Exascale Energy Storage Research

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I. Science, economic and geopolitical drivers

Changing economics of U.S. energy supply

II. Energy storage and power density

III. Capacitors, supercapacitors and batteries

IV. Exascale: why is it needed and how can it help

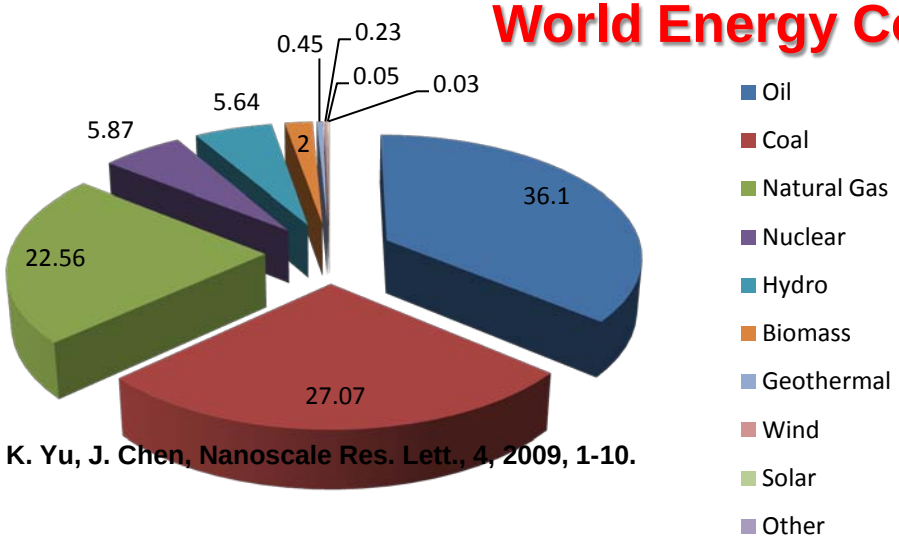
V. Broader impact on Science and Engineering

VI. Summary

Includes slides and input from Sreekanth Pannala and Bobby Sumpter. See their posters!!!

Energy Consumption and CO2 Emissions

World Energy Consumption



K. Yu, J. Chen, Nanoscale Res. Lett., 4, 2009, 1-10.

85.7% of worldwide energy consumption is from fossil fuels.

U.S. CO2 Emissions (EPA)

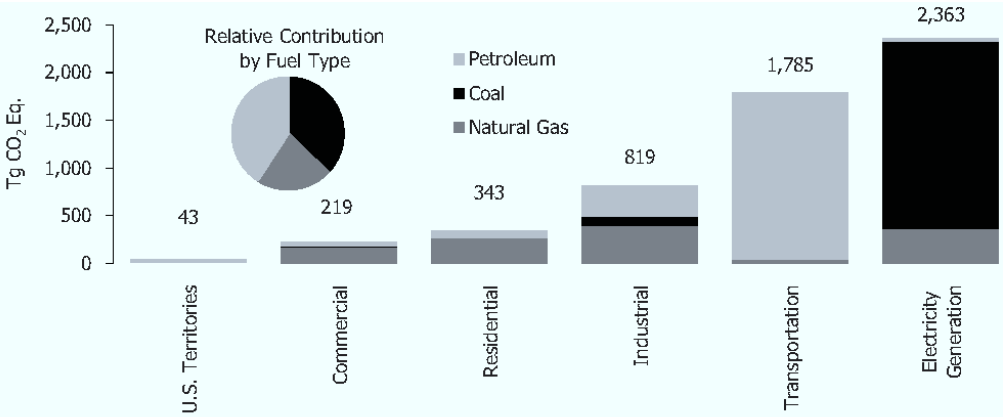
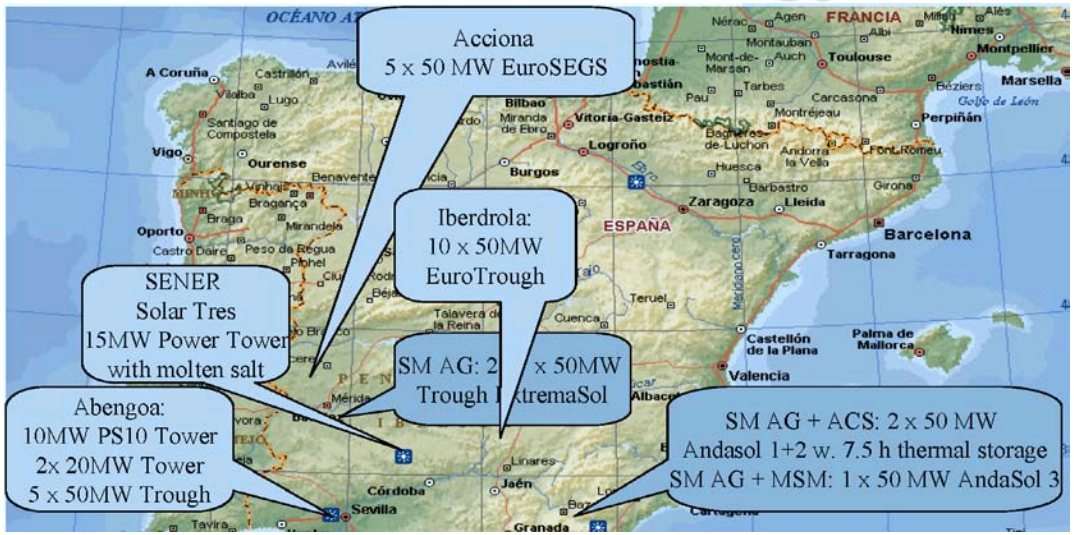


Figure ES-6: 2008 CO_2 Emissions from Fossil Fuel Combustion by Sector and Fuel Type

Transportation (oil) 32%
Coal (electricity) 34%

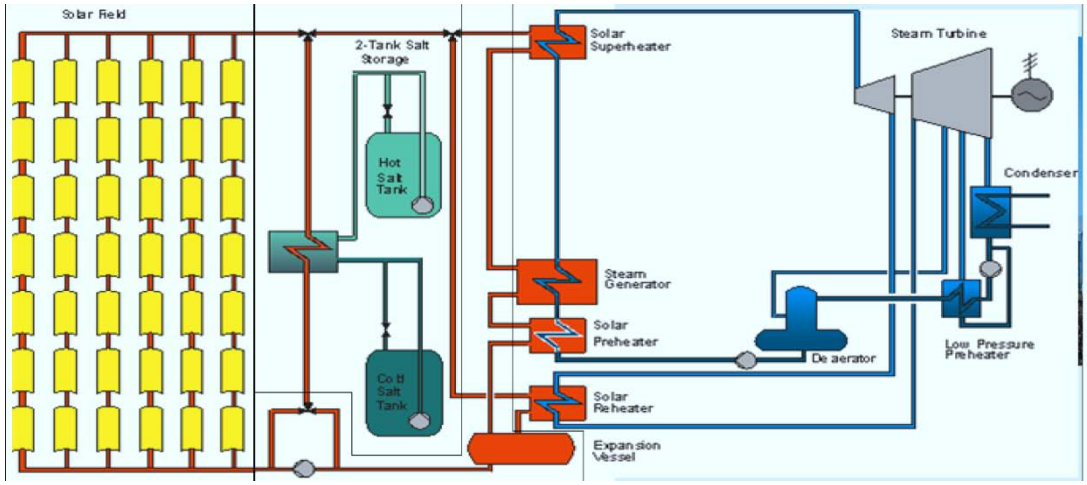
Reduction targets:
Europe 2020 20-30%
World 2050 50%

Solar-thermal plants in Spain: technology and economics



Solar heat drives a steam turbine. Excess heat is stored in molten salt for power generation at night.

Major solar-thermal power plants are planned in U.S. Southwest



Source: Solar Millenium AG

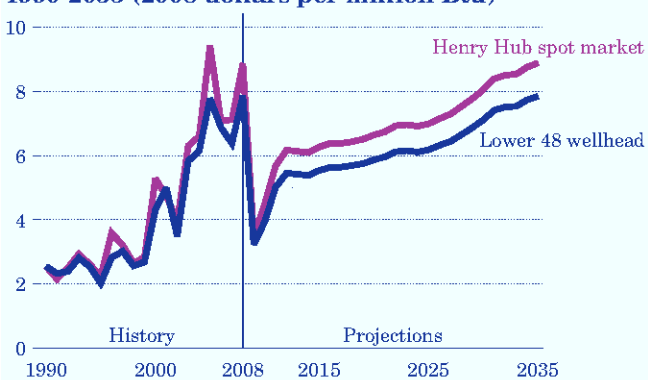
AndaSol-1 &- 2 plants in Spain: 1,020 MWh, 7.5 full load hrs, 31,000 tons of molten NaNO3/KNO3 salt

Economic crisis ends solar subsidies in Spain ⇒ stop to building of new solar plants

Changing economics of U.S. energy supply – major effect on economics of energy storage

- U.S. has coal reserves for > 200 years, but coal has v. large CO2 emissions
  - main usage – electricity generation
- Large imports of liquid fuels will continue for foreseeable future
  - main usage – transportation
- Breakthrough in mining of natural gas in the U.S.
  - New technology allows much better extraction – environmental impact??
  - New large natural gas fields discovered in the US: PA, TX, NY
  - Natural gas generates 50% less CO2 than coal.

