MATERIALS SCIENCE AND MATERIALS CHEMISTRY CHALLENGES FOR LARGE SCALE ELECTROCHEMICAL ENERGY STORAGE

JUN LIU

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SNL team:
James A. Voigt, John D. Boyes, Justine E. Johannes *and* Marjorie Tatro

Supported by Transformational Materials Science Initiative (PNNL), by Office of Electricity (DOE), ARPA-E (DOE)

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Summary of New Scientific Opportunities in Related to Storage

Low-Cost Materials & Chemistry

Beyond Lithium
Rechargeable Air Systems
Surfaces and Reactions

Minimize Need for Storage

Better Modeling, Simulation and Control Algorithms

Test-bed Capabilities

From Lab-scale to Power Lines

System Level Integration

Across traditional boundaries,
ex. Vehicle to Grid

From Mark Johnson, ARPA-E

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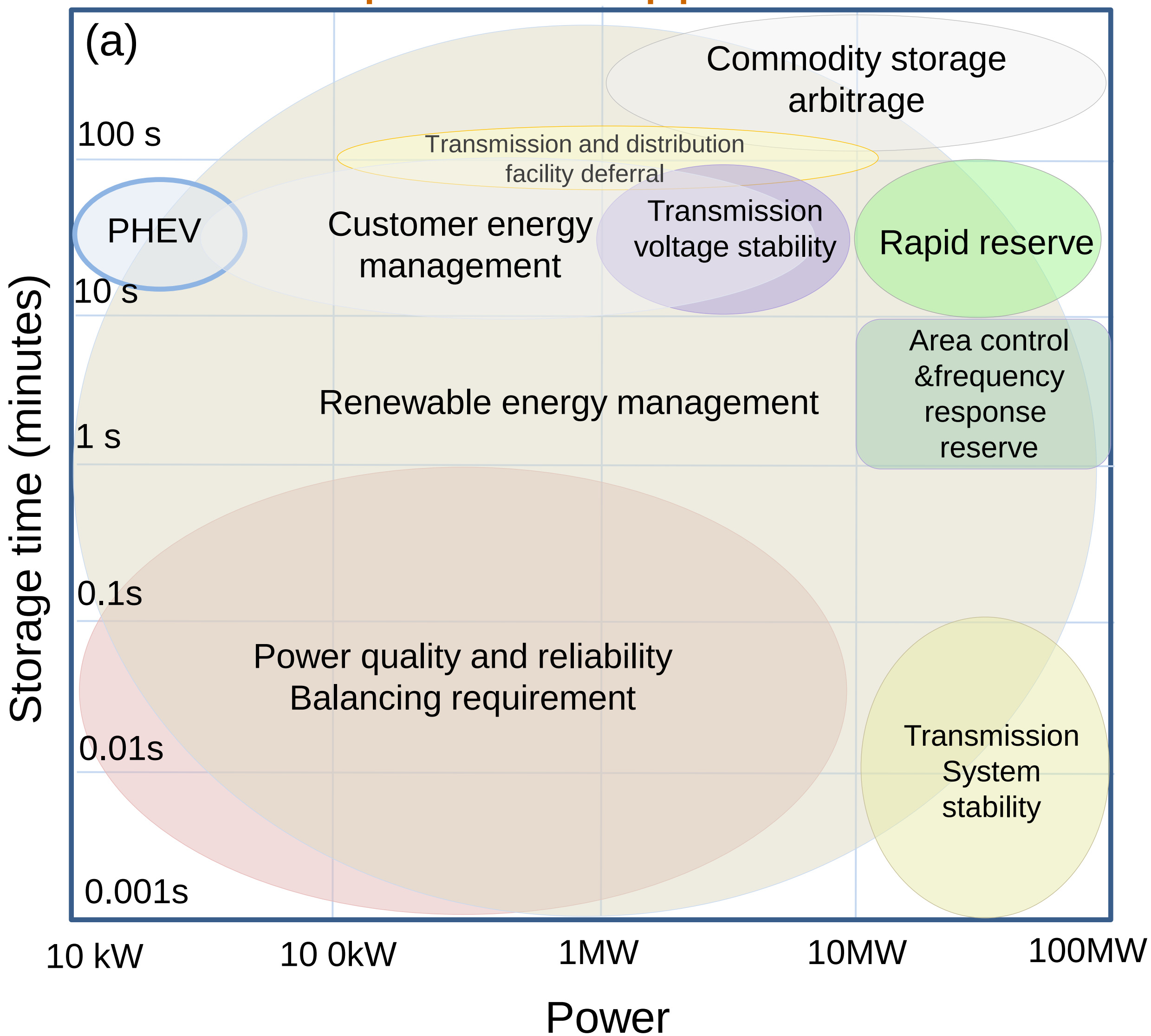
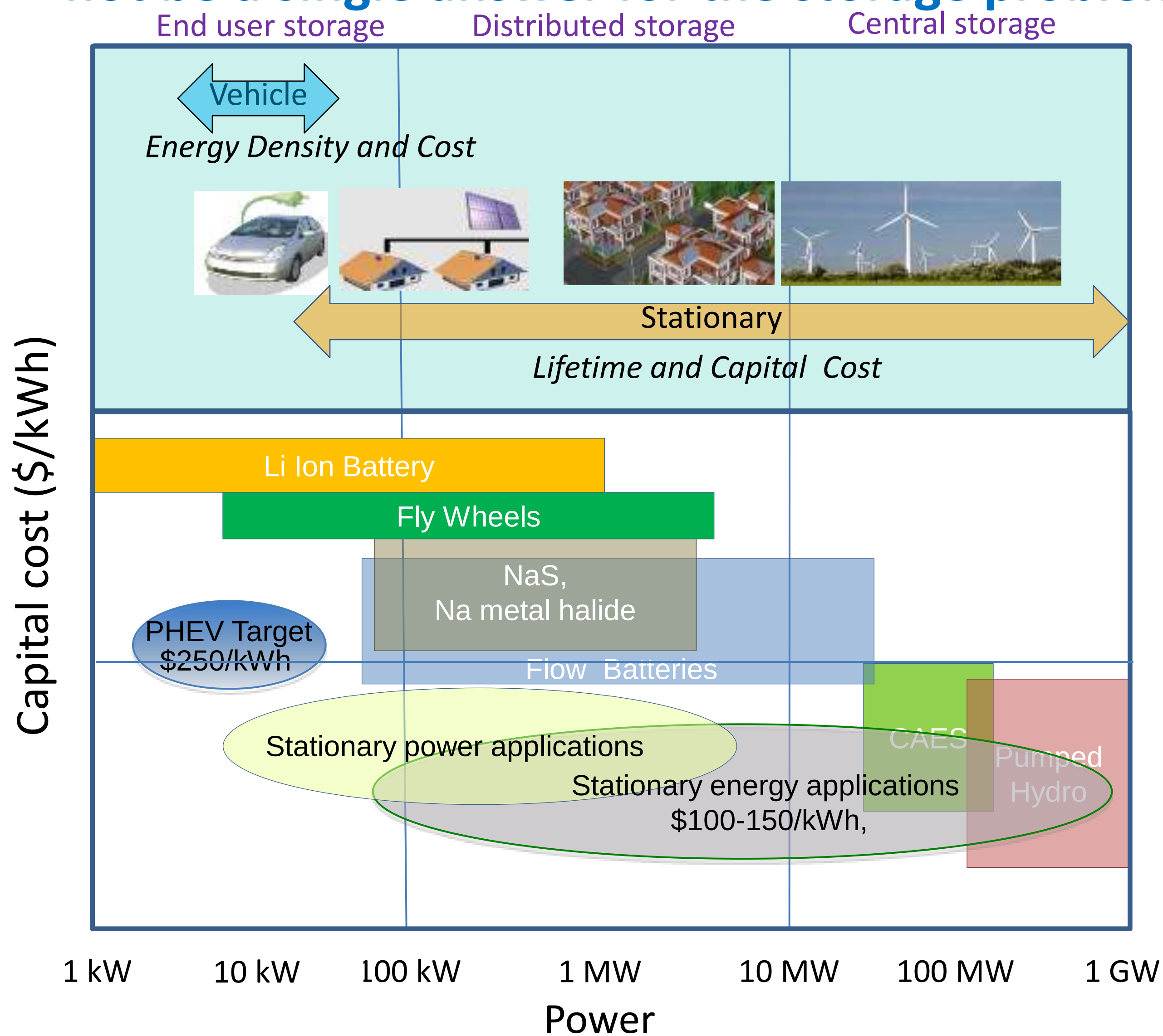
Stationary storage applications are very wide compared to transportation applications



P. Butler, J. L. Miller, P. A. Taylor, *Energy Storage Opportunities Analysis Phase II Final Report A Study for the DOE Energy Storage Systems Program, Sandia National* Laboratories, Albuquerque, New Mexico 87185 and Livermore, California 94550,**2002.**

Different technologies will have different applications. There will not be a single answer for the storage problem.



Jun Liu, Zhenguo Yang,* John P. Lemmon, Carl Imhoff, Michael Kintner-Meyer, Gordon L. Graff, Liyu Li, Jianzhi Hu, Yuliang Cao, Gordon Xia, Birgit Schwenzer, Viswanathan, Vilayanur V, Suresh Baskaran, Vincent Sprenkle, James A. Voigt, John D. Boyes, Justine E. Johannes and Marjorie Tatro,* Materials Science and Materials Chemistry for Large-Scale Electrochemical Energy Storage for the Electrical Grid, submitted

Analysis Results for Pacific Northwest Region

Questions:

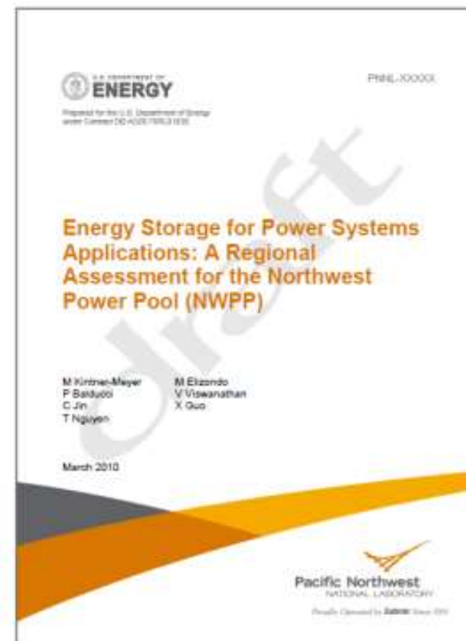
a) how much total load balancing requirements are necessary to accommodate an assumed expansion of wind energy resources of 14.4 GW in the Northwest Power Pool (NWPP) in 2019?

b) what are the most cost effective technological solutions for addressing load balancing requirements? and

c) can energy storage be cost-effectively employed for arbitrage opportunities?

Preliminary answers:

a) Balancing requirements are estimated to be about 4 GW;
b) Current practice is not the least expensive option;
c) Electrochemical storage can be cost competitive;
d) Possible solutions:
NaS, NaS+DR, NaS+PH, Li-ion+DR, NaS+PH+DR
e) Arbitrage not economical in the near future (by 2019).



ENERGY

PNNL-XXXXX

Energy Storage for Power Systems Applications: A Regional Assessment for the Northwest Power Pool (NWPP)

M Kintner-Meyer
P Balducci
C Jin
T Nguyen

M Elizondo
V Viswanathan
X Guo

March 2010

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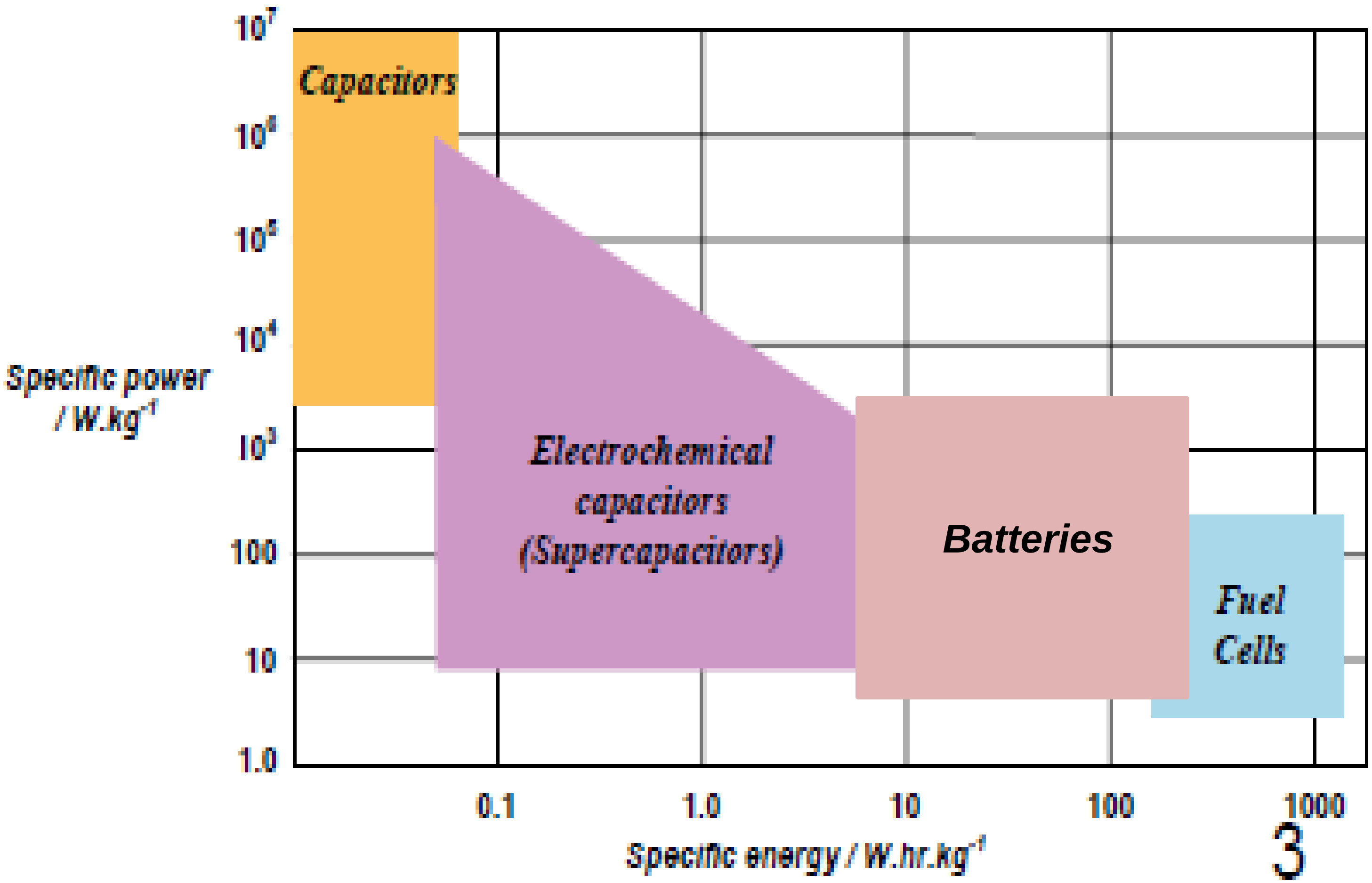
Three Gorge Dam:
$25B investment
18GW capacity

Different methods for electrochemical energy storage



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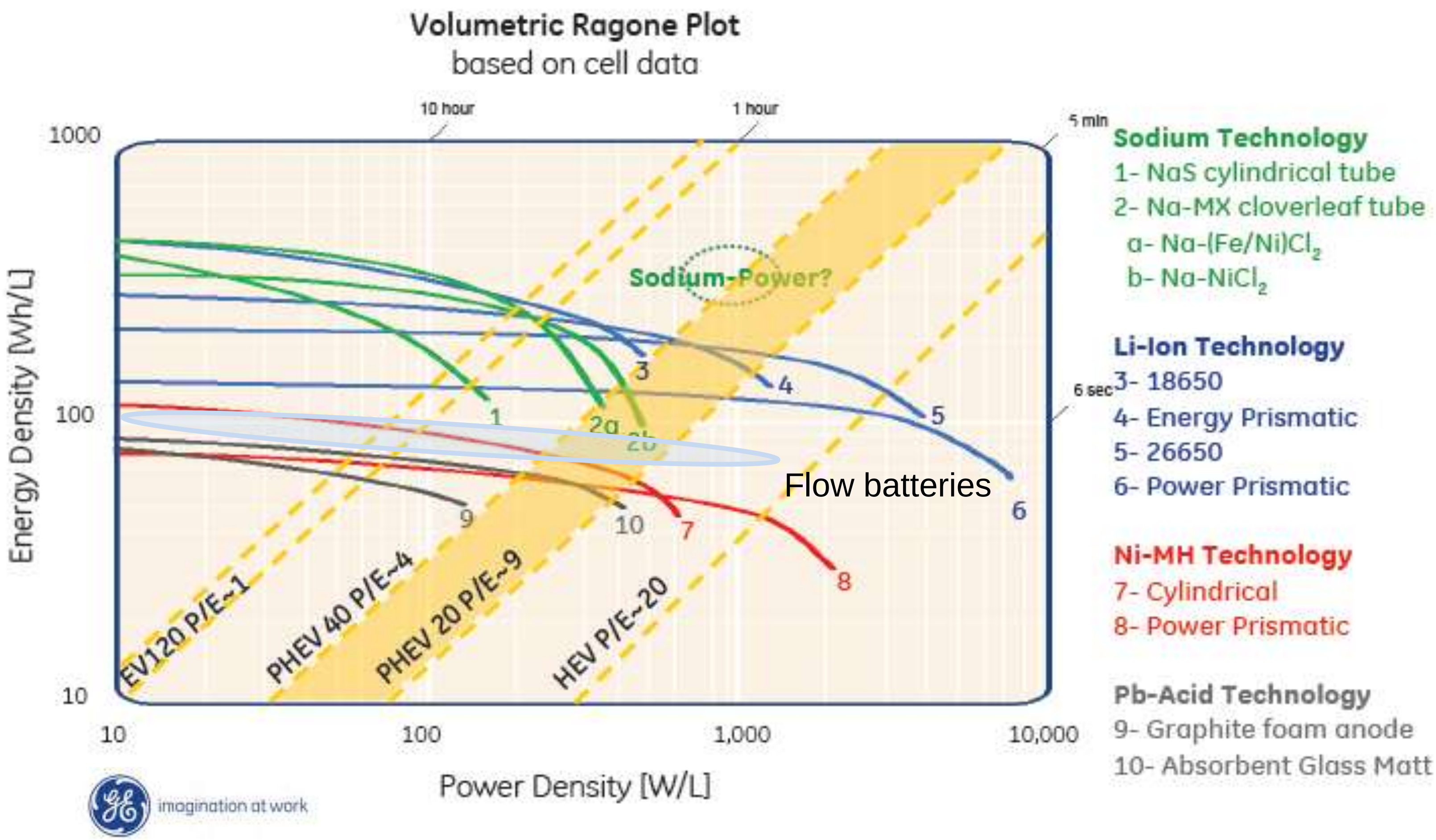
Four major battery technologies: Li, Na, Pb-acid and flow batteries



