Electrochemical/Battery Storage Technologies

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Electrical Energy Storage Technologies and Applications Workshop

March 20 – 21, 2013

Argonne National Laboratory

Illinois Institute of Technology (IIT)

- IIT is a national, technological, PhD-granting research university, with world-renowned programs in engineering, architecture, the sciences, humanities, psychology, business, law, and design.
- Currently, IIT has about 8,000 students annually among them 4,000 are graduate students.
- IIT boasts 4 research institutes and 26 research centers through which faculty and graduate students conduct basic and applied research.
- In particular, the Wanger Institute for Sustainable Energy Research & Robert W. Galvin Center for Electricity Innovation offer energy-related interdisciplinary research.

✓ IIT has five campus locations across the Chicago metropolitan area.

✓ The main Campus is located in Chicago's historic Bronzeville neighborhood.

IIT Current Niche Research Areas

- **Smart Grid and Perfect Power**
- **Optimum Design of Wind Power**

- **Energy Efficiency including Sustainable Built Environment, Energy Storage, and Plug-In Vehicles**

- **Coal and Solid Fuel Gasification, Conversion, and CO_2 Separation and Sequestration**

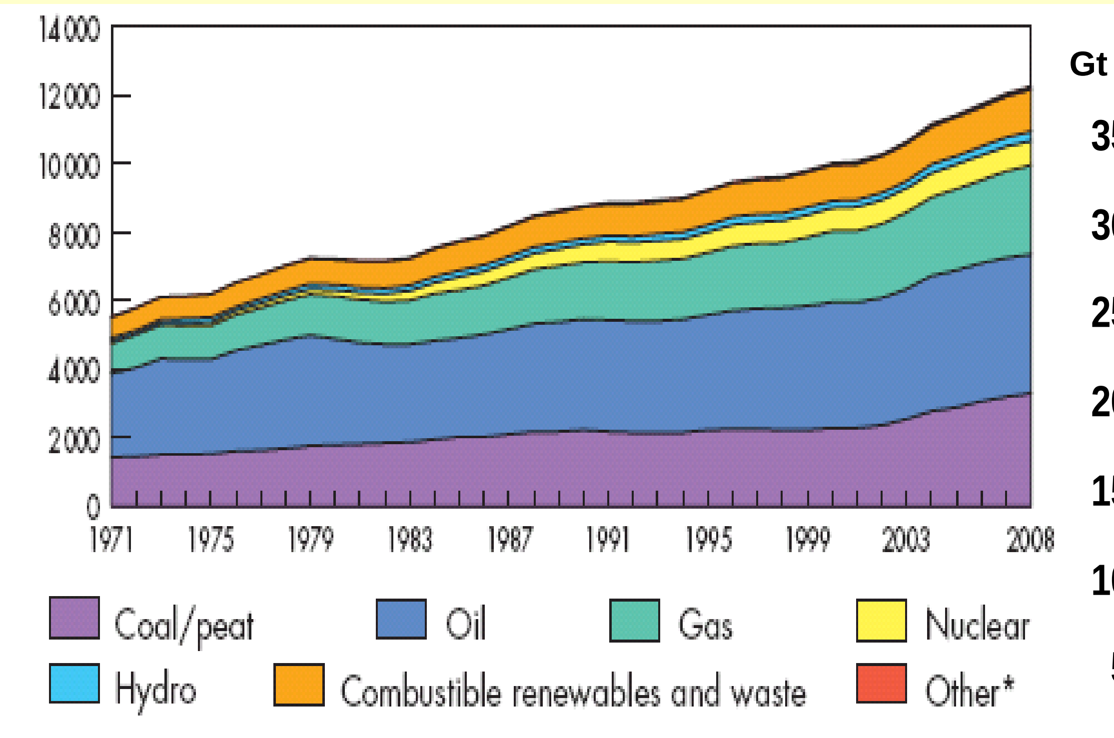
Outline

- The Need for Energy Storage
- Technology Requirements
- Introduction of Batteries
- Li-ion Batteries
- Flow Batteries
- Electrochemical Capacitors
- Conclusions

<u>The Need</u>: Global Energy and Environmental Challenges

World Energy Consumption (1971-2008)

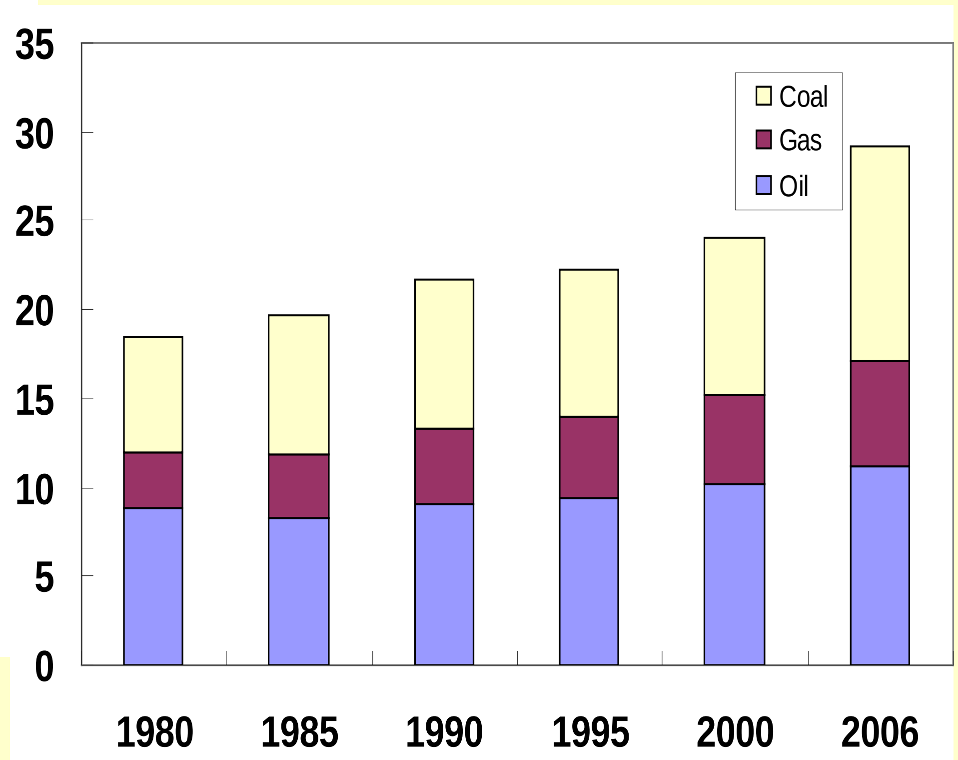
Mtoe



Source: EIA

CO_2 Emission from Consumption of Fossil Fuels

Gt



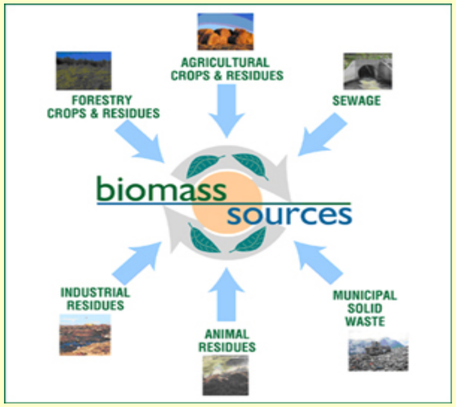
Source: EIA

Solutions?

Energy Storage: Solutions to Sustainable Energy and Environment

- **Better manage the use of renewable energy resources (Solar, Wind, Tide, Hydropower, Geothermal, Biomass, *etc*.)**

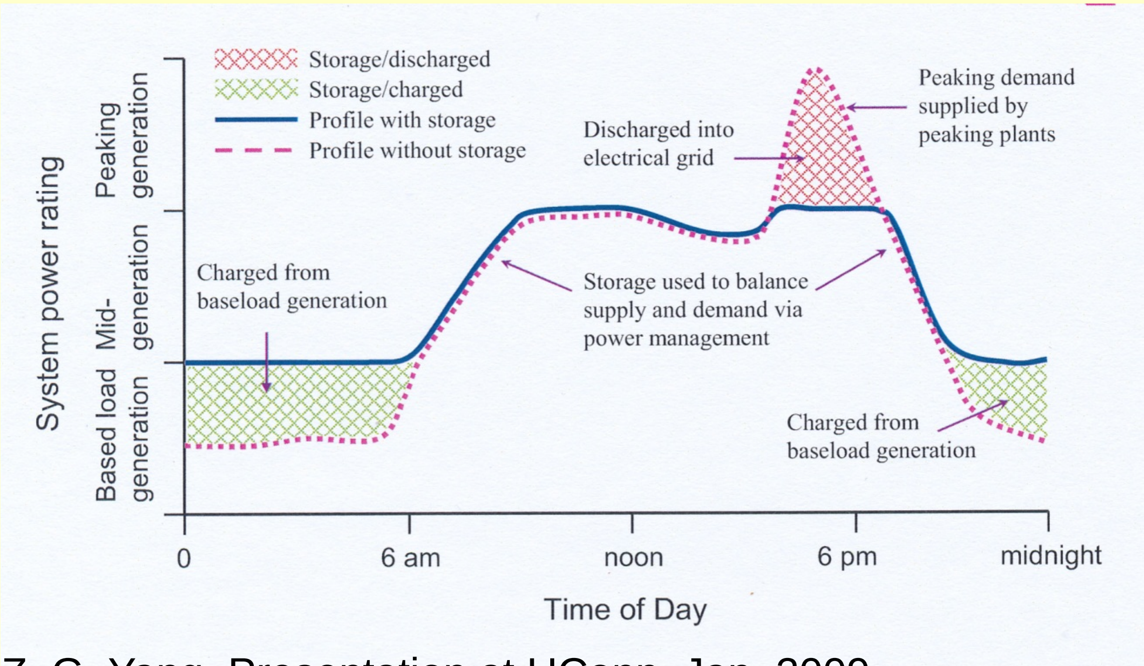


- **Develop electric vehicles to ensure efficient use of energy, diversified energy sources, and a better environment**


The Need of Energy Storage for Utility Applications

- **Renewable energy integration:** make intermittent renewable energy dispatchable and effective use
- **Peak shaving and load shifting:** improving power economy
- **Frequency regulation:** providing responsive power to meet second-to-second and minute-to-minute demands and increase operational margins against grid upsets
- **Grid reliability and stability:** preventing voltage sag and blackout



Z. G. Yang, Presentation at UConn, Jan. 2009.

The Need for Electric Vehicles

- **Energy Security:** diversify energy sources and decouple from imported petroleum – all U.S. electricity is produced from domestic coal, nuclear energy, natural gas, and renewable resources

- **Fuel Economy:** HEVs, PHEVs and Evs can reduce fuel costs because of the low cost of electricity relative to gasoline and diesel.

- **Energy Efficiency:** EVs convert 59 – 62% of the electrical energy from the grid to power at the wheels, whereas gasoline vehicles only convert 17 – 21% of the gasoline energy to power at the wheels.

- **Better Environment:** Reduce the life cycle greenhouse gas emission if electricity is produced from nuclear-, hydro-, solar-, or wind-powered plants.

Technology Requirements

Major Parameters often used to describe the requirements and performance:

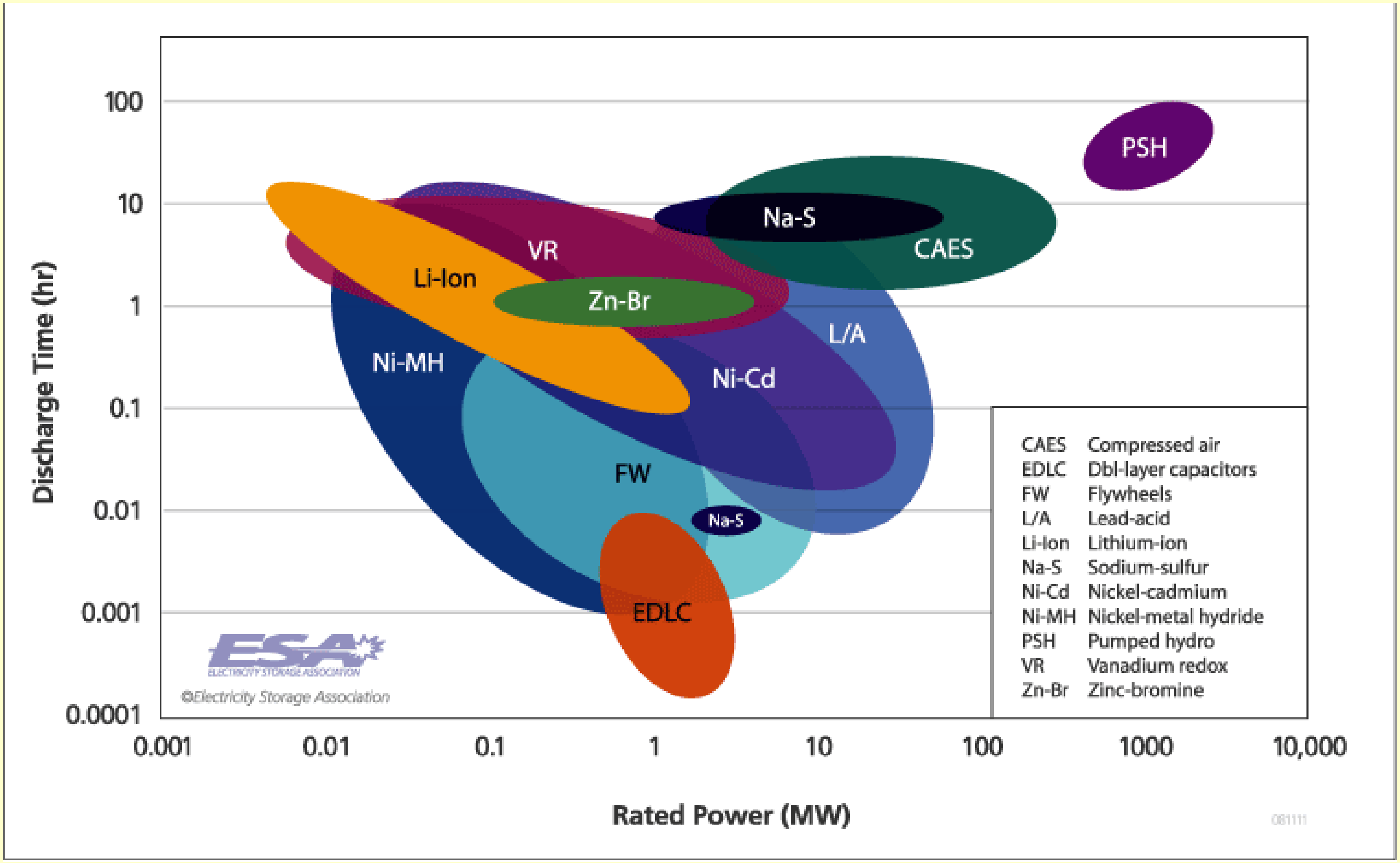
- **Charge/Discharge Time** – seconds, minutes, hours, etc.
- **Power** – the rate of energy transfer, 1 watt = 1 joule/sec = 1 ampere•volt, … KWs, MWs, GWs
- **Energy** – KWh, MWh, GWh
- **Power Density (W/L) & Specific Power (W/kg)**
- **Energy Density (Wh/L) & Specific Energy (Wh/kg)**

Technology Options for Electrical Energy Storage

Electrical Energy

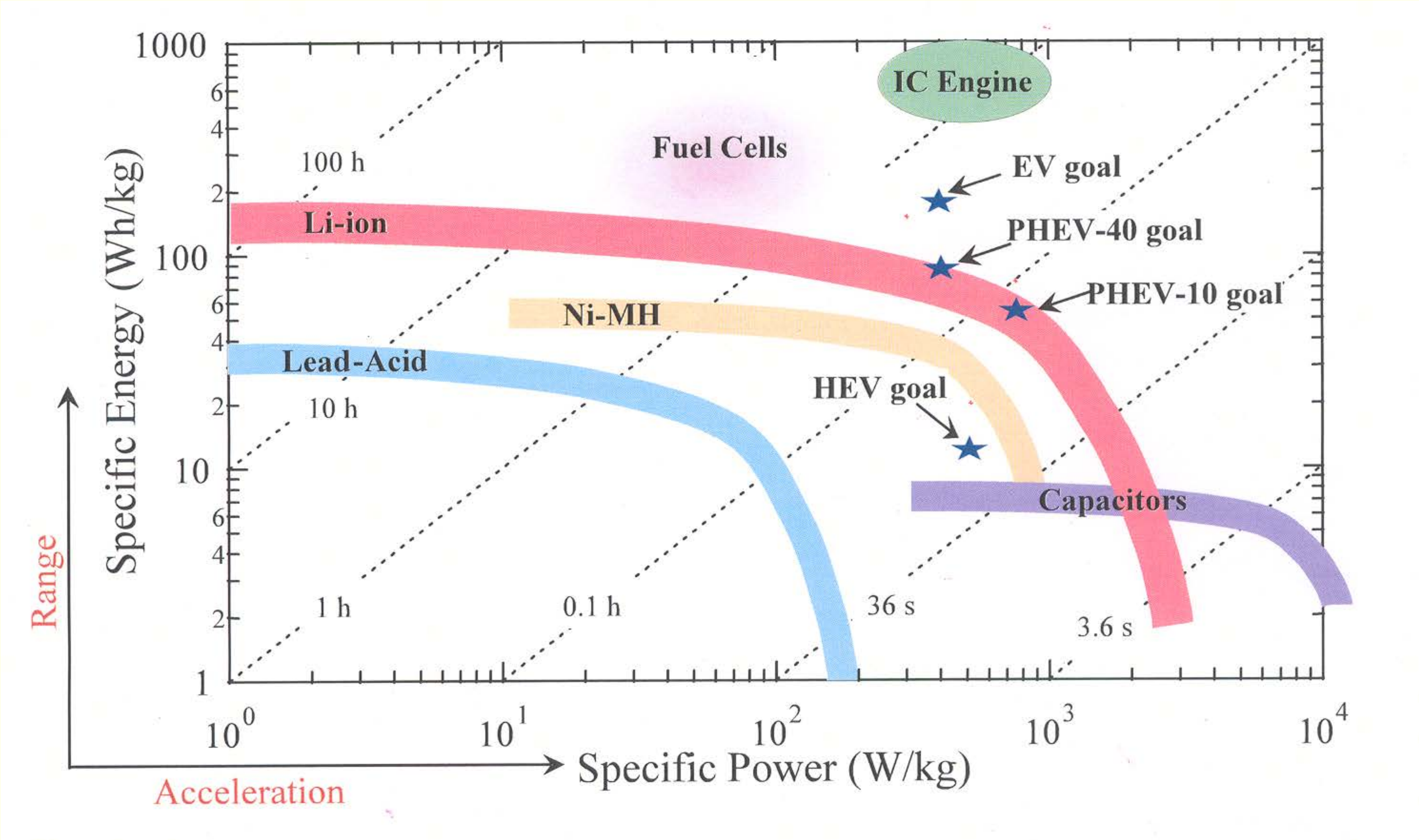
In electrical charges: supercapacitors	Direct storage, high efficiency, but low energy and seconds storage
In kinetic energy: flywheel	High efficiency, but seconds - minutes storage
In potential energy: pump hydro, compress air	Special site requirements
In thermal energy: fluid, phase transformation	Low efficiency, typical for solar energy
In electrochemical energy: batteries	Flexible, wide ranges of options
In chemical energy: hydrogen	Low efficiency

Technology Ratings for Utility Applications



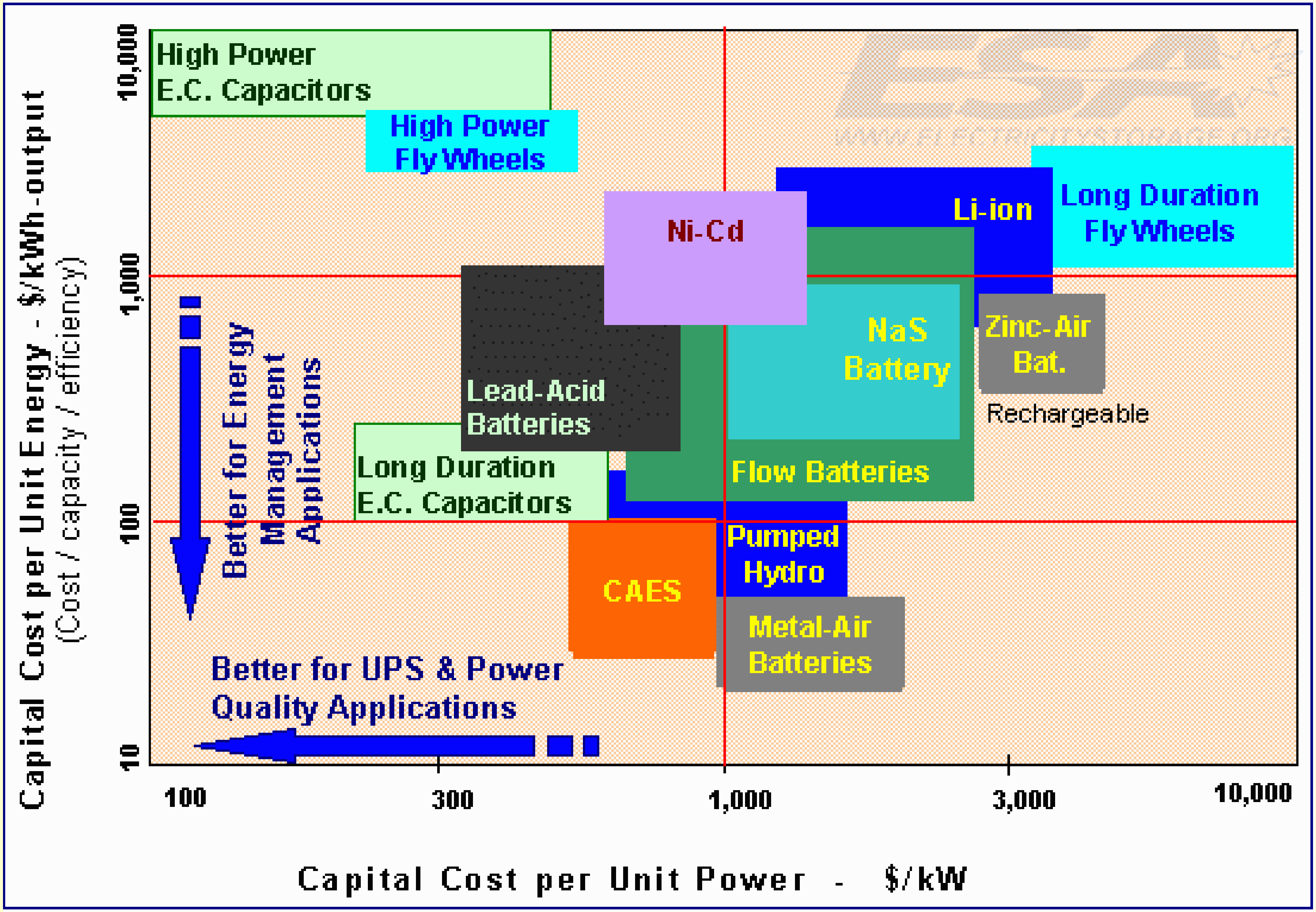
Lead-acid batteries: limit life, environmental concerns
VR flow batteries: independent power and energy ratings, low energy density
Li-ion batteries: high energy density, high efficiency, but high cost, low power

Comparison Among Electrochemical Devices
(for electric vehicles and portable devices)



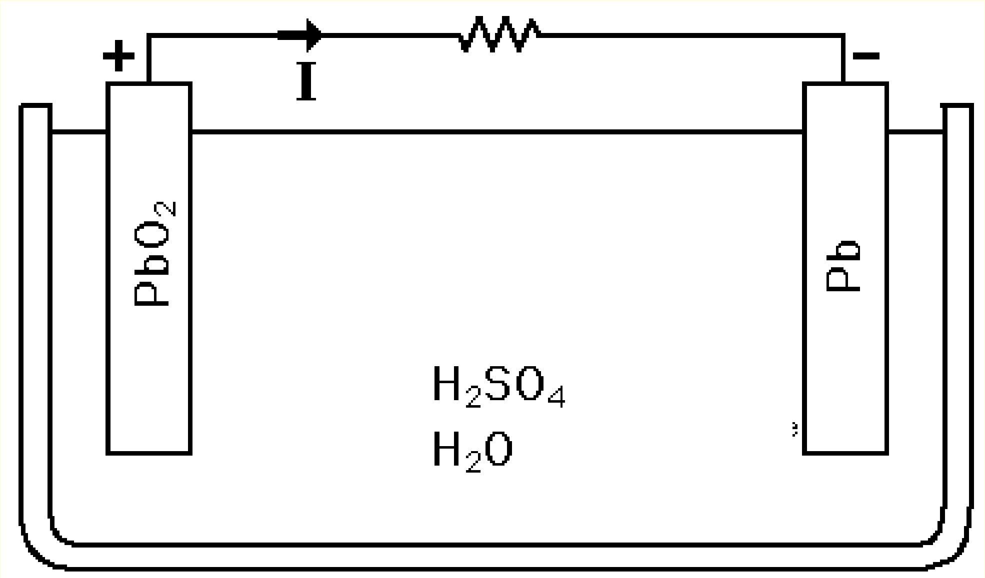
* J. Barnes, "Overview of DOE's Energy Storage R&D for Vehicles," NDIA-MI Ground-Automotive Power & Energy Workshop, Troy, Michigan, November 2008.