Figure 69. Annual average lower 48 wellhead and Henry Hub spot market prices for natural gas, 1990-2035 (2008 dollars per million Btu)



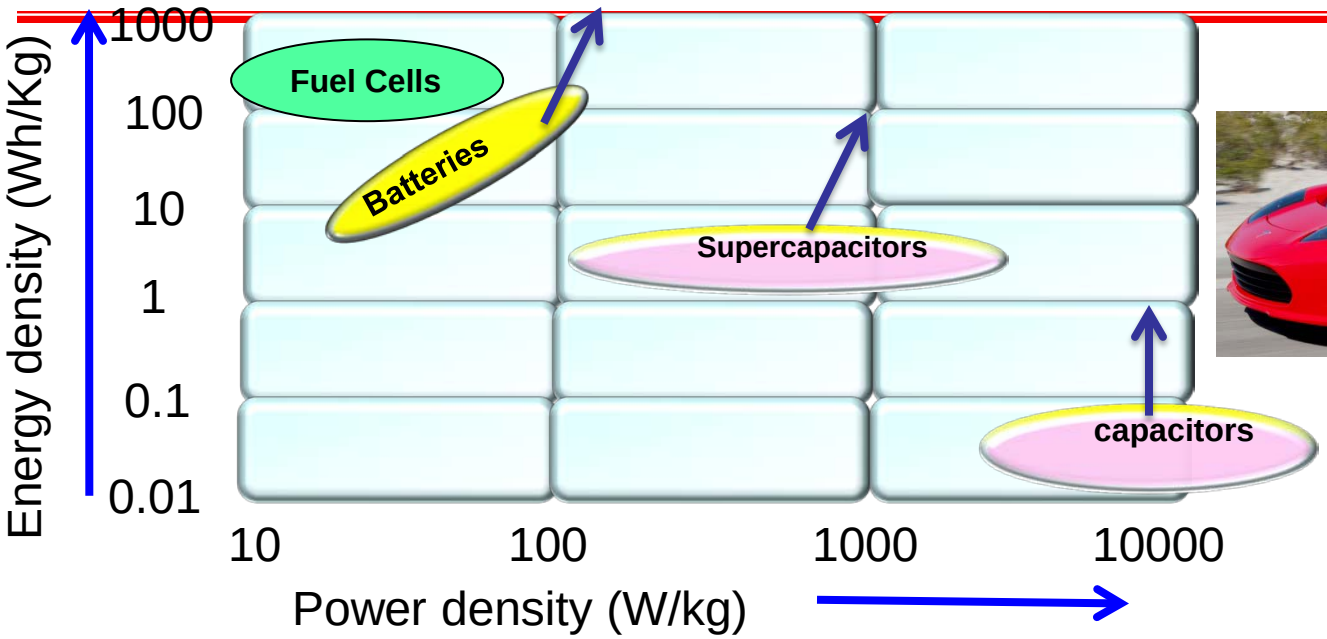
DOE/EIA April 2010

Associated Press Oct 13 2010: $3.50/MBtu
Price will stay below $4/MBtu, for next 80 y???
Current electricity generation: 48% coal, 21% gas
By 2015: 44% coal, 25% gas.

Richard Myers, VP, Nuclear Energy Institute: "*$4 natural gas challenges the economics of just about every other form of electricity generation*"

Constellation Energy just cancelled $10B nuclear plant in MD.
Wind energy investments are falling drastically

Transportation: energy storage and power density



Tesla

- **Major improvements necessary:**
  - ✓ **Higher energy-density batteries**
  - ✓ **Higher power-density capacitors**

Safety !!!
Cost !!!

Nissan Leaf – range ~ 100 miles

High Energy Density in Polymer-Based Capacitors

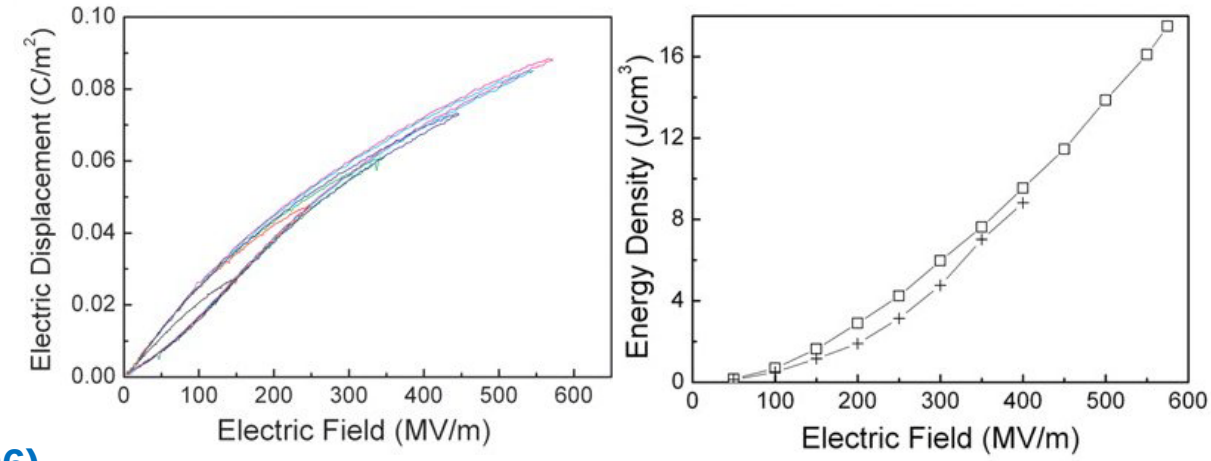
Polypropylene capacitors are most often used in high power applications:

- **low losses**
- **exceptional stability**
- **environmental friendliness**

BUT energy density ~ 4 J/cc.

Experimental Breakthrough:
Chu, Zhang *et al.*, Science (2006)

PVDF-CTFE (91/9) : ~ 18 J/cc

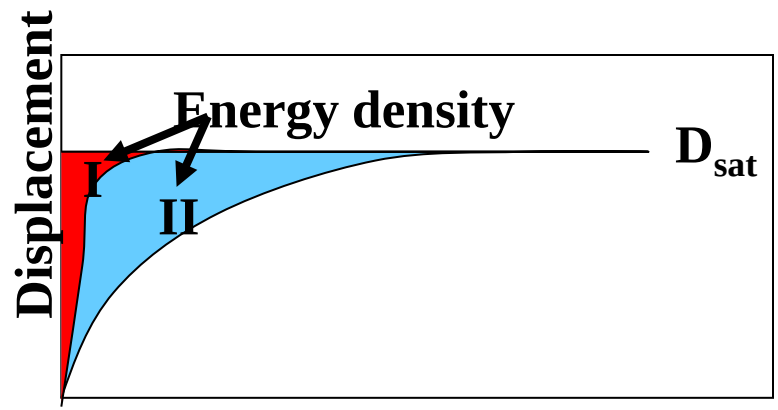


PVDF-CTFE (91/9)