Mohamed Rahmane and Chuck Iacovangelo

GE Global Research, Niskayuna, NY

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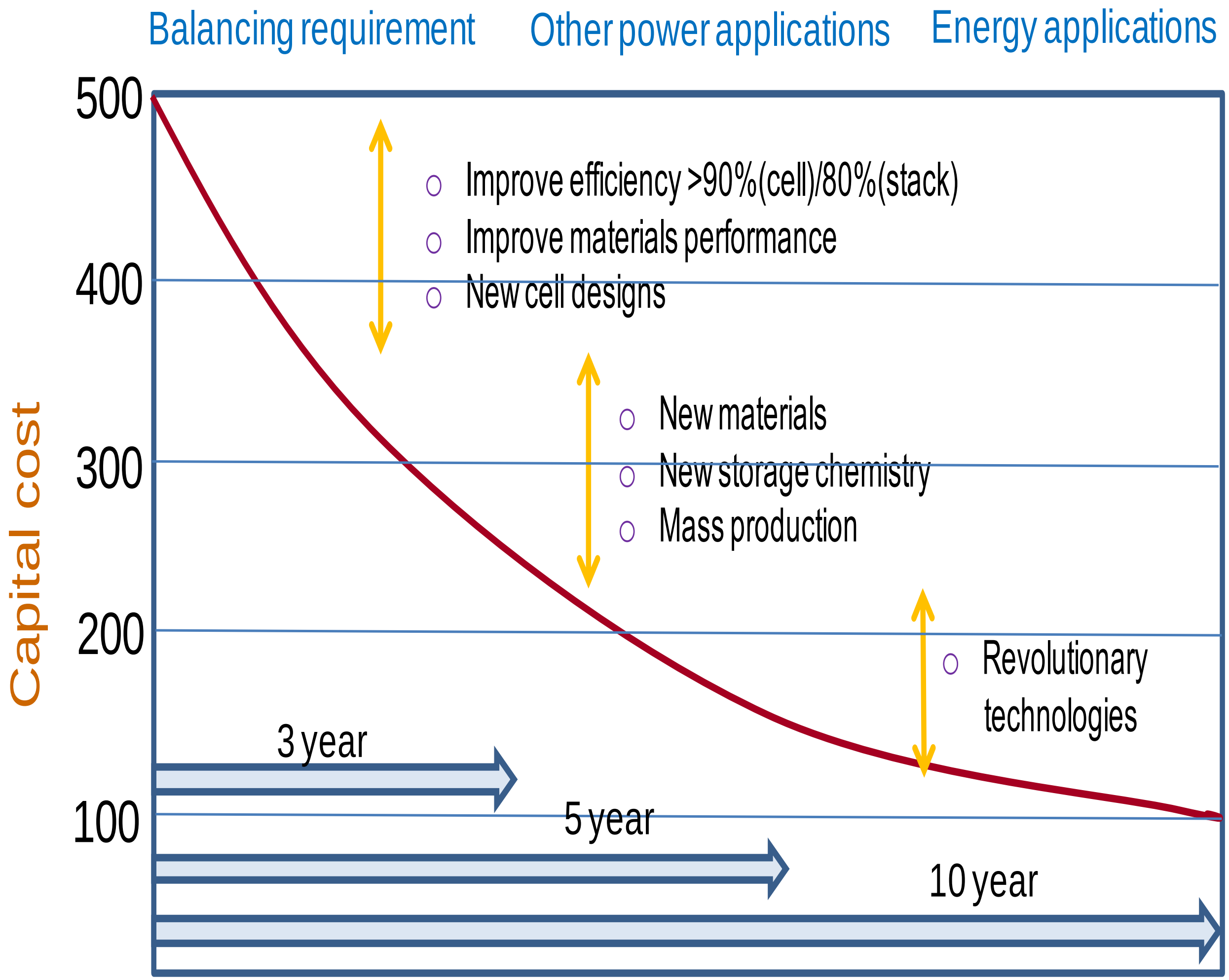
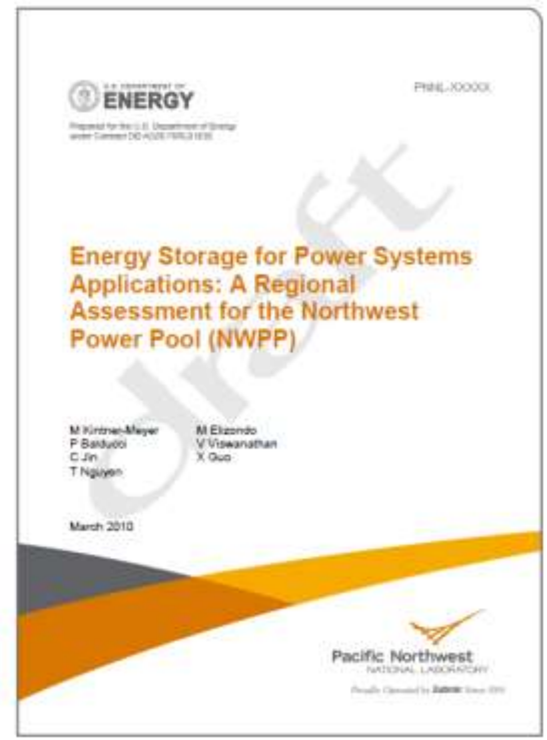
Storage technologies could be developed and implemented in several stages depending on the market requirements





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Grand Challenges for Large Scale Energy Storage

Fundamental understand of the materials properties and chemical processes in complex, reactive environments and systems;

New materials, chemistry and components to significantly improve the efficiency, reliability, safety and life span of current and future storage systems;

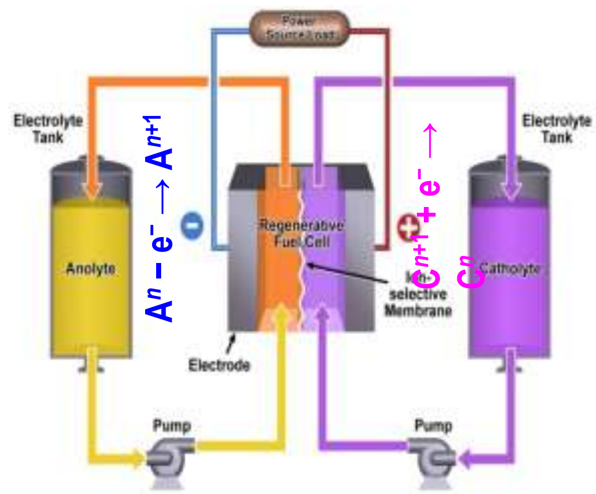
Revolutionary designs, concepts and architectures that can significantly reduce the system and maintenance cost: of large energy storage systems;

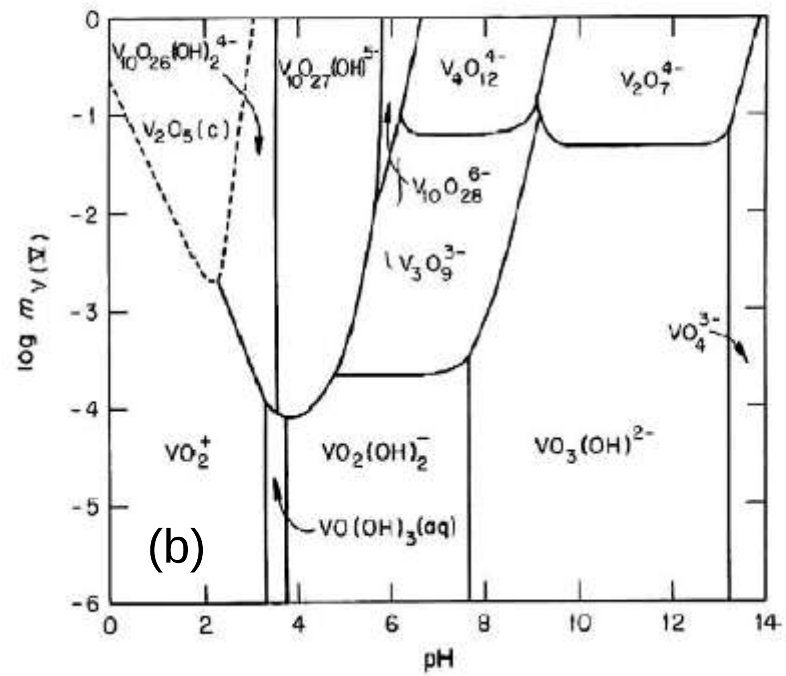
Novel energy storage mechanisms, energy storage technologies that are environmentally friendly and that are not dependent on materials and chemicals of limited supply;

Tools and methodologies to predict and analyze the economics of specific technologies for different scales/different applications and guide smart grid integration.

State-of-the-art characterization and modeling tools should be used to understand the fundamental chemistry in aggressive and concentrated electrolyte solutions encountered in redox flow batteries, Na-S batteries and Na-metal halide batteries.

Redox flow battery





Redox reaction in V flow battery:

Anode: $V^{3+} + e^- \underset{Discharge}{\overset{Charge}{\rightleftharpoons}} V^{2+}$

Cathode: $VO^{2+} + H_2O - e^- \underset{Discharge}{\overset{Charge}{\rightleftharpoons}} VO_2^+ + 2H^+$

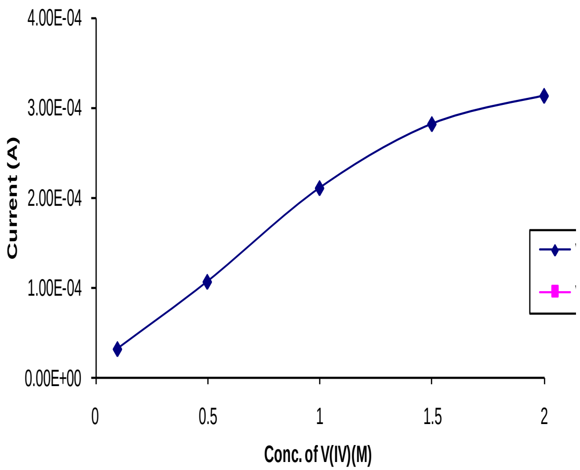
The energy density is limited by the solubility, but the solution chemistry is poorly understood in concentrated acids and salts

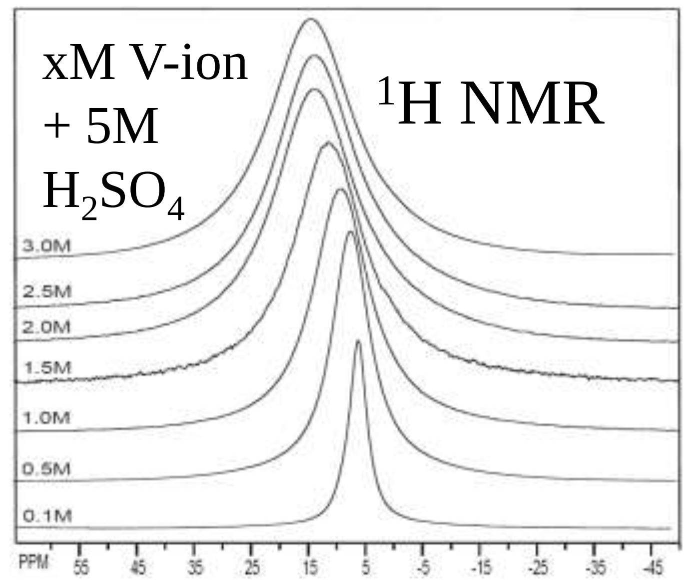
More from Professor Maria Skyllas-Kazacos

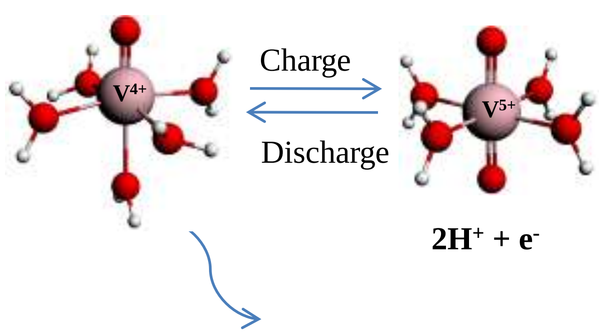
C. F. Baes Jr, R. E. Mesmer, *The Hydrolysis of Cations, Robert E Krieger Publishing Company, Malabar, Florida* 1986.

High field NMR technique is a powerful tool to study the chemical speciation and reactions in the flow batteries.

The efficiency, durability, activity are limited by the poor understanding of the chemical speciation, chemical and materials reactions.







Axial Water Molecule has Faster Exchange with solvent

Careful study of electrolyte chemistry has led to significant increase of all V flow battery (from under 2M to 3M)

M. Vijayakumar, S.D.Burton, C. Huang, L. Li, Z. Yang, G. L. Graff, J. Liu, J. Z. Hu, M. Skyllas-Kazacos, *Journal of Power Sources* **2010**.

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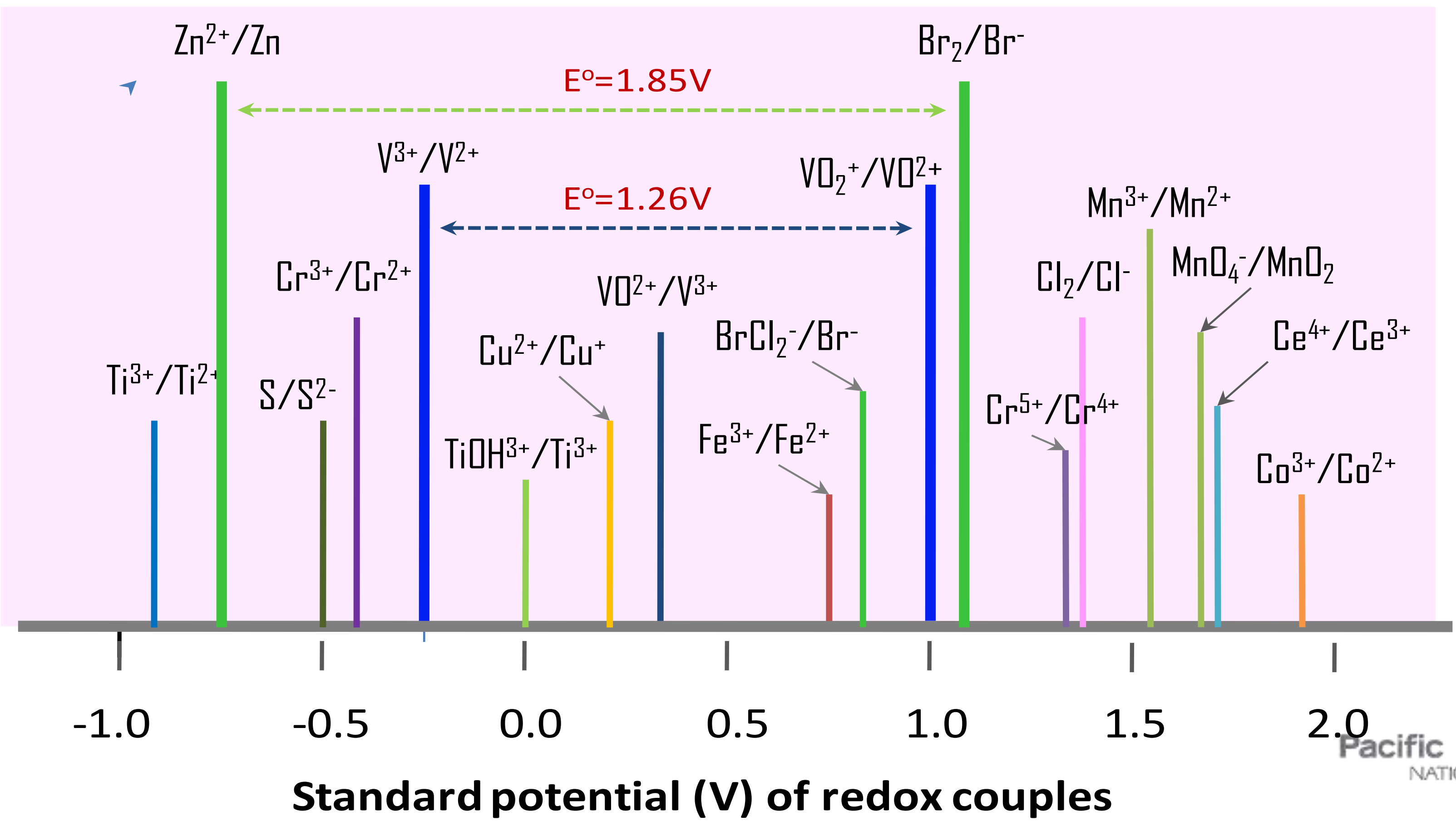
Redox chemistries and exiting technologies

