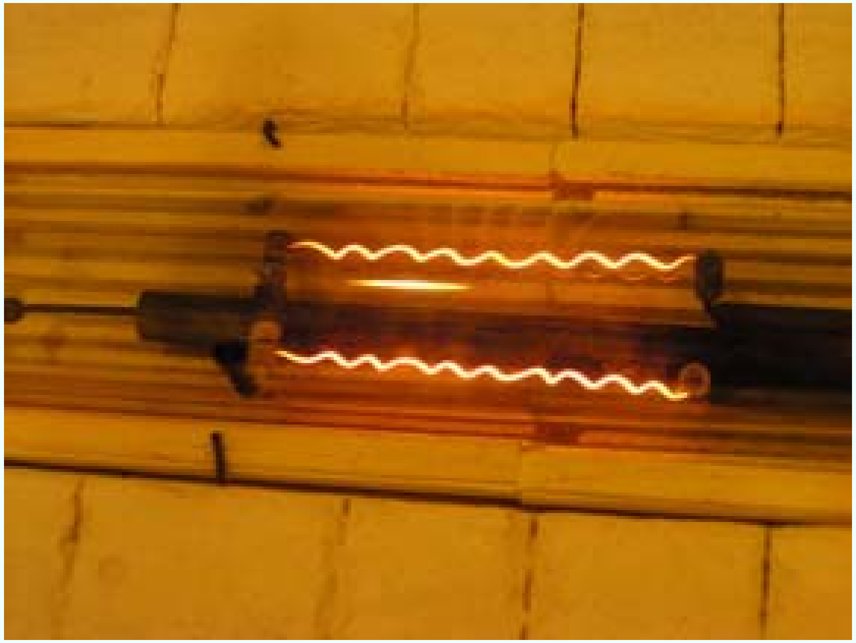
$$l \propto \sqrt{Dt}$$

- Designing a crystalline nanoparticle with a small radius is key to a material with fast insertion kinetics and superior overall performance.

Hot-Wire Chemical Vapor Deposition (HWCVD) for the Synthesis of Metal Oxide Nanoparticles





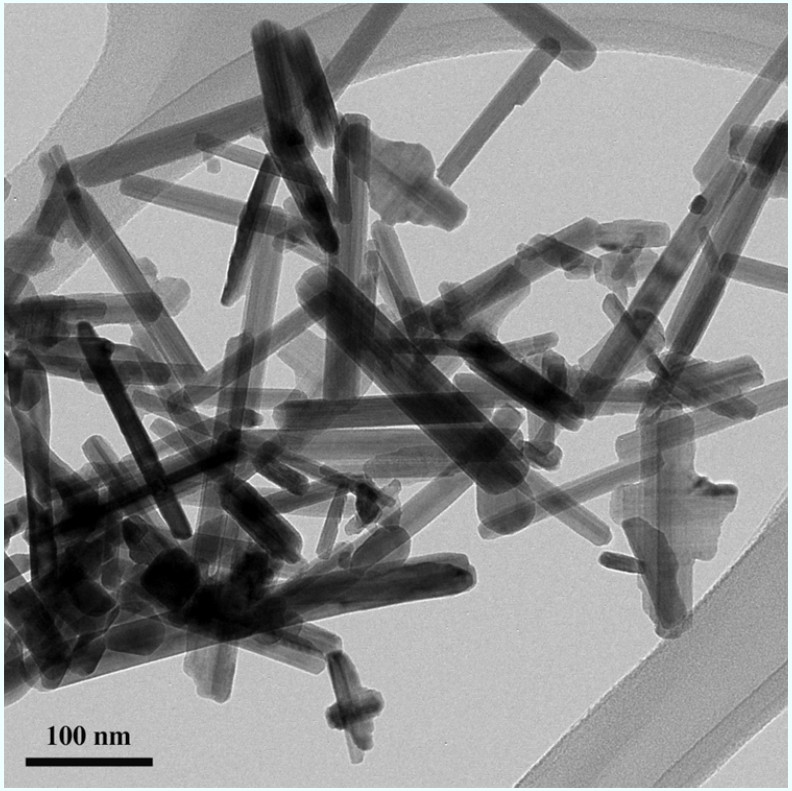


- **This technique has also been employed for the production of carbon nanotubes.**

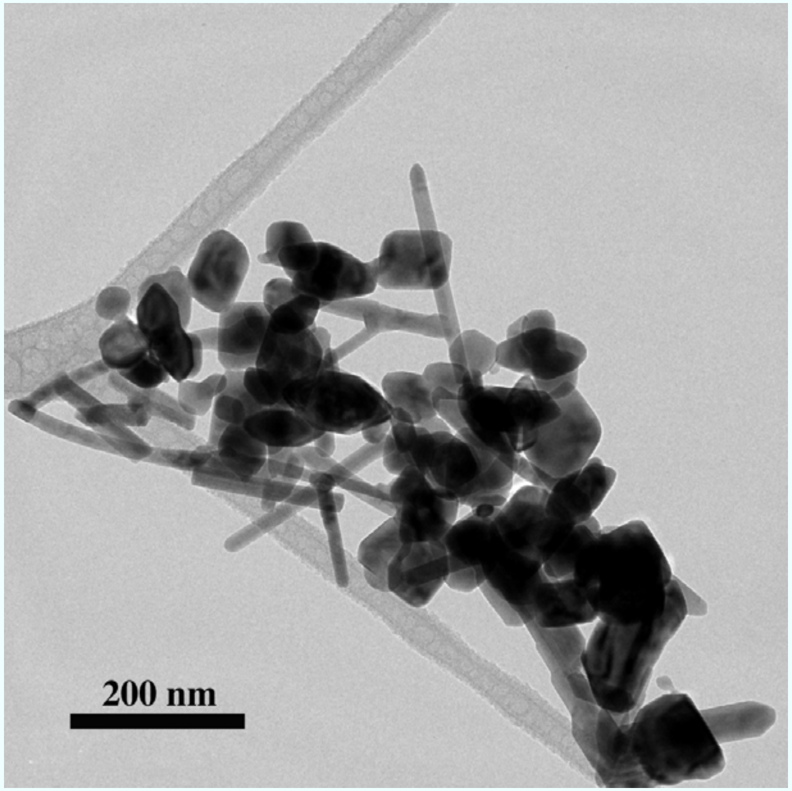
SWNTs: **A.C. Dillon, et al Appl. Phys. Lett. 81 (2002) 4061 and** ***MWNTs:*** **A.C. Dillon, et al. NanoLetters 3(2003) 1425.**