Cost Challenges



Introduction of Batteries

(Lead acid battery)



- Anode (negative): Pd
- Cathode (positive): PbO_2
- Liquid electrolyte: H_2SO_4 in water

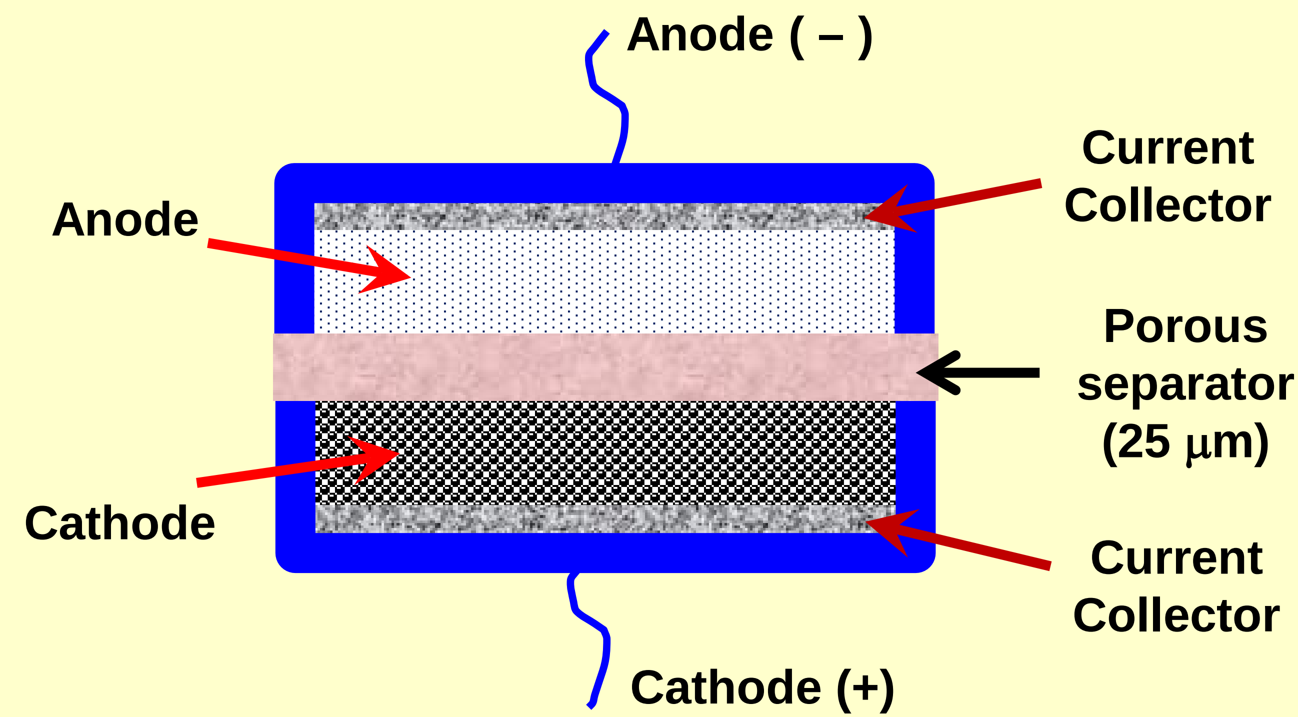
Anode: $Pb(s) + HSO_4^-(aq) \xrightarrow{\text{Discharge}} PbSO_4(s) + H^+(aq) + 2e^-$

Cathode: $PbO_2(s) + HSO_4^-(aq) + 3H_+(aq) + 2e^- \xrightarrow{\text{Discharge}} PbSO_4(s) + 2H_2O$

Cell voltage, $E^o = E^o_{red} + E^o_{ox} = 0.359\ V + 1.69\ V = \sim 2.0\ V$

Introduction of Batteries

(Li-ion battery)



- ❑ Anode: $Li_4Ti_5O_{12}$ + 10 wt% CB + 10 wt% PVDF
- ❑ Cathode: $LiFePO_4$ + 10 wt% CB + 10 wt% PVDF
- ❑ Liquid electrolyte: 1M $LiPF_6$ in EC:DMC (1:1)
- ❑ Current collectors: Cu mesh for the anode & Al mesh for the cathode

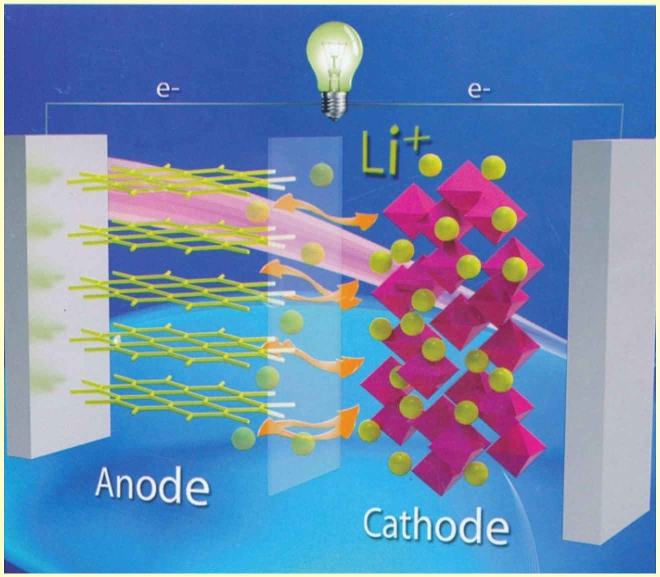
Anode: $Li_4Ti_5O_{12} + 3Li^+ + 3e^- \xrightarrow{\text{Charge}} Li_7Ti_5O_{12}$ $\quad E_{anode} = 1.5$ V vs Li/Li^+

Cathode: $LiFePO_4 \xrightarrow{\text{Charge}} Li_{1-x}FePO_4 + xLi^+ + xe^-$ $\quad E_{cath} = 3.4$ V vs Li/Li^+

Cell voltage, $E = E_{cath} - E_{anode} = 3.4\text{ V} - 1.5\text{ V} = \sim 1.9\text{ V}$

Introduction of Batteries

(Li-ion battery, Cont.)



Li-ion batteries store energy through redox reactions of the host materials induced by Li-ion intercalation & deintercalation.

- **Why intercalation? Why not direct conversion?**
- **How can we increase energy and power densities of Li-ion batteries?**
- **What are the limiting factors?**

Introduction of Batteries
(Li-ion batteries)

Current Status and Challenges for EV applications:

Nissan Leaf:

- **Driving range: ~100 miles, 80 kWh electric motor**
- **Full charging time: 20 hr for 110V, 8 hr for 220V**
- **Cost: $33,000 before tax incentives**

Fiat's 500e:

- **Driving range: 80 miles**
- **Charging time: 4 hr with a 240-volt charging station**
- **Cost: ~$33,000 before tax incentives**

Tasla Model S:

- **Driving range: ~250 miles**
- **Charging time: 0.5 hr for a driving distance of 150 miles using the best technology available today**
- **Cost: $90,000 before tax incentives**

Driving range too short, recharging time too long, cost too high!

Li-ion Batteries (LIBs)

Li-ion Batteries (LIBs)

DOE's Cell Level Goals for PHEVs and Evs*:

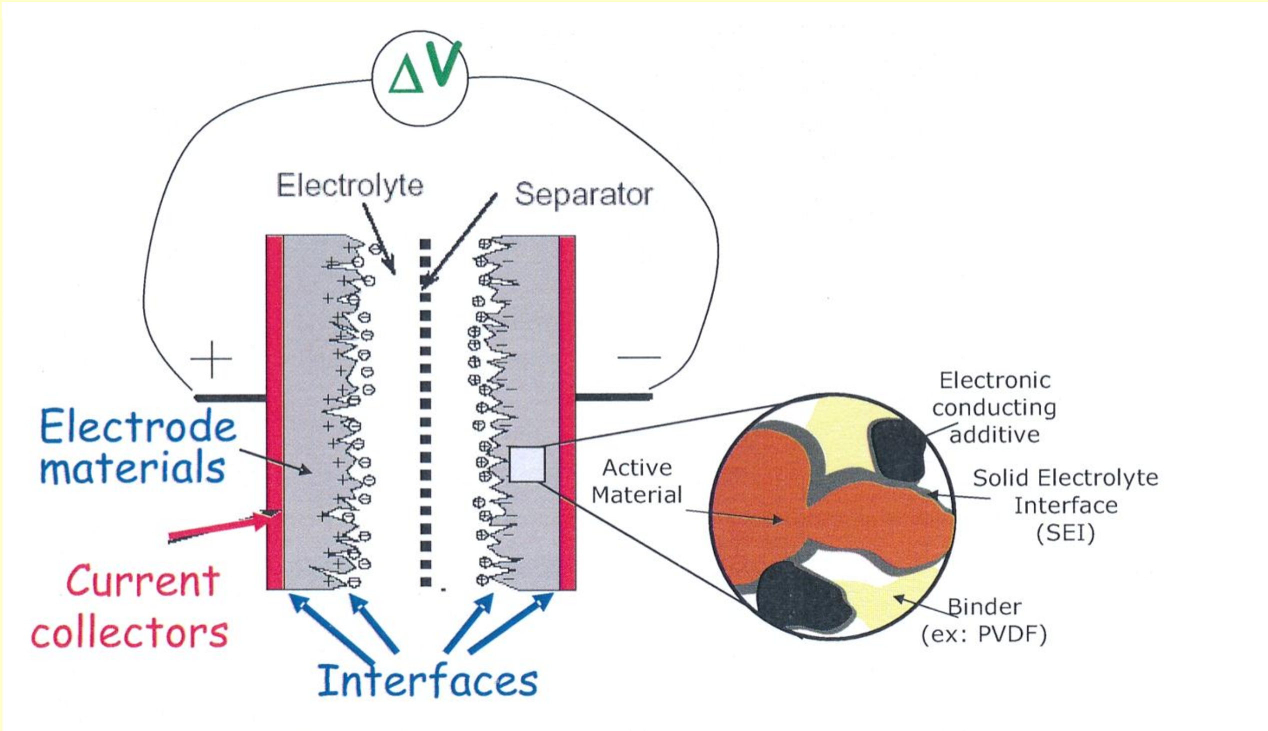
Characteristics	Unit	PHEV40	EV
Recharge Rate		C/3	C/3
Specific Energy	Wh/kg	200	400
Energy Density	Wh/L	400	600
Calendar Life	Year	10+	10
Cycle Life (30^{o}C, C/3)	Cycles	5,000	1,000
Operating Temp. Range	^{o}C	-30 to +52	-30 to +65

***** U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, DE-FOA-0000793 (2013) .

Li-ion Batteries (LIBs)

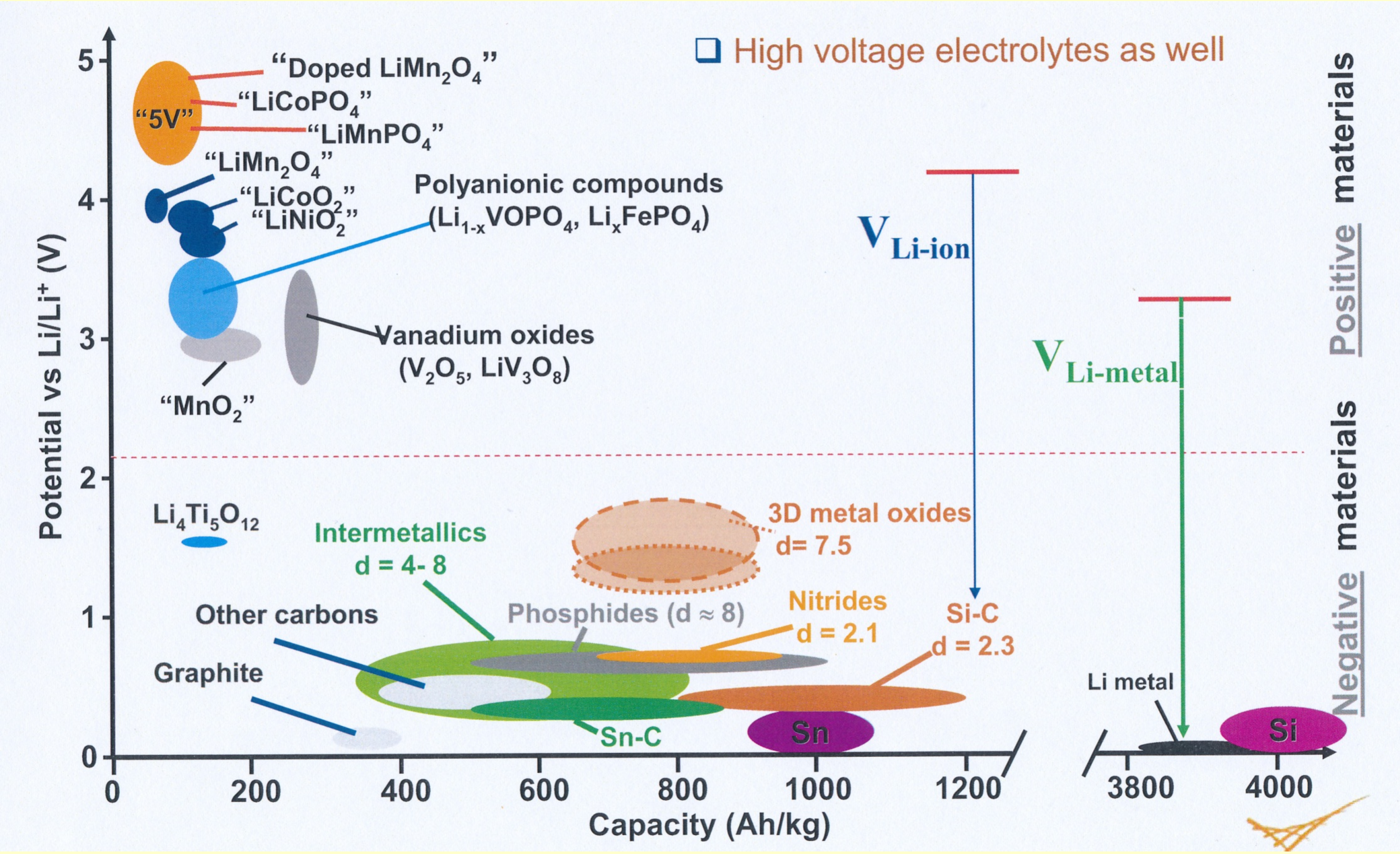
Requirements and Challenges:

- **Anode: high capacity, dendrite free, long cycle life**
- **Cathode: high capacity, high voltage, long cycle life**
- **Electrolyte: wide electrochemical window, stable against reduction and oxidation, high ionic conductivity**
- **All: rapid charge/discharge rates, 4 interfaces to master**



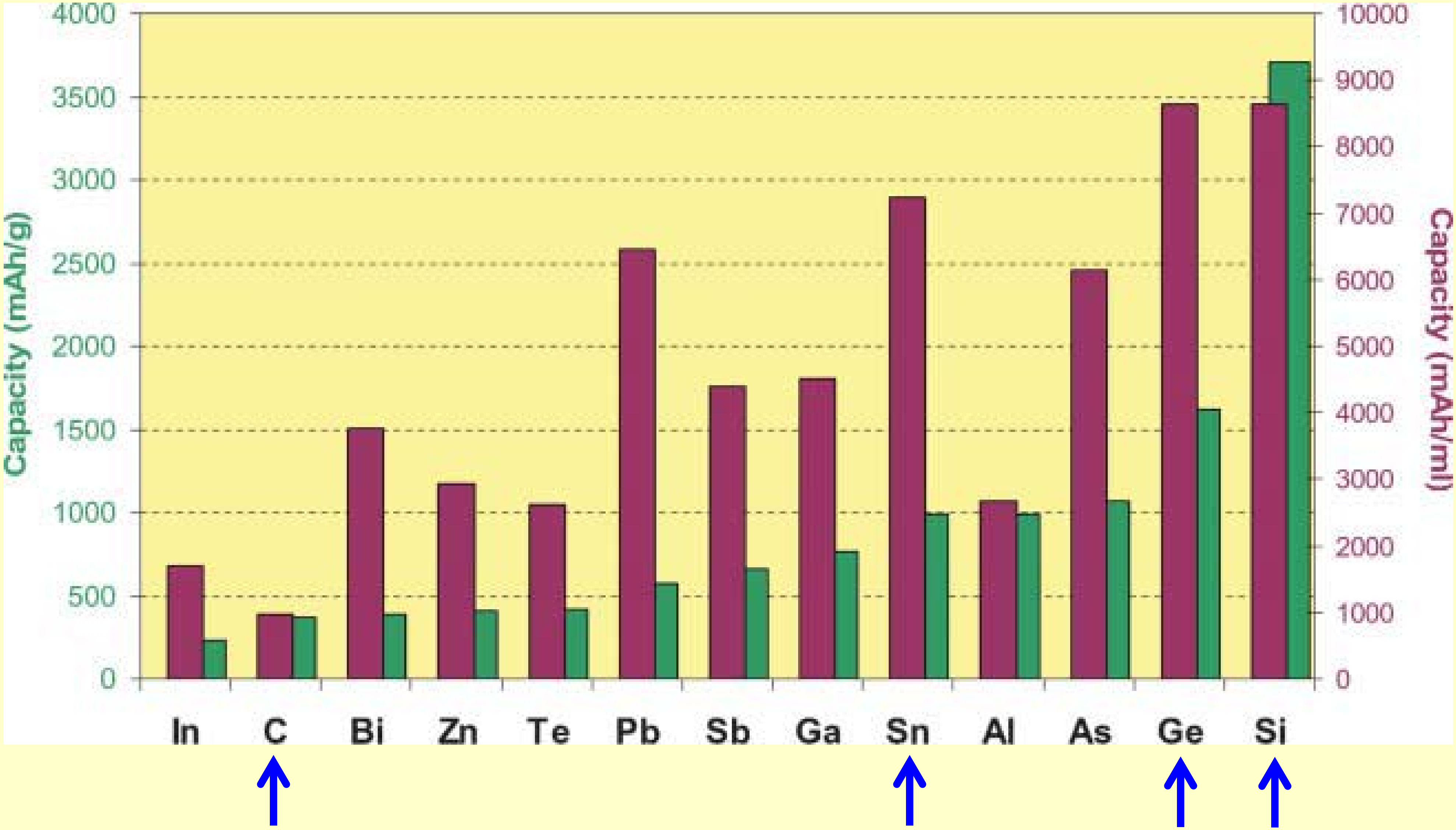
Z. G. Yang, Presentation at UConn, Jan. 2009.