- VRB: V^{2+}/V^{3+} vs. VO_2^+/VO^{2+}
- ICB: Fe^{3+}/Fe^{2+} vs. Cr^{3+}/Cr^{2+}
- ZBB: Br^-/Br^{2-} vs. Zn^{2+}/Zn
- PSB: Br^2/Br^- vs. S/S^{2-}

Up to 100 kw or multi-MW demonstrated

Others:
V^{2+}/V^{3+} vs. $Br^-/ClBr_2^-$;
Ce^{4+}/Ce^{3+} vs. V^{2+}/V^{3+};
Fe^{3+}/Fe^{2+} vs. Br_2/Br^-;
Mn^{2+}/Mn^{3+} vs. Br_2/Br^-;
Fe^{3+}/Fe^{2+} vs. Ti^{2+}/Ti^{4+}, …



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Non-aqueous electrolytes for redox flow batteries with wide operation voltage range

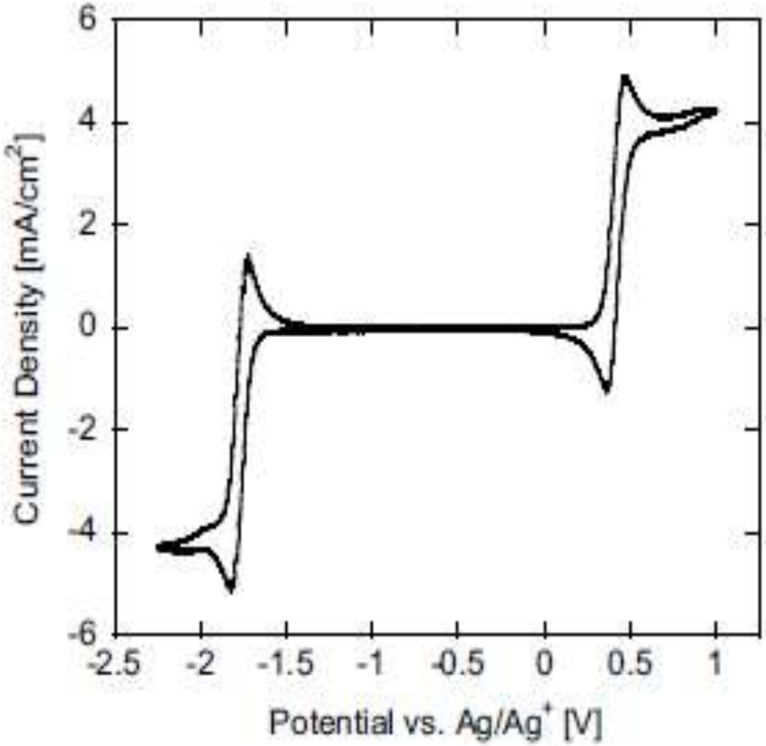


Figure 1: A non-aqueous all-vanadium redox flow battery chemistry supports a cell potential of 2.2 V. Cyclic voltammograms (100 mV/s) for 0.01 M vanadium acetylacetonate, supported by 0.05 M tetraethylammonium tetrafluoroborate in acetonitrile, in contact with a gold microelectrode.

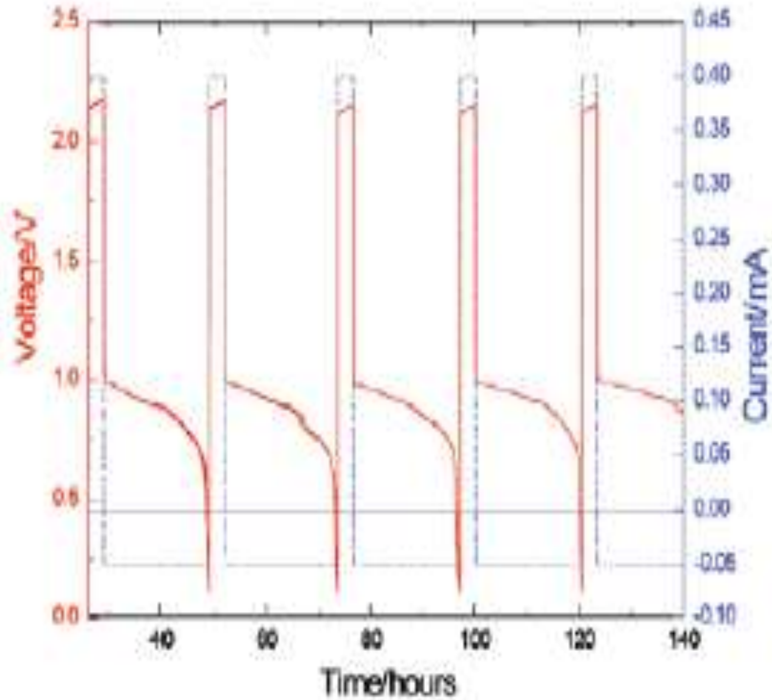


Figure 2: High coulombic efficiency is achieved at low depth of discharge. Constant current charge/discharge experiments with 0.4 mA charge current and 0.05 mA discharge current. The system consisted of 0.1 M vanadium acetylacetonate supported by 0.5 M tetraethylammonium tetrafluoroborate in acetonitrile solvent. Charged to 4% theoretical state of charge.

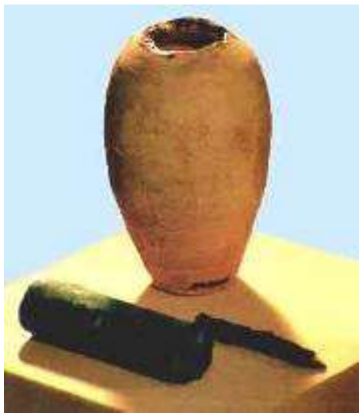
Aaron Shinkle, Qinghua Liu, Alice Sleightholme, Levi Thompson, and Charles Monroe

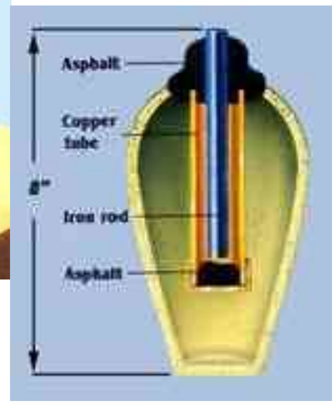
University of Michigan
2300 Hayward St.
Ann Arbor, MI 48109

More from Professor Austen Angell

Requirement of energy storage materials.

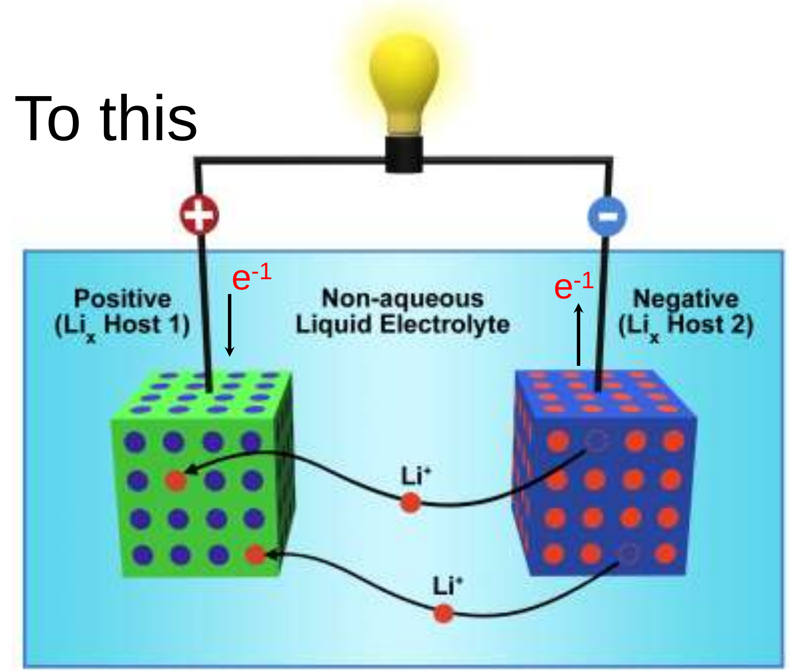
From this





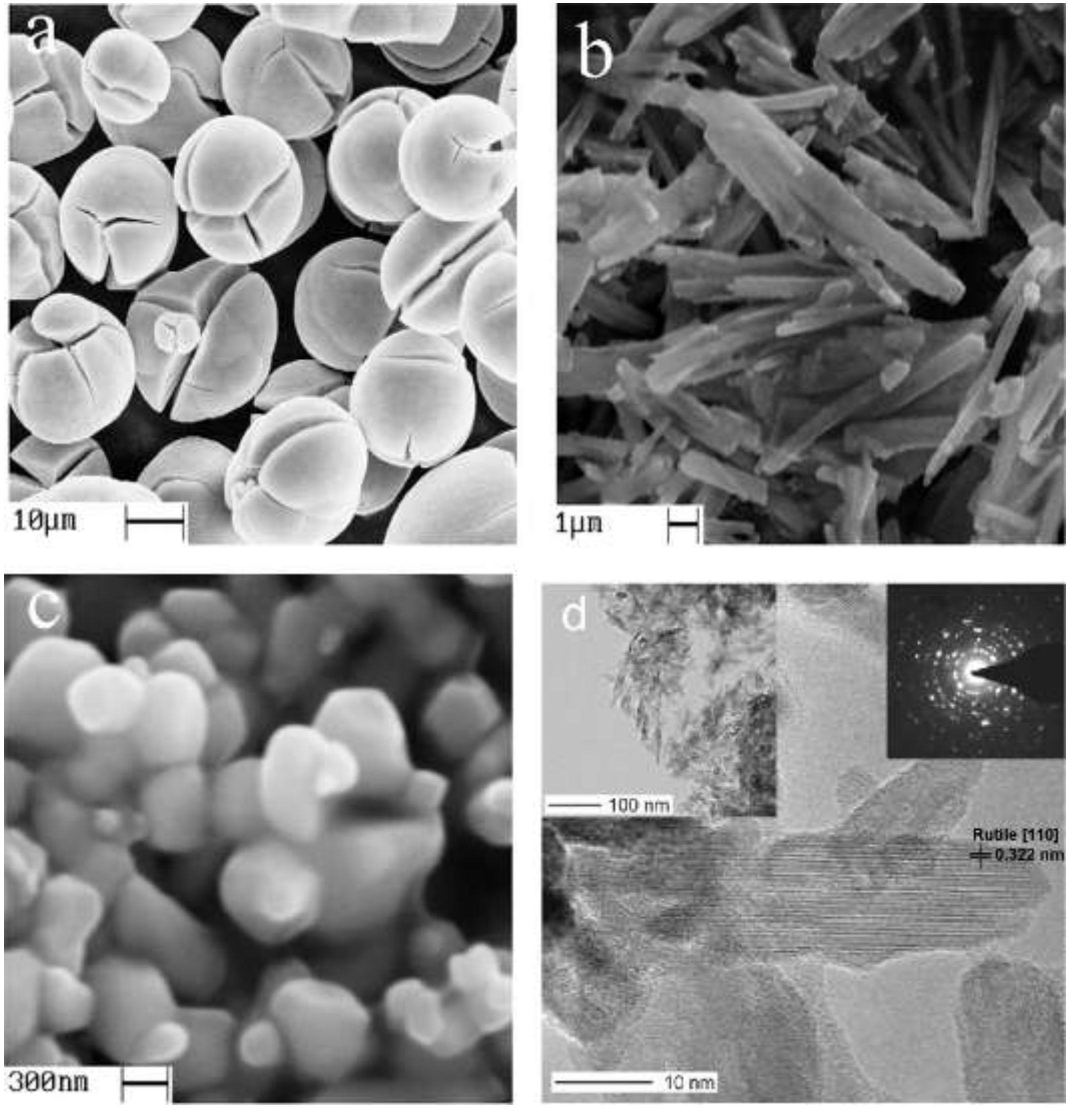
2000 year old
Baghdad “battery”

To this



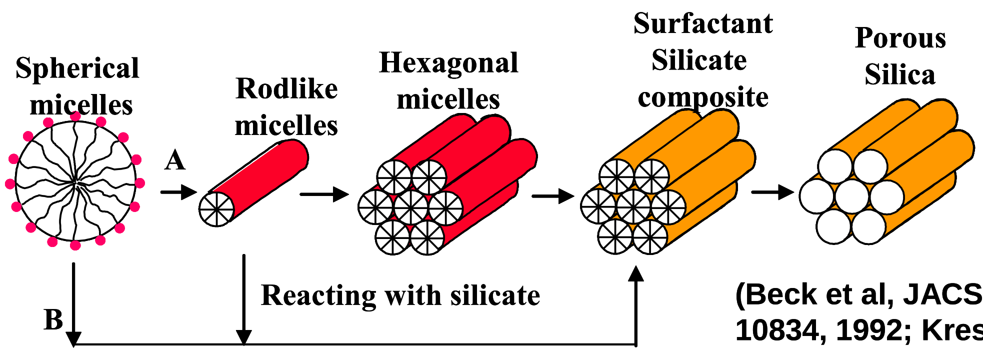
- Controlled hierarchical architectures for maximum flow
- High surface area
- Multifunction: electron and ion conductivity,
- Multi-component
- Chemical, thermal and mechanical stability

TiO_2 anode materials prepared by hydrothermal methods

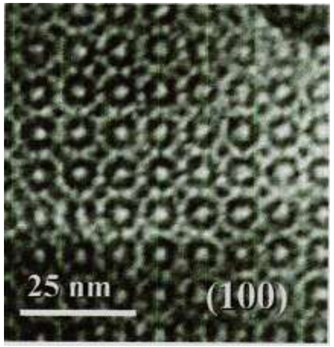


Y. S. Hu, L. Kienle, Y. G. Guo, J. Maier, Adv. Mater. 2006, 18, 1421.

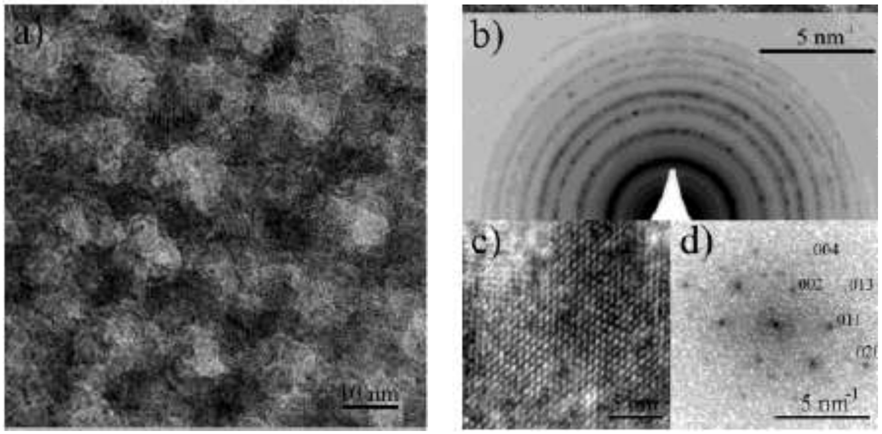
High quality mesoporous silica can be easily made with surfactant templated, self-assembly approaches, but other crystalline materials are very difficult.



(Beck et al, JACS, 114, 10834, 1992; Kresge, et al. Nature, 359, 710, 1992.)