HWCVD Production of Tungsten-oxide Nanostructures

300 ^{o}C



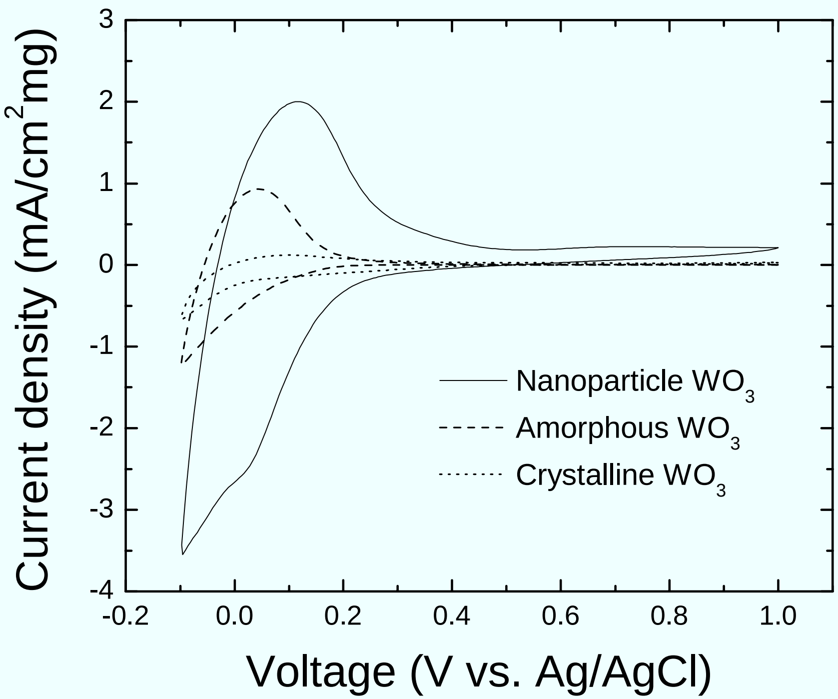
600 ^{o}C

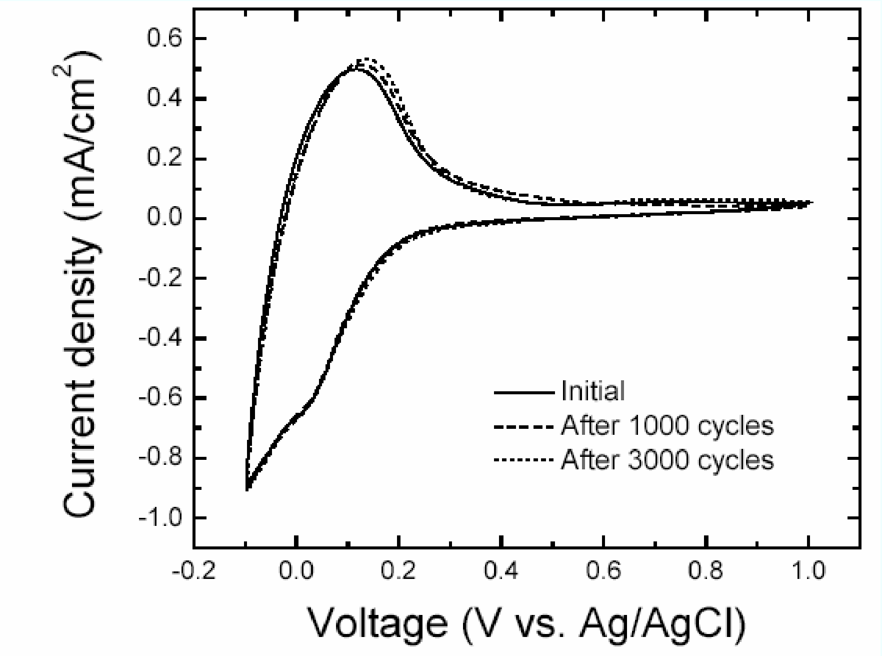


Synthesis at 150 torr 4% O_2 in Ar, filament temperature ~ 2000 ˚C. Nanoparticles are observed at high density with the furnace at either 300 or 600 ˚C. Slightly larger particles observed at higher temperature.

A.H. Mahan, et al., *Chem. Phys. Lett.* 413 (2005) 88.

Electrochromic performance comparison



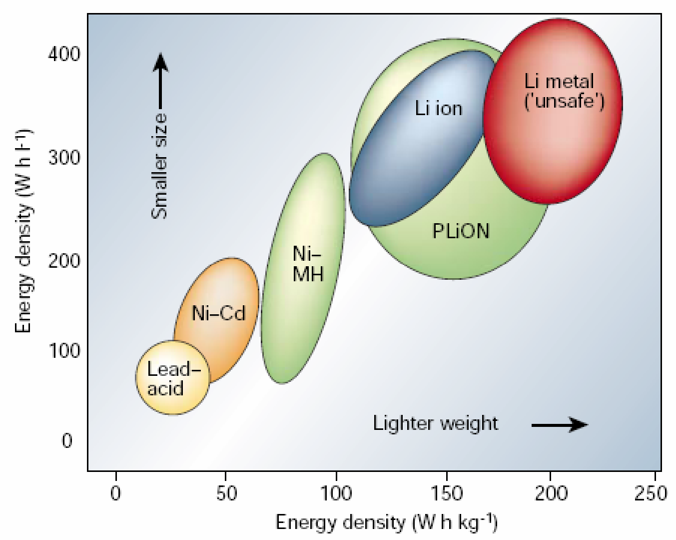


Higher charge insertion than the state-of-the-art amorphous films with similar coloration efficiency

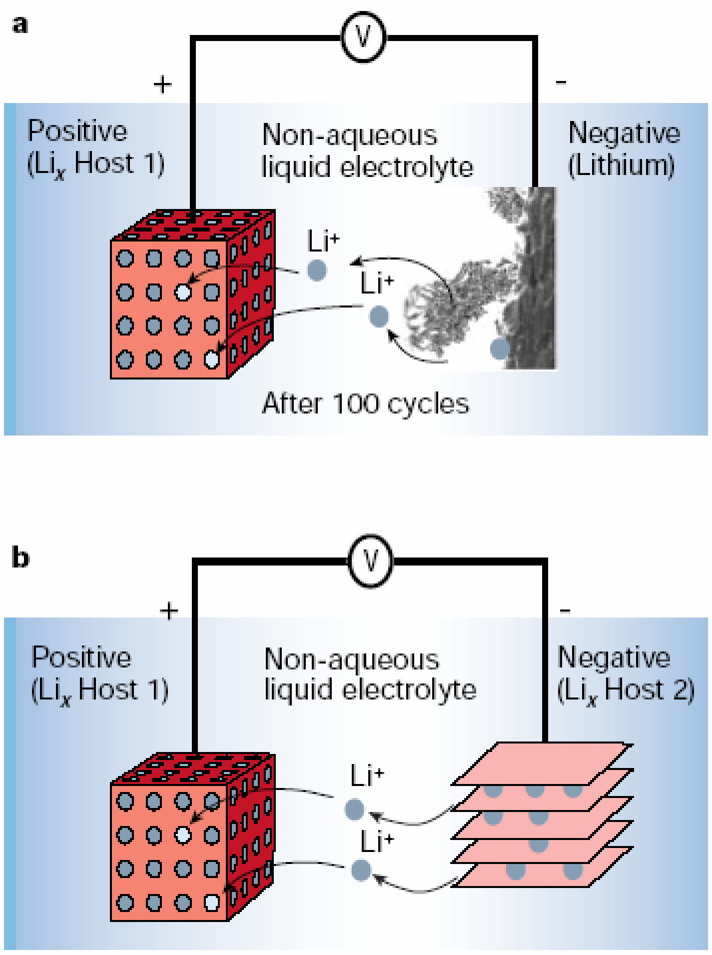
As anticipated these nanoparticle crystalline films are much more stable than state-of-the-art amorphous films!