Materials Status and Challenges for LIBs



Z. G. Yang, Presentation at UConn, Jan. 2009.

Li-ion Batteries: Design of Anodes



D. Larcher, et al., J. Mater. Chem., 17, 3759-3772 (2007).

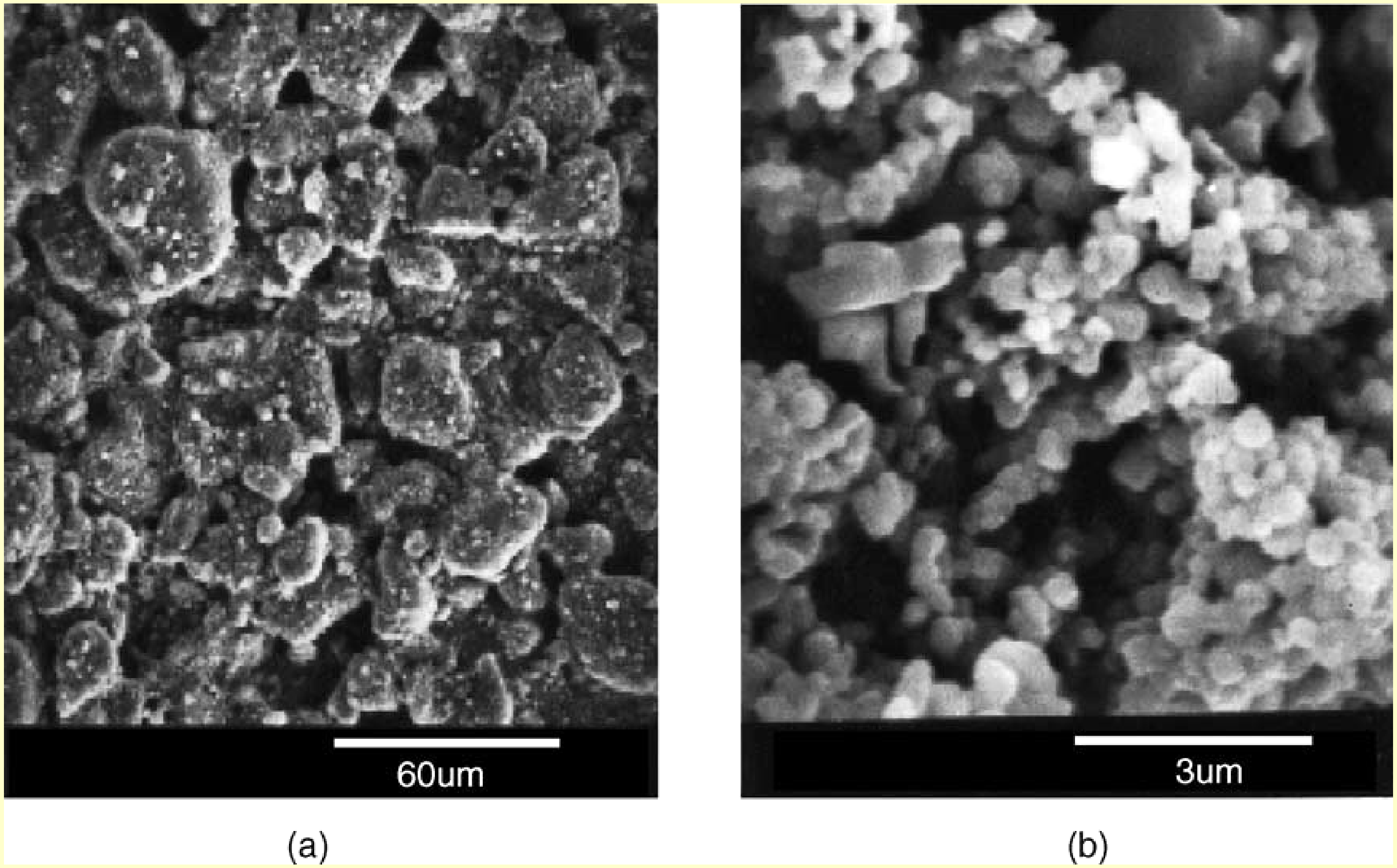
Example 1: Sn-Based Anodes Derived from Li_2SnO_3 for LIBs

Take-home message: **Nanoparticles can enhance the performance of LIBs**

Sn-Based Anodes Derived from Li_2SnO_3 for LIBs

Li_2SnO_3 made via solid-state reaction

(large agglomerates)



(a) (b)

Li_2SnO_3 made via sol-gel

(200 – 300 nm)

Discharge vs Li anode

$Li_2SnO_3 + 4Li^+ + 4e^-$ ================➔ $3Li_2O + Sn$

$Sn + xLi^+ + xe^-$ <===========➔ Li_xSn $(x < 4.4)$ $\Delta V = \sim 300\%$

D. W. Zhang, et al., J. Alloys Compd., 415, 229-233 (2006).

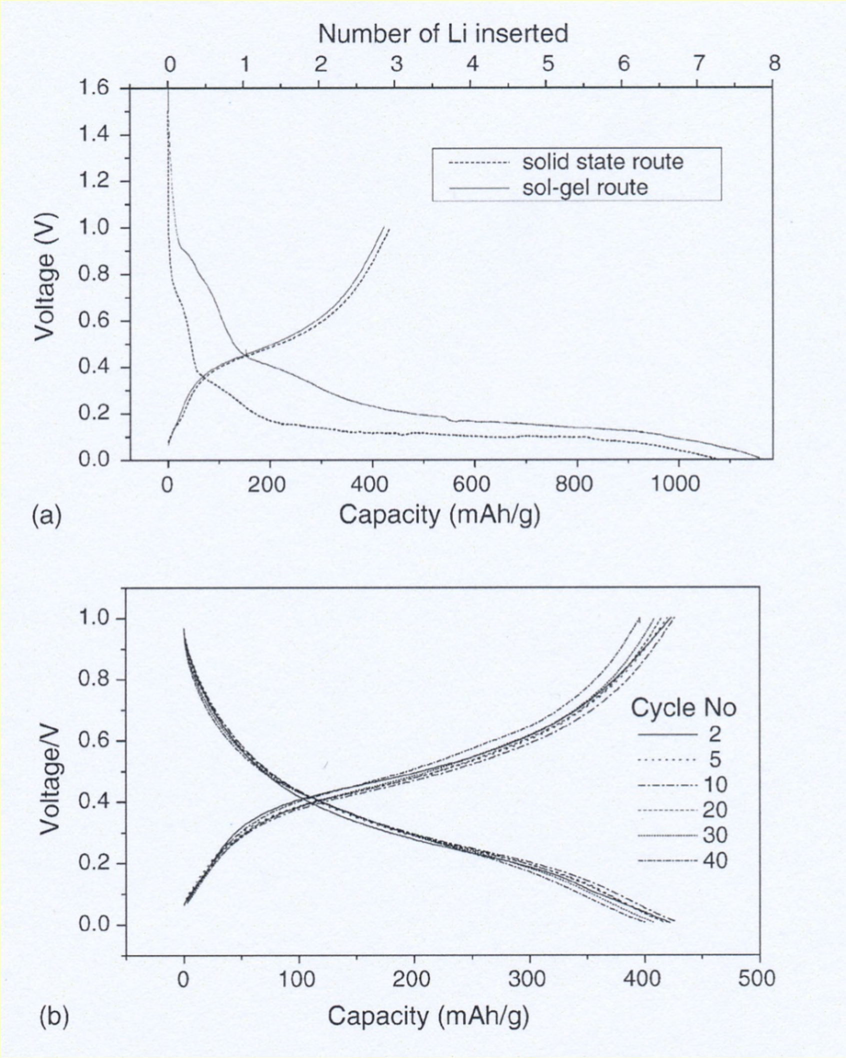
Sn-Based Anodes Derived from Li_2SnO_3 for LIBs (Cont.)

Discharge vs Li anode

$Li_2SnO_3 + 4Li^+ + 4e^-$ ========➔ $3Li_2O + Sn$

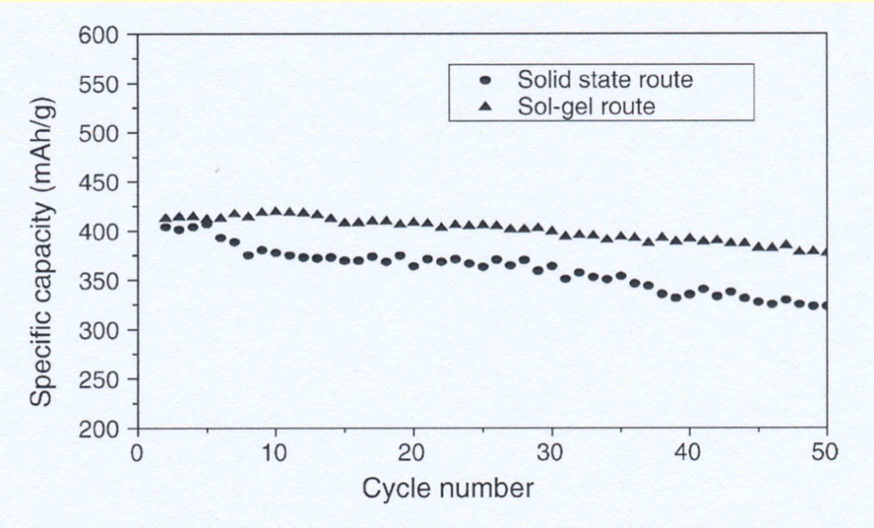
$Sn + xLi^+ + xe^-$ <=======➔ Li_xSn $(x < 4.4)$

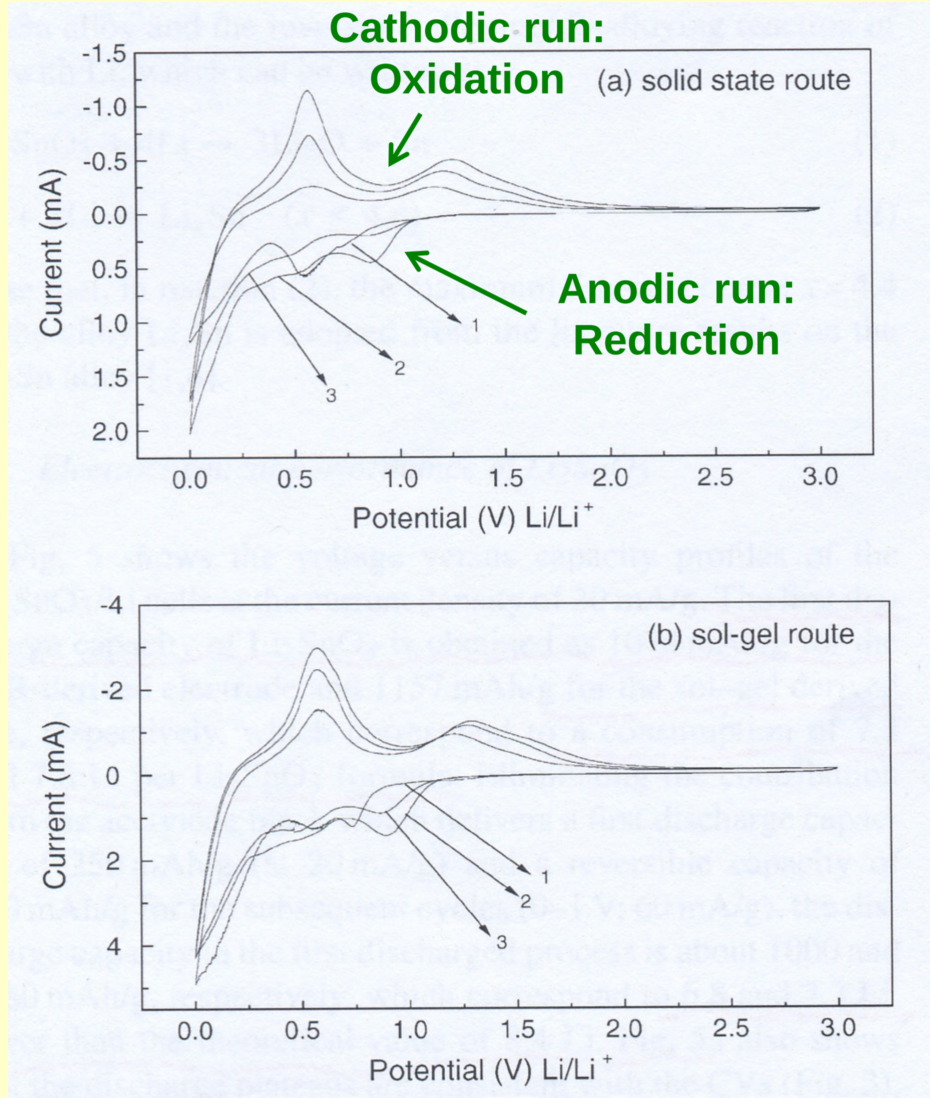
- The first discharge capacity of Li_2SnO_3 is higher than 1000 mAh/g, corresponding to > 7 Li per Li_2SnO_3 formula.
- The subsequent charge/discharge cycles only exhibite ~400 mAh/g capacity, which is 40% of the theoretical capacity of the second reversible reaction.
- The 400 mAh/g capacity remains after 40 cycles.
- Sol-gel processed powder is better than solid-state processed powder, indicating that nanoparticles are essential.



D. W. Zhang, et al., J. Alloys Compd., 415, 229-233 (2006).

Sn-Based Anodes Derived from Li_2SnO_3 for LIBs (Cont.)





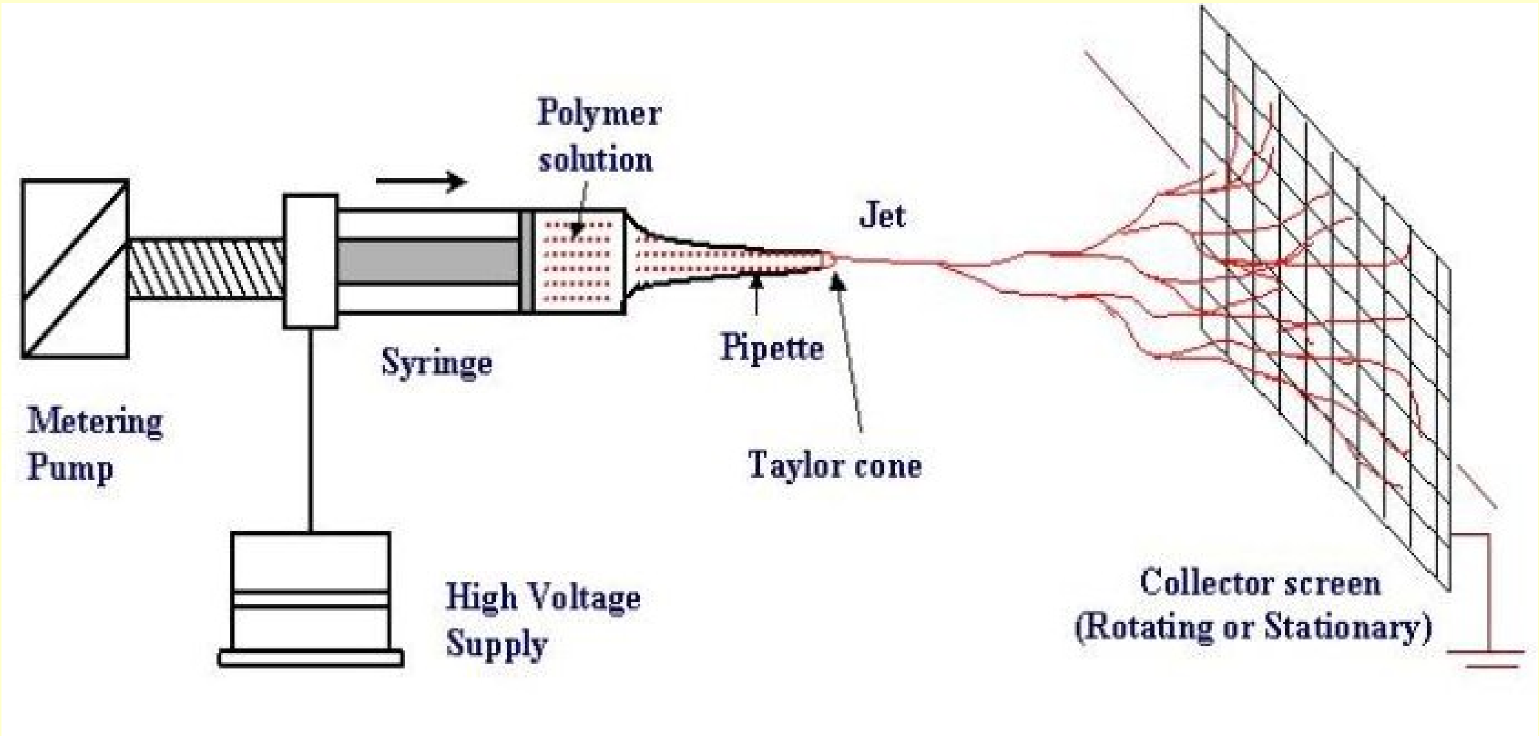
- The specific capacity as a function of cycle number for Li_2SnO_3 /Li cells shows better properties of the sol-gel processed powder than the solid-state processed powder.
- Cyclic voltammograms reveal that the reversible alloying process between Li and Sn results in two reduction peaks at 0.8 and 0.46 V and two oxidation peaks at 0.58 and 1.2 V.

D. W. Zhang, et al., J. Alloys Compd., 415, 229-233 (2006).

<u>Example 2:</u> Fabrication of Double-Walled Si–SiOx Nanotube (DWSiNT) for the Anode of LIBs via Electrospinning

<u>Take-home message:</u> Advanced processing methods can result in the best anode of LIBs ever reported in the literature.

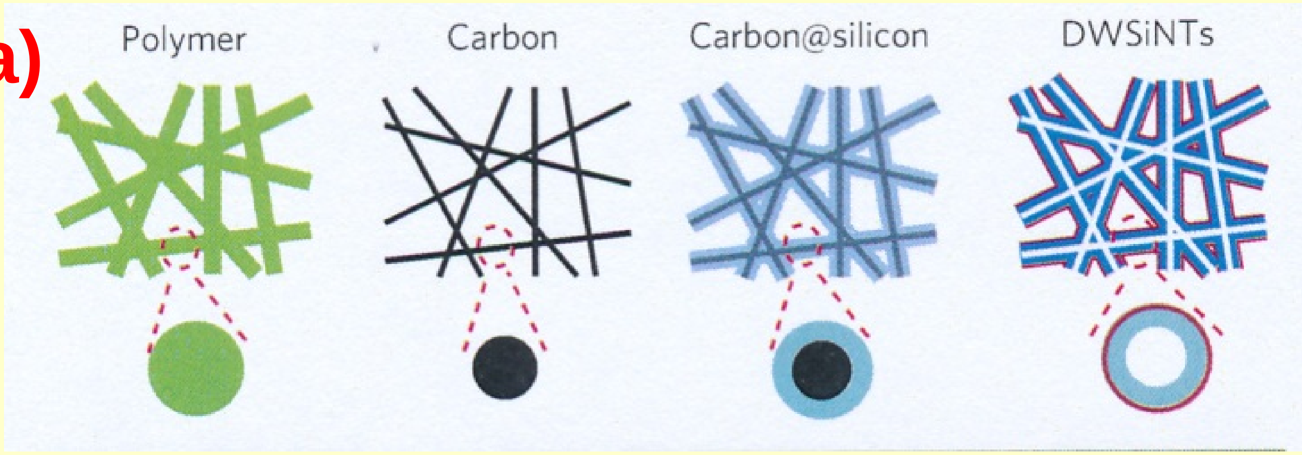
Fabrication of Double-Walled Si–SiOx Nanotube (DWSiNT) for the Anode of LIBs via Electrospinning

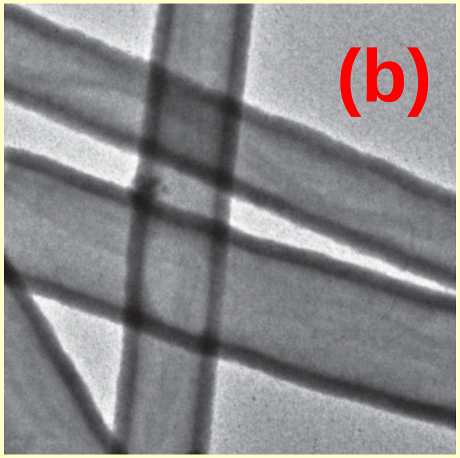


Electrospinning uses an electrical charge to draw very fine fibers from liquid.

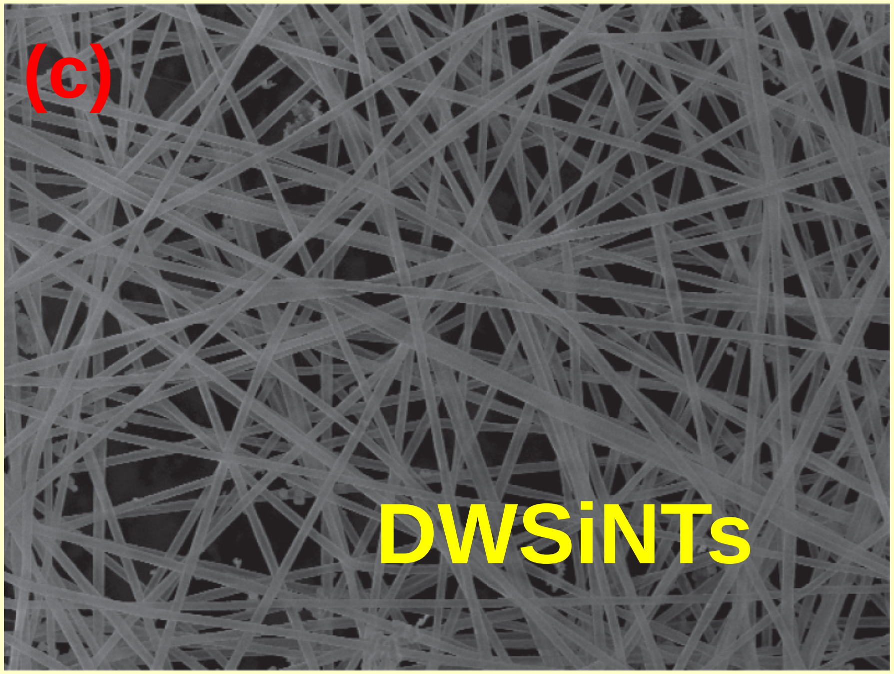
Fabrication of Double-Walled Si–SiOx Nanotube (DWSiNT) for the Anode of LIBs

(a)





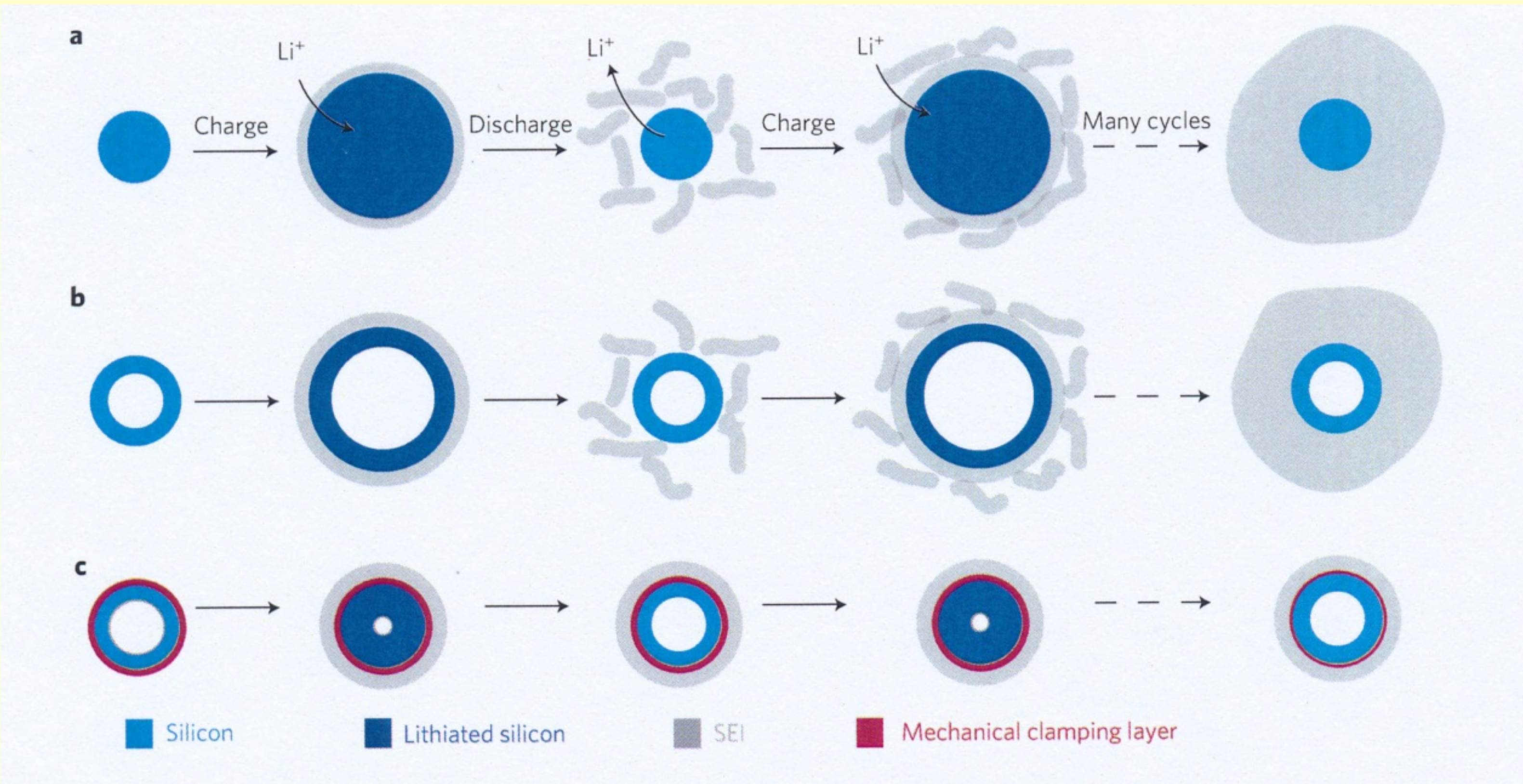
Fabrication process for DWSiNTs: (i) polyacrylonitrile (PAN) fibers via electrospinning; (ii) carbonization of PAN fibers at 500^{o}C; (iii) Si coating of 30 nm thick via SiH_4 chemical vapour deposition (CVD); (iv) carbon core removal at 500^{o}C in air and oxidation of the Si nanotube surface.