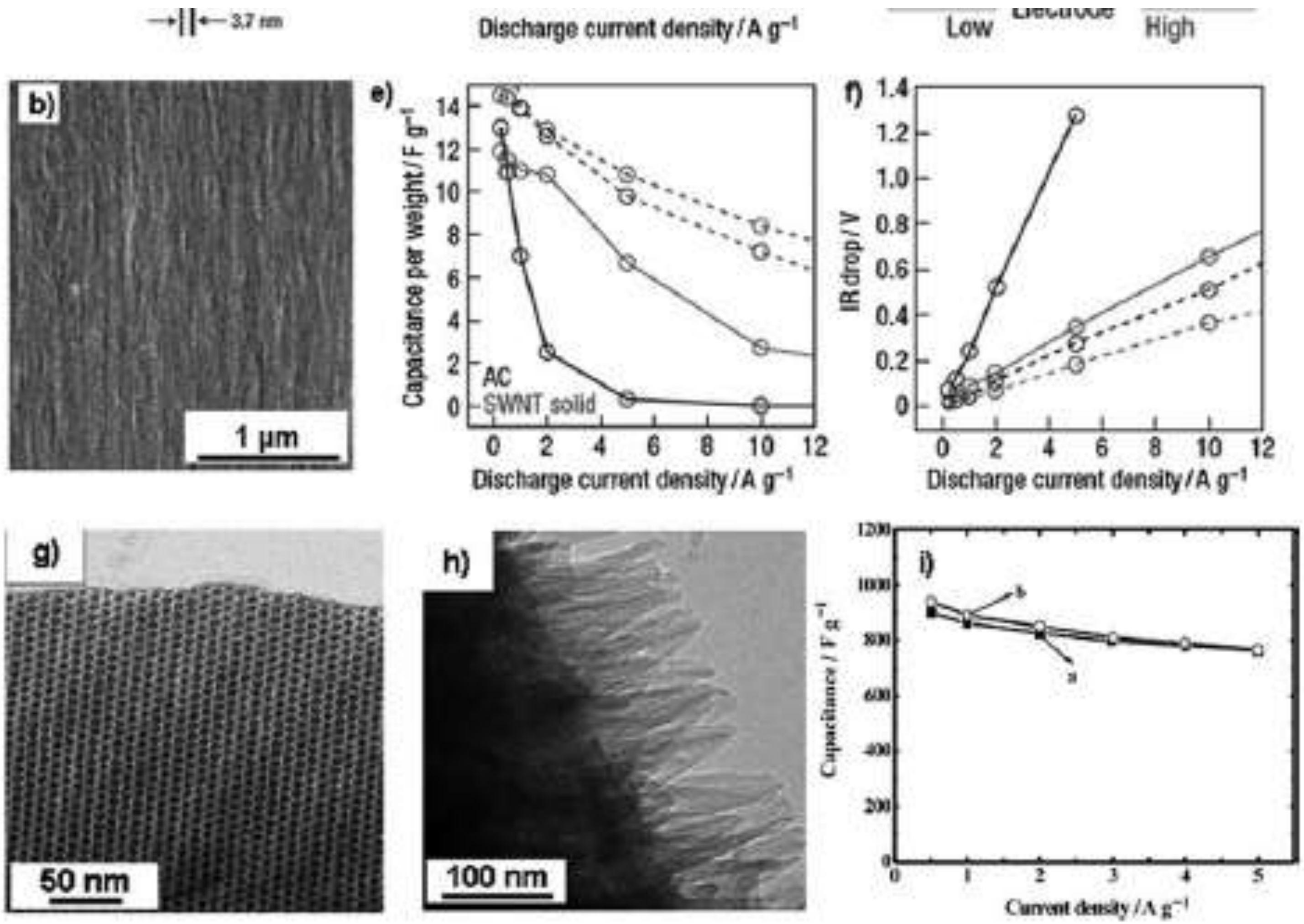
Lu et al., Nature 1997



B. Smarsly et al, Chem. Mat., 2004, 16, 2948

Surfactant templated mesoporous TiO_2 is usually made of nanocrystalline, anatase walls. Crystal growth and phase transition causes pore structure collapse during heat treatment.

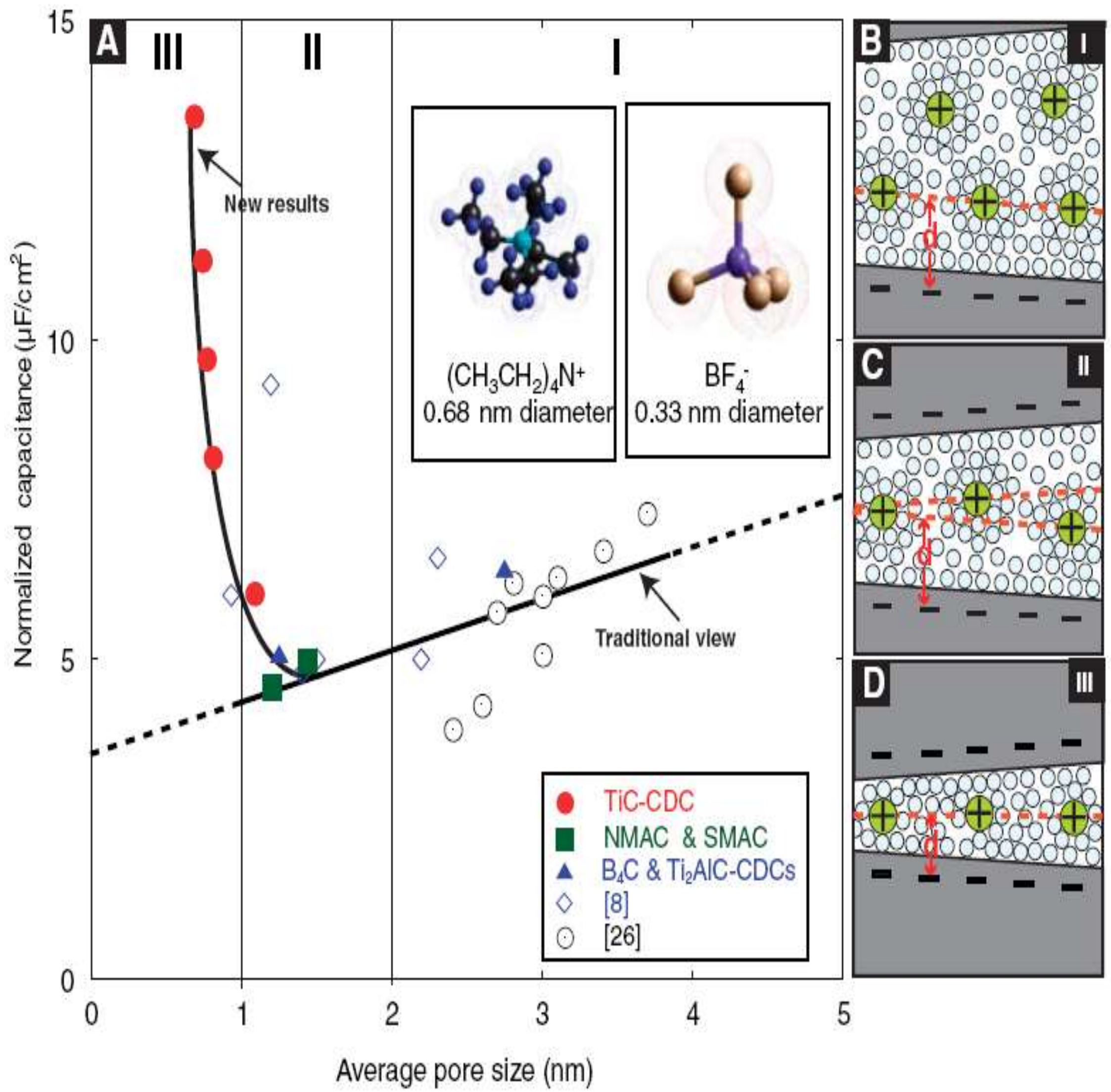
Novel nanoporous carbon materials have potential for high energy density and high power



D. N. Futaba, K. Hata, T. Yamada, T. Hiraoka, Y. Hayamizu, Y. Kakudate, O. Tanaike, H. Hatori, M. Yumura, S. Iijima, *Nat. Mater.* **2006**, *5*, 987.

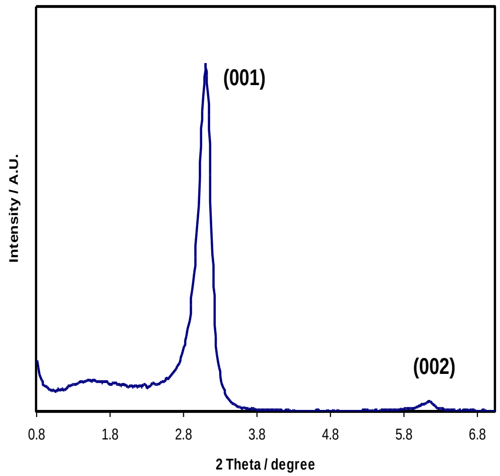
[248] Y. G. Wang, H. Q. Li, Y. Y. Xia, *Adv. Mater.* **2006**, *18*, 2619.

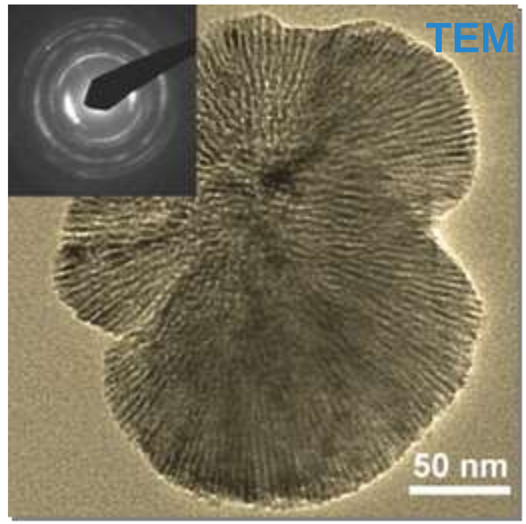
Pore sizes matters for transport properties

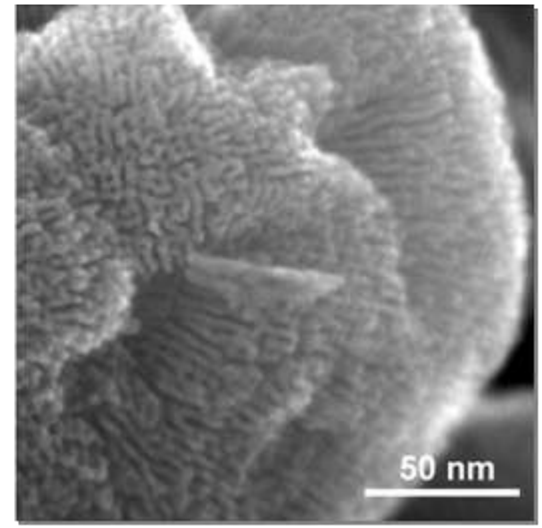


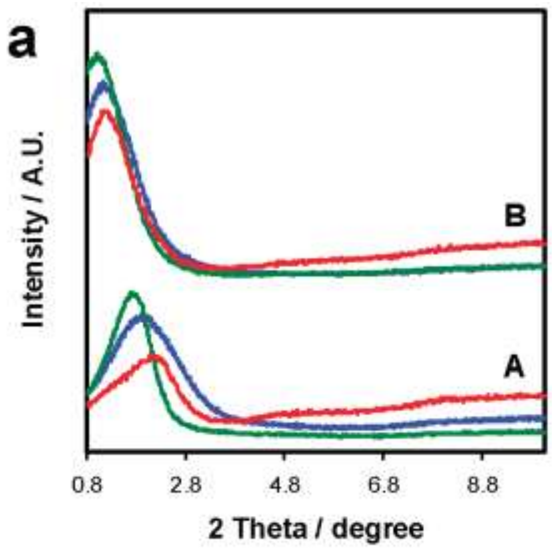
J. Chmiola, G. Yushin, Y. Gogotsi, C. Portet, P. Simon, P. L. Taberna, *Science* **2006**, *313*, 1760.

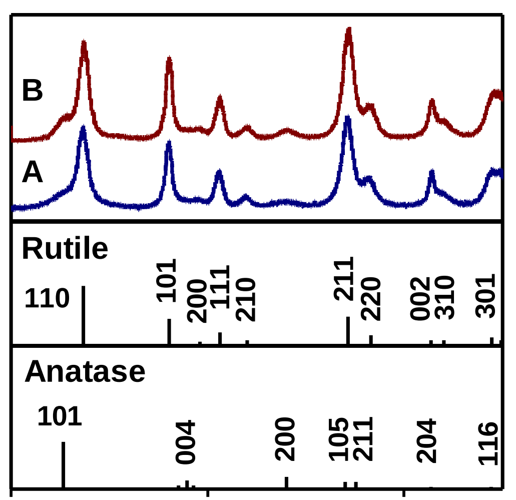
Highly Crystalline Mesoporous TiO_2











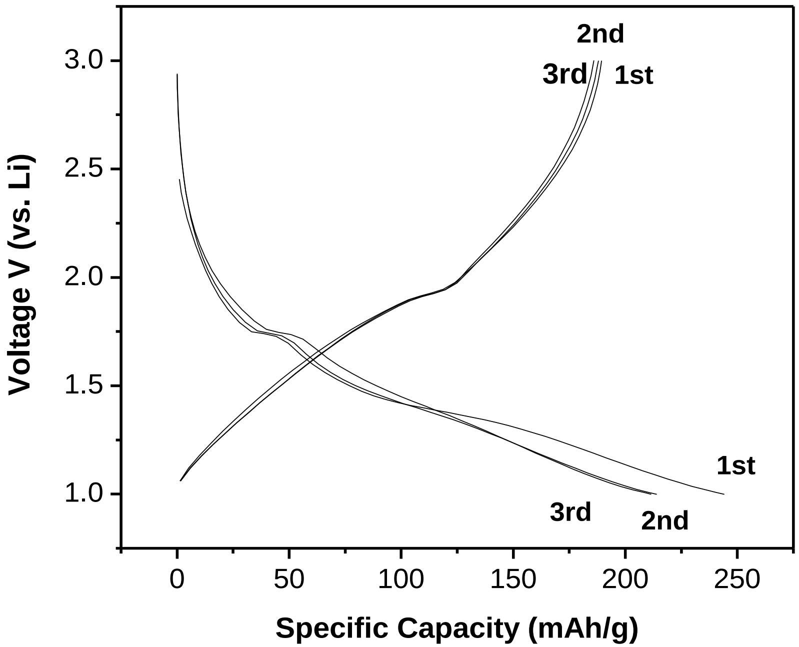
High angle XRD

SEM

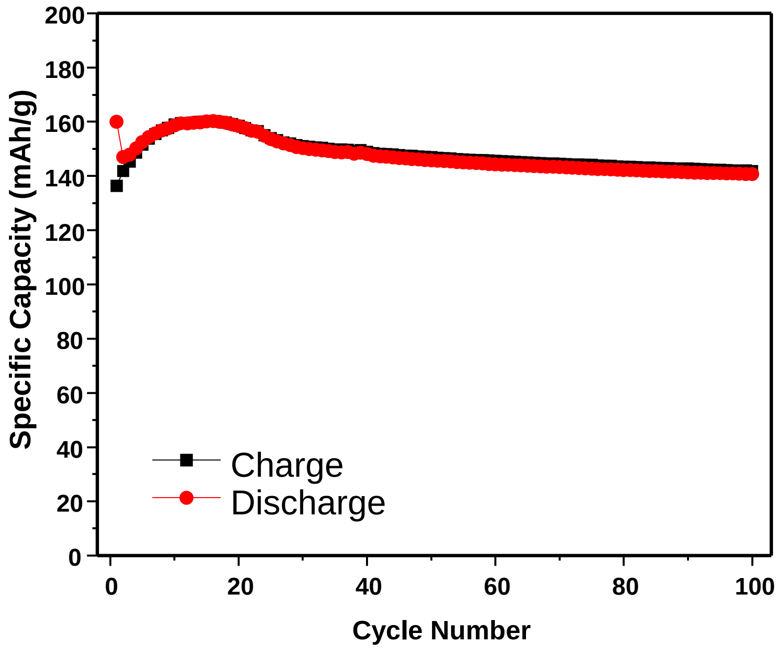
Crystalline rutile phase before and after calcination.

Wang, D. Liu, J. et. al, Chem. Mater. 2008.