S.-H. Lee, et al. Advanced Materials 18, 763 (2006)

Comparison of the different battery technologies

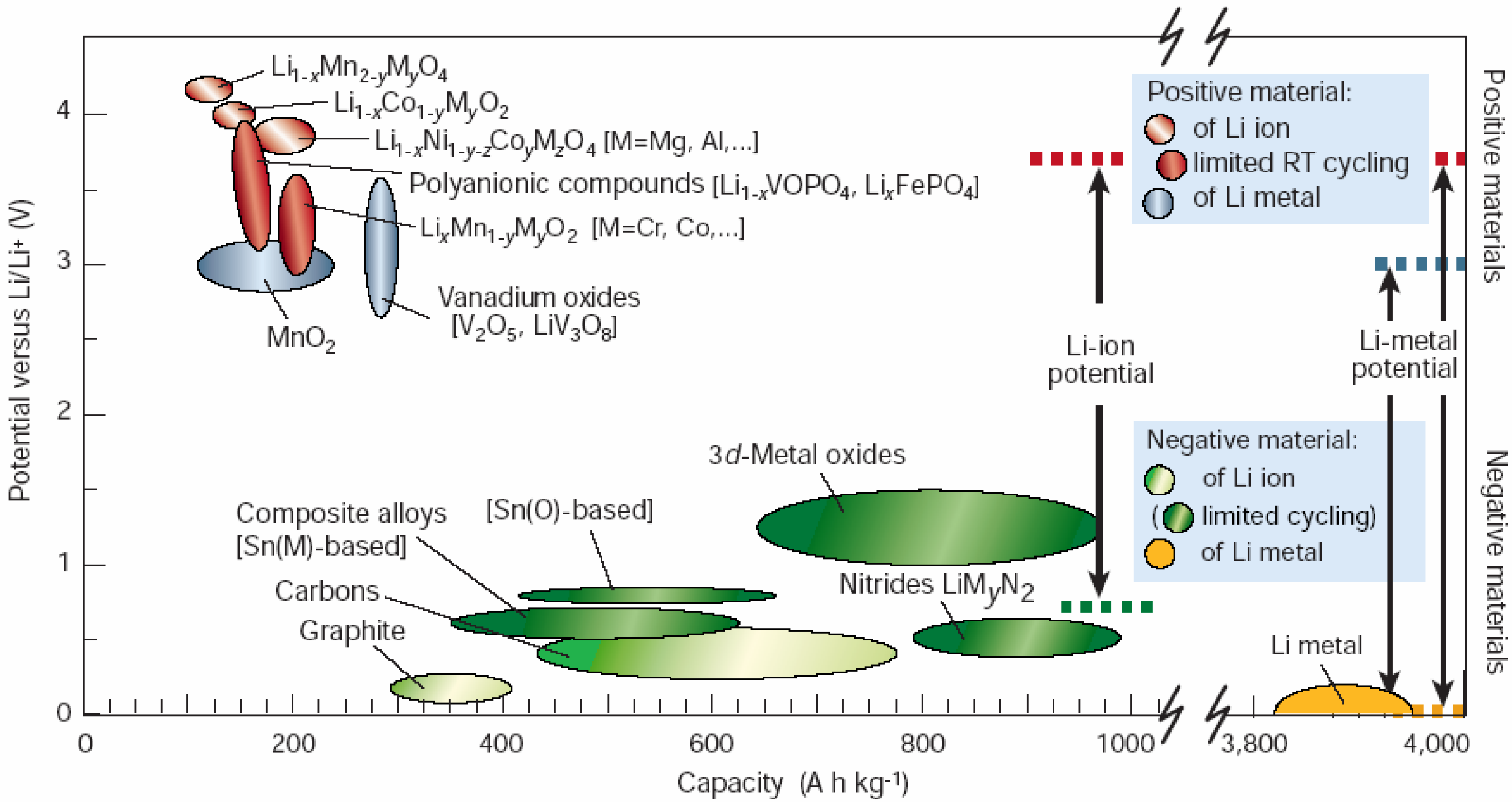


Operating Principles



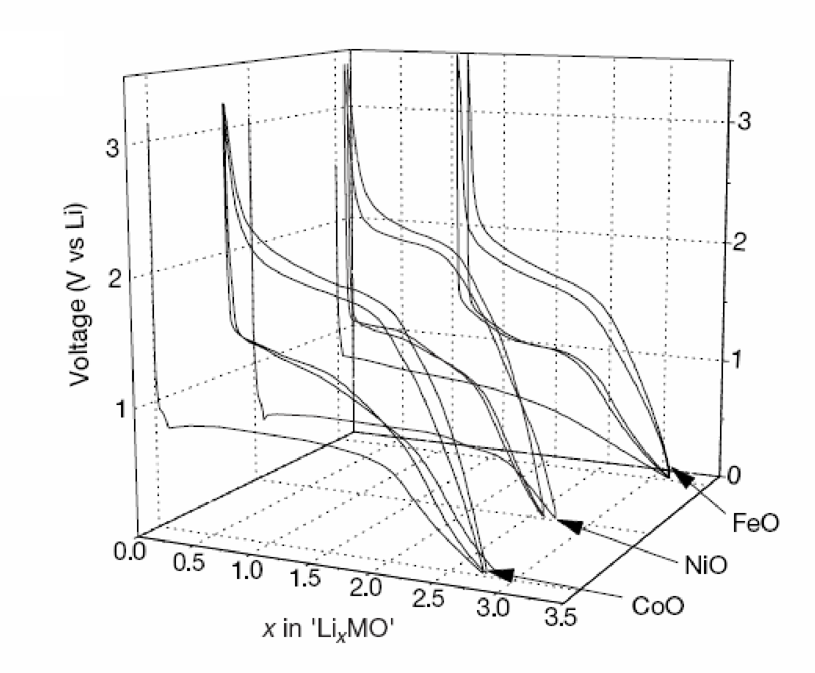
After J.-M. Tarascon & M. Armand, Nature 414, 359 (2001)

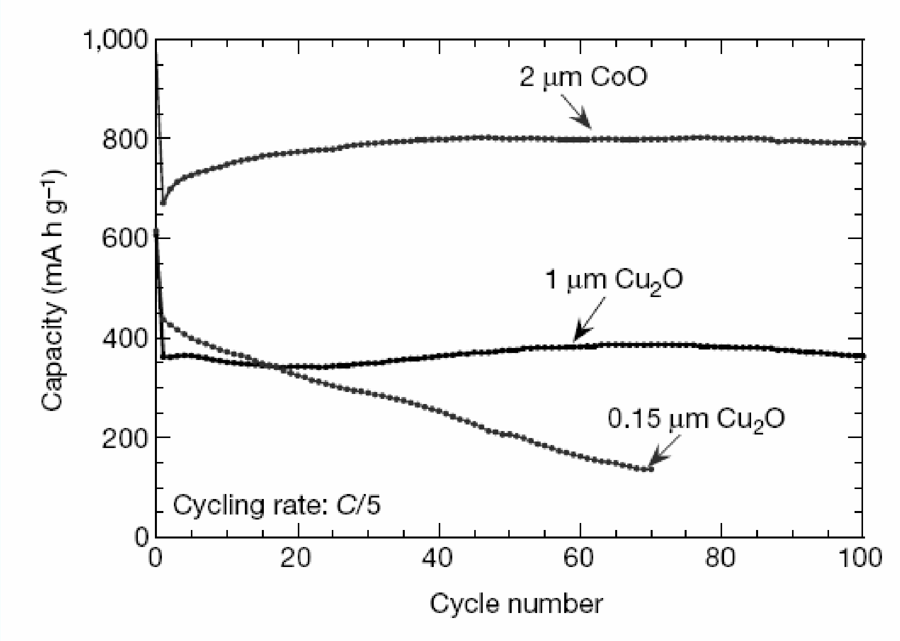
Voltage versus Capacity for Positive and Negative Electrode Materials