H. Wu, et al., Nature Nanotechnology, DOI: 10.1038/NNANO.2012.35 (2012).

Advantages of Double-Walled Si–SiOx Nanotubes (DWSiNT)

Comparisons in solid electrolyte interlayer (SEI) formation on different Si surfaces during charge/discharge



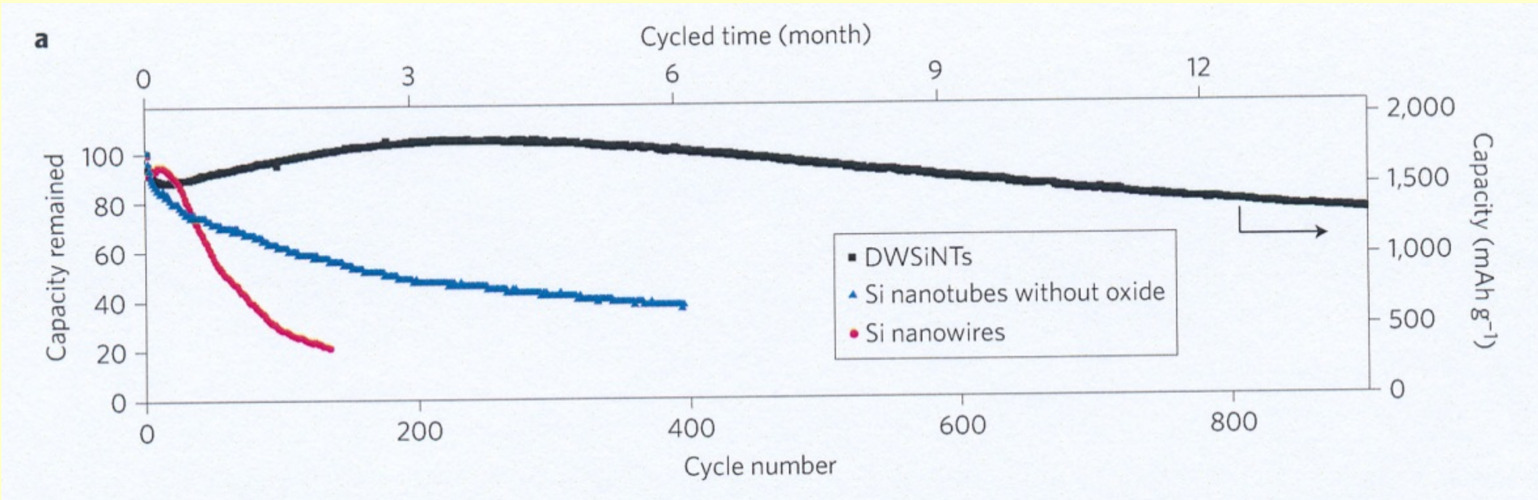
Solid Si nanowire

Si nanotube

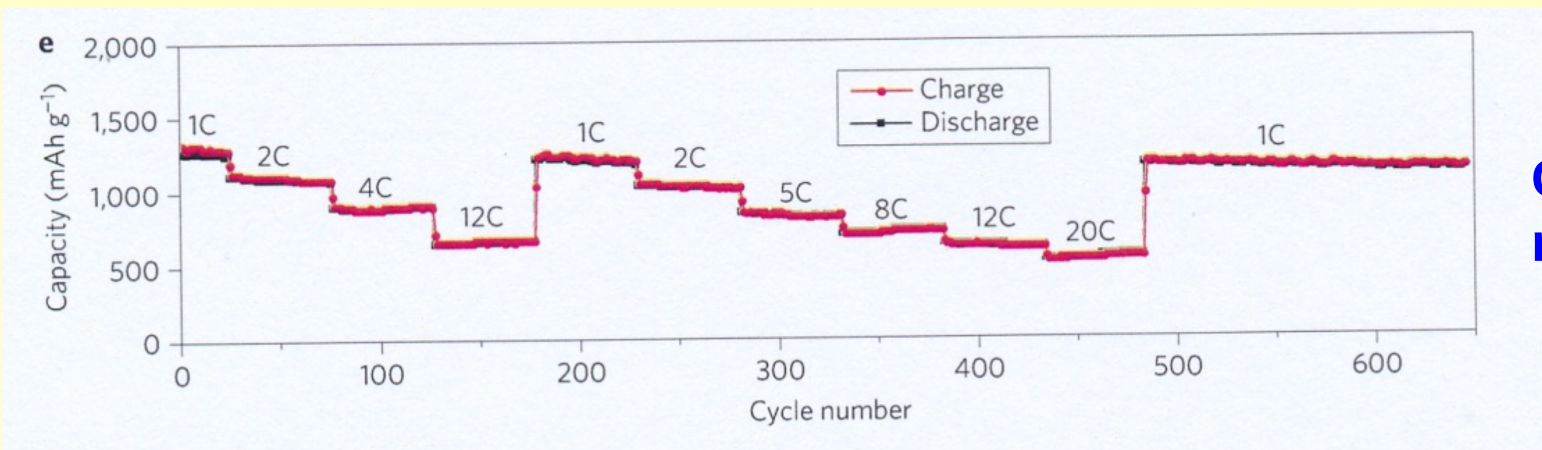
Si nanotube with SiOx coating

H. Wu, et al., Nature Nanotechnology, DOI: 10.1038/NNANO.2012.35 (2012).

Electrochemical Characteristics of Double-Walled Si–SiOx Nanotubes (DWSiNT)



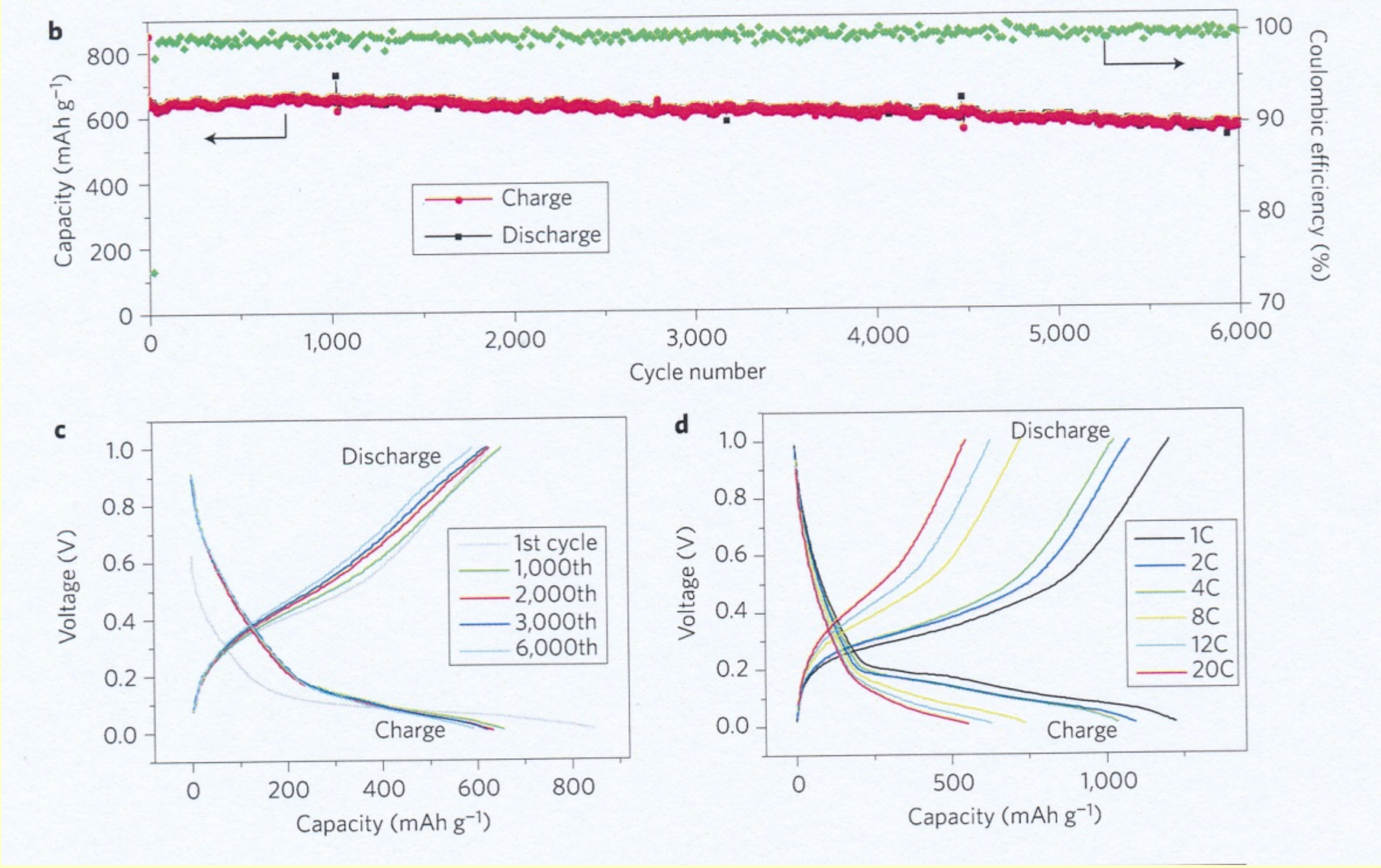
Charge/discharge rate in C/5



Capacity at 1,250 mAh/g in 1C

H. Wu, et al., Nature Nanotechnology, DOI: 10.1038/NNANO.2012.35 (2012).

Electrochemical Characteristics of Double-Walled Si–SiOx Nanotubes (DWSiNT)



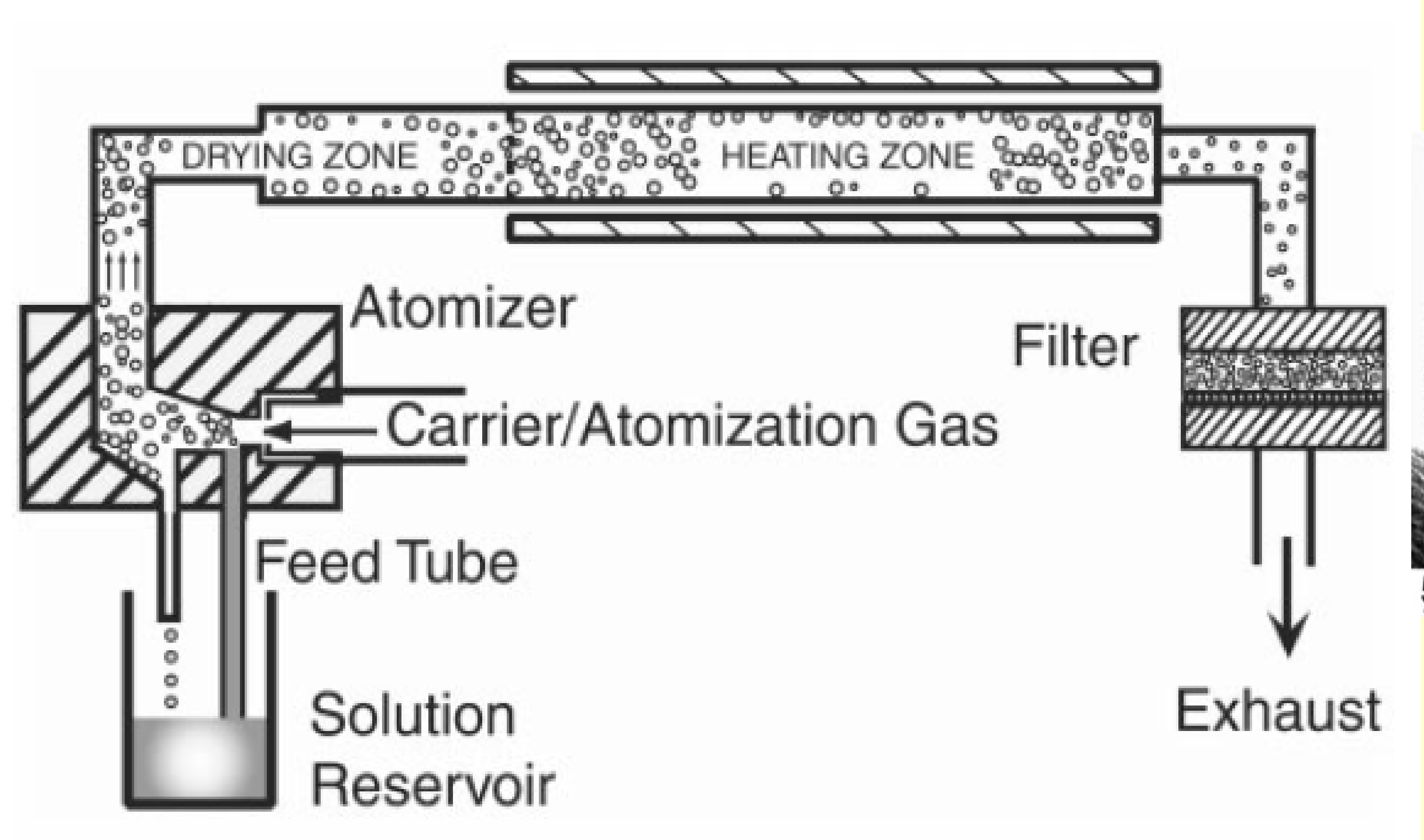
Charge/discharge rate in 12C over 6,000 cycles with a capacity of 600 mAh/g.

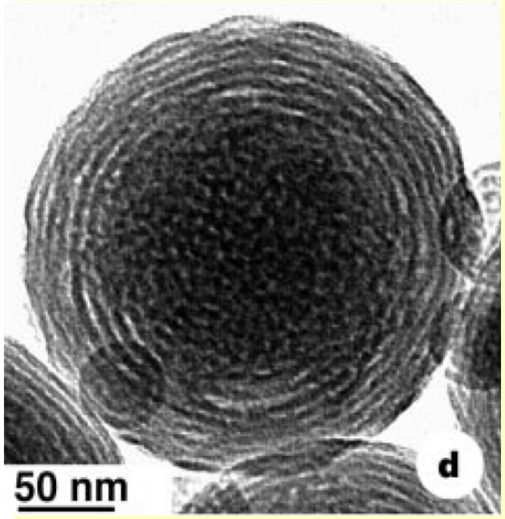
H. Wu, et al., Nature Nanotechnology,
DOI: 10.1038/NNANO.2012.35 (2012).

<u>Example 3:</u> Spray Pyrolysis of Porous $LiFePO_4$/C Particles for the Cathode of LIBs

<u>Take-home message:</u> Novel material synthesis can lea to the best $LiFePO_4$ cathode of LIBs ever reported in the literature. The $LiFePO_4$ cathode is used widely in commercial LIBs .

Nanoporous Electrodes Made via Spray Pyrolysis





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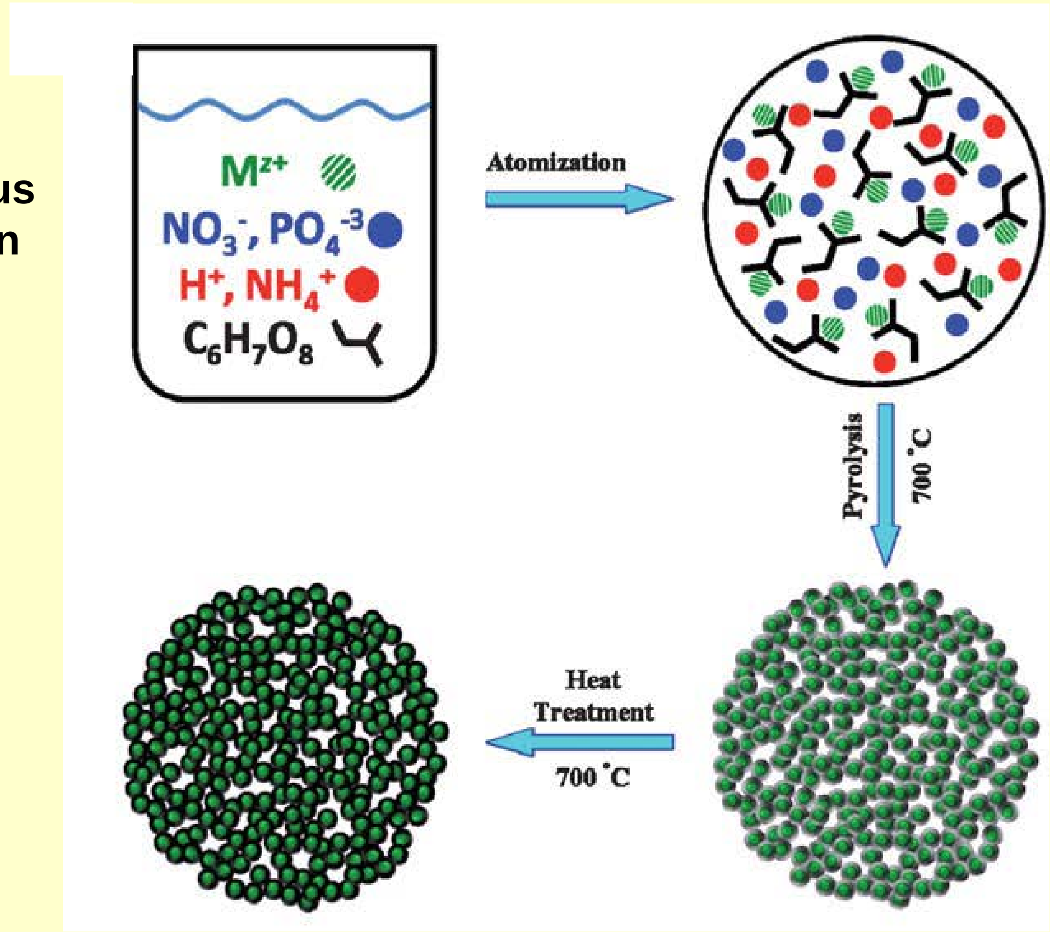
Y. Lu *et al.* Nature, 398, 223-226 (1999).

Spray Pyrolysis of Porous $LiFePO_4$/C Particles for the Cathode of LIBs

Aqueous solution



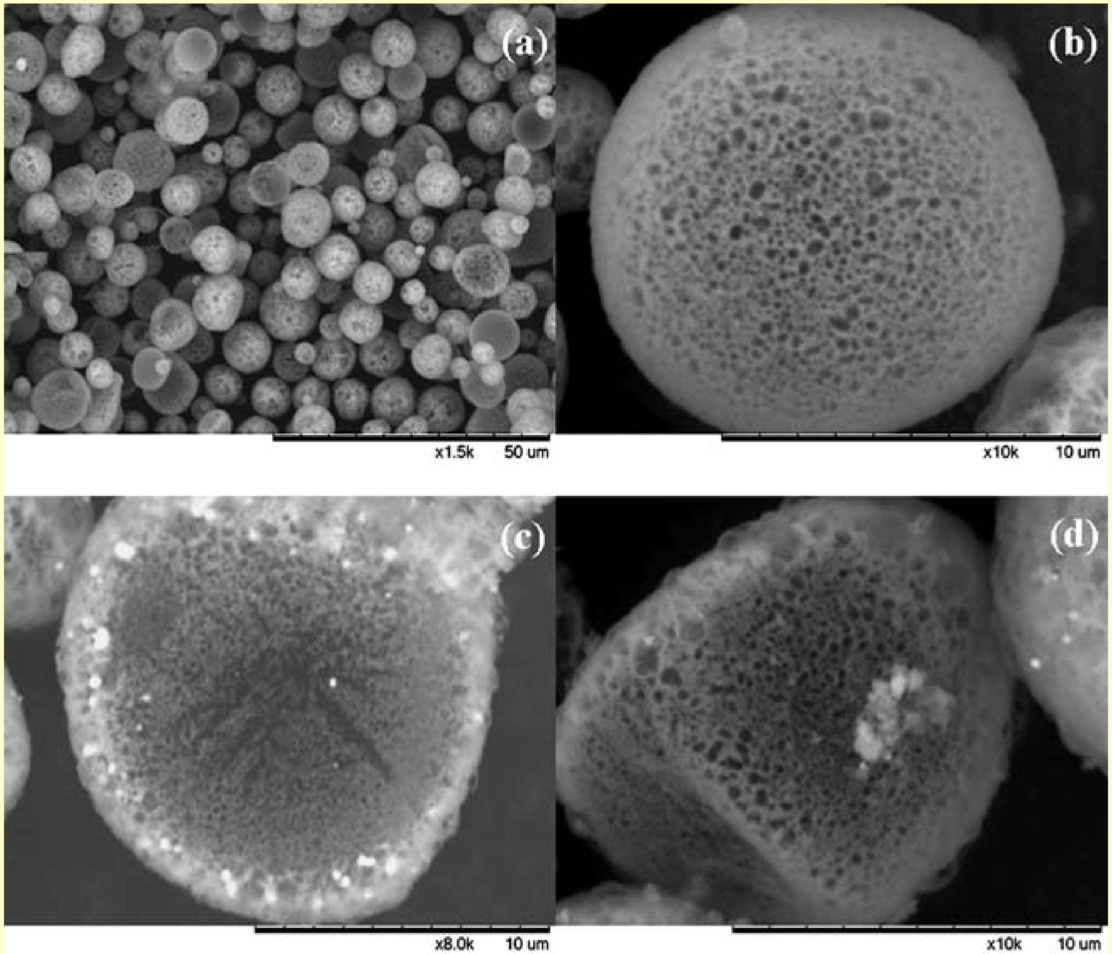
Steps for the formation porous $LiFePO_4$/C particles via spray pyrolysis.