Electrochemical Performance of Mesoporous Rutile ad Anode for Li-ion Battery



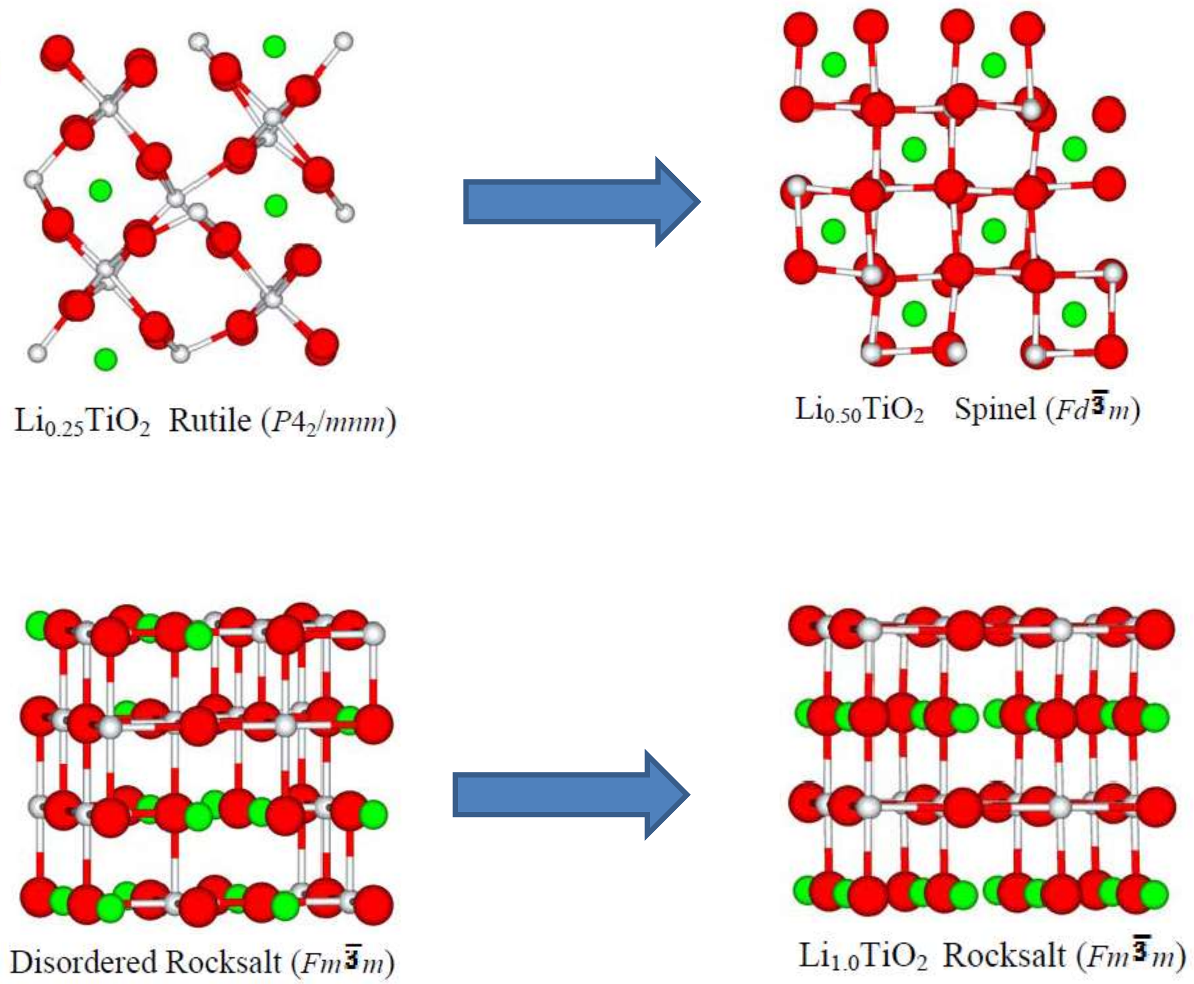
Voltage-capacity profile at C/5 rate



Low capacity loss (8%) after 100 cycles at 1C charge and discharge rates

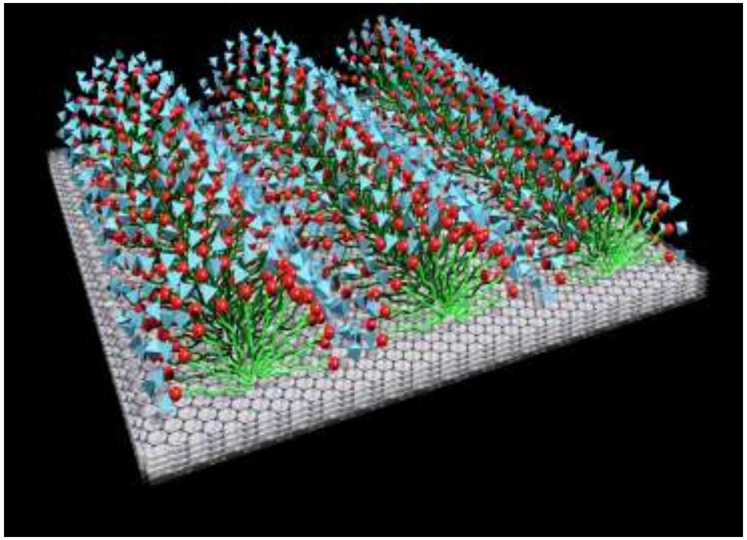
- **Excellent structure and interface stability — good cyclability, low fade rate**
- **Capacity higher than theoretical value of bulk anatase (168 mAh/g) at C/5 rate.**

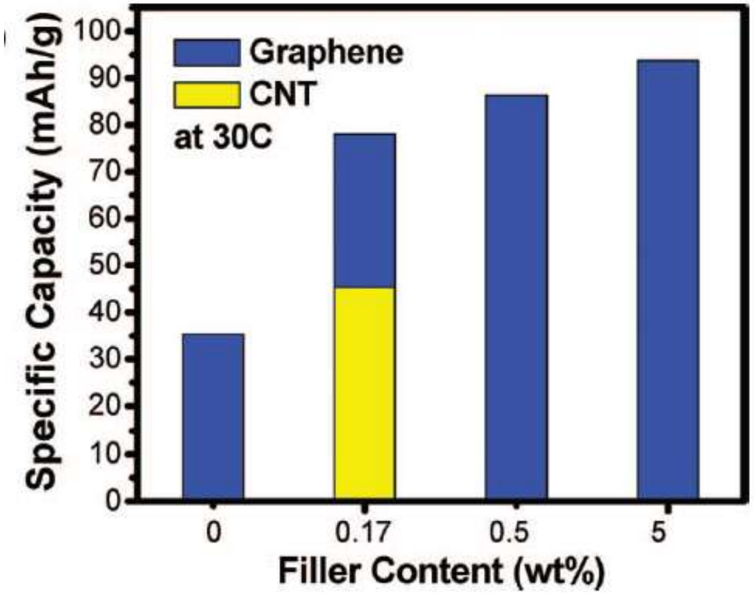
Modeling of charge transport and structural evolution complements experimental results from electrochemical characterization and NMR.

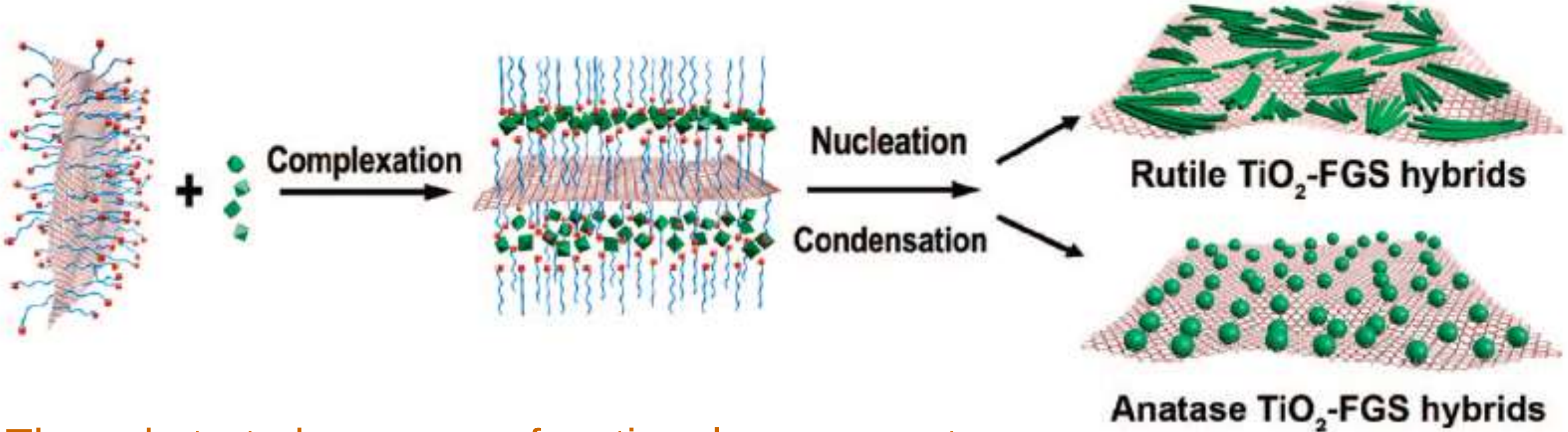


Rock salt cubit structure should have a capacity high than 300 mAh/g

Step 3: From single phase to mutliphase self-assembly using extended nanostructural building blocks

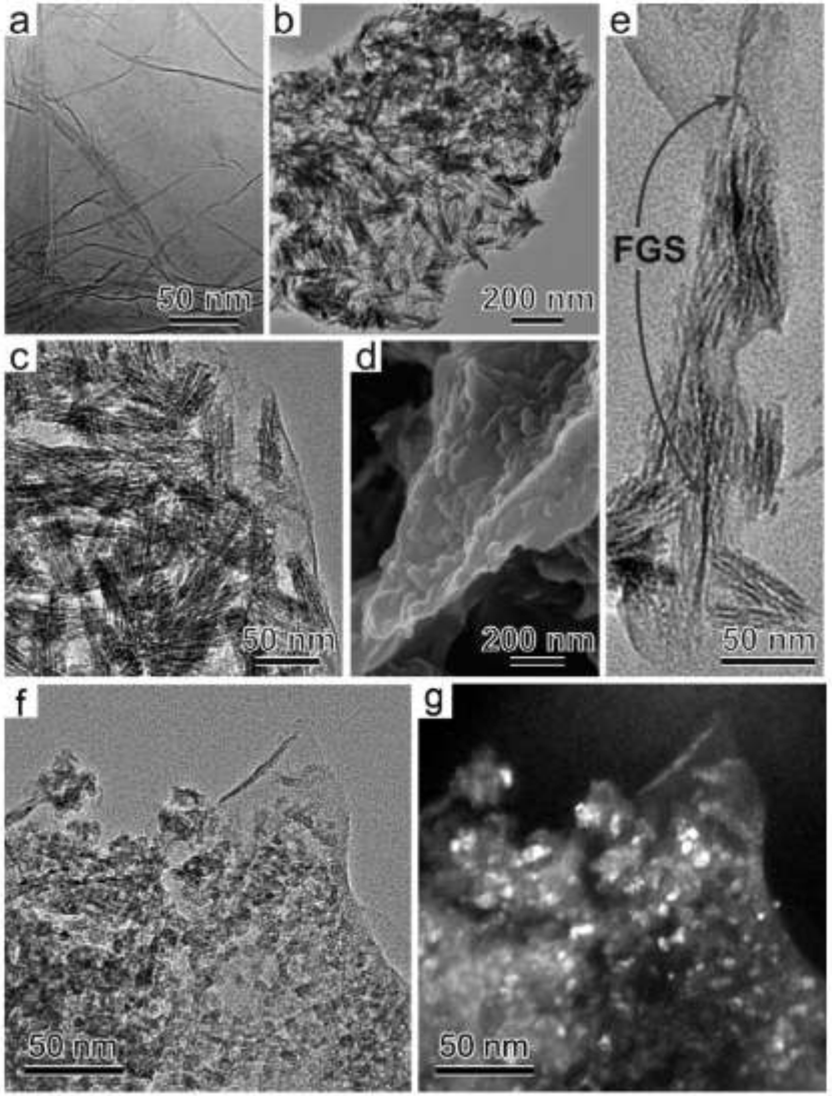






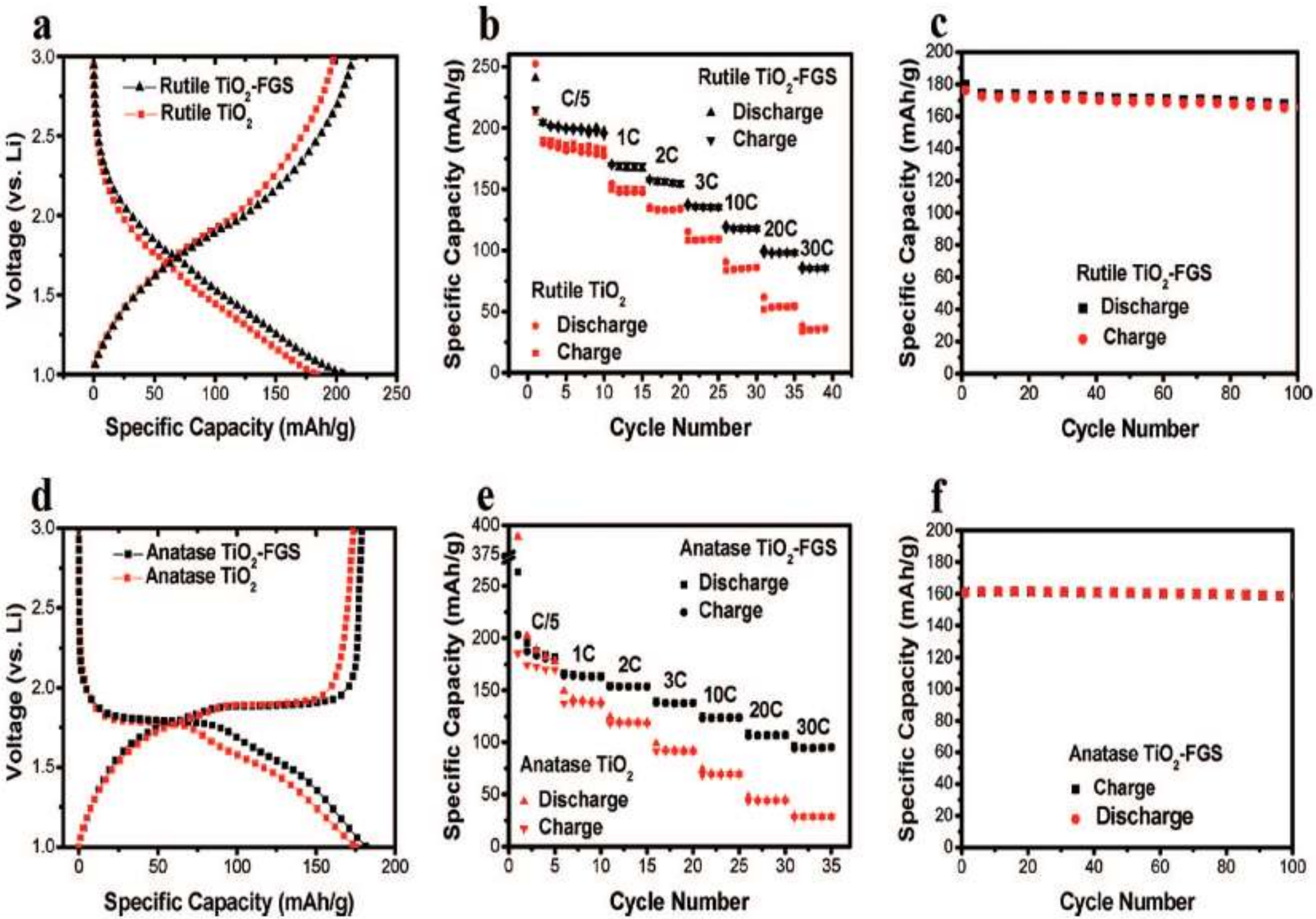
The substrate becomes a functional component

Graphene TiO_2 nanocomposites

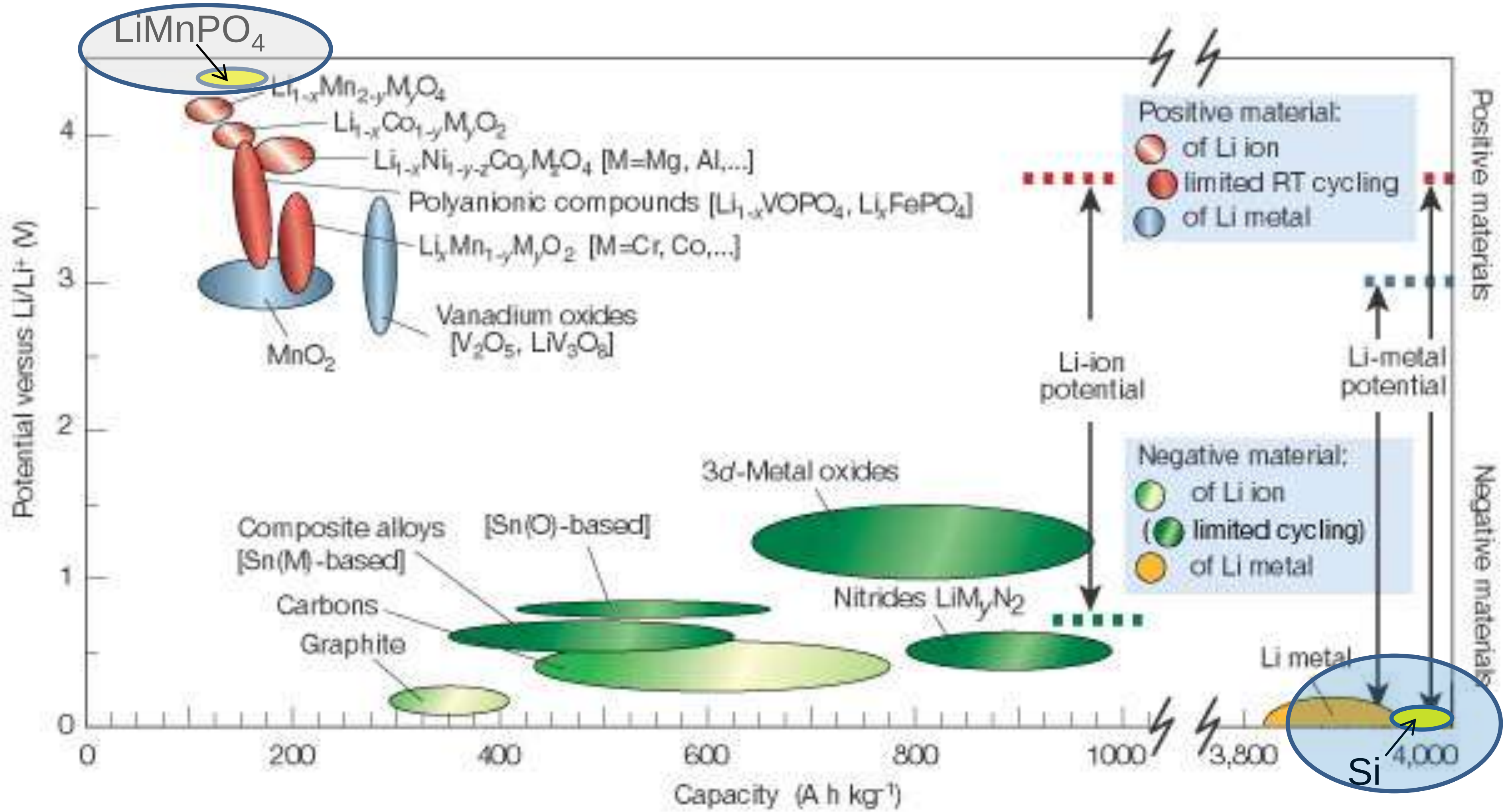


Want et al, ACS Nano, 2009

Improvement of high charge rate behavior for Both rutile and anatase



Challenges for Li-ion batteries: high voltage, high capacity cathode materials, and stable anode materials