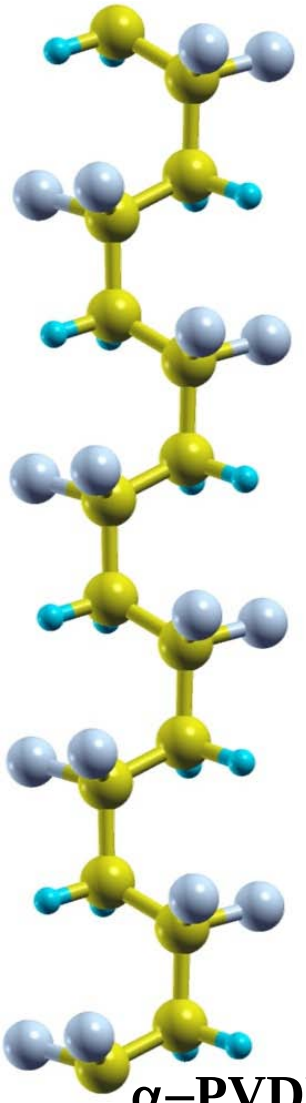
$$\xi = \int E dD$$ **Shaded area**

For the same D_{sat} the energy density is larger if D increases slowly

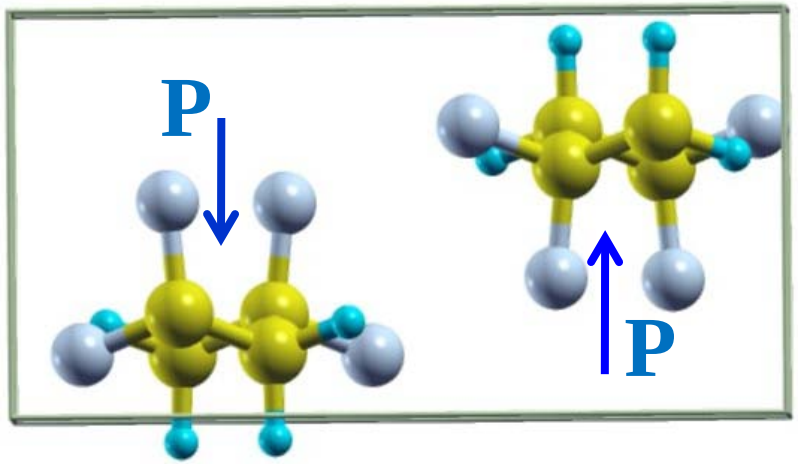
Area II > **Area I**



Two common phases of PVDF



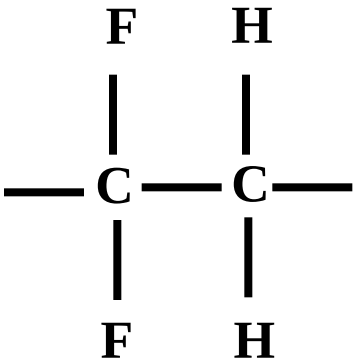
α–PVDF



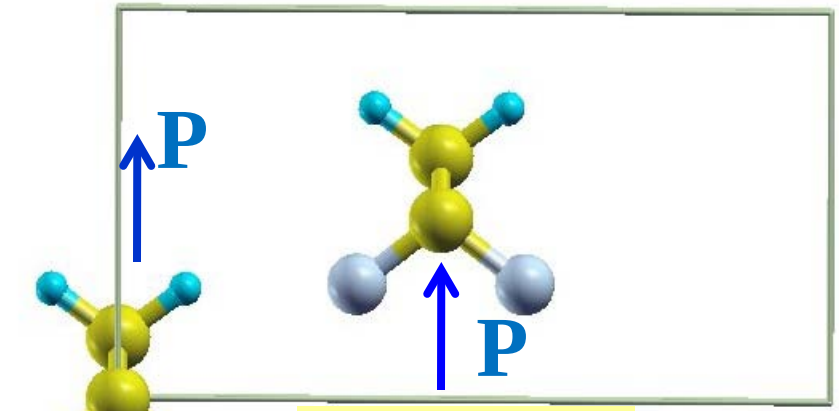
α–PVDF: non-polar

V = 222.55 Å^3
E = -490.6793 Ry

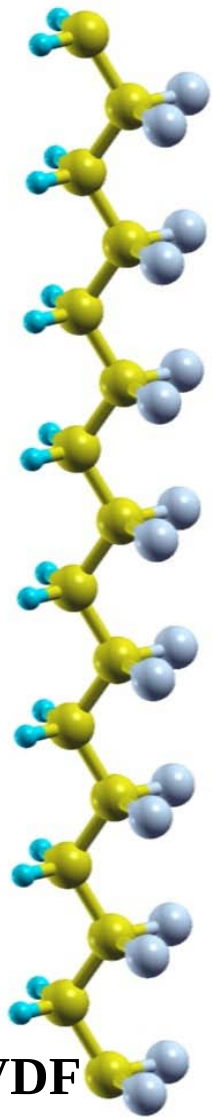
Ground state



β–PVDF: P = 0.19 C/m^2

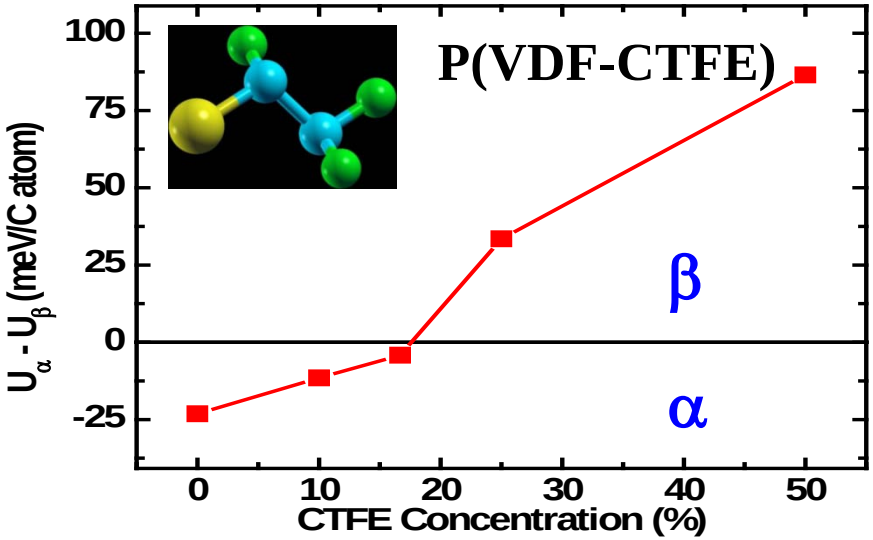


V = 212.47 Å^3
E = -490.666 Ry



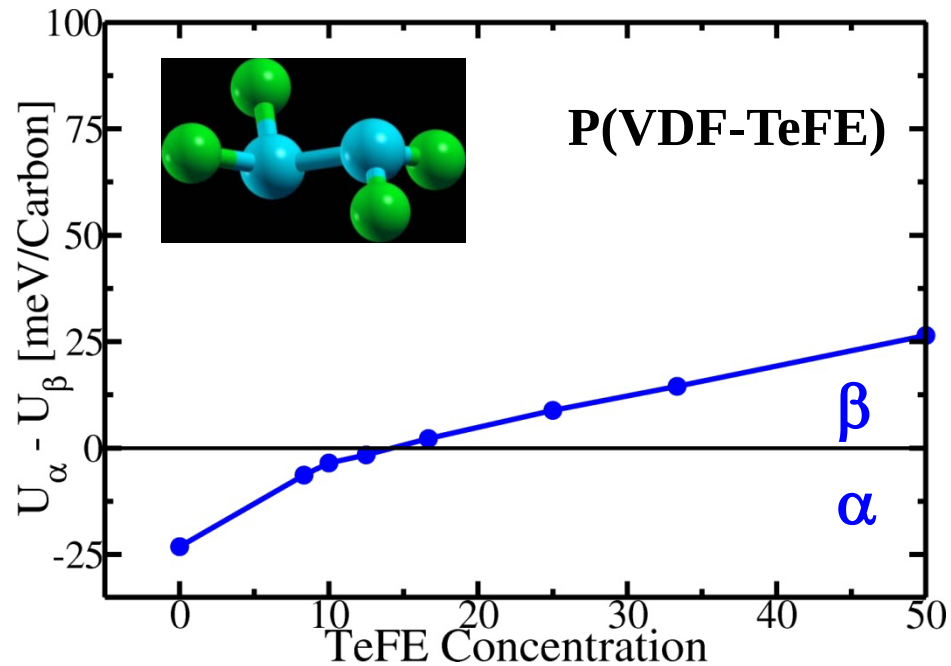
β–PVDF

Phase stability: CTFE and TeFE concentration in PVDF



- α phase is stable up to 20 % CTFE
- the energy difference decreases as CTFE concentration increases

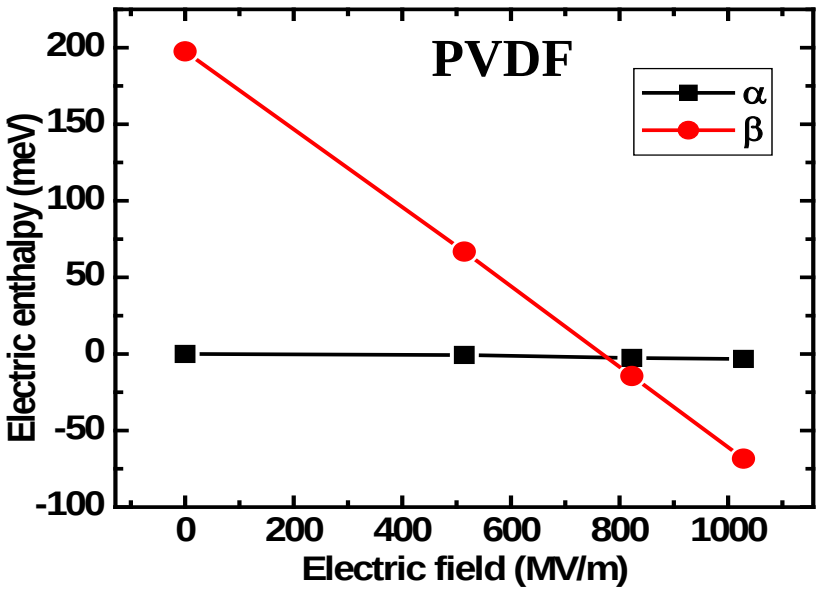
$$E_{crit} = \frac{U_\alpha - U_\beta}{P_\beta}$$



- α phase is stable up to 15 % TeFE
- energy difference is smaller between α and β for TeFE than for CTFE