J. Liu, et al., Energy & Environmental Sci., 4, 885 (2011).

Spray Pyrolysis of Porous $LiFePO_4$/C Particles for the Cathode of LIBs

Surface view

Cross-section view



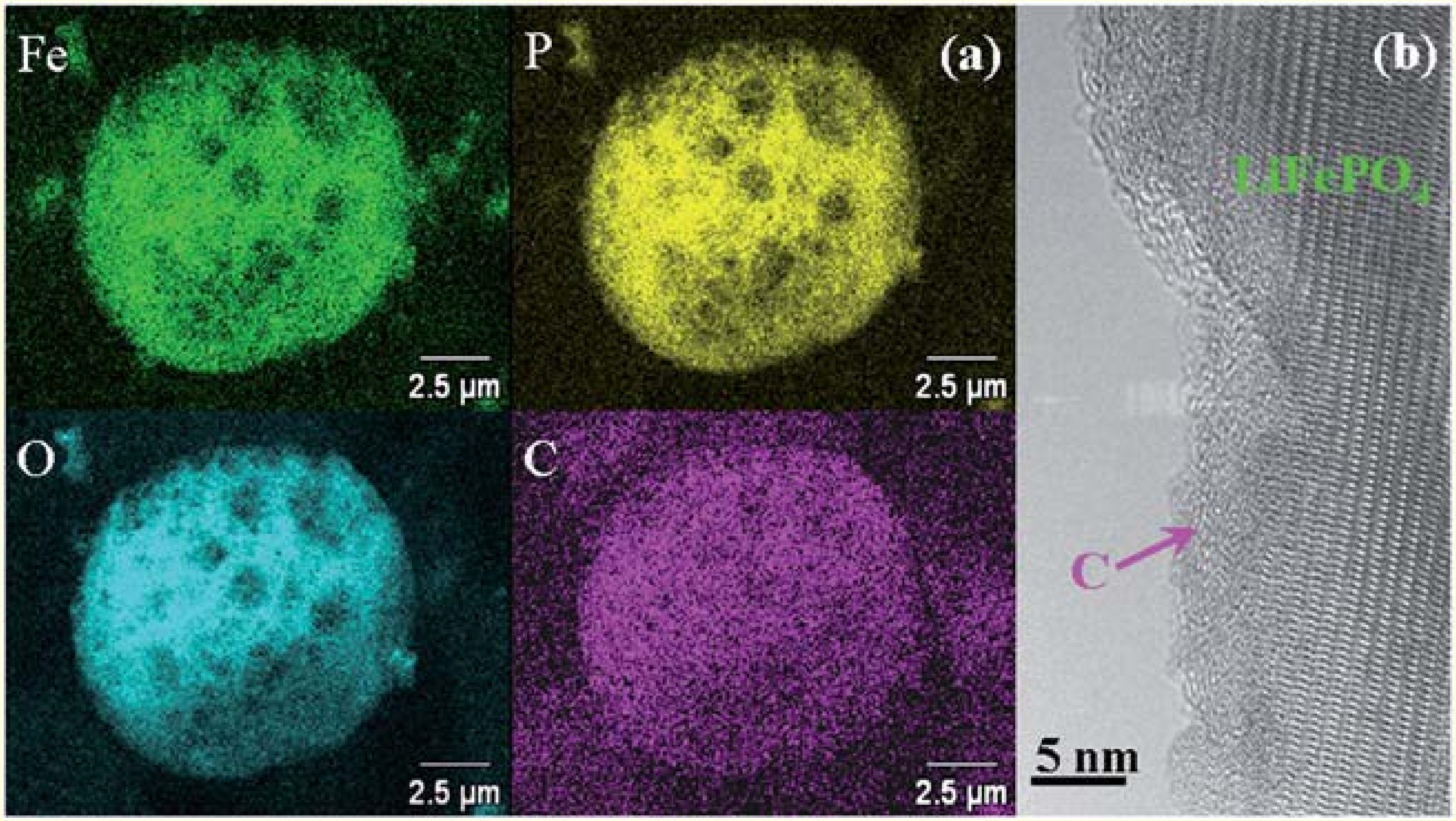
Surface view

Cross-section view

SEM images of 3D porous $LiFePO_4$/C spheres via spray pyrolysis.

J. Liu, et al., Energy & Environmental Sci., 4, 885 (2011).

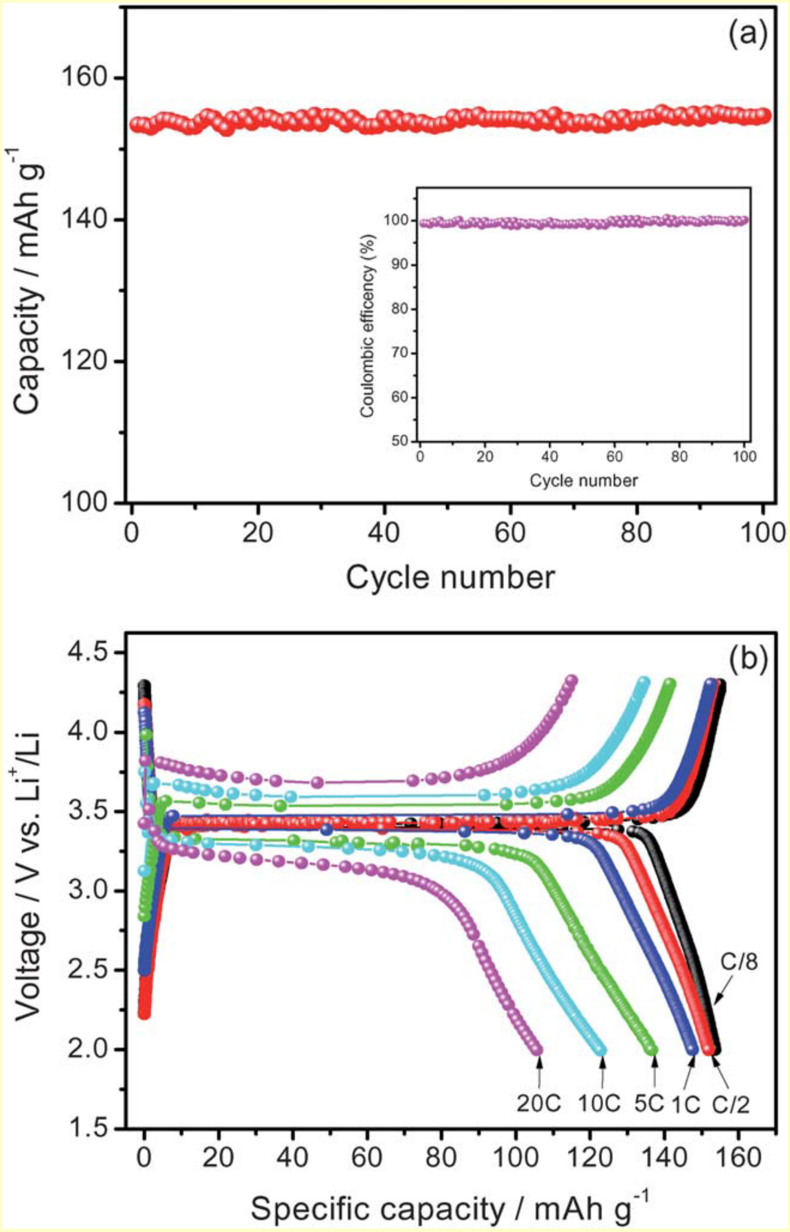
Spray Pyrolysis of Porous $LiFePO_4$/C Particles for the Cathode of LIBs



- **EDS indicates that Fe, P, and O distributions are quite uniform within the particle; C is also well distributed over all surfaces, suggesting a well-interconnected conducting network.**
- **HRTEM reveals that the C coating on the pore surface is 3 to 4 nm.**

J. Liu, et al., Energy & Environmental Sci., 4, 885 (2011).

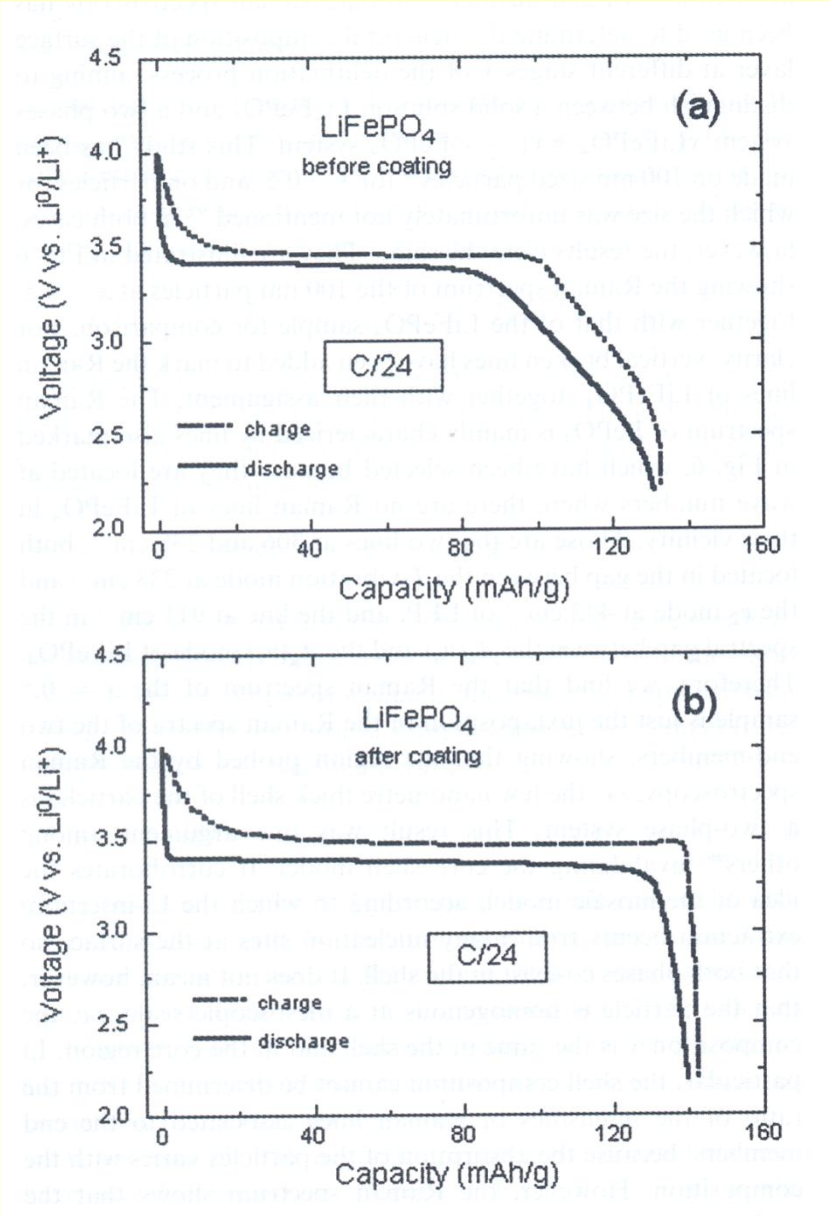
Spray Pyrolysis of Porous $LiFePO_4$/C Particles for the Cathode of LIBs



- At low current density (20 mA/g, ~C/8), the composite electrode can deliver a capacity of 153 mAh/g (corresponding to 165 mAh/g of $LiFePO_4$, very close to the theoretical capacity of 170 mAh/g), with 100% capacity retention over 100 cycles.
- Capacities as high as 123 mAh/g and 106 mAh/g were achieved at 10C and 20C, respectively. The best ever reported in the literature.
- Even at high current density (1700 mA/g, 10C), the capacity retention over 100 cycles is 98% and the average coulombic efficiency is 99.2%.

J. Liu, et al., Energy & Environmental Sci., 4, 885 (2011).

$LiFePO_4$ Nanoparticles with and without Carbon Coating for the Cathode of LIBs

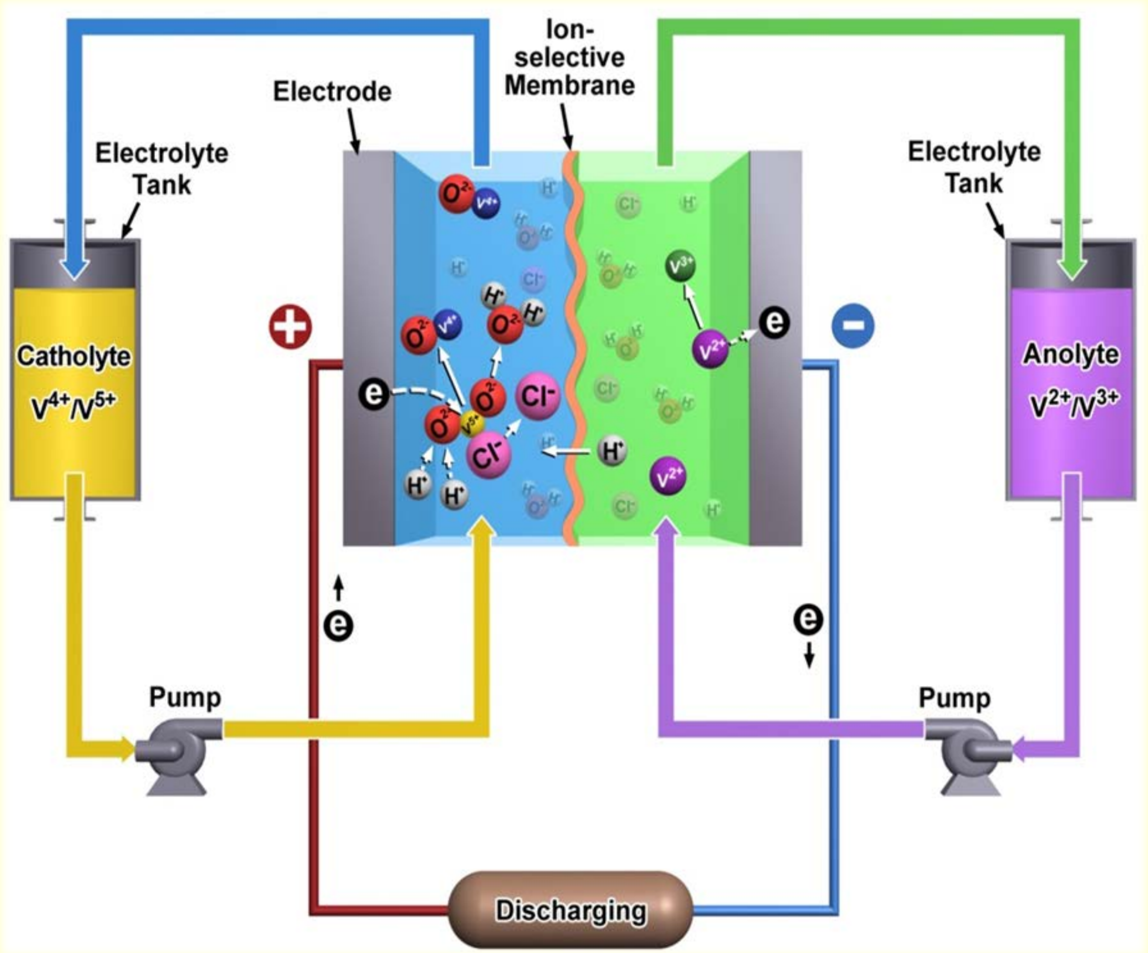


- **Charge/discharge profiles of $LiFePO_4/LiPF_6$-EC-DEC/Li cells with the cathode prepared using the 40-nm sized $LiFePO_4$ particles and the charge/discharge rate of C/24.**
- **Carbon coating greatly improves charge/discharge performance because of the improved electronic conductivity.**

C. M. Julien, et al., J. Mater. Chem., 21, 9955-9968 (2011).

Flow Batteries

The State-of-the-Art Redox Flow Battery



- **However, low energy density 20~33 Wh/liter, low specific energy 15~25 Wh/kg, & low current densities (<100mA/cm^2), ……**

- **Separate design of**
  - **- energy (KWh) – electrolytes**
  - **- power (KW) – cell stack**
- **"Inert" electrodes – no structural changes and stress buildup in electrodes**
  - **- potential long cycle life**
  - **- cycle life independent of SOC/DOD**
  - **- High fuel utilization**
- **Active heat management – flowing electrolytes carry away heat generated from ohmic heating and redox reactions- super safe**
- **Capable of storing a large energy/power (MWhs/MWs) in a simple design, for durations of hours**

Wang, Li, Yang, *Adv. Functional Mater.*, in press, 2012, **DOI: 10.1002/adfm.201200694**.

Advantages of Flow Batteries

- **Independent power and energy ratings**
- **High capacity**
- **Well suitable for utility applications**

- **To power the entire IIT campus for 1 h, ~8 MWh energy is required. Using the existing flow battery technology (~30 Wh/L), only one flow battery with a volume of 6.43 x 6.43 x 6.43 m^3 is required.**
- **To power the entire IIT campus for 10 h, ~80 MWh is required, and one flow battery with a volume of 13.87 x 13.87 x 13.87 m^3 would be required.**
- **In contrast, if LIBs are used, one needs 3,333 packs of LIBs with each pack having 2,400 Wh energy (e. g., 48V 50Ah Li-ion batteries) to provide 8 MWh energy. To provide 10h operation, then 33,333 packs of LIBs would be required.**

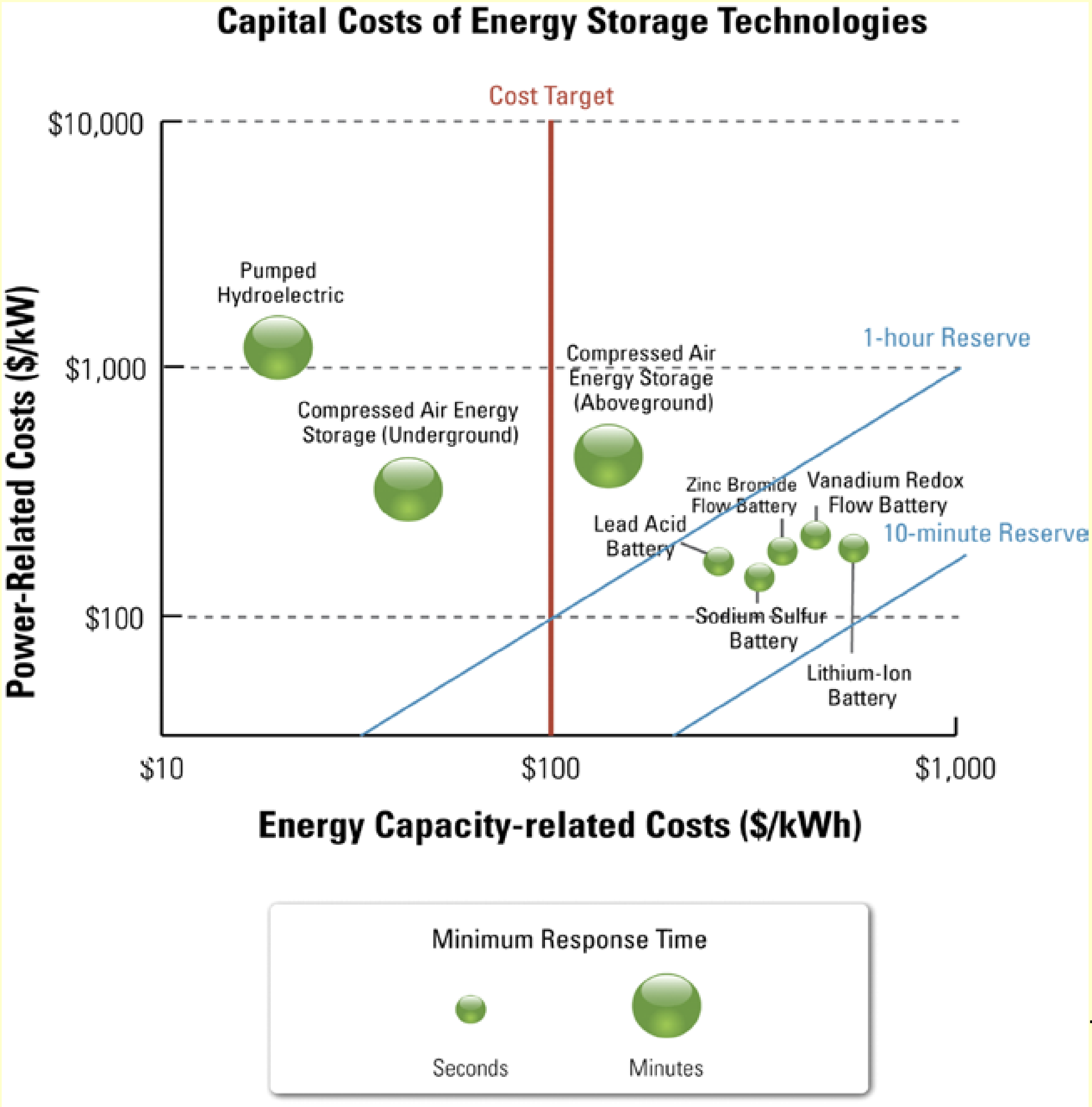
Technology Comparison of Potential Batteries for Utility Applications

Type	Open circuit voltage (V)	Specific energy (Wh/kg)	Specific power (W/kg)	Operating temperature (^oC)	Discharge time	Self-discharge % per day	Cycle life (cycles)	Round-trip DC energy efficiency
VRB	1.4	10 (29)*	16-33	35	Sec-10 hr	0.1-0.3	>6,000	72~85%
PSB	1.5	20 (41)	-------	35	Sec-10 hr	0.1~0.3	>2,000	60~75%
ZBB	1.8	65 (429)	30-60	30~50	Sec-10 hr	0.4~0.5	>2,000	65~75%
NSB	*2.1*	*150-240*	*150-230*	*300~350*	*Sec-hrs*	*20*	*>2,500*	*75~90%*
ZEBRA	*2.6*	*120*	*170*	*300~350*	*Sec-hrs*	*15*	*>2,500*	*85~90%*
C-LC	3~4	155	220	-25~40	Min-hrs	0.1-0.3	<1,000	94~99%
LT-LFP	1.7	50-70	>1,000	-25~40	Min-hrs	0.1-0.3	>5,000	94~99%

VRB: all-vanadium redox flow batteries; PSB: polysulfide-bromide batteries; ZBB: zinc-bromide batteries; *NSB: sodium-sulfur battery*; *ZEBRA: sodium-nickel chloride battery*; C-LC: Li-ion batteries of C anode and $LiCoO_2$ cathode; LT-LFP: Li-ion batteries of $Li_4Ti_5O_{12}$ anode and $LiFePO_4$ cathode.
* Theoretical energy density

X. Lu, et al., presentation at the Conference of Materials Challenges in Alternative & Renewable Energy, Cocoa Beach, FL, Feb. 2010.