After J.-M. Tarascon & M. Armand, Nature 414, 359 (2001)

Transition-metal Oxides as Negative-Electrode Materials

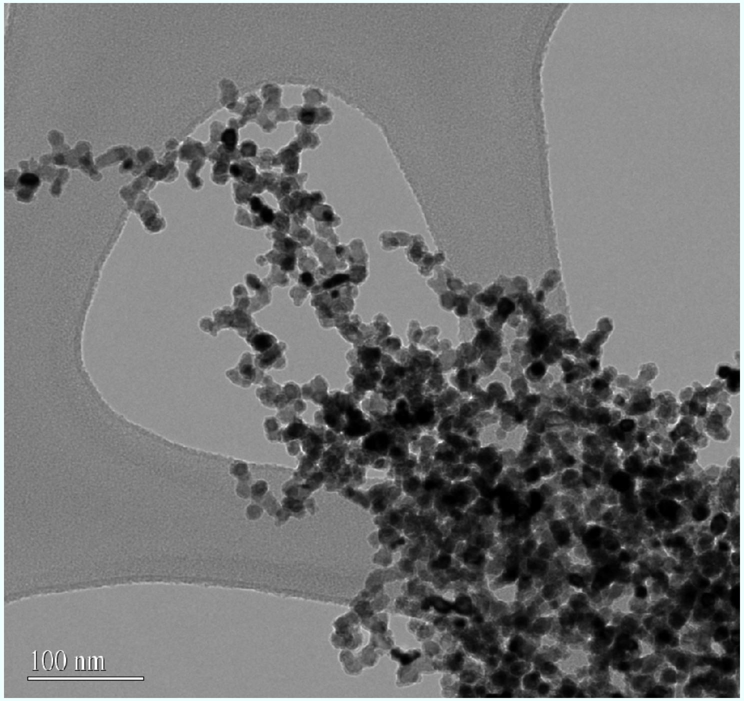




$$\begin{aligned} CoO + 2Li^+ + 2e^- &\rightleftarrows Li_2O + Co \\ 2Li &\rightleftarrows 2Li^+ + 2e^- \\ \hline CoO + 2Li &\underset{2}{\overset{1}{\rightleftarrows}} Li_2O + Co \end{aligned}$$

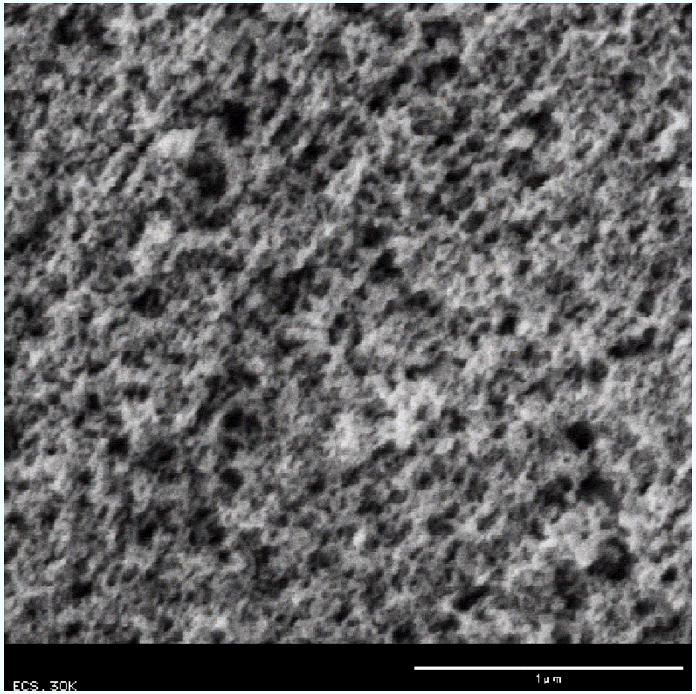
After P. Poizot et al., Nature 407, 496 (2000)

Electrophoresis for Creating MoO_x Nanostructured Anodes



Starting Material

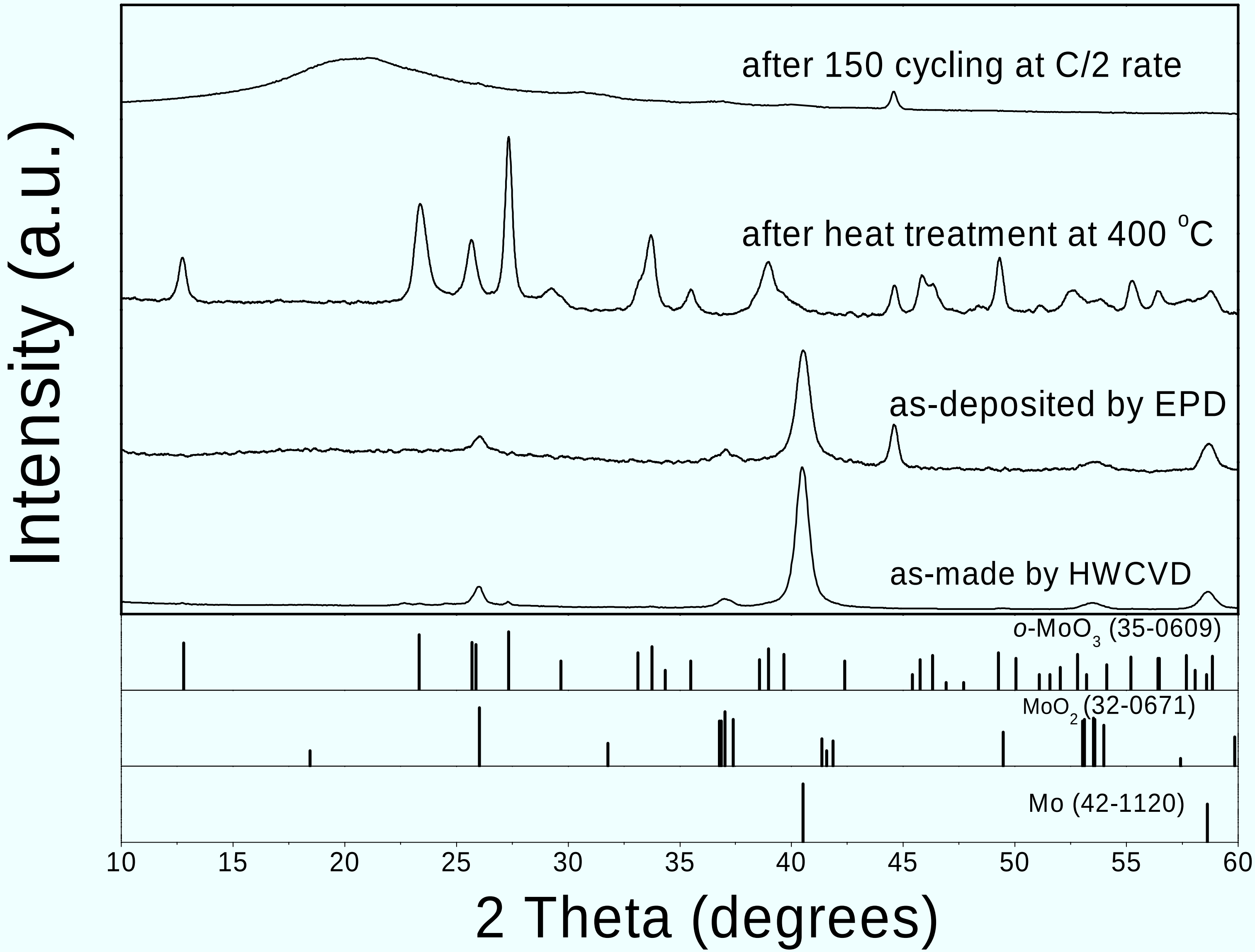
TEM image of nanospheroids synthesized in a static argon and 4 % oxygen at a pressure of 75 Torr, furnace being maintained at 300 ^{O}C.