Computational details : one impurity monomer in a progressively larger supercell

PVDF phase transformation in homogeneous electric field



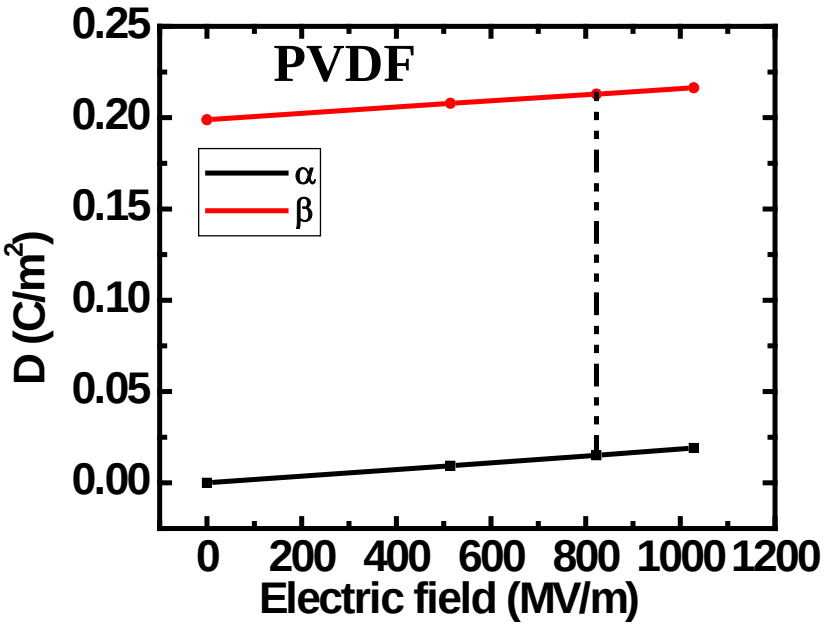
- At E=0 (and T=0) α–phase is the ground state.

$$F(E) = F(0) - V(P \cdot E)$$

- β–phase becomes favorable above 800 MV/m

PVDF

D in each phase does not change much with field

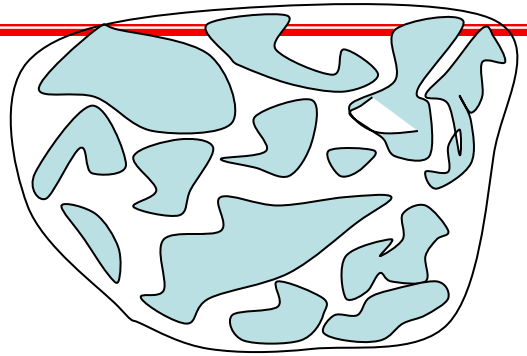


Phase transformation accompanied by

- Large change in polarization
- Volume change 4.5 %

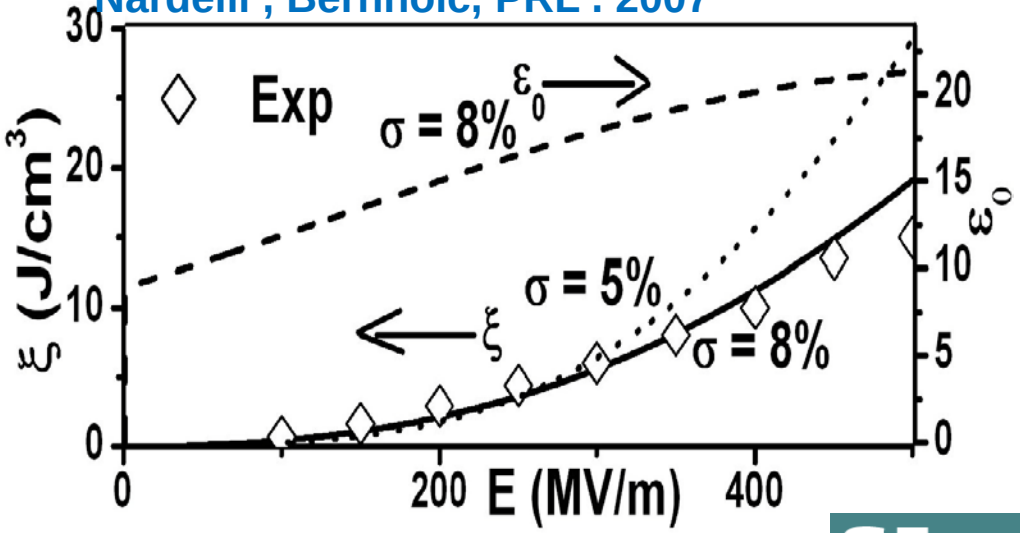
First order phase transition

High energy & power density in capacitors

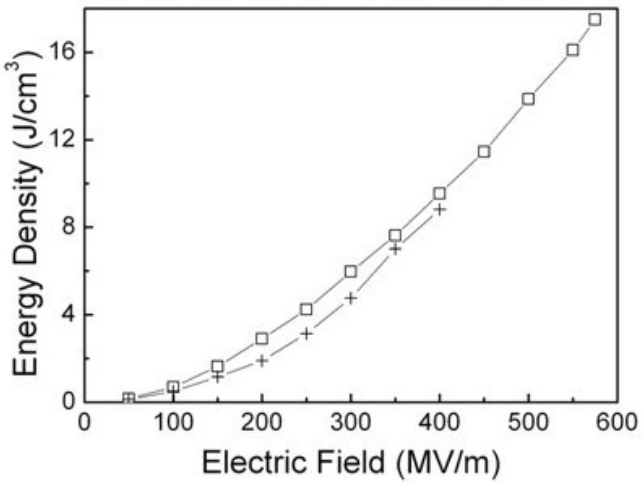


Assume disordered P(VDF-CTFE) consisting of nano domains with varying CTFE concentrations

Theory: Ranjan, Yu, Buongiorno Nardelli , Bernholc, PRL . 2007



Chu, Zhang *et al.*, Science 313, 334 (2006)



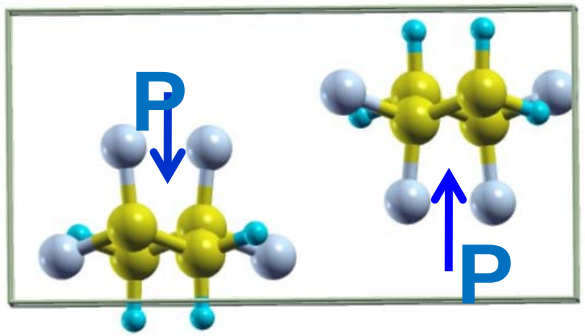
Inquiries from Tesla Motors and venture capitalists such as Kleiner & Perkins, Lux, Goldman-Sachs, etc.

Slashdot News for Nerds. Stuff that Matters.
Improved High-Performance Energy Storage