Cost Challenges and DOE Goals



Capital costs based on energy capacity for the existing technologies:

- **Vanadium Redox Flow Battery: ~$500/kWh**
- **Li-ion Battery: ~$600/kWh**

If energy density is increased by 10 times while keeping the cost the same, the redox flow batteries would provide an energy capacity-related cost at $50/kWh.

The ARPA-E, DE-FOA-0000290, March 2, 2010

Chemistries for All-Vanadium Flow Batteries

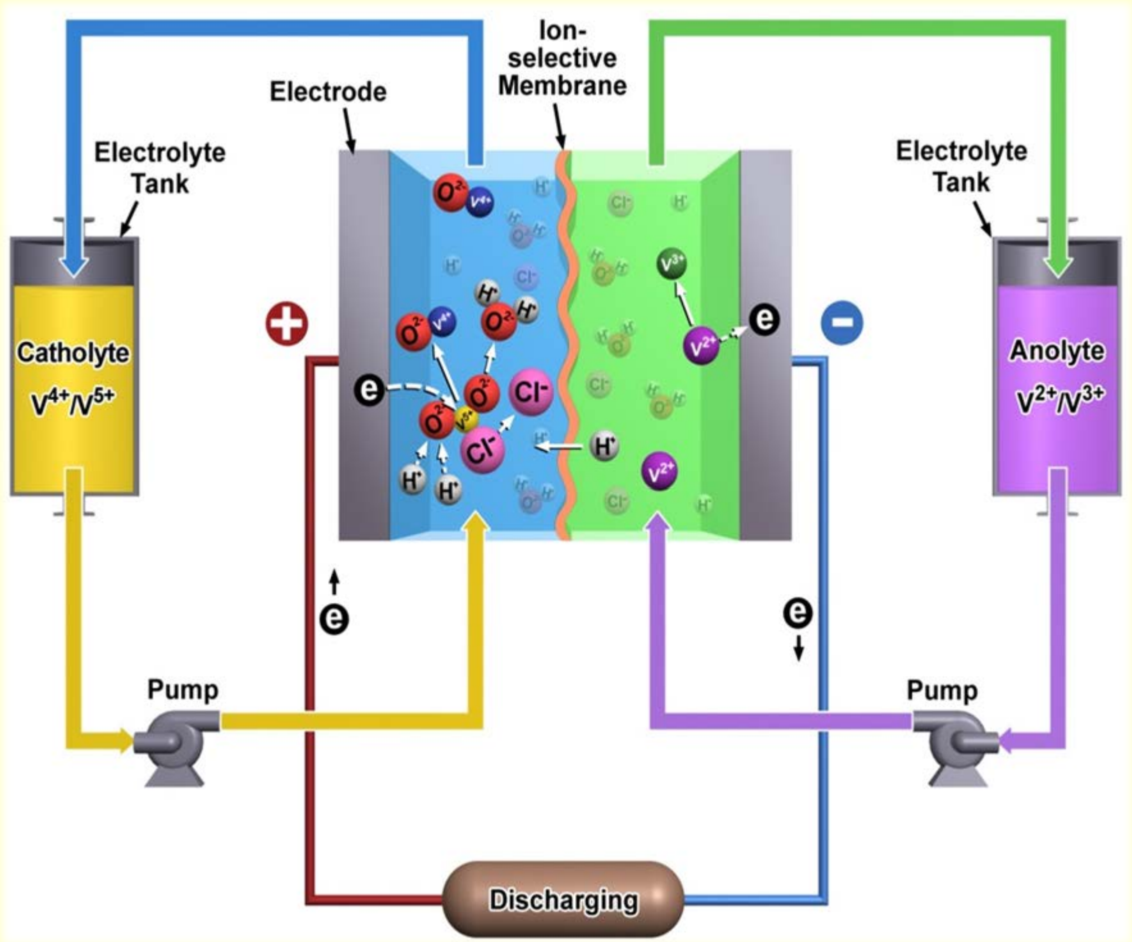
Catholyte: $VO^{2+} + H_2O \xrightarrow{\text{charge}} VO_2^{+} + 2H^{+} + e^{-}$

$E^{o} = +1.0$ V vs. SHE

Anolyte: $V^{2+} \xleftarrow{\text{charge}} V^{3+} + e^{-}$

$E^{o} = -0.26$ V vs. SHE

<u>Cell voltage, E = 1.26 V</u>



- Same elements (V) at both sides, mitigating cross transport
- Unlimited cycle life, (270,000 deep cycles demonstrated)
- Up to multi-MW/MWh demonstrated

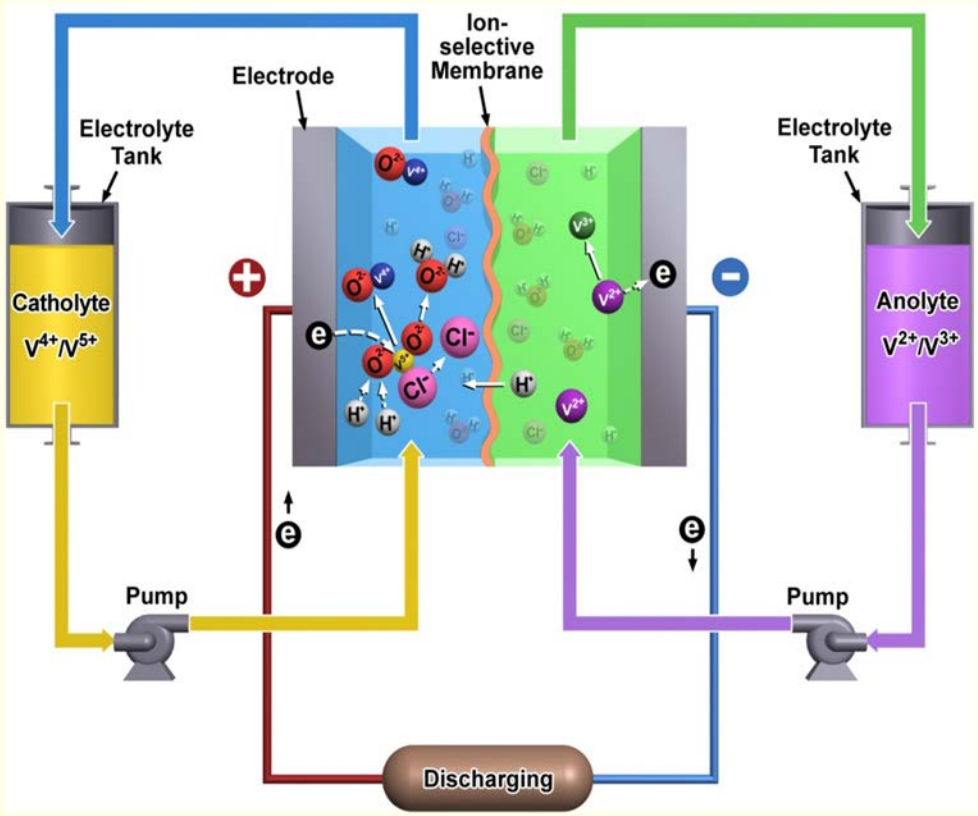
- **Low energy capacity:** < 1.75 M in the sulfate systems, resulting in low energy density 20~33 Wh/liter & low specific energy 15~25 Wh/kg.
- **Issue of stability:** > 35°C, V^{5+} precipitates out, ~RT, V^{4+} out, & < 10°C, V^{2+} out, leading to a narrow operation temperature window, 10 – 40°C, and requiring active heat management.

A New Vanadium Redox Chemistry Based on SO_4^{2-}/Cl^{-1} Supporting Electrolytes

Catholyte: $VO^{2+} + Cl^{-} + H_2O - e \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} VO_2Cl + 2H^{+}$ ε_{co}=1.0 V

Anolyte: $V^{3+} + e \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} V^{2+}$ ε_{ao}=*-0.25*

Overall: $VO^{2+} + Cl^{-} + H_2O + V^{3+} \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} VO_2Cl + 2H^{+} + V^{2+}$ E_o=1.25 V

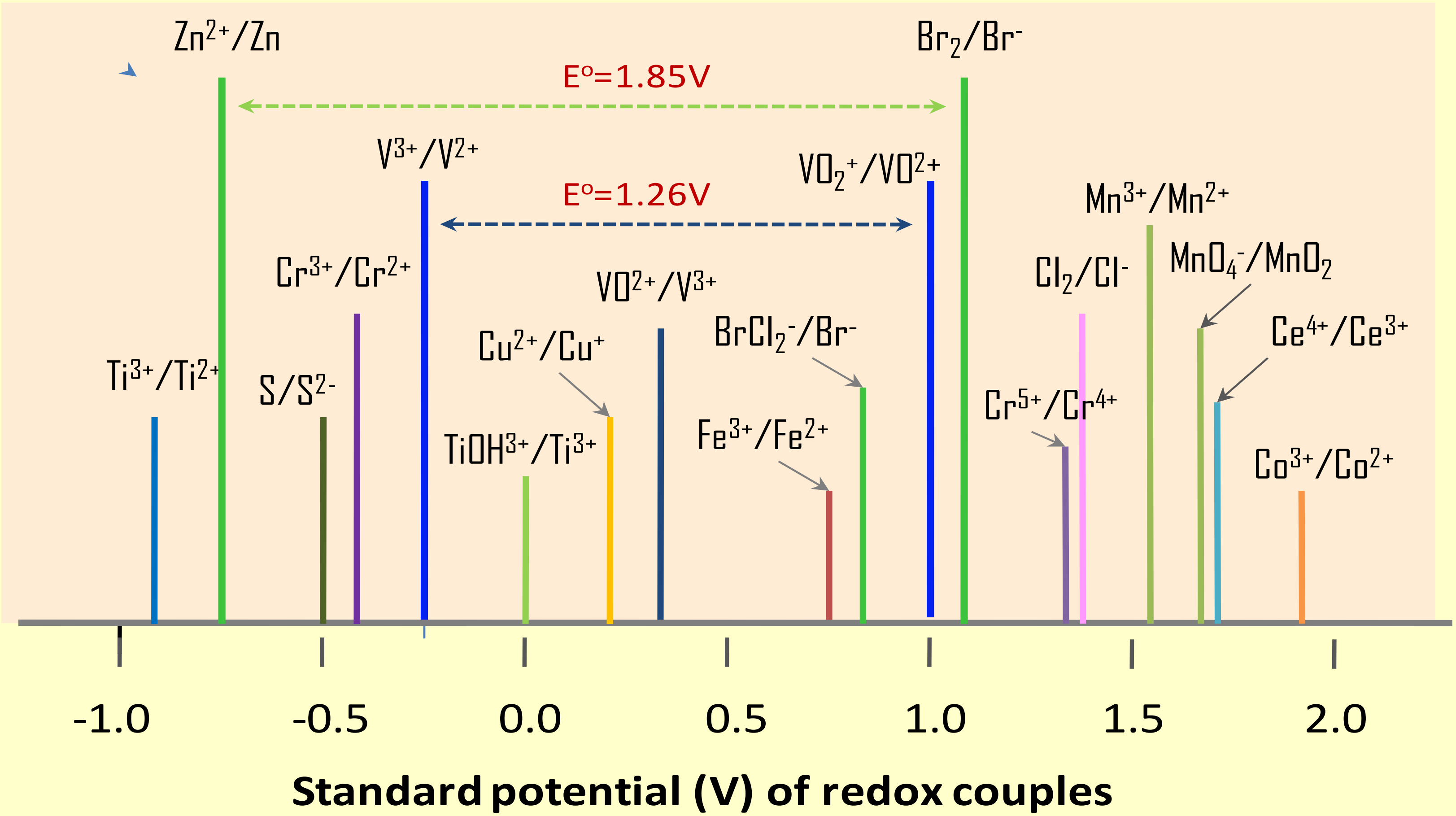


- **Excellent redox reversibility**
- **Significantly improved stability**
- **Increased energy density**

Li, et al, *Advanced Energy Materials*, 1, 394, 2011

Other Existing Redox Flow Battery Chemistries

- Varied redox couples studied
- Dominated by aqueous supporting electrolytes, SO_4^{2-}, Cl^-, Br^-, …
- A few non-aqueous electrochemistries explored



Needs:

- High cell voltage
- High energy density redox couples

Yang, et al, ***Chemical Reviews***, 111 (2011) 3577.

Major Parameters for Flow Batteries

- Redox couples chemistry
- Supporting electrolyte chemistry
- Aqueous versus non-aqueous systems
- Ion exchange membranes
- Flow rates of the anolyte and catholyte
- Electrode structure in the negative and positive electrodes
- State of charge at the inlet of the flow cell
- Operation temperature
- Oxygenated vs deoxygenated electrolytes
- Catalytic activities of the electrode material

A New Hybrid Redox Flow Battery with Multiple Redox Couples

Catholyte 1: $VO^{2+} + H_2O \xrightarrow{\text{charge}} VO_2^{+} + 2H^{+} + e^{-}$ $E^{o} = +1.0$ V vs. SHE

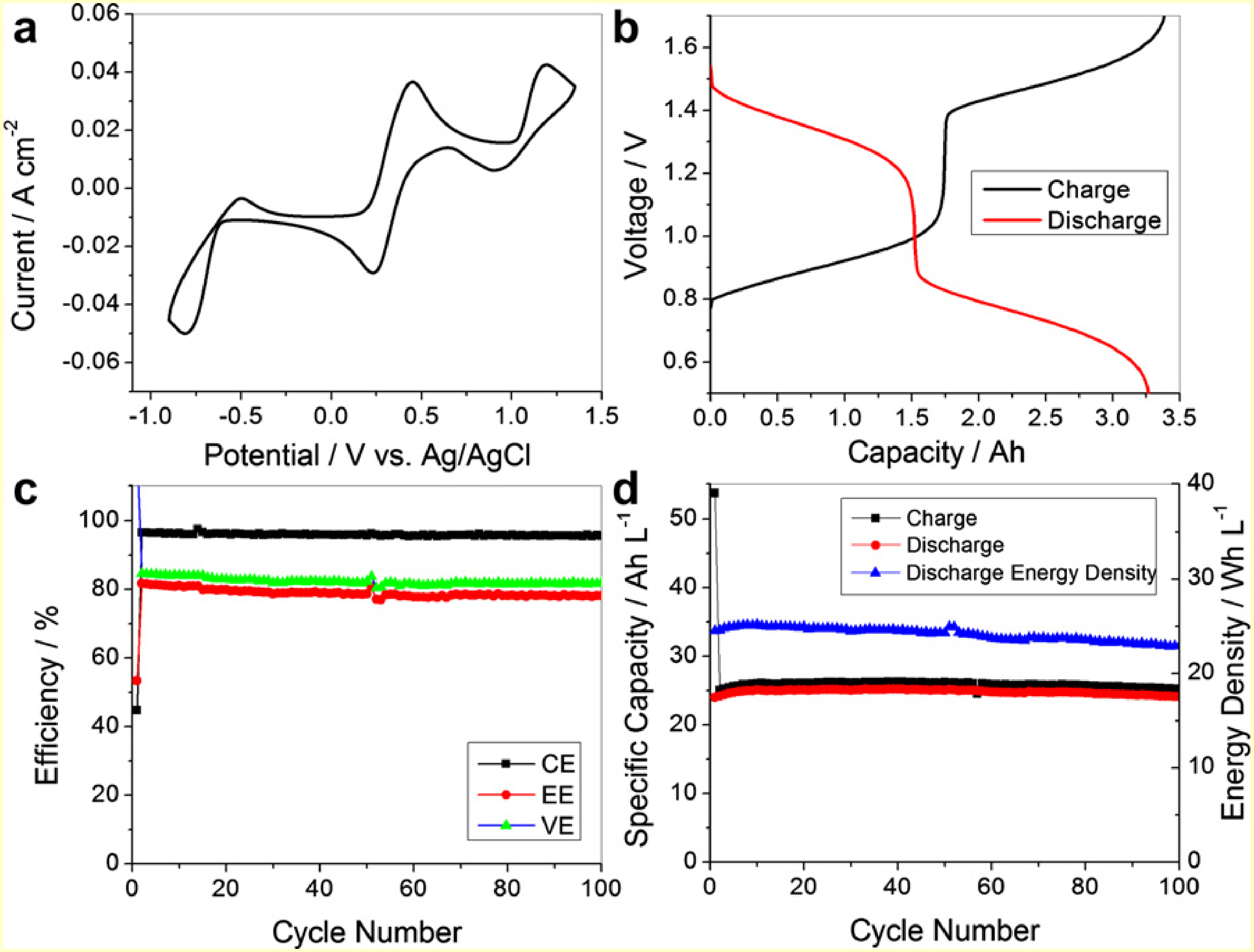
Catholyte 2: $Fe^{2+} \xrightarrow{\text{charge}} Fe^{3+} + e^{-}$ $E^{o} = +0.77$ V vs. SHE

Anolyte: $V^{2+} \xleftarrow{\text{charge}} V^{3+} + e^{-}$ $E^{o} = -0.26$ V vs. SHE

Compared with the Fe/V cell using the sulfate-chloride mixed acid electrolyte, the Fe/V hybrid cell achieved a >60% increase in the volumetric energy density attributed to the contribution from the second redox reaction pair.

W. Wang, et al, *J. Power Sources*, 216, 99-103 (2012).

A New Hybrid Redox Flow Battery with Multiple Redox Couples

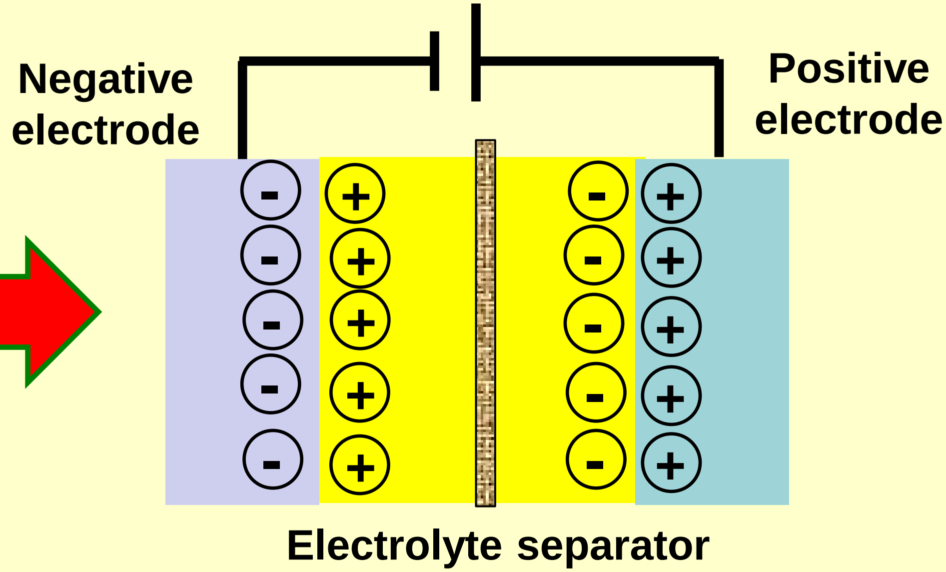


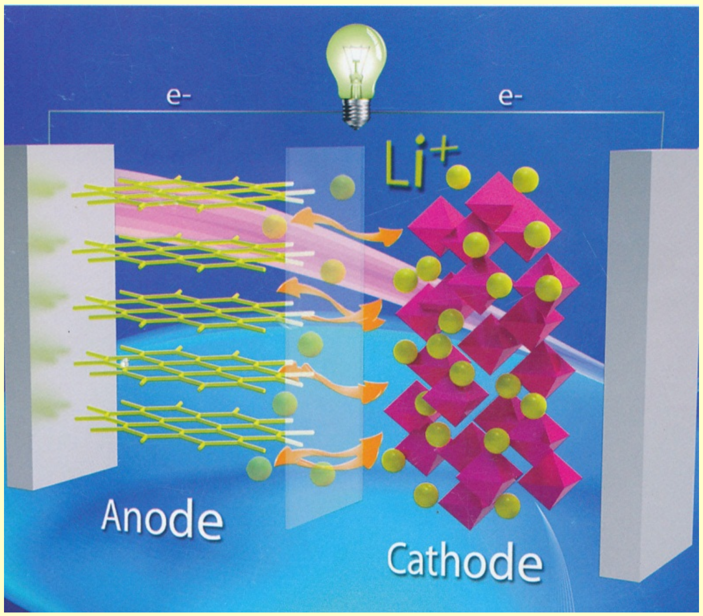
W. Wang, et al, *J. Power Sources*, 216, 99-103 (2012).