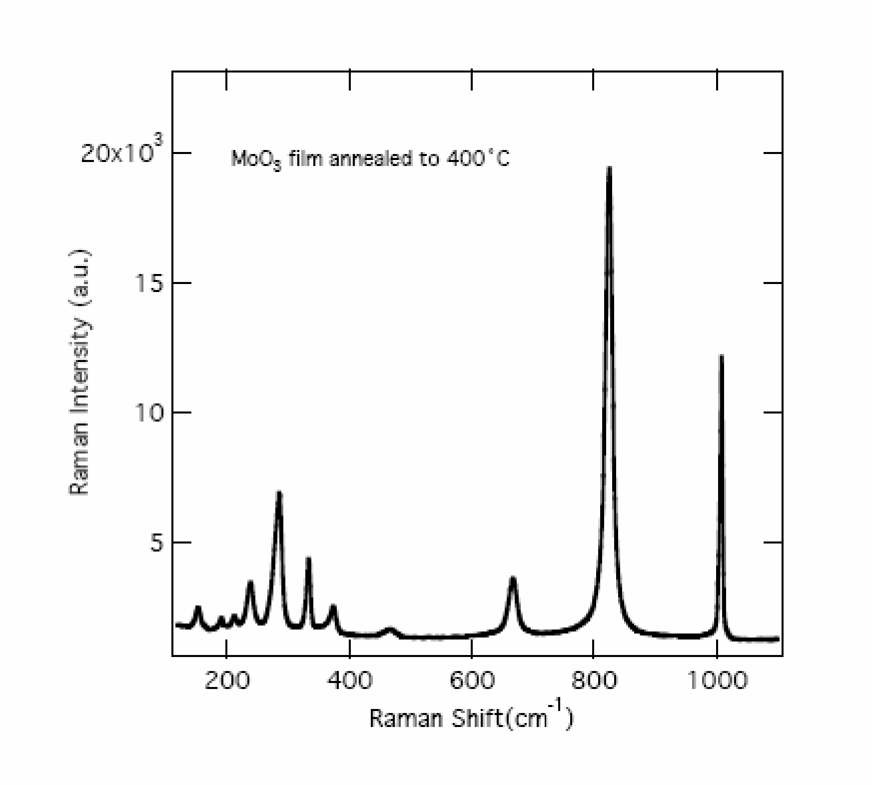
Porous High Surface Area Anode

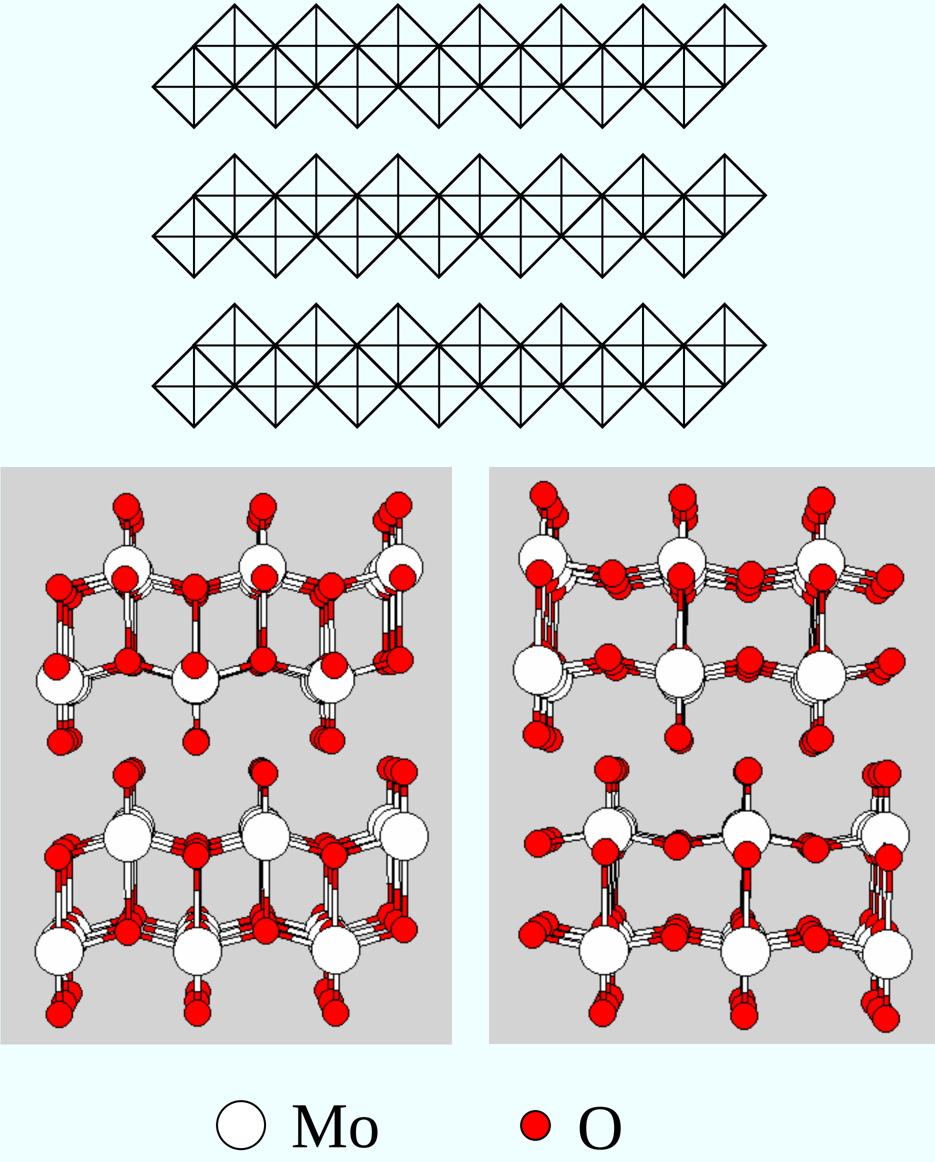
SEM image of the film electrode synthesized using electrophoretic deposition technique.