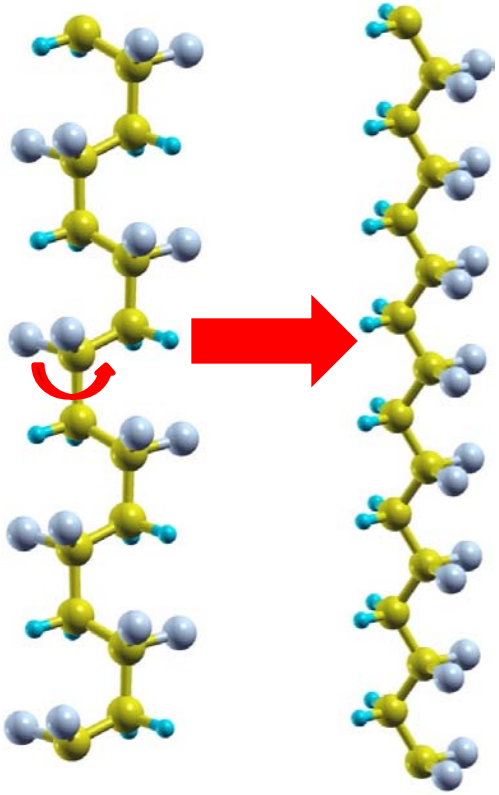
APS physics

UPI.com 100 YEARS OF JOURNALISTIC EXCELLENCE

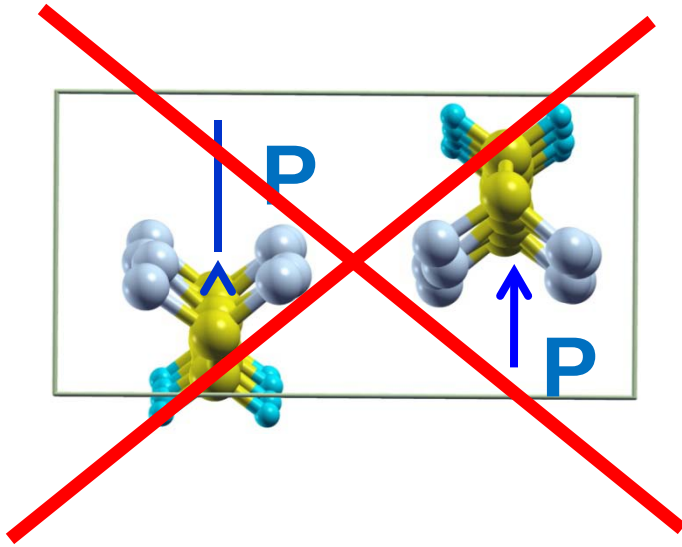
α to β transition



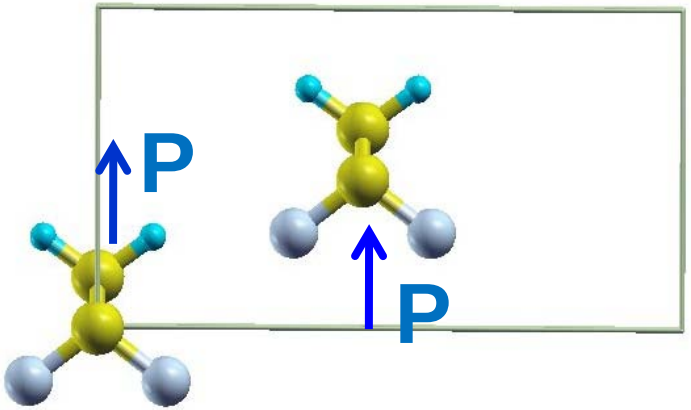
α-PVDF



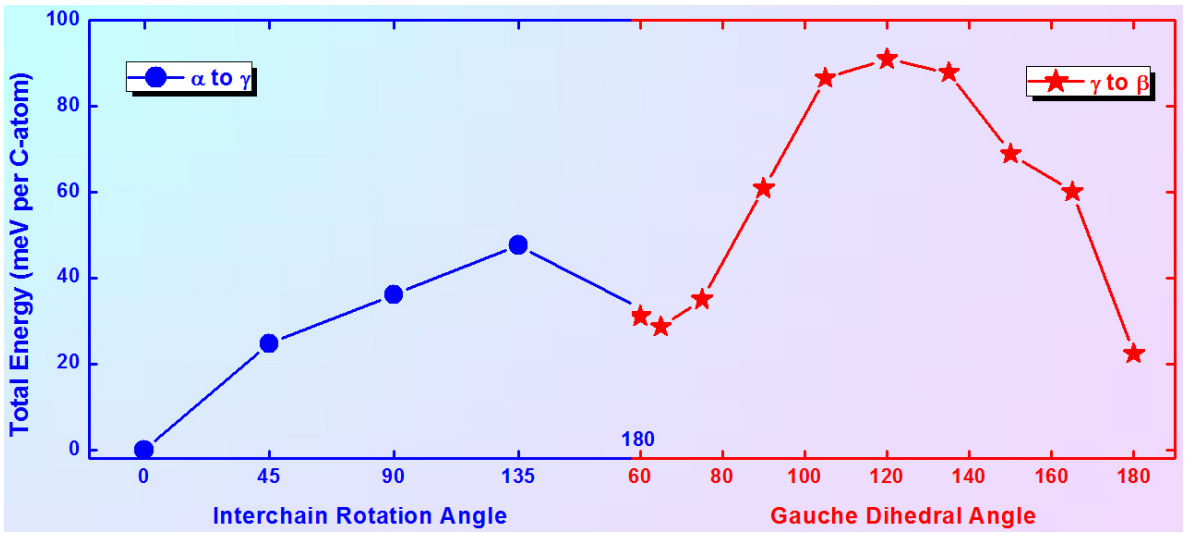
anti parallel β-PVDF



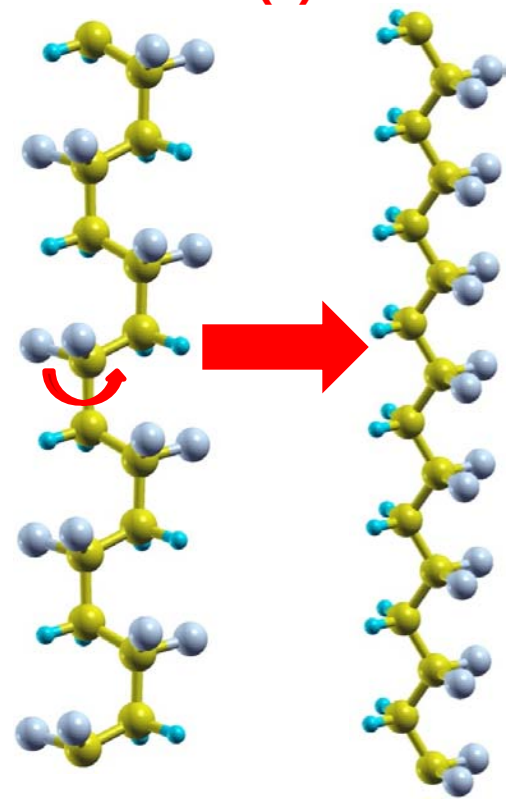
β-PVDF

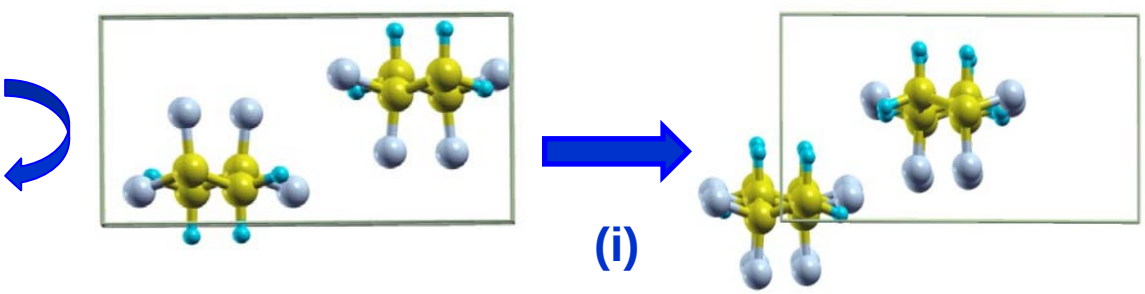


Energetics & Mechanism of Phase Transitions in PVDF



(ii)



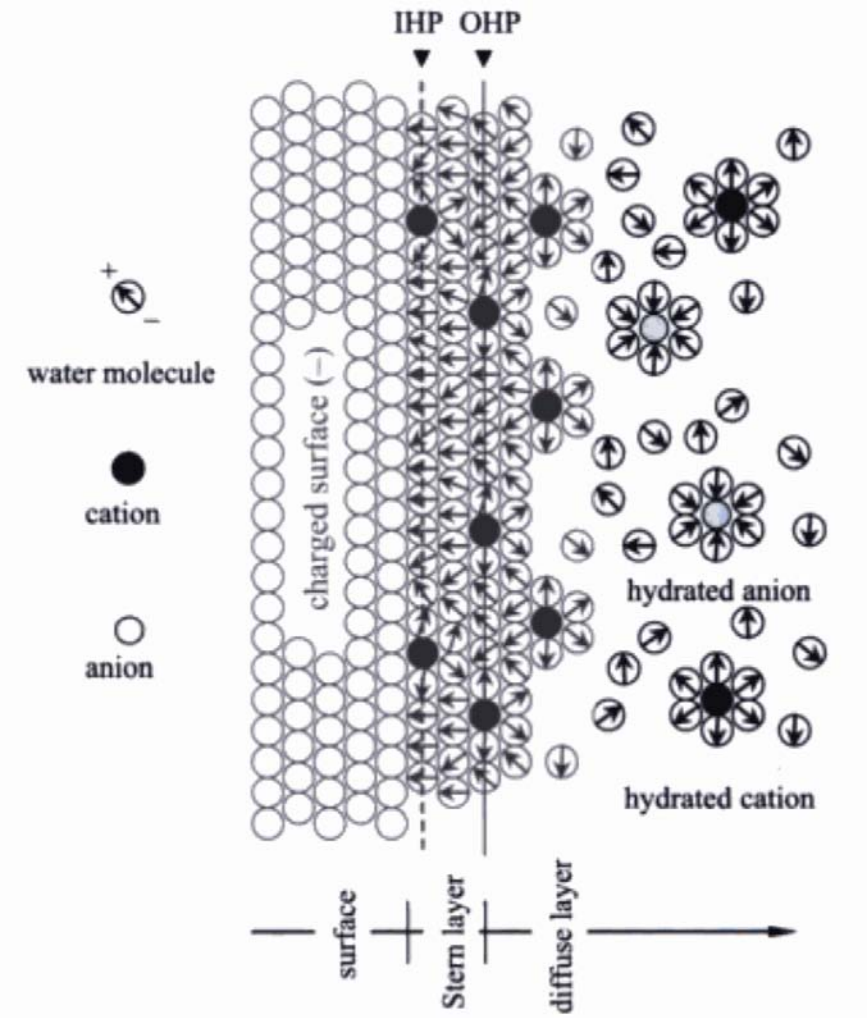


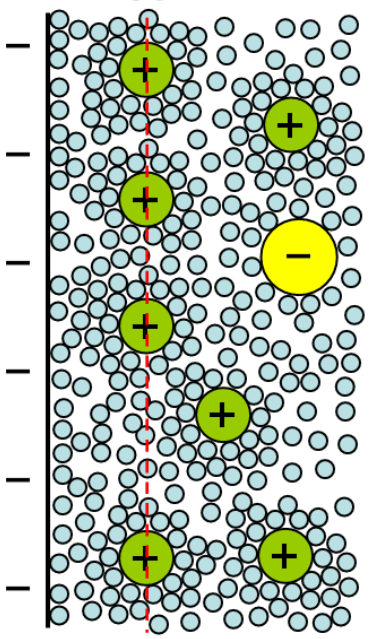
(i)

(i) Inter-chain rotation angle (θ) : α to γ.

(ii) Dihedral angle (ϕ): γ to β.