Tarascon & Armand, Nature 2001 414, 359-367

More cathodes work from Dr. Mike Thackeray

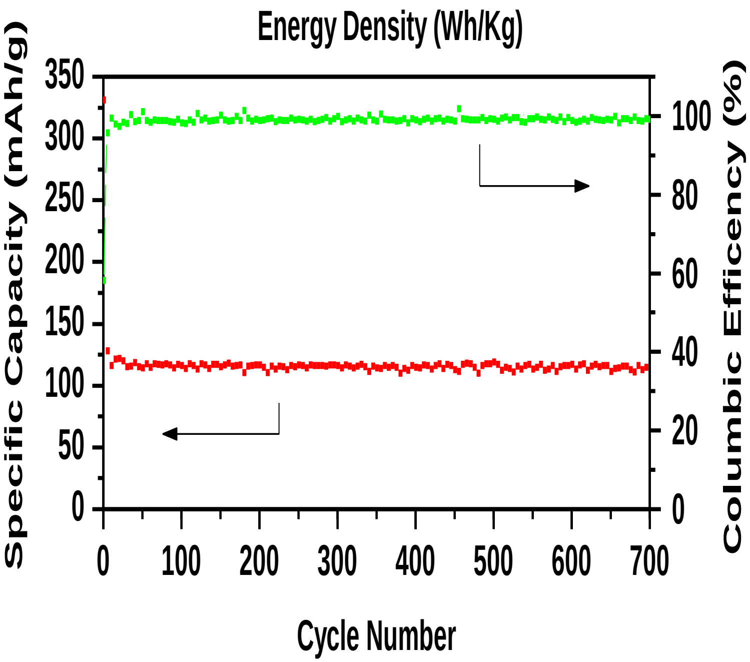
Pacific Northwest NATIONAL LABORATORY

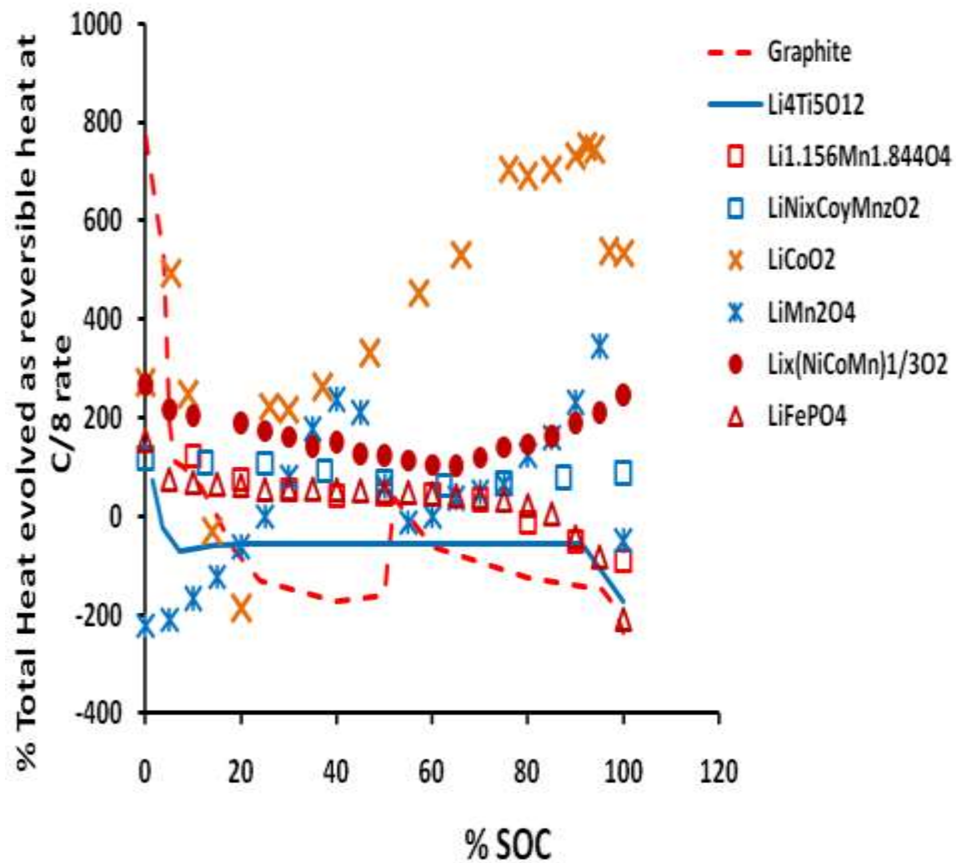
Potential low cost long lasting Li-ion batteries based on $LiFePO_4$ and TiO_2

More on safety from SNL

$LiFePO_4$

TiO2 (anatase)



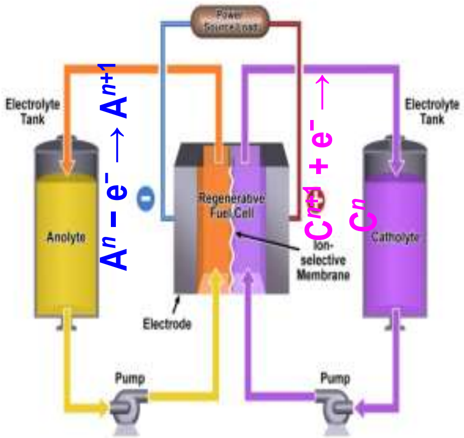


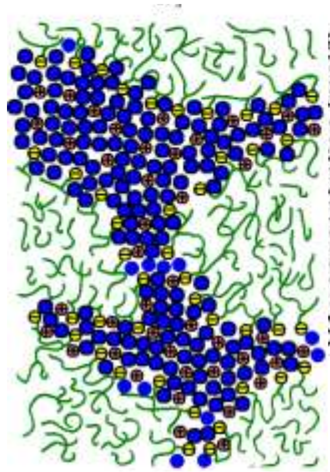
D. W. Choi, D. H. Wang, V. V. Viswanathan, I. T. Bae, W. Wang, Z. M. Nie, J. G. Zhang, G. L. Graff, J. Liu, Z. G. Yang, T. Duong, *Electrochemistry Communications* **2010**, *12*, 378.

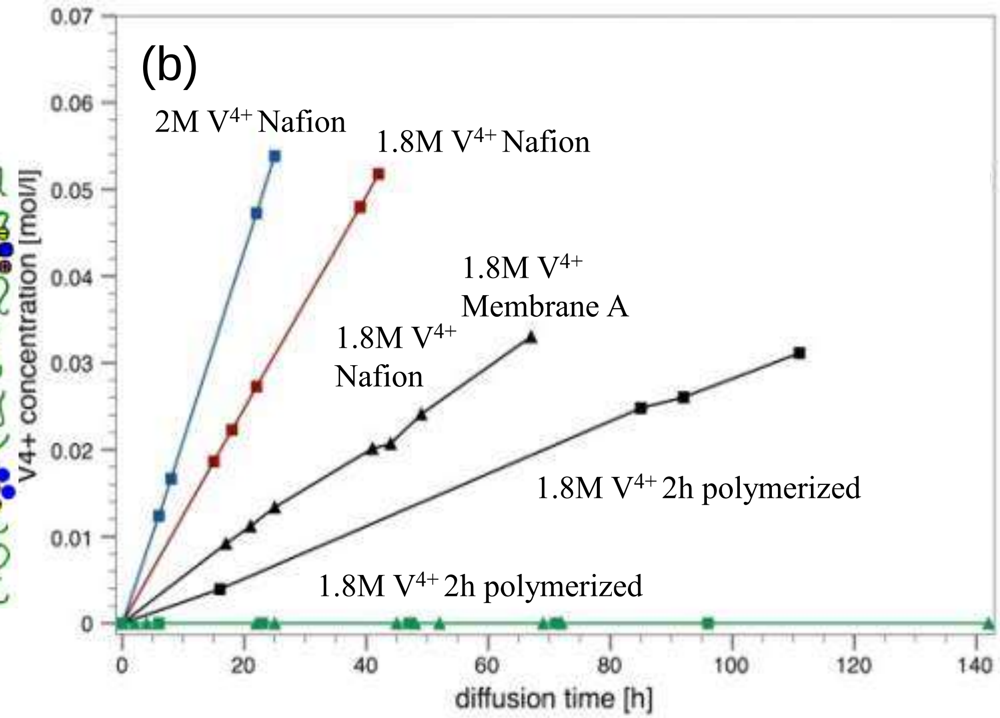
R. E. Williford, V. V. Viswanathan, J. G. Zhang, *Journal of Power Sources* **2009**, *189*, 101.

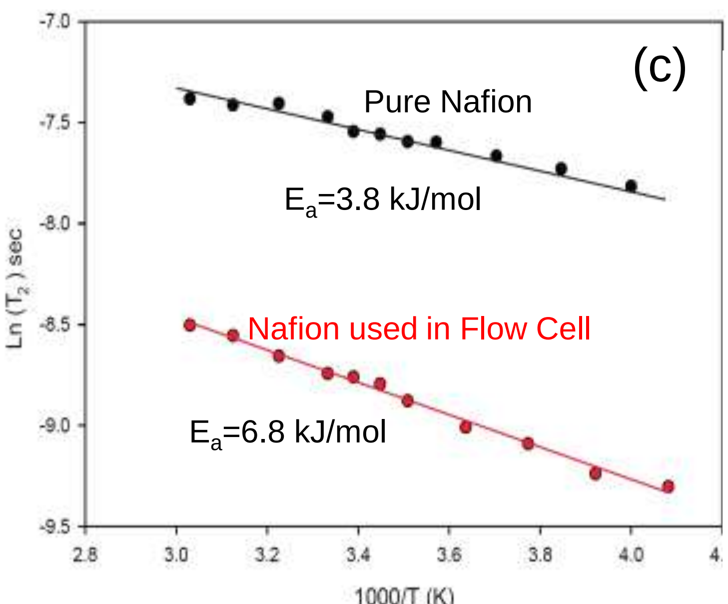
Separators and membranes are widely used, but suffer cross-contamination and fouling.

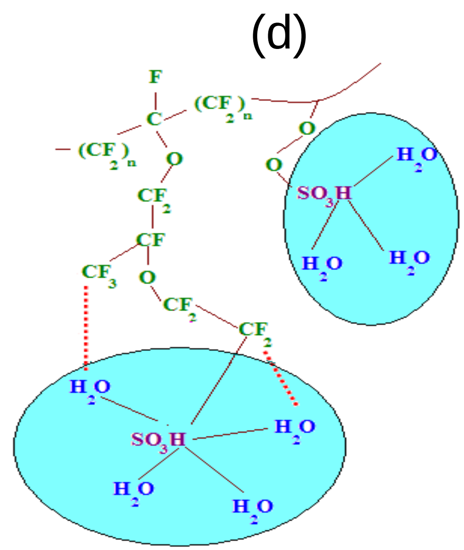
Schematic of Nafion membrane

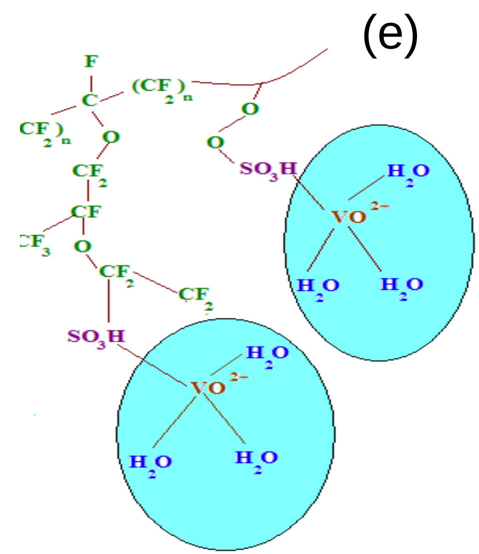




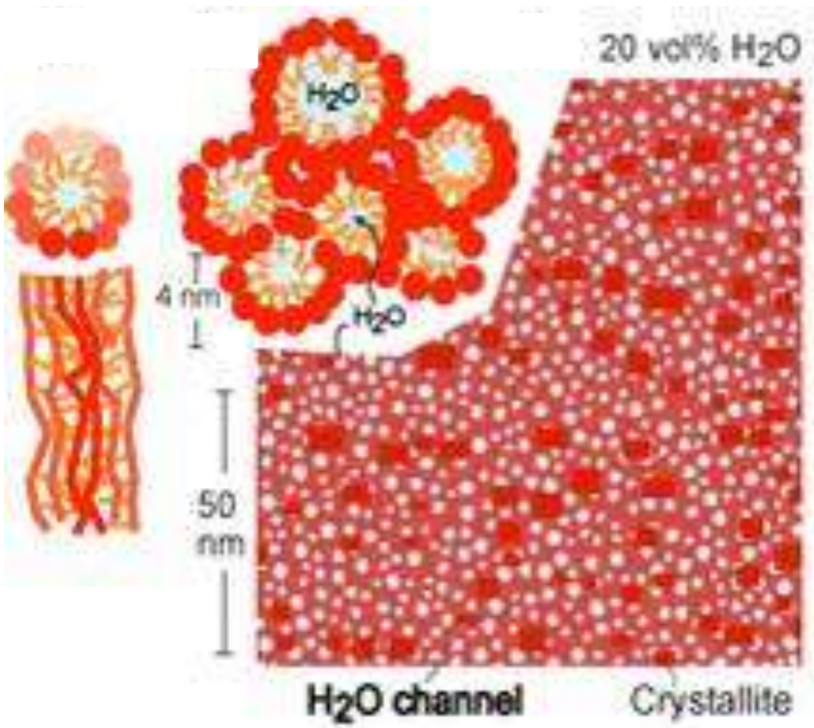


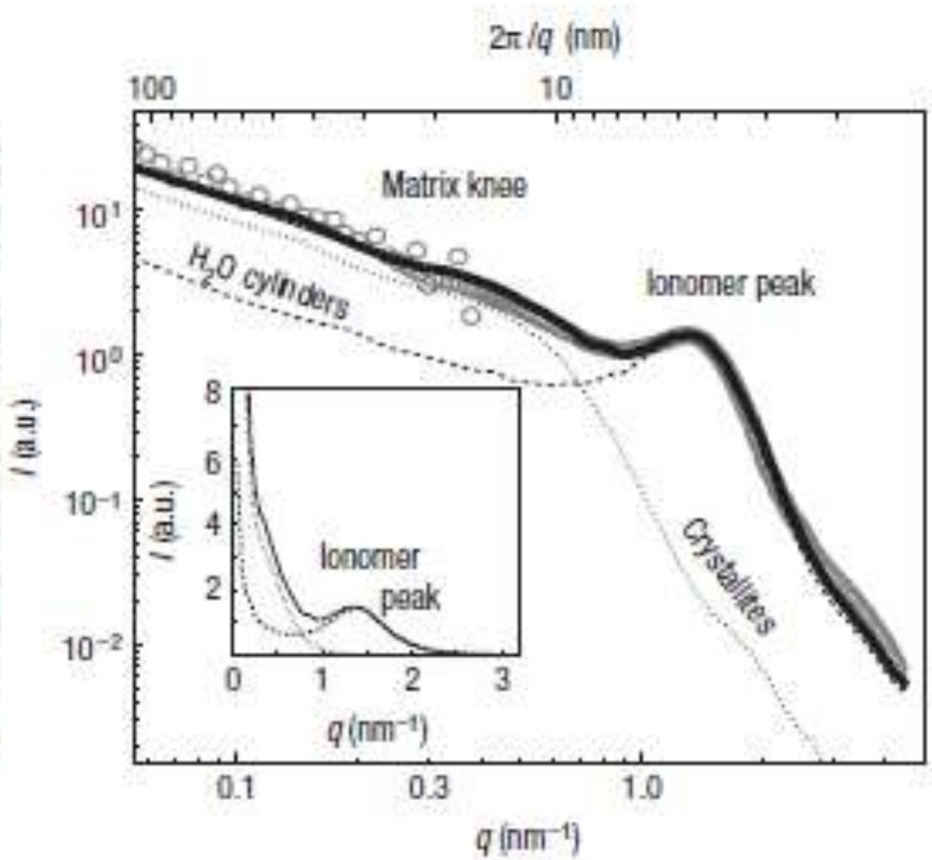






New understanding of Nafion membranes: wide pore channels (2.4 nm), suggesting the importance of water diffusion for H conducting. Such water diffusion mechanism will also favor the diffusion of hydrated cations.