Electrochemical Capacitors
(Supercapacitors)

Supercapacitors versus Li-ion Batteries

Supercapacitors (SCs) store energy in the electric double layer at the electrode-electrolyte interfaces

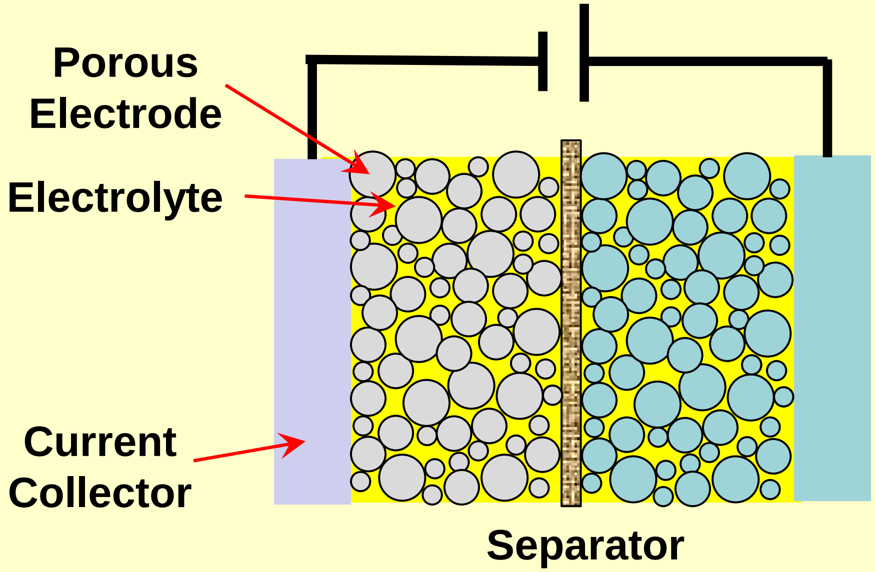


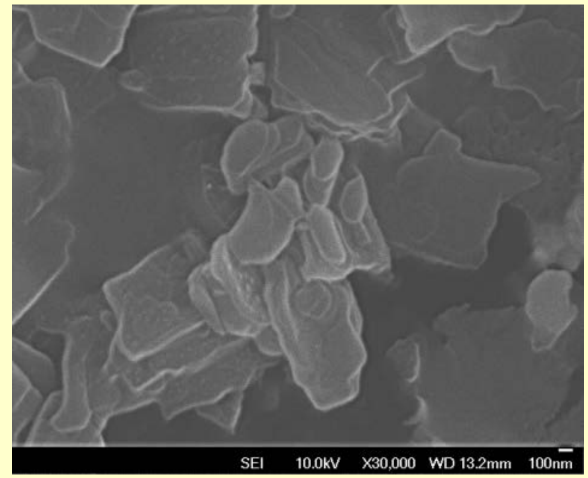


Li-ion batteries store energy through redox reactions of the host materials induced by Li-ion intercalation & deintercalation.

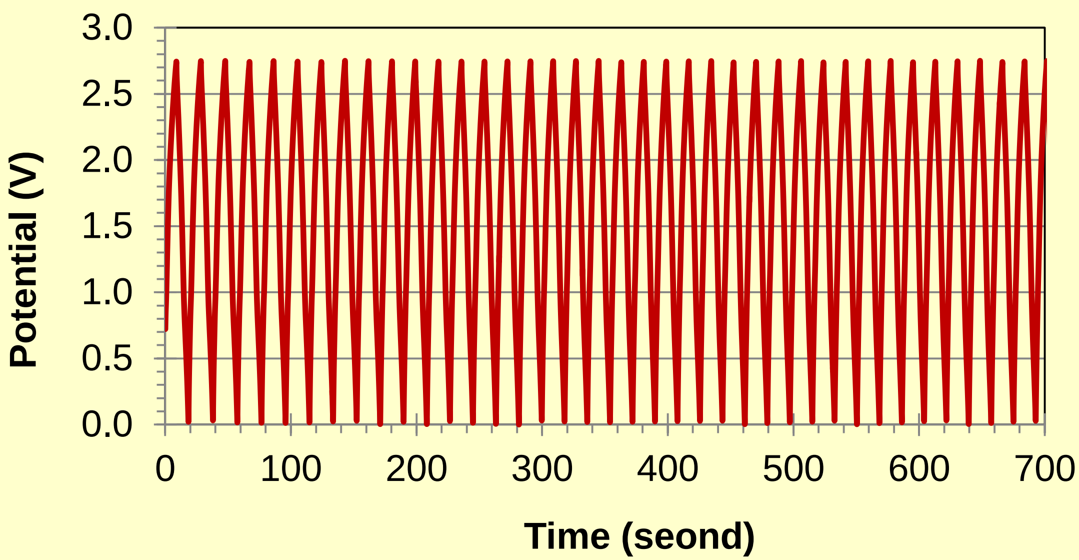
SCs: Fast charge/discharge rates, long cycling life, but low energy storage capacity.

Strategy 1: Improve the Energy Density of Supercapacitors via High Surface Area



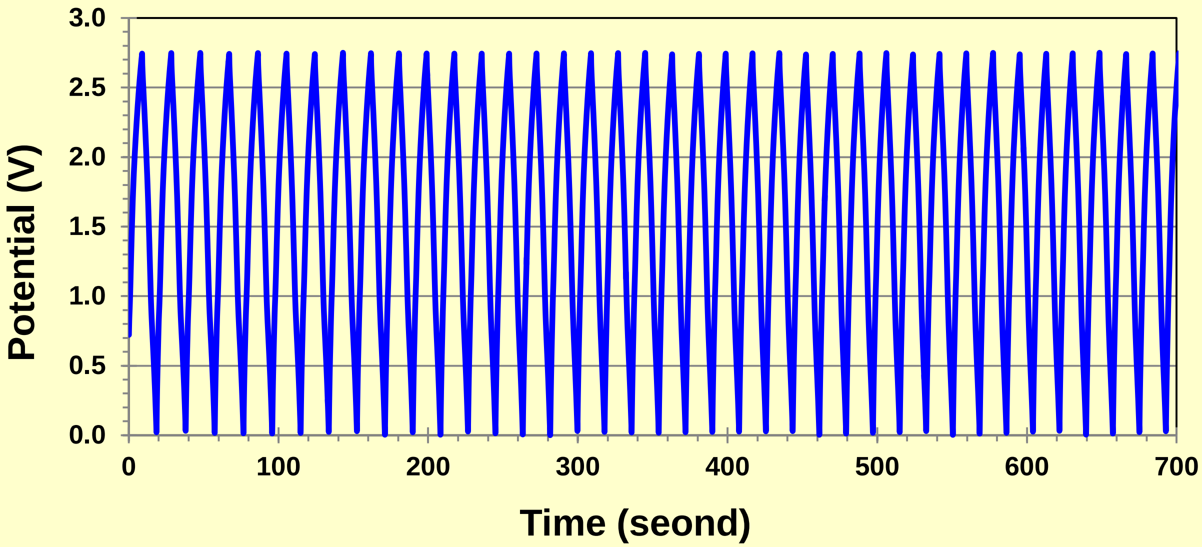


SEM image of graphene nanosheets (GNs)



Graphene is a good electrode material because of its exceptional electrical conductivity, excellent chemical stability, and very high specific surface area.

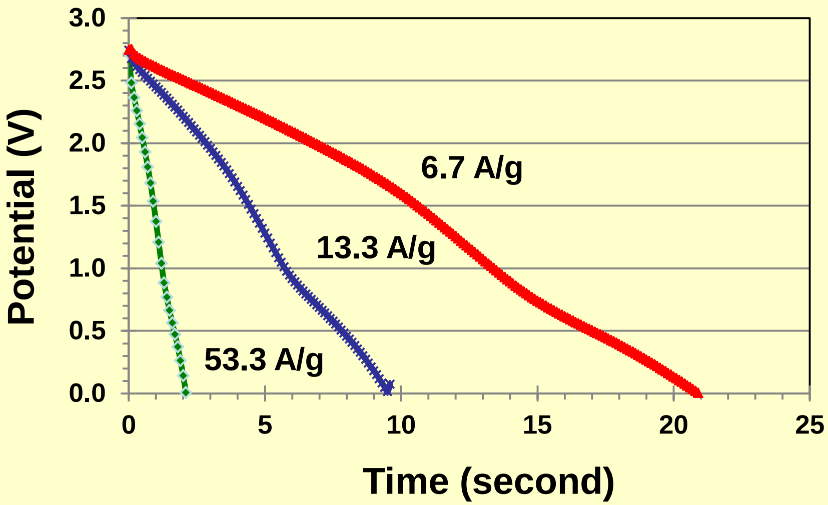
Properties of SCs with Planar Electrodes Made through Slurry Sedimentation Enhanced by Filtration



Galvanostatic charge/discharge cycling curves with a current density of 13.3 A/g.

The specific energy, E, can be computed from the double layer capacitance, *C*, and the applied voltage, V, via

$$E = \frac{1}{2} CV^2$$



A comparison of galvanostatic discharge curves for 3 different current densities as indicated

The GN-based SCs with planar electrodes in an organic electrolyte:

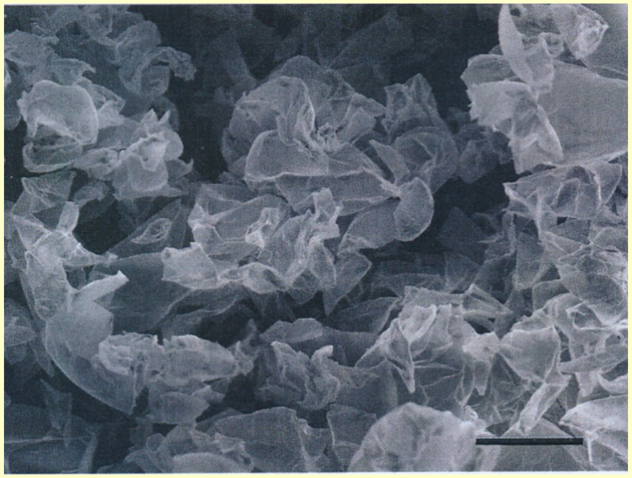
Current density (A/g)	Specific power (W/kg)	Specific capacitance (F/g)	Specific energy (Wh/kg)
6.7	8,645	103.2	26.2
13.3	17,290	89.8	22.4
53.3	69,290	83.0	21.0

Comparison of Various SCs with Planar Electrodes Made of Graphene or Activated Carbon

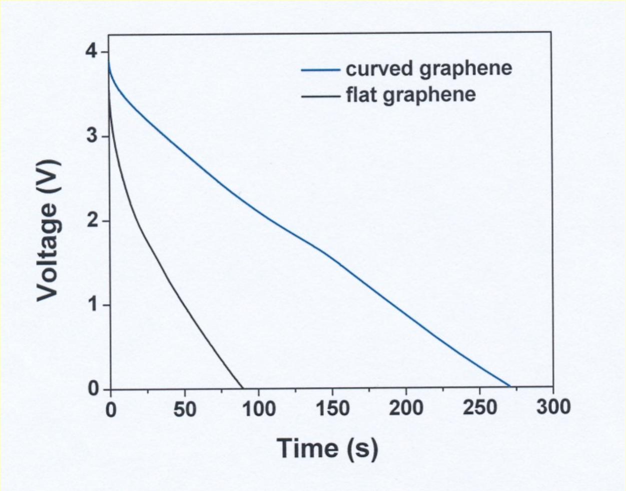
Electrode material	Electrolyte (voltage)	Current density (mA/g)	Specific power (W/kg)	Specific capacitance (F/g)	Specific energy (Wh/kg)	Ref.
Activated carbon	KOH (1 V) Organic (2.7 V)		~10,000 ~10,000	160 100	< 5 < 5	1
Flat G	KOH (1 V) $TEABF_4$/PC (2.7V) $TEABF_4$/AN (2.7 V)			128 91 95	4.4 23.0 24.0	2
Flat G	H_2SO_4 (1 V) Ionic liquid (3.5 V)			117 75	4.0 31.9	3
Flat G	KOH (1 V)	100	10,000	205	7.1*	4
Flat G	Ionic liquid (4 V)	1,000		48	26.0	5
Curved G	Ionic liquid (4 V)	1,000		158	85.6	5
Laser irradiated G	$TEABF_4$/AN (2.7 V) Ionic liquid (4 V)			265 276	67.1 149.5	6
Flat G	$TEMABF_4$/PC (2.7 V)	6,700	8,645	103	26.2	Our data

1) P. Simon and A. Burke, Electrocchem. Soc. Interface, 17 (2008) 38; 2) M. D. Stoller, et al., Nano Lett., 8 (2008) 3498; 3) S. R. C. Vivekchand, et al., J. Chem. Sci., 120 (2008) 9; 4) Y. Wang, et al., J. Phys. Chem., 113 (2009) 13103; 5) C. Liu, et al., Nano Lett., 10 (2010) 4863; 6) M. F. El-Kady, et al., Science, 335 (2012) 1326.

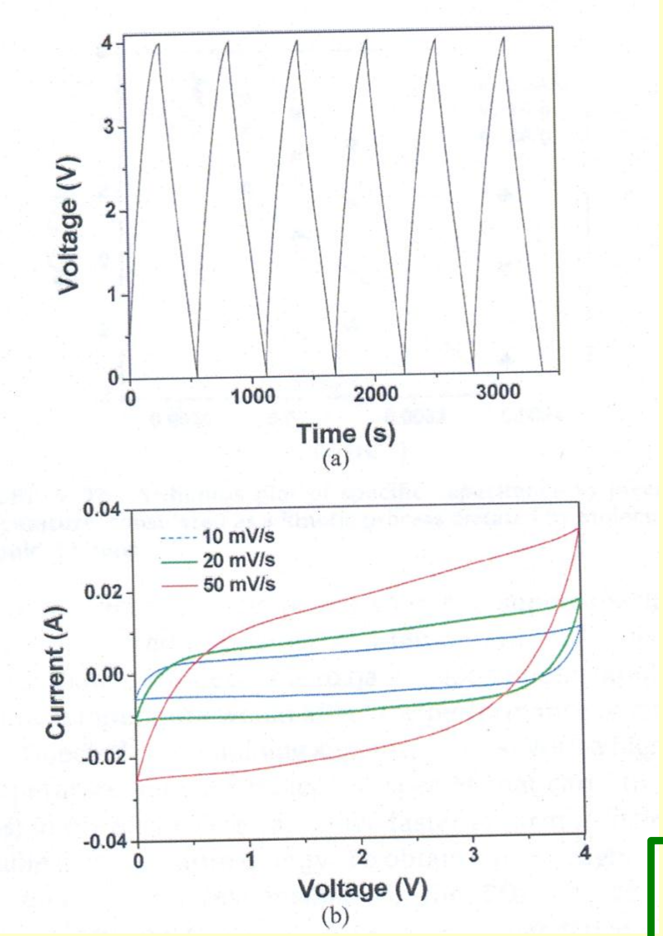
Curved Graphene Prevents Re-stacking and Results in High Energy Densities



SEM image of curved graphene



Discharge curves of curved graphene vs flat graphene electrodes



Galvanostatic charge-discharge curves of a curved graphene electrode (1 A/g, IL electrolyte)

Cyclic voltammograms as a function of the scan rate (IL electrolyte)

Specific capacitance:

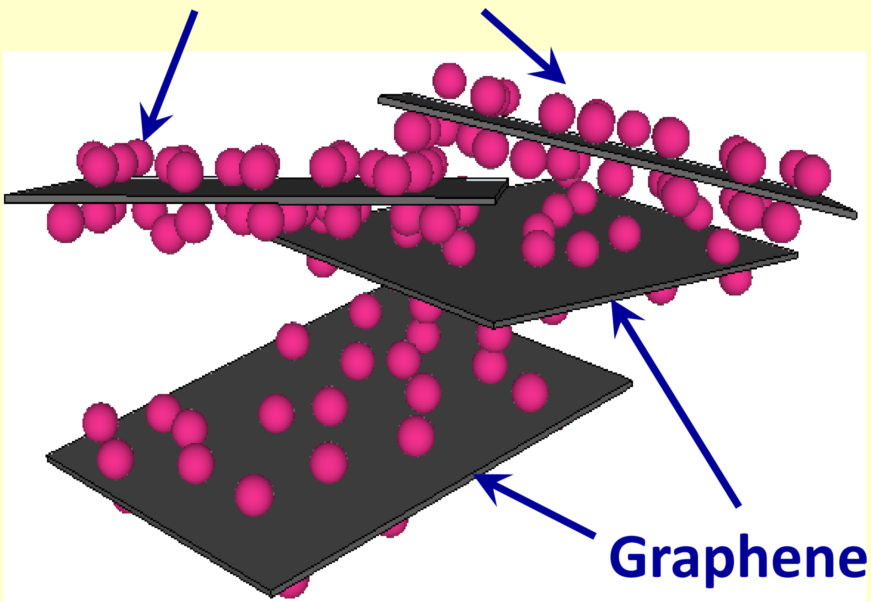
158 F/g

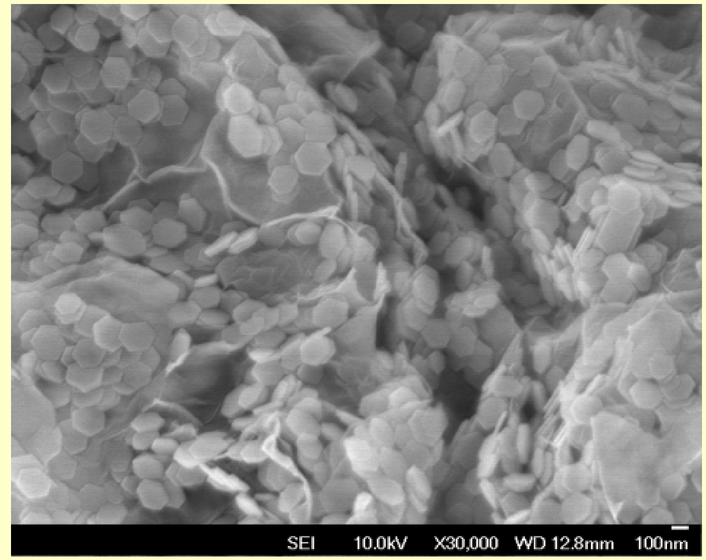
Specific energy:

85.6 Wh/kg

C. Liu, et al., Nano Lett., 10 (2010) 4863.

Strategy 2: Improve the Energy Density of Supercapacitors via Pseudocapacitance

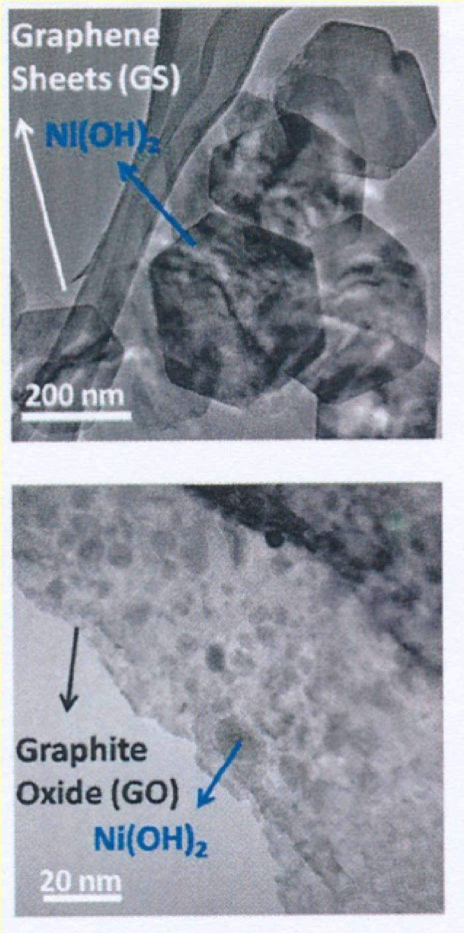


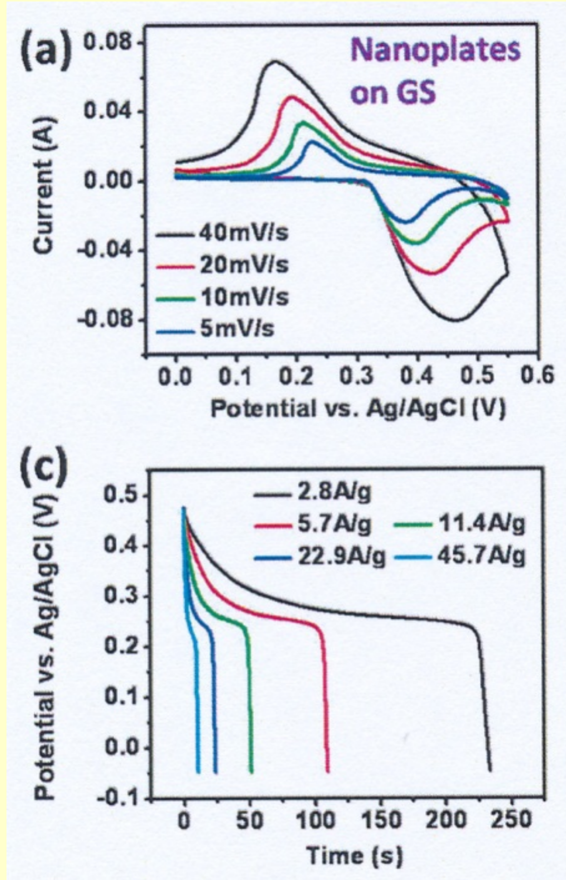


SEM image of $Ni(OH)_2$/graphene assembly

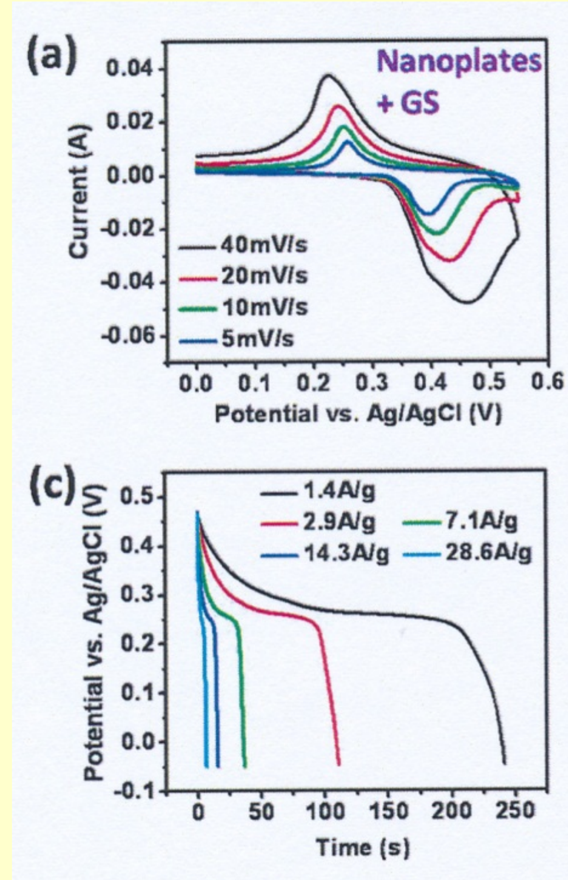
- ❑ Pseudocapacitance can increase the specific energy density by 10 to 100 times over that of the double-layer capacitors.
- ❑ Pseudo-capacitance can be due to (i) two-dimensional deposition of adatom arrays on electrode surfaces, (ii) redox reactions at electrode surfaces without intercalation (known as redox pseudocapacitance), and/or (iii) ion intercalation into electrode surfaces (known as intercalation pseudocapacitance).