Electrical double-layer dictates the functioning principle of a supercapacitor





"Super"-Capacitor

$$C = \frac{\varepsilon A}{d}$$

Surface area

Thickness

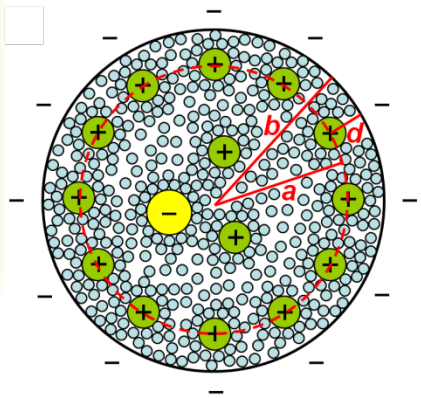
Courtesy of Bobby Sumpter

Beyond the parallel plate model

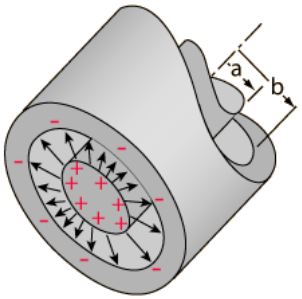
$$C = \frac{\varepsilon A}{d}$$

Plate capacitor

EDCC (electrical double cylinder capacitor)



$$C/A = \frac{\varepsilon_r \varepsilon_0}{b \ln\left(b/(b-d)\right)}$$

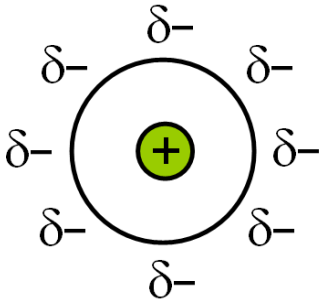


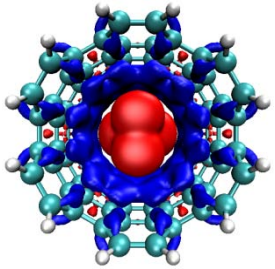
$$C = \frac{2\pi \varepsilon_r \varepsilon_0 L}{\ln(b/a)}$$

Cylindrical capacitor

EWCC (electrical wire in cyclinder capacitor)

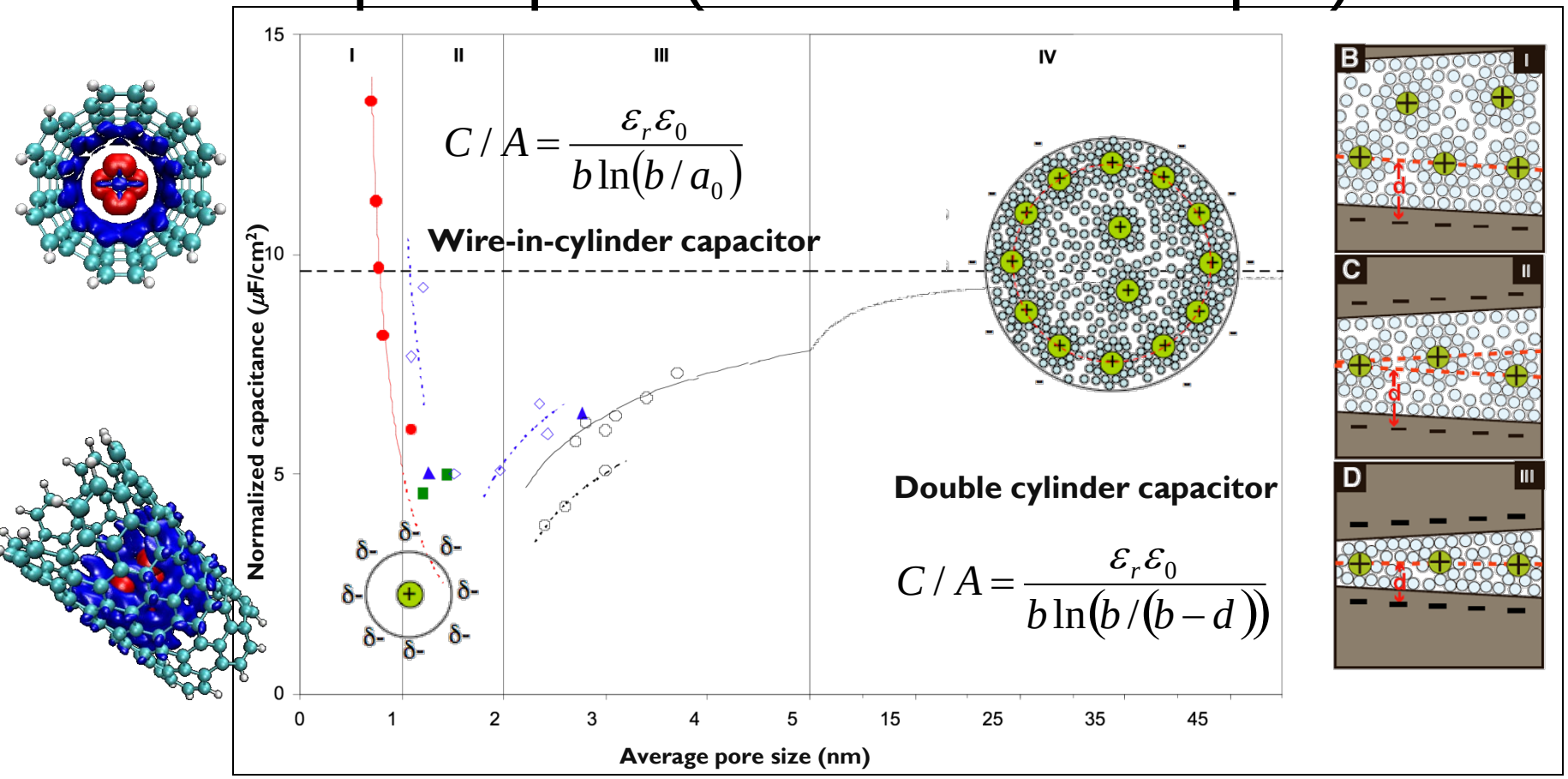
$$C/A = \frac{\varepsilon_r \varepsilon_0}{b \ln(b/a_0)}$$





Courtesy of Bobby Sumpter

Dramatic raise in capacitance for nanoporous supercapacitors explained from first-principles (with minimum input)



Exp: Chmiola, J.; Yushin, G.; Gogotsi, Y.; Portet, C.; Simon, P.; Taberna, P. L. *Science*, 2006, *313*, 1760.
First Principles Theory: J. Huang, B. G. Sumpter, V. Meunier, Angew. Chem. Int. Ed. 2008, 47, 520.

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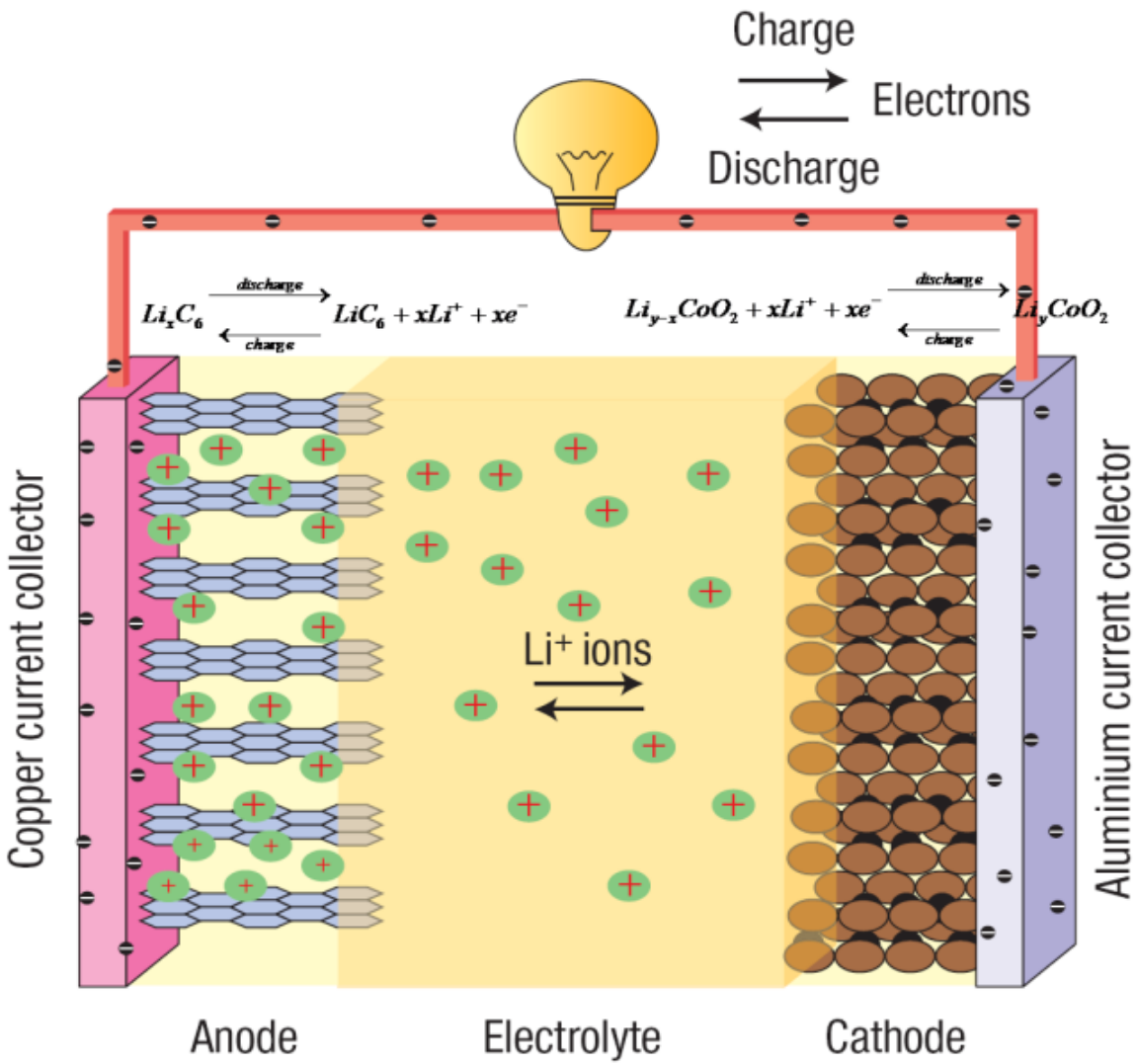
Courtesy of Bobby Sumpter