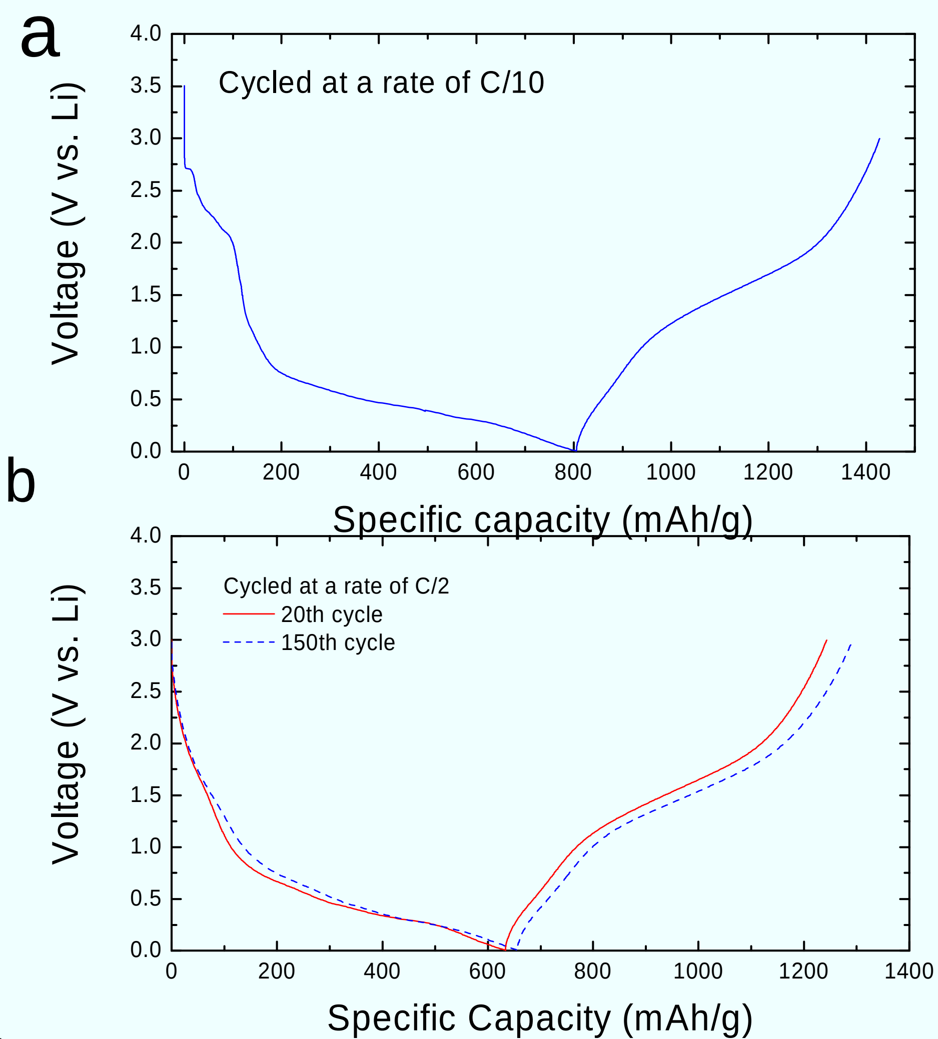
XRD analysis of MoO_x Nanoparticles



Raman Spectroscopy of as-synthesized nanostructures





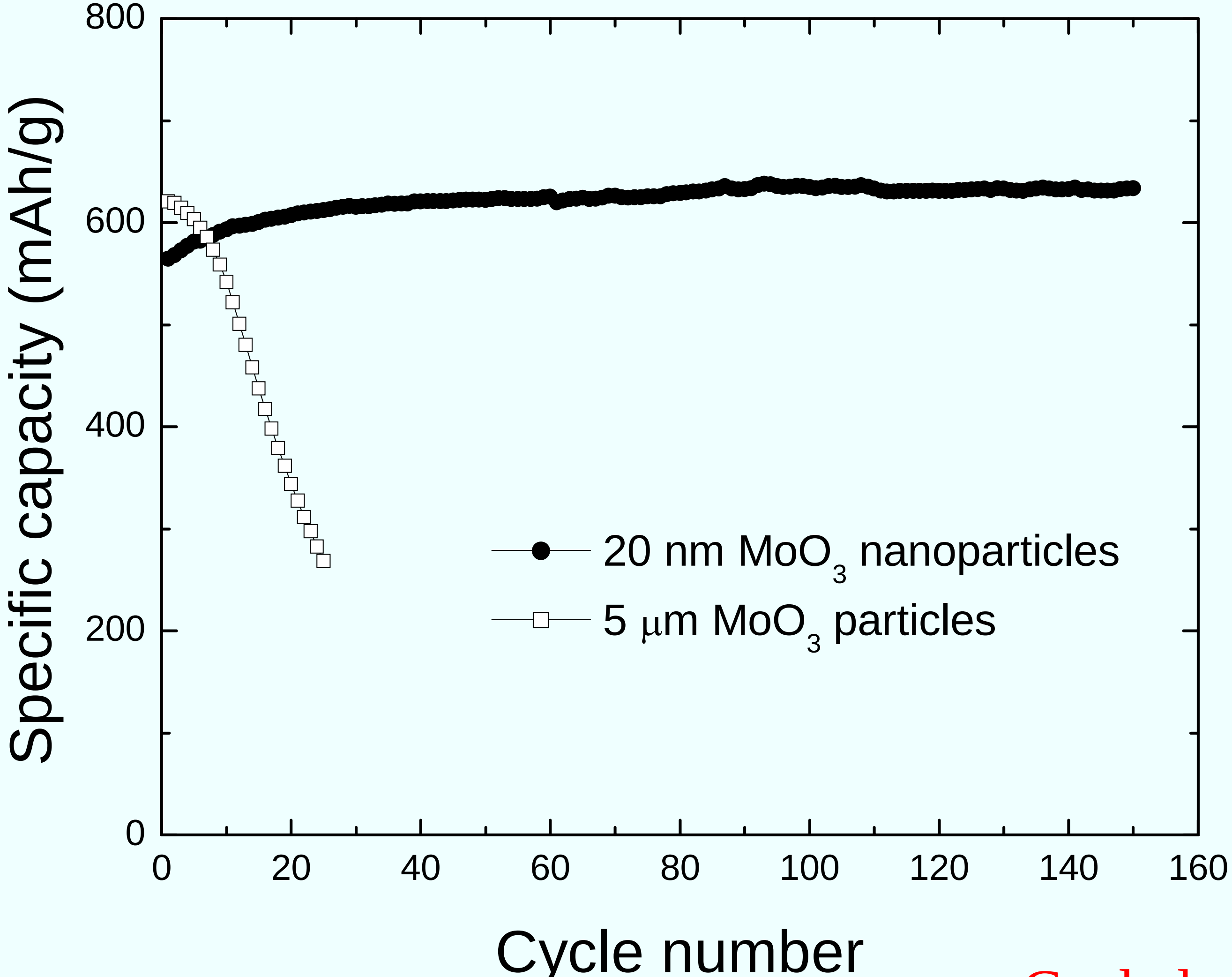


A negative electrode fabricated with MoO_3 crystalline nanoparticles showed a reversible capacity of approximately 630 mAh/g.

The state-of-the-art graphite anodes employed in commercial lithium batteries have a reversible capacity of approximately 350 mAh/g.