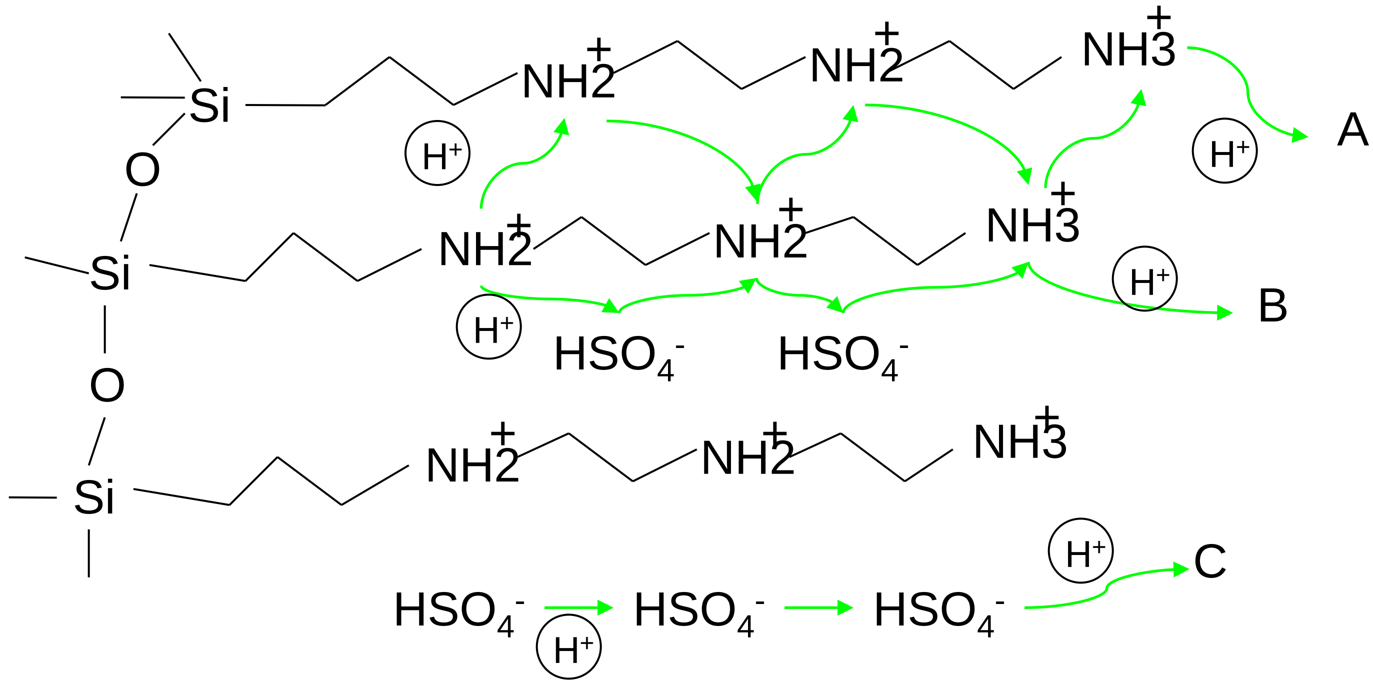




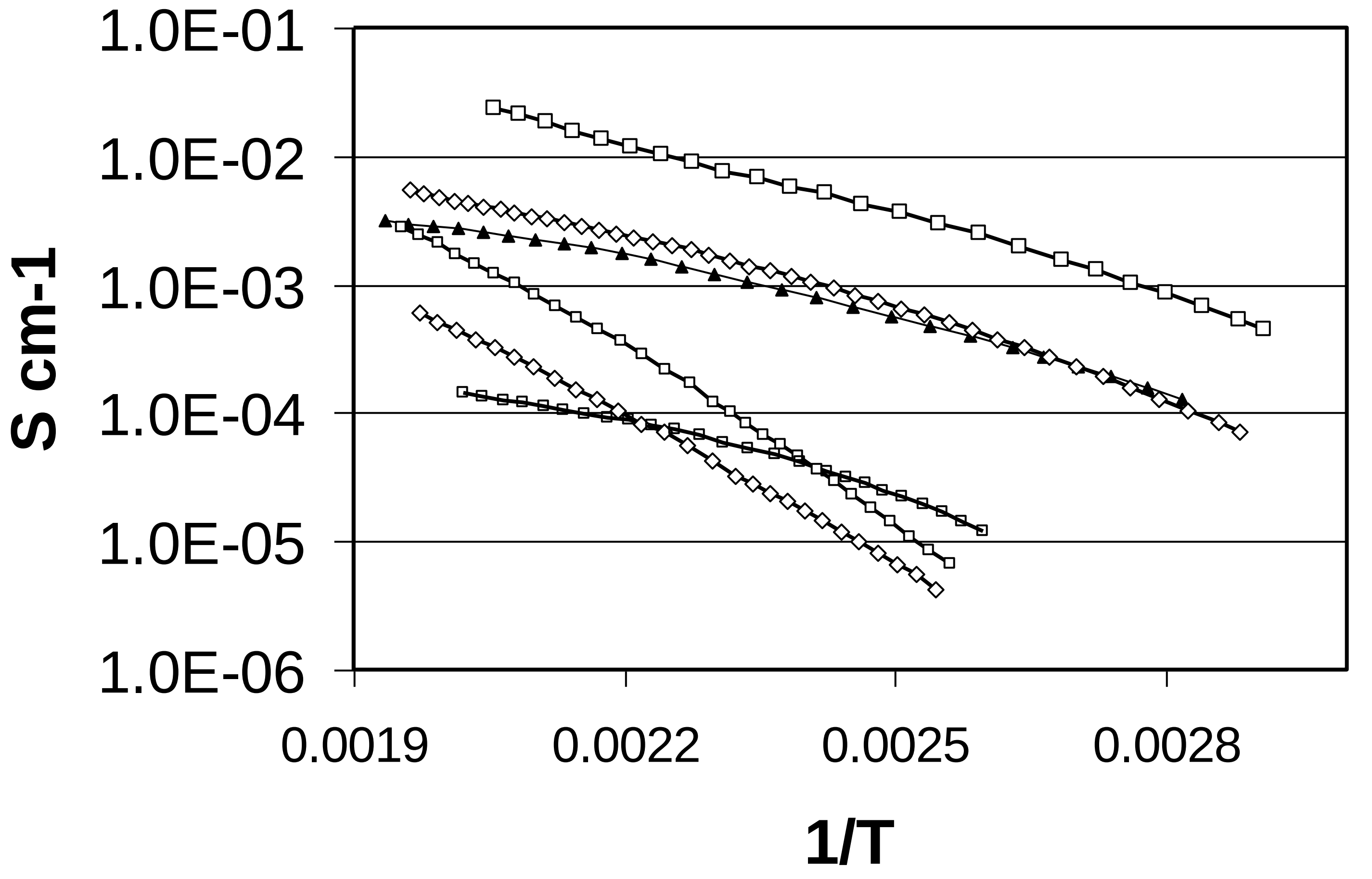
K. Schmidt-Rohr, Q. Chen, *Nature Materials* ***2008, 7, 75.***

More membrane work from Dr. Thomas Zawodzinski

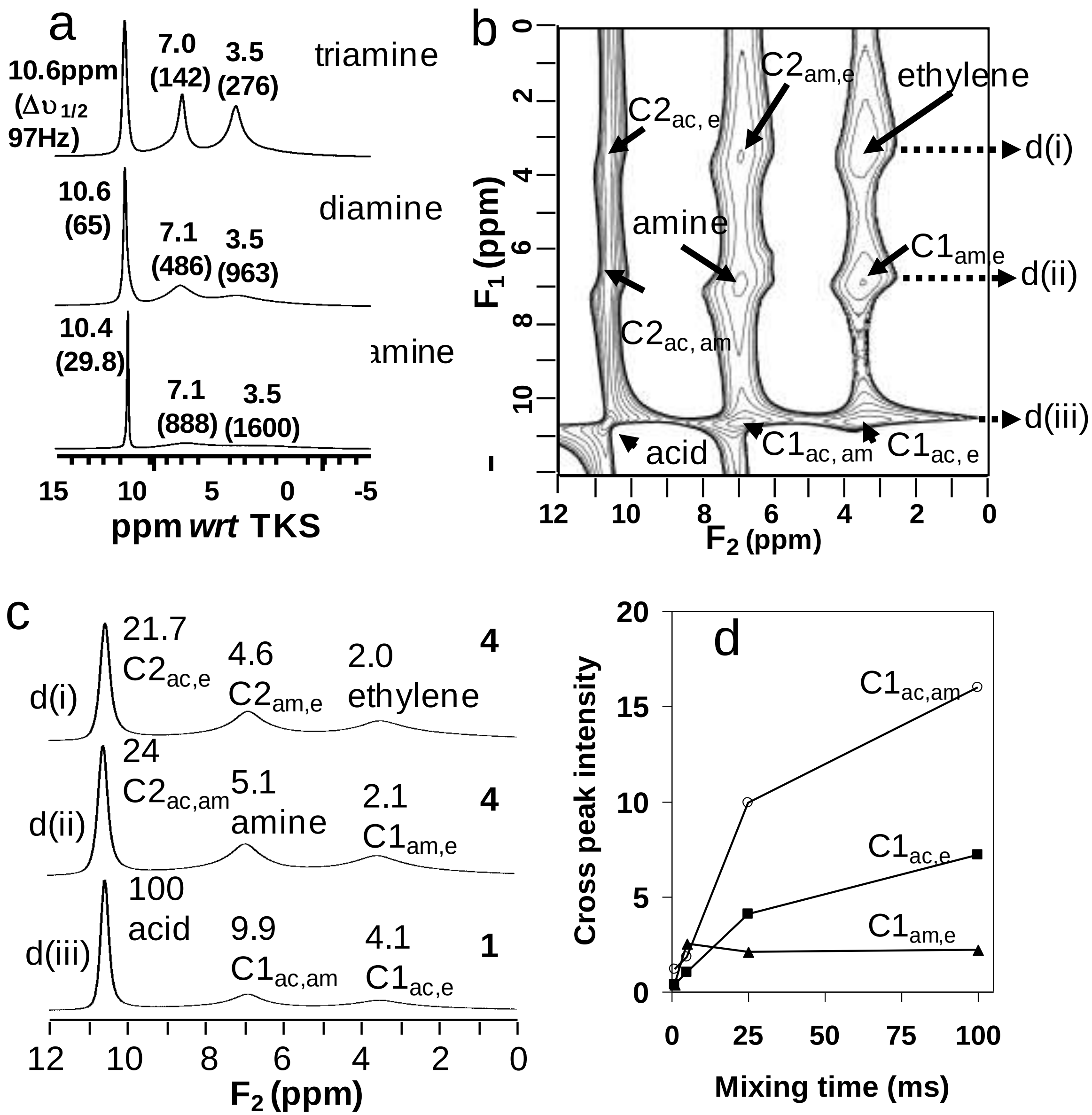
Is it possible to make proton conducting materials that is not dependent on water diffusion?



Proton conductivity of solid state silica based materials

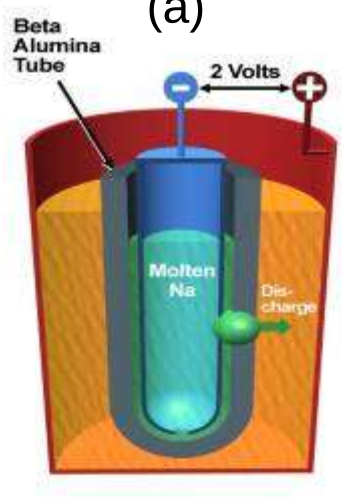


The proton hopping mechanism is supported by high resolution and 2D NMR spectroscopy results

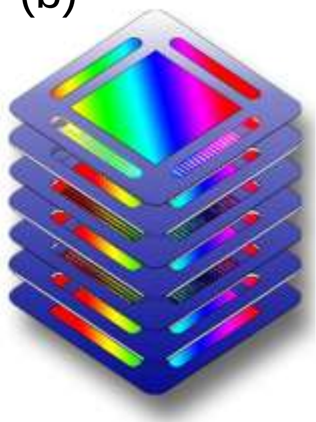


New designs and architectures: new thinking is needed on how the large batteries work much more efficiently and safely

(a)

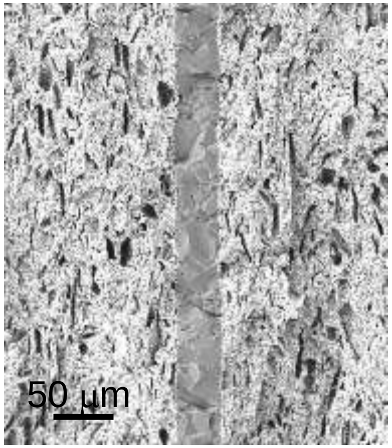


(b)



(c)

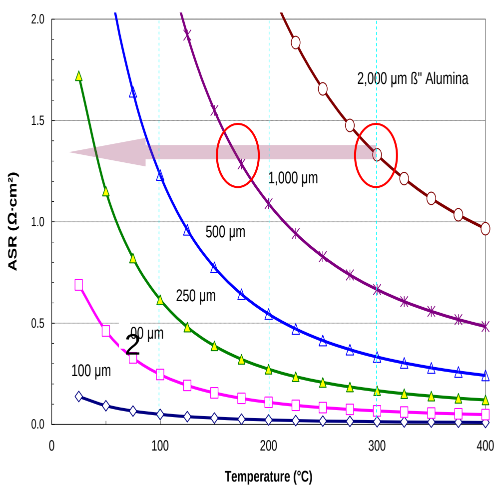
(d)

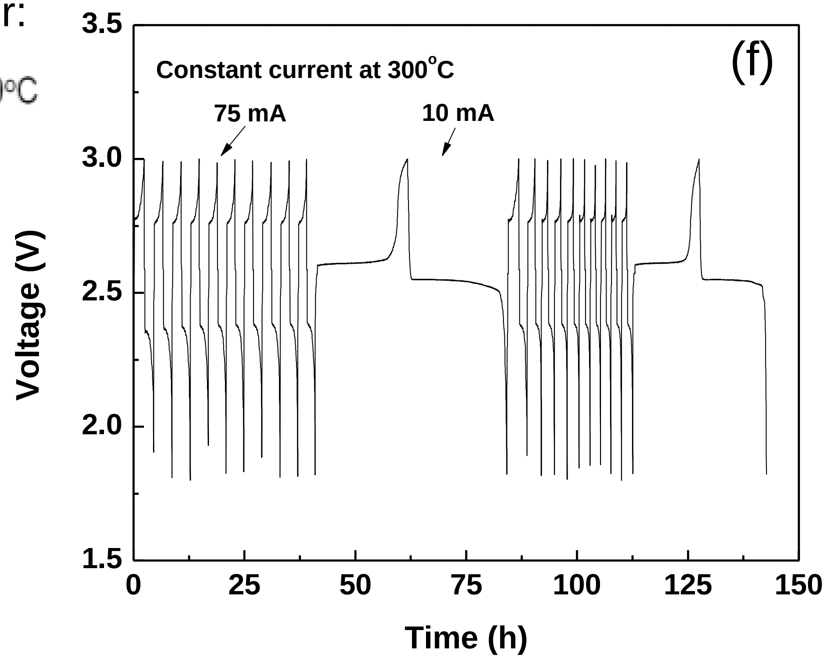


$2Na + xS \leftrightarrow Na_2S_x$ $(x = 5\text{-}3)$, E = 2.08-1.78V at 350°C or:

$2Na + NiCl_2 \leftrightarrow 2NaCl + Ni$ (ZEBRA), E = 2.58V at 300°C

(e)





More from EeaglePitcher (Dr. Jim Degruson)

Beta'' alumina – Design considerations

Design considerations

Performance, reliability and cost

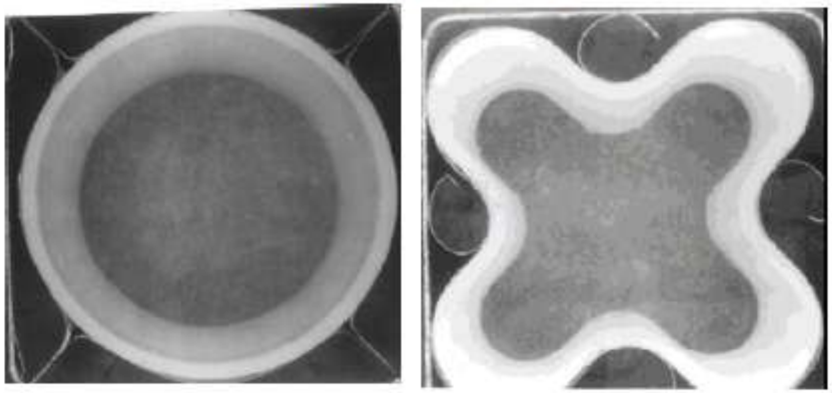
Performance (power)

- Na+ conductivity (increase Na+ flux)
- Shape (Increase surface area while maintaining minimum required tube strength)

Reliability

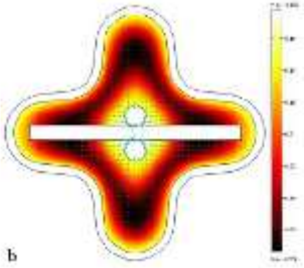
- Strength (Material & shape)
- Cell assembly (Residual stress from sealing process)
- Pressure cycling during cell operation
- Current density

After J. Sudworth (2001)