Modeling Li-ion batteries

Anode:
LiC_6

Cathode:
$LiCoO_2$
$LiFePO_4$

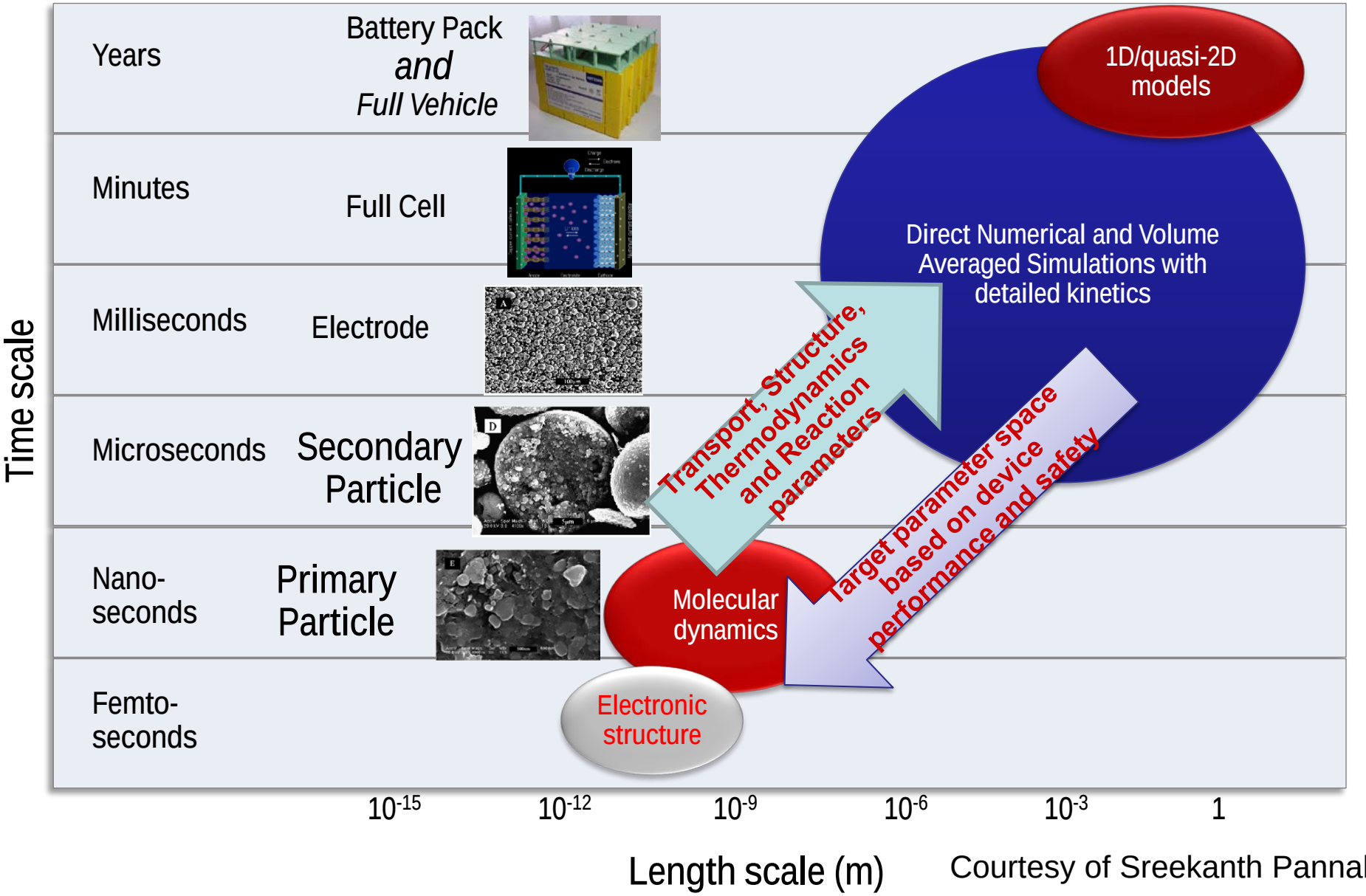
Better cathode and nanostructure needed



Schematic of a typical Li-ion cell sandwich (adapted from Scrosati, 2007).

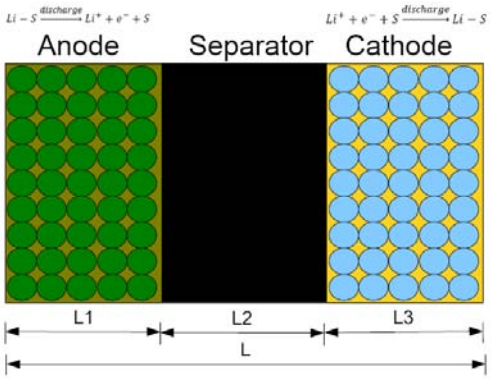
Courtesy of Sreekanth Pannala

Time and Length Scales for Modeling



Courtesy of Sreekanth Pannala

Continuum simulation of Li-ion cell



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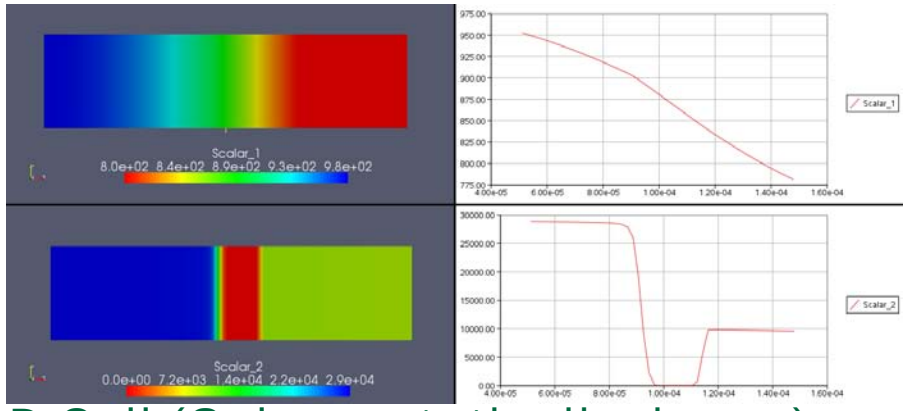
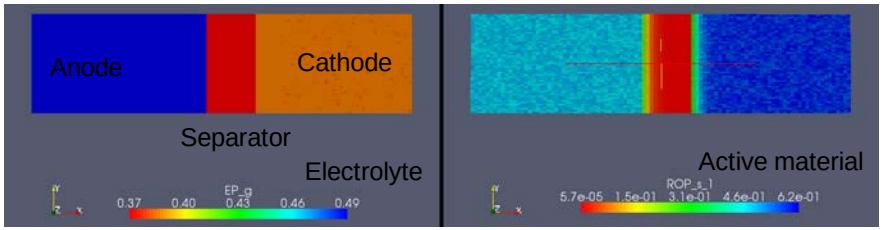
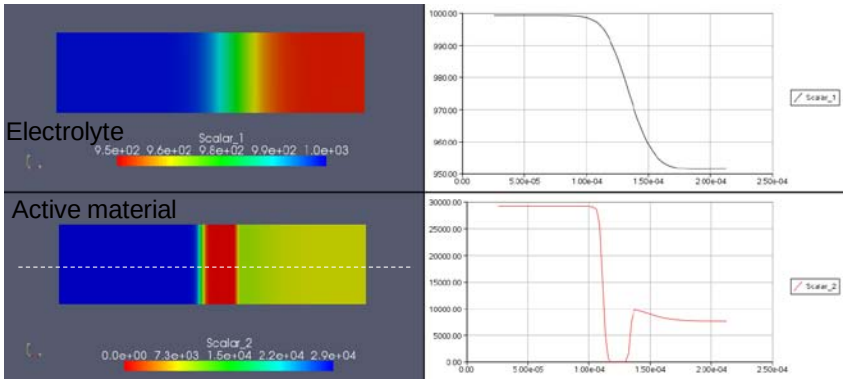
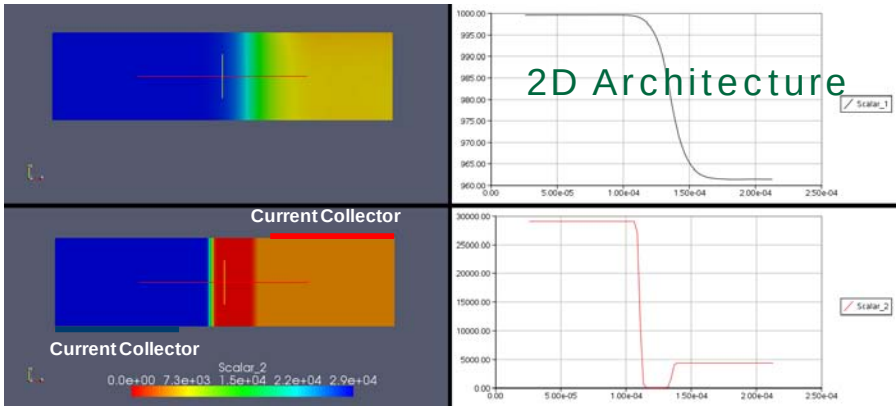