Pseudocapacitors Derived from Nano-Ni(HO)$_2$ on Graphene Electrodes





CV and galvanostatic discharge curves of nano-Ni(HO)$_2$ on graphene

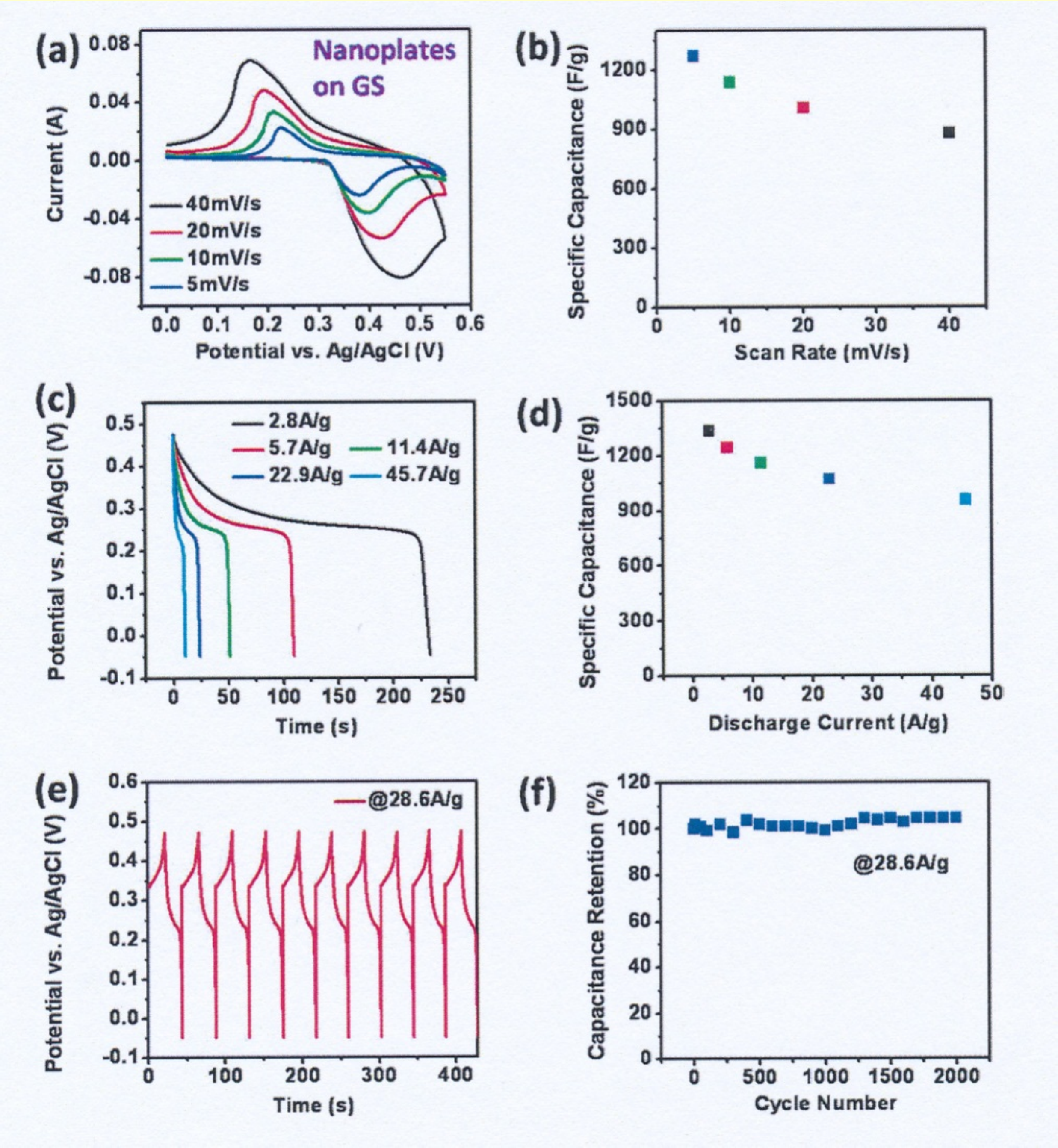


CV and galvanostatic discharge curves of nano-Ni(HO)$_2$ physically mixed with graphene

- ❑ C = 1267 F/g based on the mass of Ni(HO)$_2$ or 887 F/g based on the total sample mass at a scan rate of 5 mV/s.
- ❑ The redox current peaks correspond to the reversible reactions of Ni(II) ⟷ Ni(III).
- ❑ The C of physically mixed nano-Ni(HO)$_2$ with graphene is only about 50% C of nano-Ni(HO)$_2$ on graphene.

H. Wang, et al., J. Am. Chem. Soc., 132 (2010) 7472.

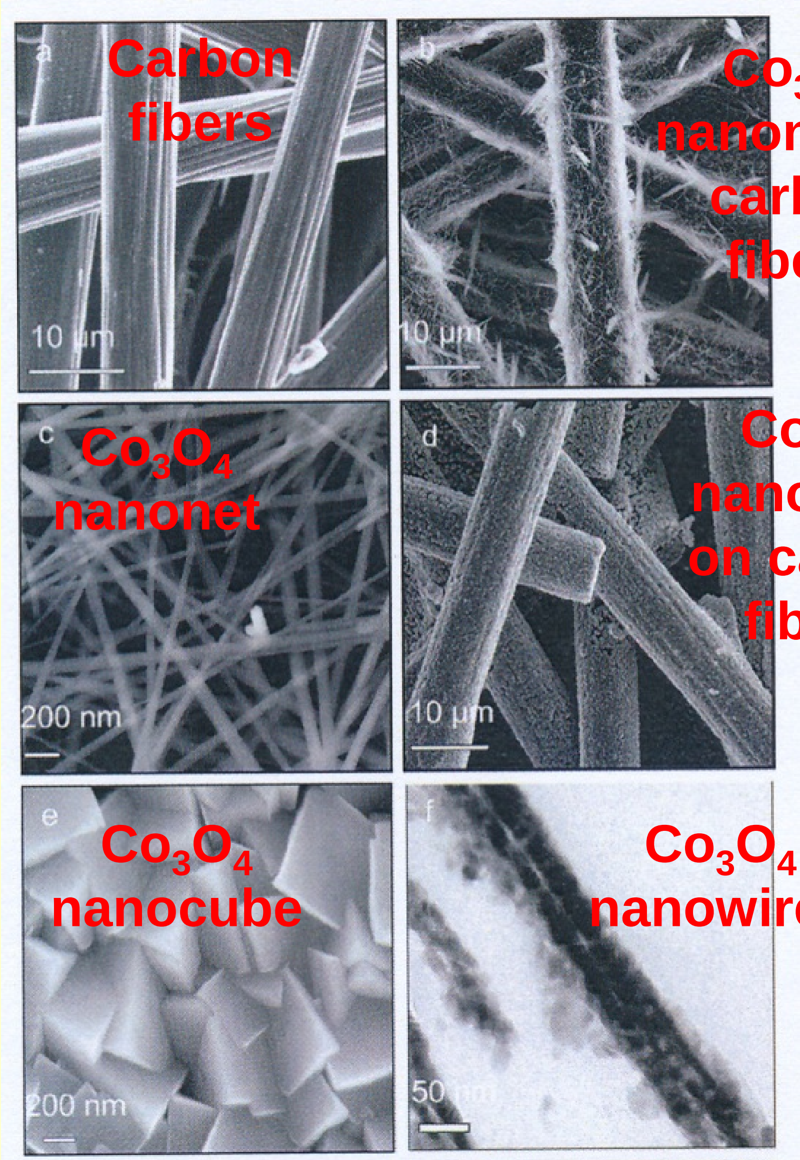
Pseudocapacitors Derived from Nano-$Ni(HO)_2$ on Graphene Electrodes

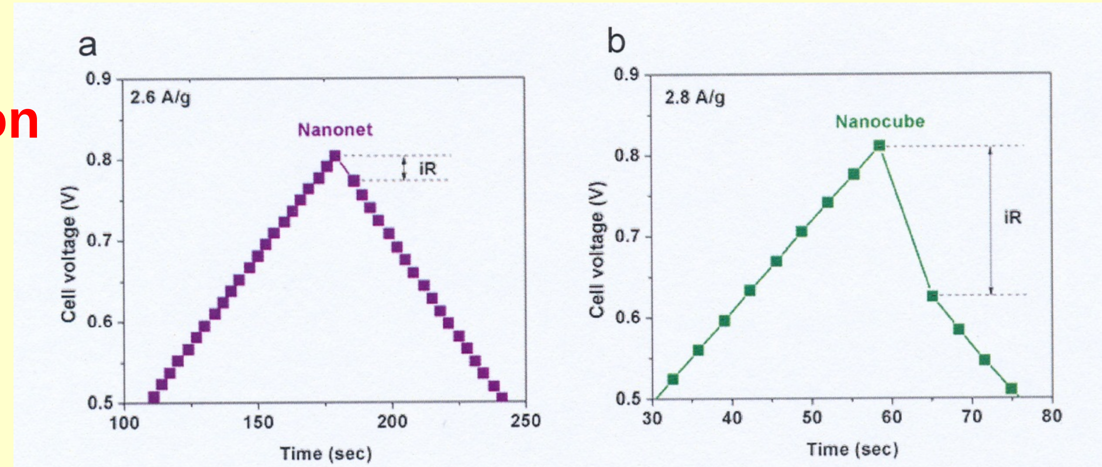


- Very high specific capacitance (~1,335 F/g) at current density of 2.8 A/g.
- The specific capacitance still very high (~953 F/g) at current density of 45.7 A/g.
- Capacitance retention is excellent with no discernable capacitance degradation over 2000 cycles.
- The Columbic efficiency is nearly 100% for each charge/discharge cycle.

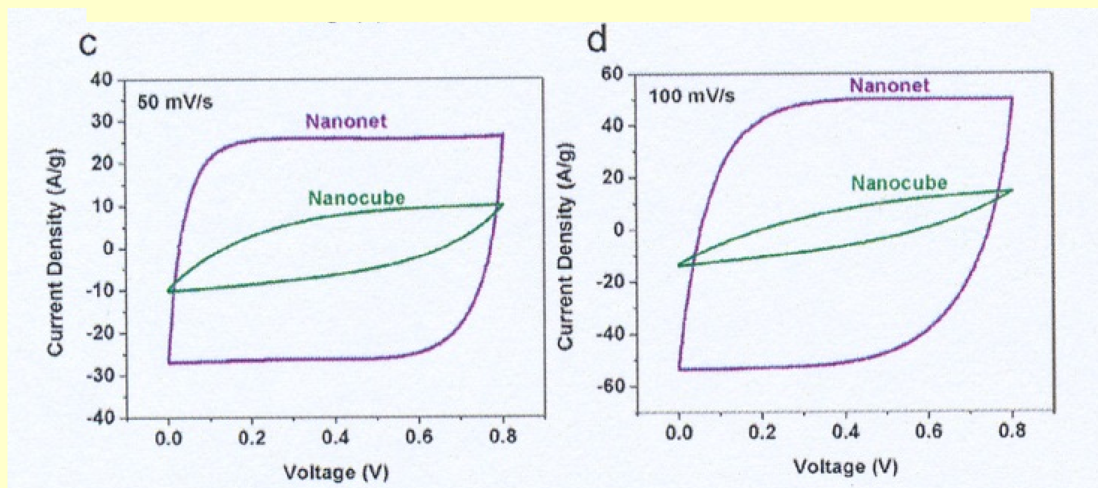
H. Wang, et al., J. Am. Chem. Soc., 132 (2010) 7472.

Pseudocapacitors Derived from Carbon Fiber Paper Supported Cobalt Oxide





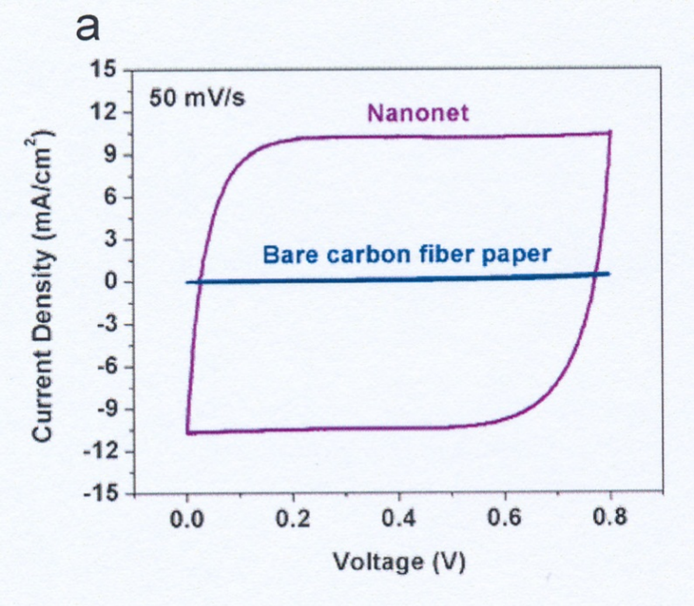
Nanonet has better rate capability and higher coulombic efficiency than nanocube.

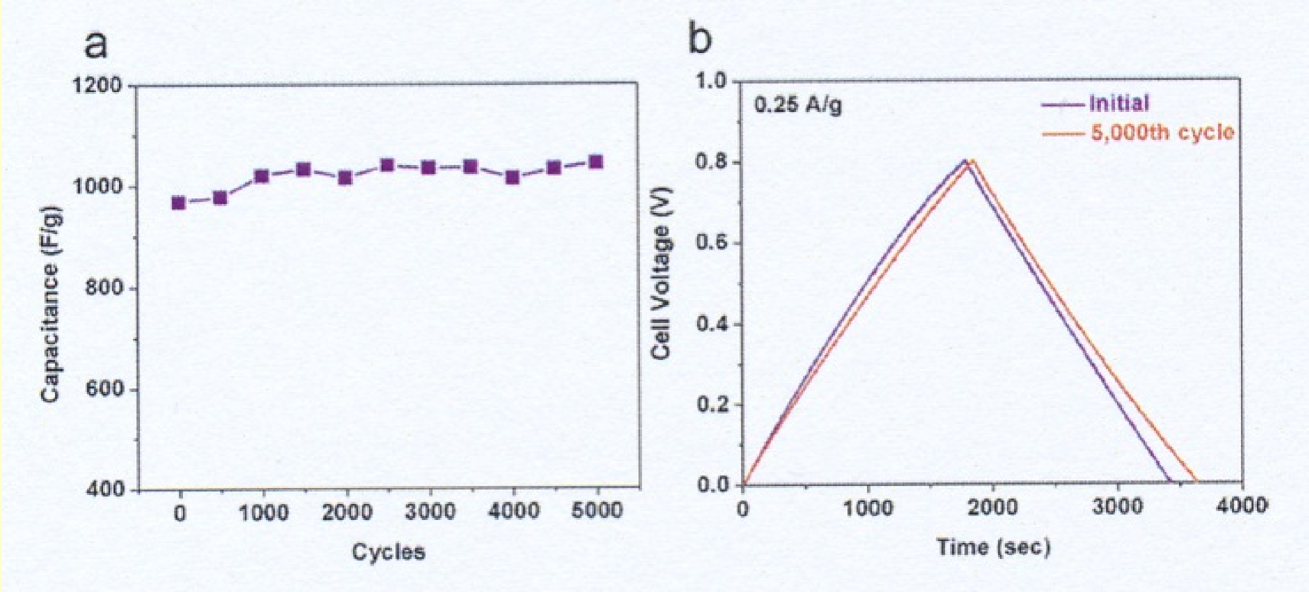


Nanonet has excellent "rectangular-shape" cyclic voltammograms, whereas nanocube has "distorted" CV curves.

L. Yang, et al., Nano Lett., 12 (2012) 321.

Pseudocapacitors Derived from Carbon Fiber Paper Supported Cobalt Oxide





Contribution of the carbon fiber paper to the capacitance is negligible. Nearly all capacitance is due to the pseudo-capacitance of Co_3O_4 nanonet.

- **The specific capacitance of the nanonet electrode is 1,124 F/g at a charge/discharge rate of 25.3 A/g.**
- **Capacitance degradation is negligible over 5,000 charge/discharge cycles.**
- **In spite of very high specific capacitance, the specific energy is only ~39 Wh/kg.**

Proposed mechanism:

Redox reactions due to rapid OH^- intercalation/deintercalation at the surface of Co_3O_4, as shown below.

$$Co_3O_4 + OH^- + H_2O \longleftrightarrow 3CoOOH + e^-$$
$$3CoOOH + 3OH^- \longleftrightarrow 3CoO_2 + 3H_2O + 3e^-$$

L. Yang, et al., Nano Lett., 12 (2012) 321.

Major Conclusions from Various SCs with Pseudocapacitance

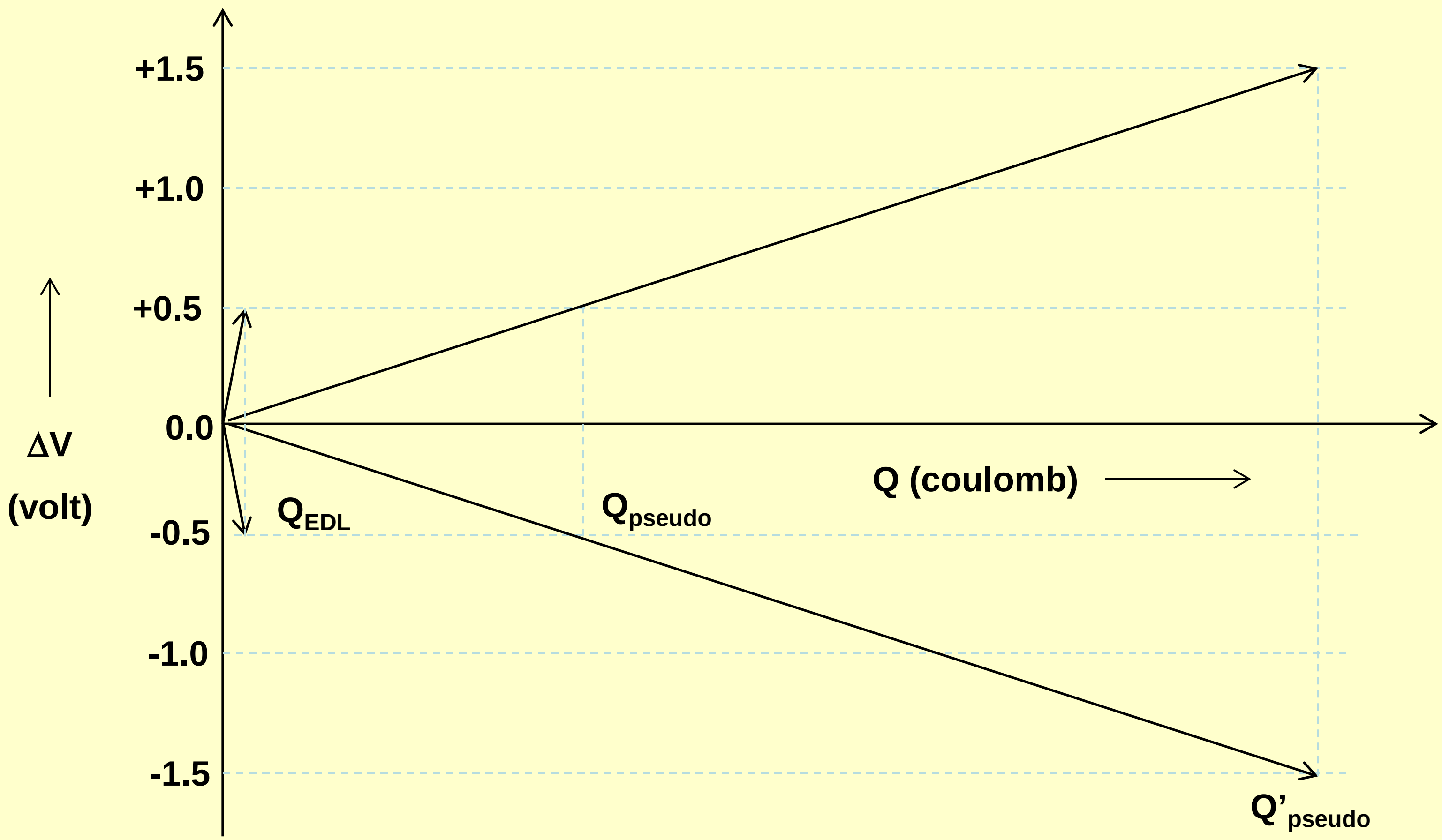
- ❑ Pseudocapacitance can increase the specific energy density by 10 to 100 times over that of the double-layer capacitors.
- ❑ Pseudocapacitors can have excellent cycle stability if the issue of their electron conduction is addressed properly.
- ❑ In spite of the enormous progress made recently, the specific energy of pseudocapacitors is still low (< 100 Wh/kg) comparing with that of Li-ion batteries.

✓**Can we further improve the specific energy of pseudocapacitors?**

✓**How can we achieve pseudocapacitors with specific energy > 600 Wh/kg (based on active electrode materials)?**

Increasing the Energy Density of Pseudocapacitors by Increasing the Cell Voltage

The specific energy, E, of supercapacitors: $E = \frac{1}{2} CV^2$



Schematic of the storage capacity: (i) pseudocapacitance, Q_{pseudo}, can increase the energy density by ~ 10 times, (ii) pseudocapacitance along with increasing the cell voltage from 1 to 3 V, Q'_{pseudo}, can increase the energy density by ~30 times.

Calculated Energy Densities of Pseudocapacitance with Multi-Electron Transfer Redox Reactions

Specific capacitance of electrodes (F/g)	150/150	150/700	700/700	700/700	700/700
Cell voltage (V)	5 (2+3)	5 (2+3)	4 (2+2)	5 (2+3)	3 (1.5+1.5)
Specific energy based on active electrode materials (Wh/kg)	260	429	778	1,215	437
Specific energy of assembled devices (Wh/kg)	65 – 86	107 – 143	194 – 259	303 - 405	146 – 109

Conclusions

- Li-ion batteries have revolutionized portable electronic devices in the past two decades, and have the potential to make great impact on vehicle electrification.
- Currently, Li-ion batteries, flow batteries and super-capacitors are undergoing a period of unprecedented changes in improving energy and power densities.
- Supercapacitors have the potential to compete with Li-ion batteries in both power and energy densities.
- Advancements in materials synthesis and processing play a critical role in all of the advancements achieved in LIBs, flow batteries and supercapacitors.
- Technological breakthroughs in LIBs, flow batteries and supercapacitors in the next five years will enable board market penetration of vehicle electrification, renewable energy integration, and smart grids.

Acknowledgements

Past & Current Students:

Dr. W. Osborn, NIST; Dr. X. Wan, Intel; Dr. T. Markmaitree, Lightening Energy; Dr. Y. Zhong, Saint-Gobain Corp.

Jack Shamie, Ling Li, Monica Sawicki, Imran M Ayub, Chuanlong Wang, Xiong Xie, Kyle Crosby, Xuzhe Zhao, Pasquale Lavorato

Collaborators:

Dr. J.-Z. Hu, PNNL; Dr. Z. G. Yang, UniEnergy Technologies; Prof. A. L. Ortiz, Spain; Prof. C. Shen, China; Prof. R. Ren, China

Funding Agencies:

DOE DE-FC36-05GO15008; NSF CBET-1252924; NSF CMMI-1228888.