Increased surface area → Increased power density

b



18

imagination at work

J. Sudworth, *J. Power Sources*, 100 (2001) p 149

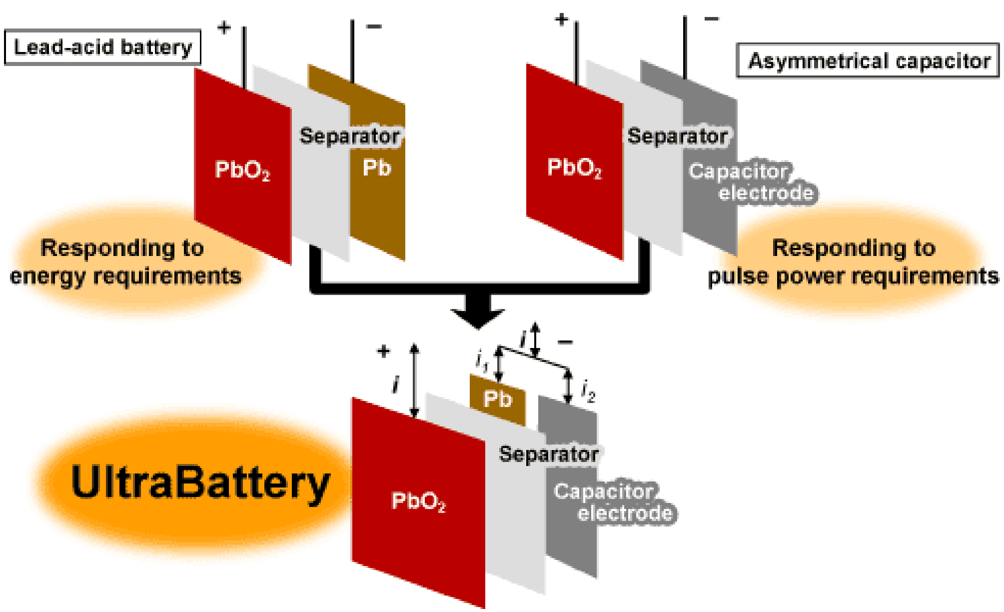
2010 Ceramic Leadership Summit

Mohamed Rahmane and Chuck Iacovangelo
GE Global Research, Niskayuna, NY

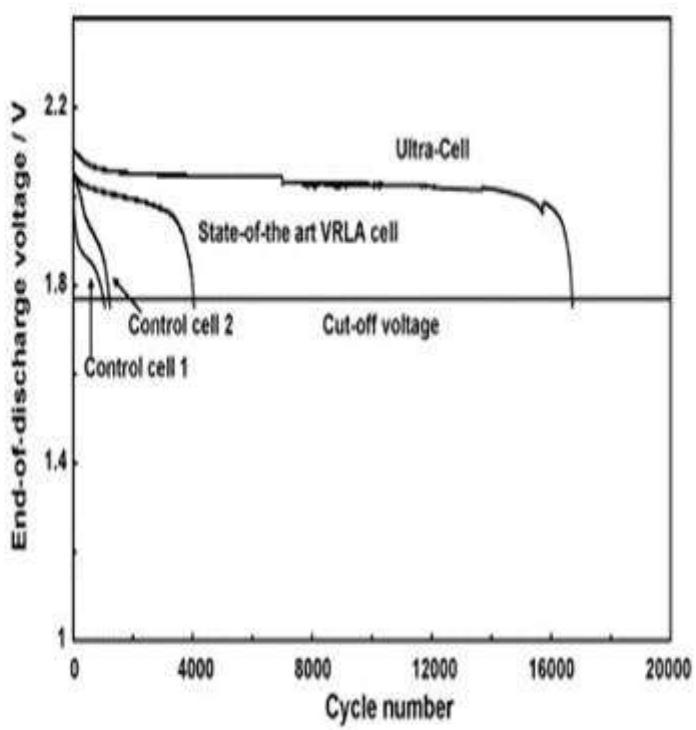
More from GE (Dr. Glen Merfeld)

Lead-carbon batteries

- Asymmetric capacitor – hybrid of lead-acid and carbon ultra-capacitor
- Lead electrode in lead-acid replaced by carbon electrodes of capacitor
- Energy stored at anode by double layer and possible H^+ pseudo-capacitance
- Carbon electrode acts as a buffer to charge/discharge currents, preventing high rates on lead negative electrode
- Improved cycle life and power



Courtesy The Furukawa Battery Co.

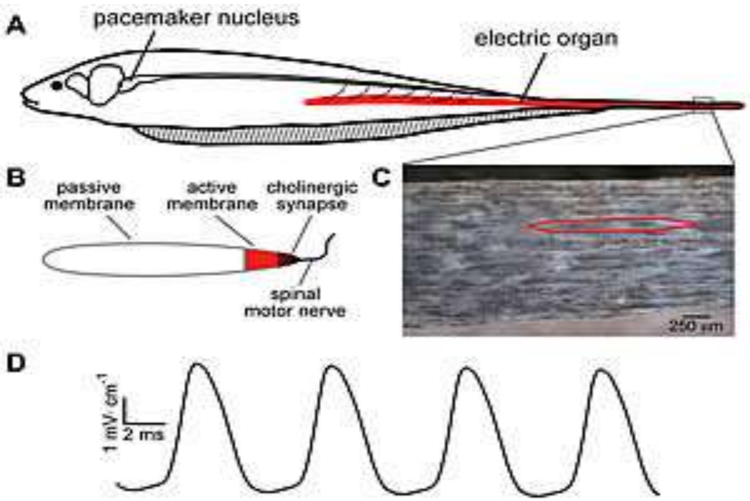


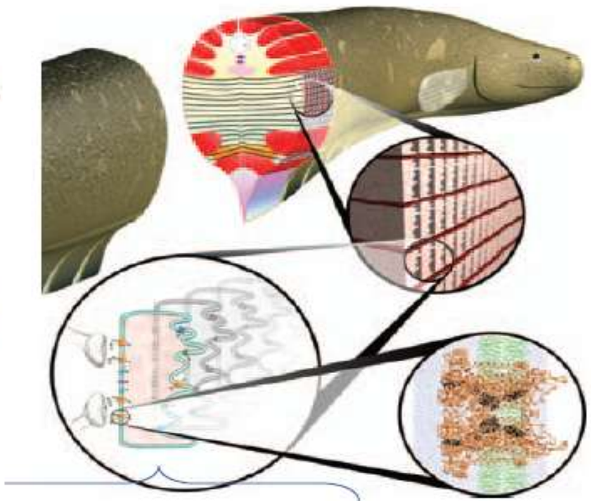
L. T. Lam, R. Louey, *Journal of Power Sources* **2006, 158, 1140;** ***b)P. T. Moseley,*** R. F. Nelson, A. F. Hollenkamp, *Journal of Power Sources* ***2006, 157, 3;***

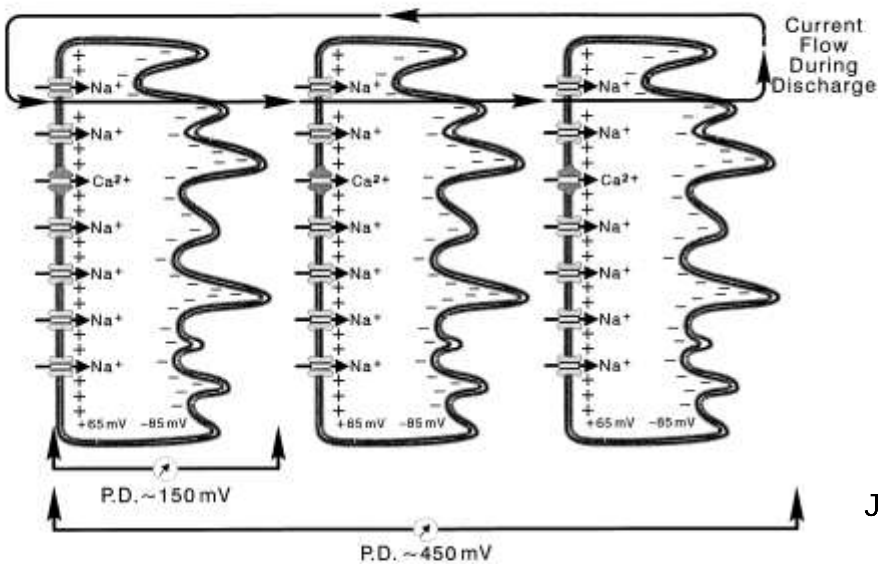
More from East Penn

Fundamental discoveries and total new mechanisms could lead to room temperature batteries for $100/kWh for large scale applications?

Biology stores energy with Na, K, Ca ions, not Li ions (electrical eels).



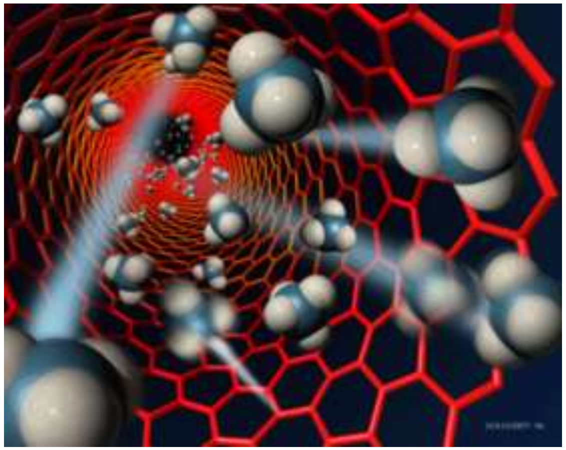


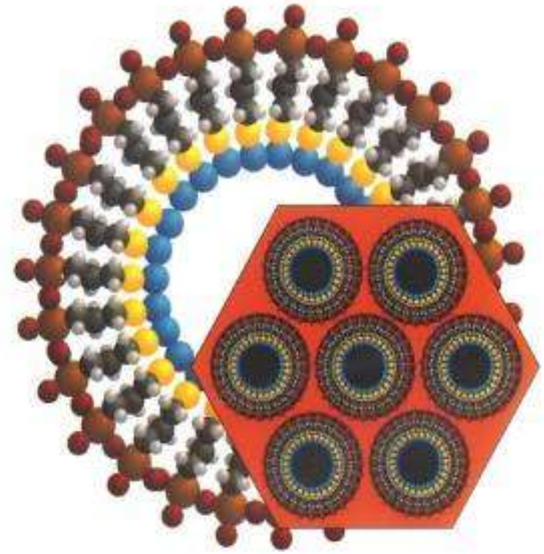


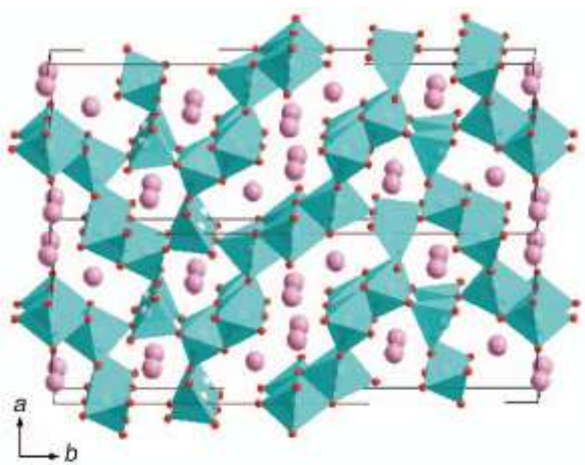
Storing large amount of energy using NaCl?

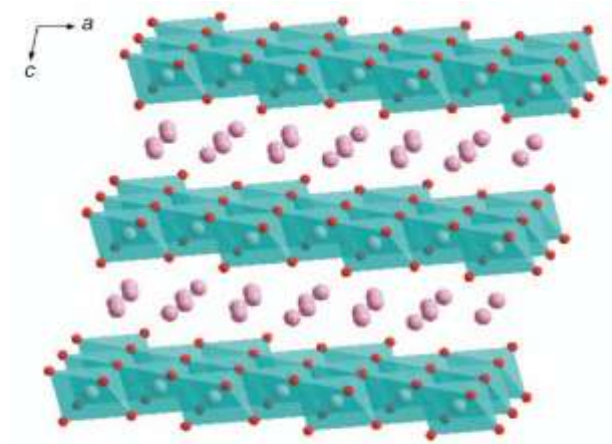
J. Xu, D. A. Lavan, *Nature Nanotechnology* ***2008, 3, 666.***

A wide range of host materials can be sued to Na ion storage

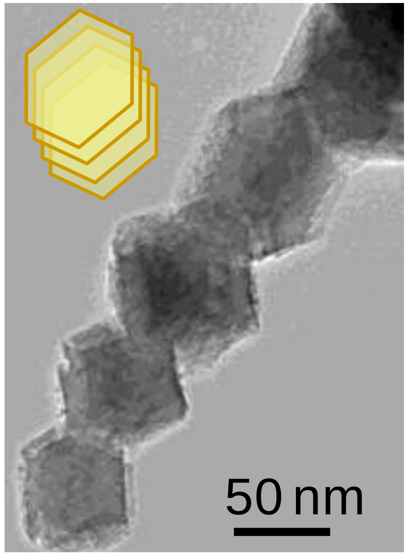


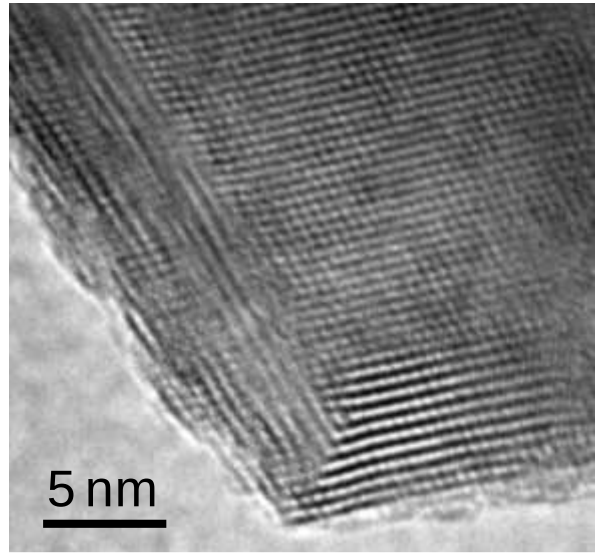


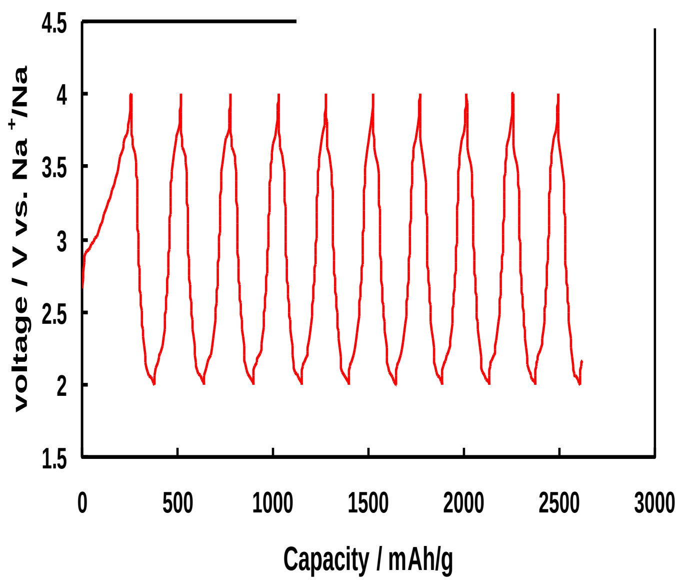


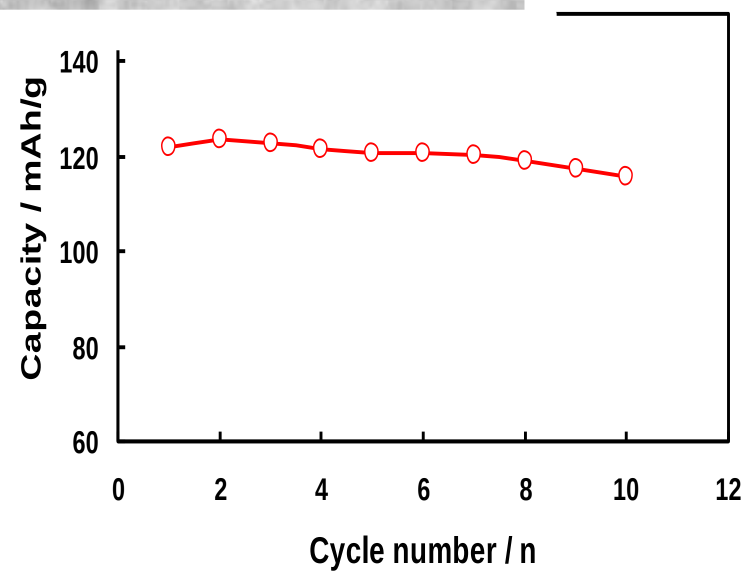


Fundamental discoveries and total new mechanisms could lead to room temperature batteries for $100/kWh for large scale applications?









A whole new class of materials that can store energy using Na ions or other environmentally friendly materials are yet to be discovered.

Pacific Northwest
NATIONAL LABORATORY

Grand Challenges for Large Scale Energy Storage

Fundamental understand of the materials properties and chemical processes in complex, reactive environments and systems;

New materials, chemistry and components to significantly improve the efficiency, reliability, safety and life span of current and future storage systems;

Revolutionary designs, concepts and architectures that can significantly reduce the system and maintenance cost: of large energy storage systems;

Novel energy storage mechanisms, energy storage technologies that are environmentally friendly and that are not dependent on materials and chemicals of limited supply;

Tools and methodologies to predict and analyze the economics of specific technologies for different scales/different applications and guide smart grid integration.