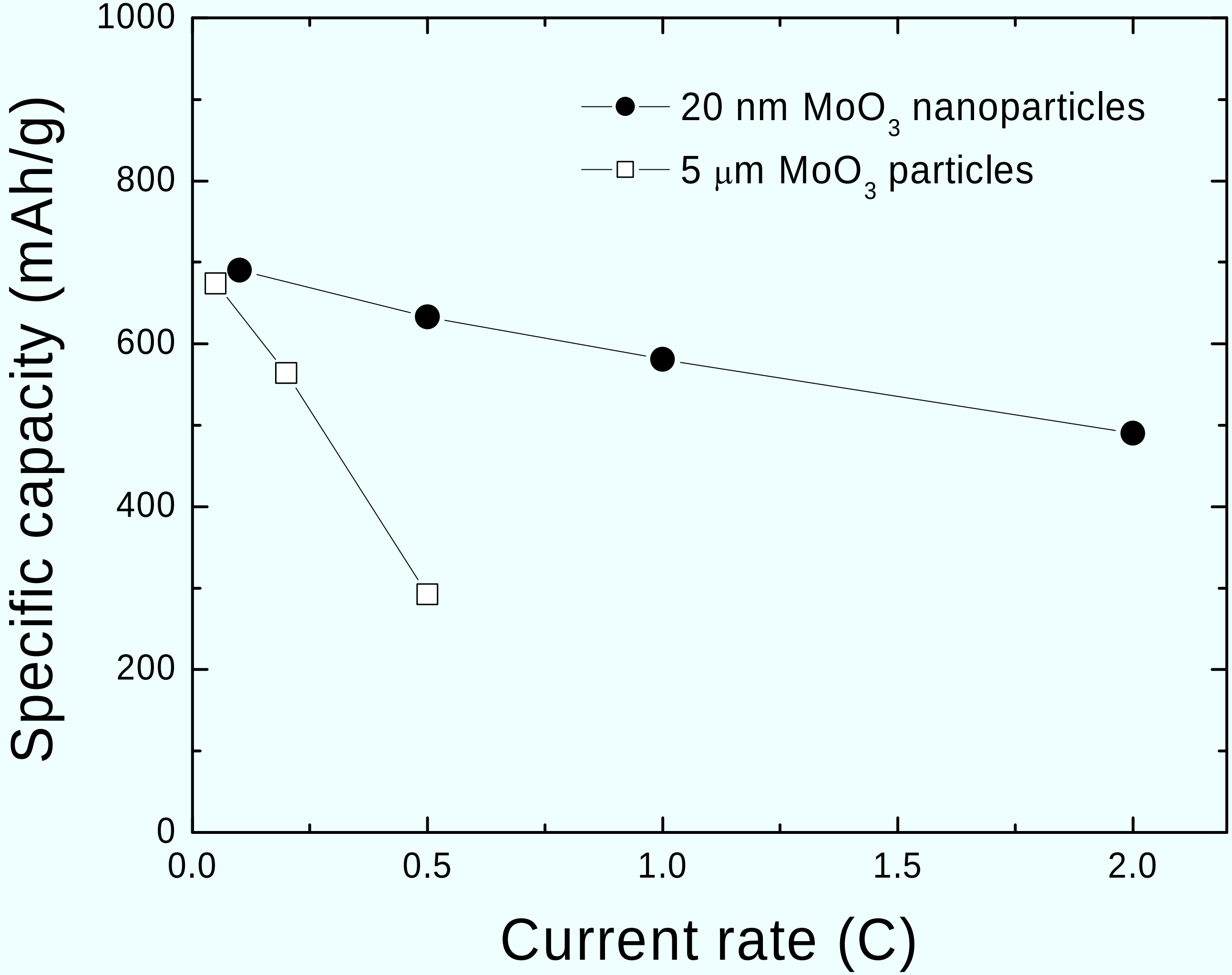
C-rate is defined as one full discharge in 1 hour.