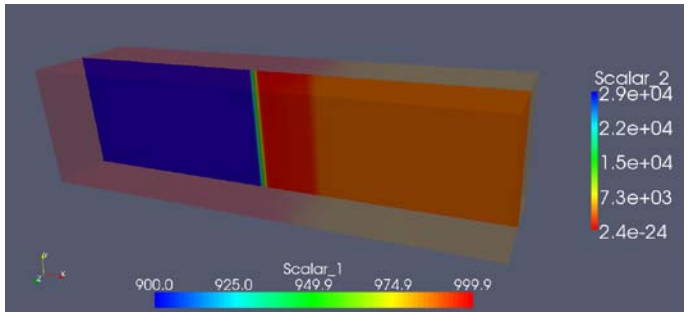
1D Cell (Galvanostatic discharge)





Random Microstructure – Galvanostatic discharge





3D Cell

Pannala et al., ECS Spring 2010

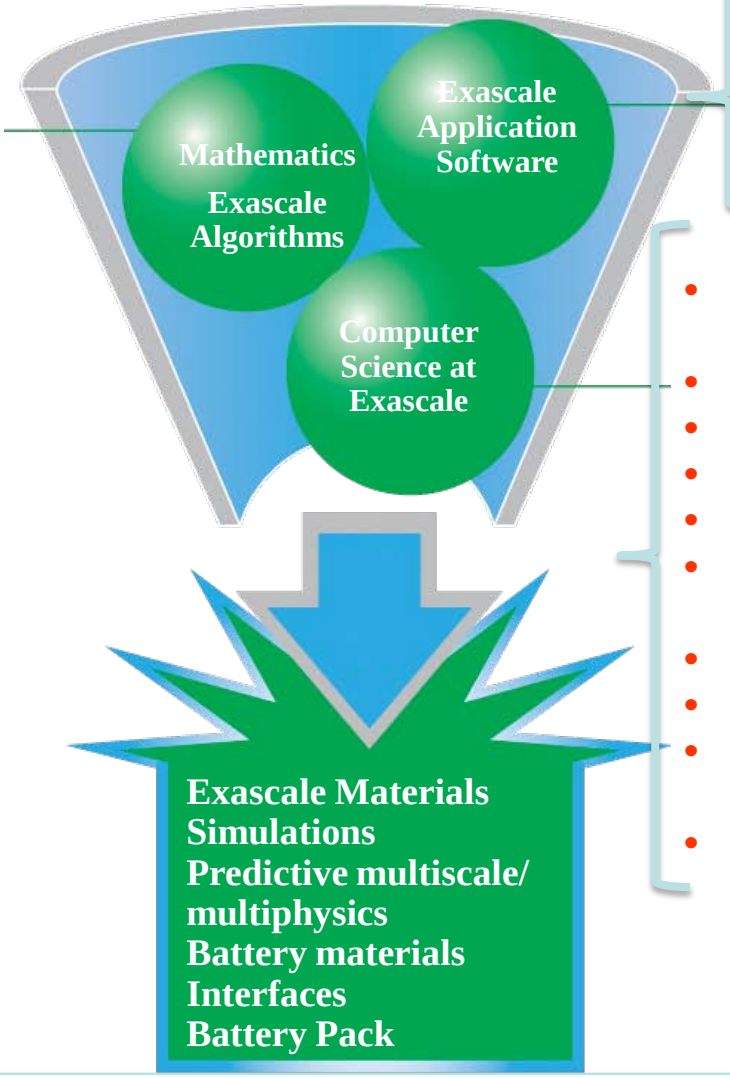
Adding electronic structure, atomistics, multiscale ⇒Exascale challenges

Case Study	Method	Computational Details
Accurate model for cathode material	QMC	1000 atoms; 10,000 electrons
Screening of cathode material	DFT/AIMD	10,000 atoms; 1000s of realizations
Solid-electrolyte interface formation and stability	RxMD/MD	mm^3 volume, several electrode/electrolyte combinations
Battery pack simulations resolving electrode/ electrolyte interfaces	3D transient continuum solvers	10 cm^3 volume, 10^{12-13} grid points with adaptivity

Courtesy of Sreekanth Pannala

Development of Exascale Simulation Tools for Batteries

- Linear and non-linear solvers
- Uncertainty Quantification
- PDE Solver framework
- Exascale algorithms
- Optimization



- Quantum
- Atomistic
- Mesoscopic
- Continuum

- Tools for hierarchical systems
- EDSL
- Run-time system
- Load balancing algorithms
- Fault resilient approaches
- Communication-avoiding algorithms
- Exascale I/O
- Data and Metadata
- Multiple precision algorithms/software
- Software V&V

Courtesy of
Sreekanth Pannala

- Uncertainty quantification, verification and validation
- Experimental collaboration and validation
- Industrial applications and collaboration

Challenge for computational nanoscience

	atoms molecules	nanostructures	bulk
size & time scale	1-100 atoms	1000-10^6 atoms	Infinite (1-10 atoms in a unit cell)
method	*ab initio* method $O(N^3)$	Algorithms do not scale; continuum methods not applicable; Codes may not parallelize	• *ab initio* method • Effective mass method

ab initio elements and reliability

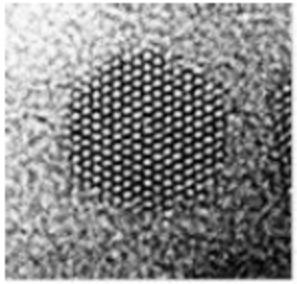
New algorithms

Exascale Supercomputers

Adapted from John Meza

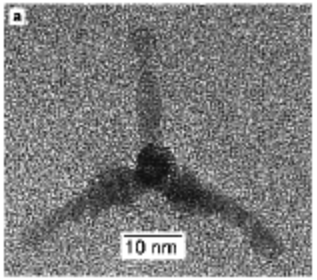
Why are large scale electronic structure calculations required?

- Nanosystems often involve 1,000 to 1,000,000 atoms



CdSe QD

~1000-5000

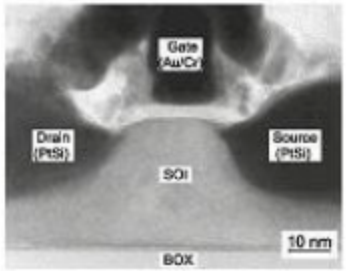


Tetrapod

>10,000

A Solar Cell

>50,000



CMOS

~1,000,000 atoms

- Atomic details are still important:
  - surface charge, impurity, dopant, symmetry, passivation
- Thus, *ab initio* total energy electronic structure calculations are needed.

From John Meza

Other areas and fields would also benefit from exascale "battery" simulation tools

Discipline	Simulation Need	Significance
Biochemistry and Molecular Biosciences	Structure/property relationships; mechanisms of enzymatic reactions	Understanding of novel biochemical function and of essentials of life processes, enabling realistic, high-level models of biological systems; Tailoring antibiotics to fight new strains of bacteria
Chemistry	Ab initio simulation of (nano) catalytic reactions in solution, charge-transfer reactions in solution, light-induced reactions	Understanding and design of novel catalytic and bio-inspired reactions; Efficient conversion and trapping of pollutants, better routes to biofuels, simpler synthesis of new drugs
Computer Science and Engineering	Simulation and design of photonic, molecular and nanoscale devices	Novel, ultrahigh-speed logic and memory with very low power requirements. Quantum computers
Earth Science	Understanding of matter at extreme conditions	Prediction of seismic shocks and volcano eruptions; understanding of planetary evolution
Engineering	Simulation of chemical and biochemical processing; material stresses at extreme conditions	Cleaner manufacturing methods; novel and nanostructured materials; much reduced waste reduced-energy input engines and buildings
Environmental Sciences	Formation, reactivity and transformation of pollutants, corrosion and breakdown processes.	Efficient conversion and trapping of pollutants, environmental sensors, new environmentally friendly cleanup processes
Homeland Security	Development of chemical and biological sensors, design of impenetrable but breathable fabrics	Sensors with nearly single-molecule detection limit and high selectivity, new protective clothing.
Materials Science	Multiscale modeling of complex and nanostructured. Design of new materials. Simulation of processes, including self-assembly.	"Virtual" design of materials with specified properties from first principles; Design of nanostructured materials with novel properties; Understanding and prediction of material response, damage, and failure

Summary

- **Transportation – THE frontier for energy storage**
  - **Very strong <u>drivers</u>: CO2 emisions, economics, geopolitics**
  - **Enhanced materials with either high-energy or high-power density storage are needed. Nanostructure is key!**
  - **Nanosimulations require exascale. So does modeling of processing, device function, and safety.**
  - **Materials simulation tools developed for batteries will have much broader impact.**

Past

Almost here

Future