Cycling Stability of MoO_3 Electrodes



Cycled at C/2 rate

Excellent Rate Capability of MoO_3 Nanoparticles



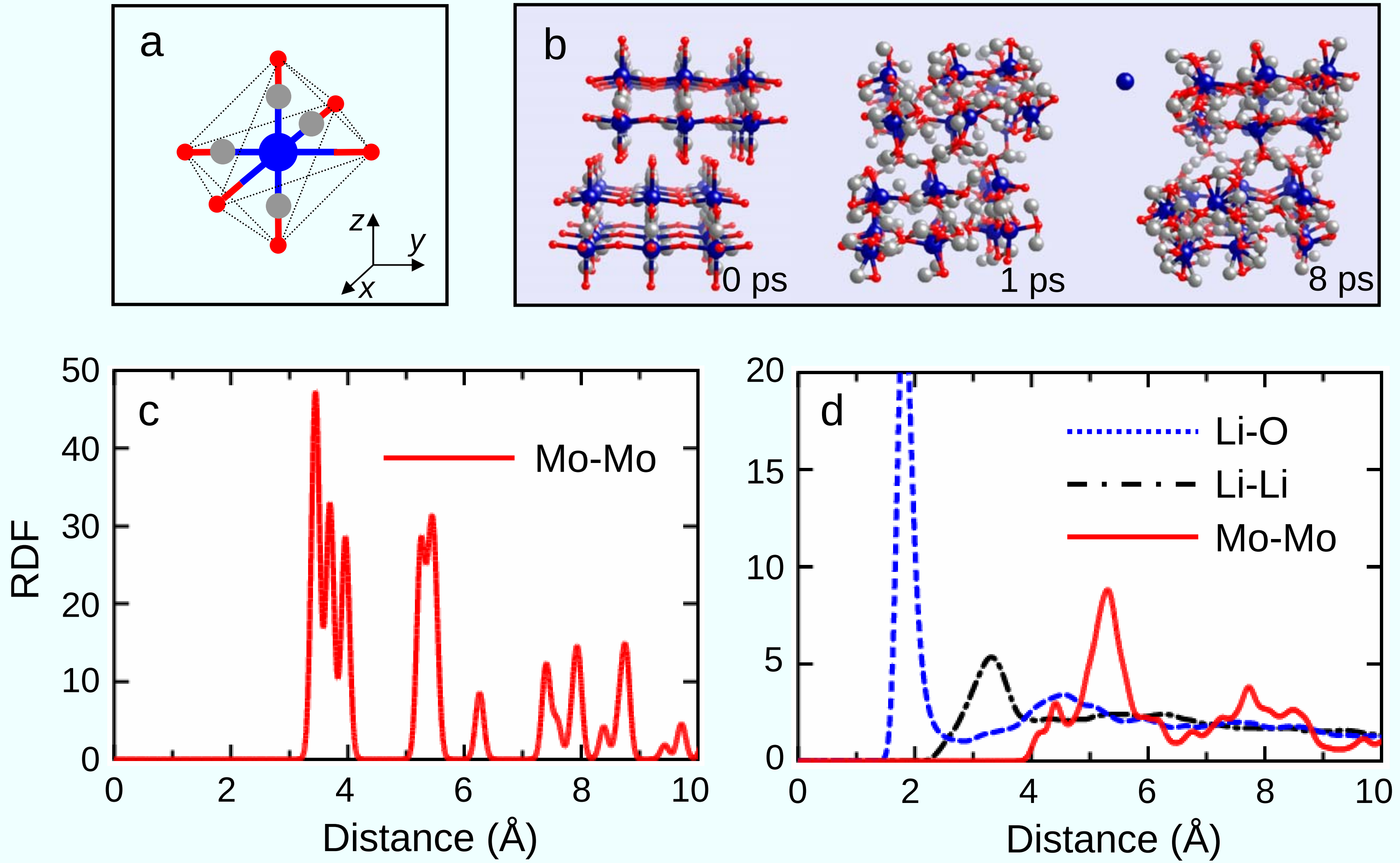
Possible Mechanism…

$$MoO_3 + 4.3(Li^+ + e^-) \rightarrow 0.5(Li_2O) + Li_{3.3}MoO_{2.5}$$

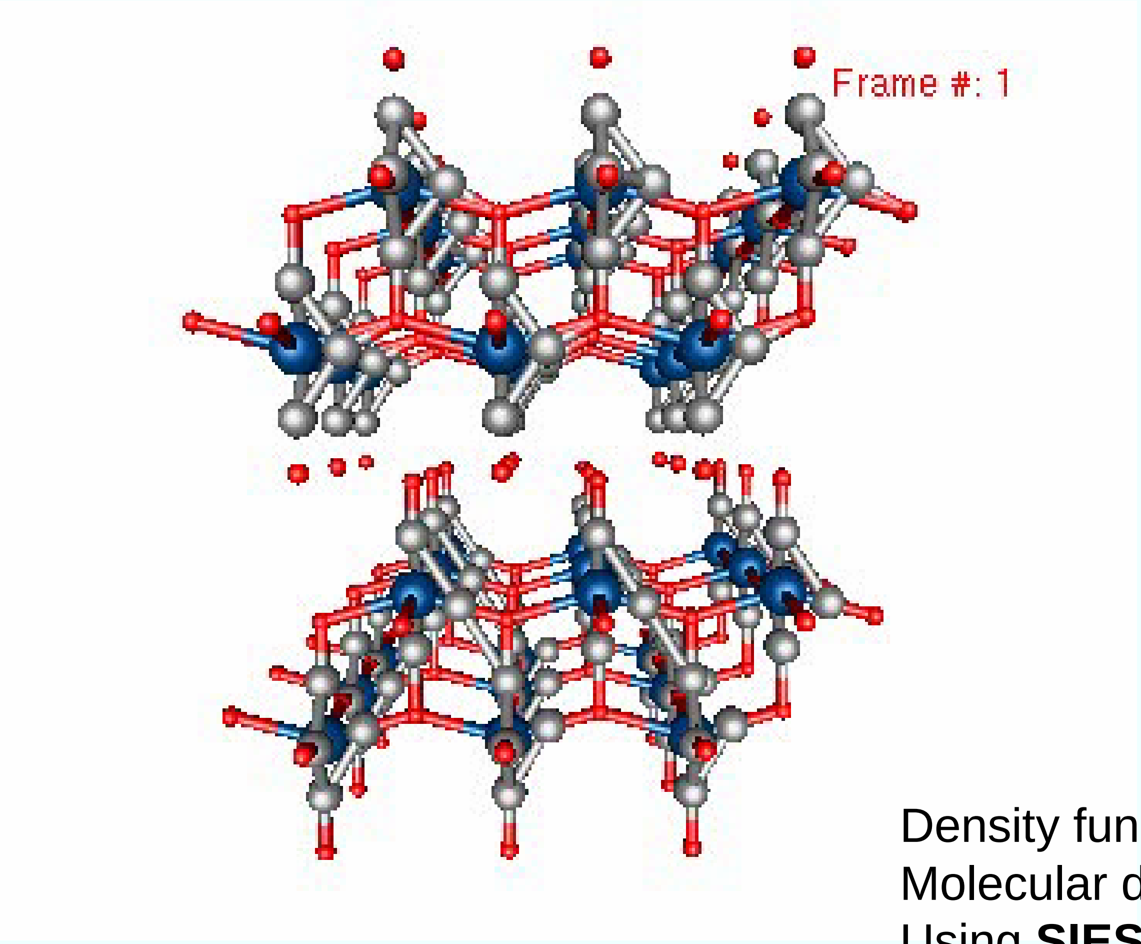
Why do MoO_3 nanoparticle electrodes exhibit a Stable Cycling?

- Small particle size to begin with
- Plenty of pores can accommodate volume changes during cycling

Li-intercalated MoO_3 nanoparticle



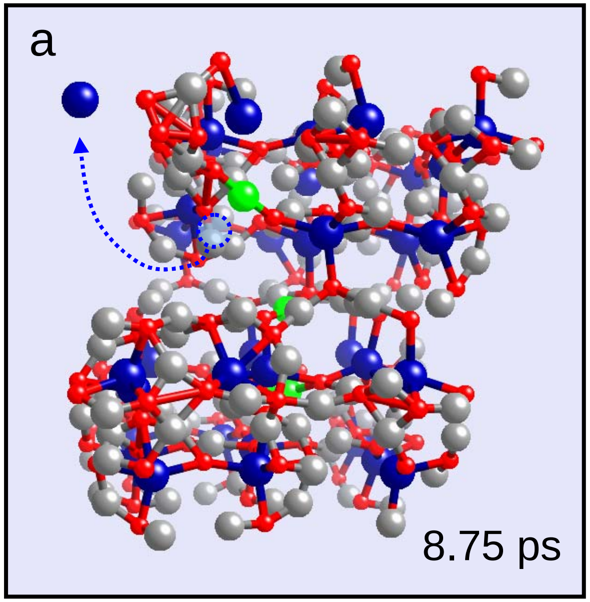
MoO_3 Amorphization (DFT-MD) by Lithium Insertion



1 frame = 10 femto second

Density functional theory
Molecular dynamics
Using **SIESTA**
3 pico seconds @ 400 K

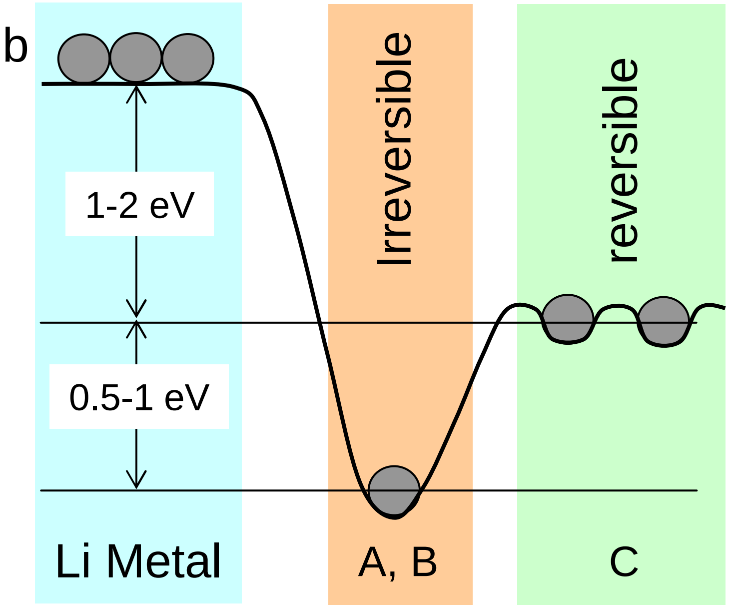
First-principles energetics of the Li intercalated MoO_3 nanoparticle



A: –0.4 eV

B: –0.6 eV

C: 0.0 eV



Summary

- Hot-wire chemical vapor deposition has been employed for the economical controlled growth of metal-oxide nanostructures at high density.
- The tungsten oxide nanoparticle films exhibit excellent cycling stability in 1 M sulfuric acid in which amorphous tungsten oxide films suffer high dissolution problems.
- Molybdenum-oxide nanoparticles have been employed as the negative electrode in Li^+ batteries. The dramatically improved capacity and rate capability could possibly make these materials suitable for the next generation of hybrid electric vehicles.
- Preliminary DFT-MD calculation clearly illustrates an initial irreversible amorphization process and reveals a mechanism for the unanticipated reversible capacity in the MoO_3 nanoparticle anode.

R. Deshpande, P.A. Parilla, K.M. Jones, E. Whitney, Y.H. Kim, S. Zhang, A.H. Mahan, and A.C. Dillon