# Energy Storage Technology

## Maxwell Technologies, Inc

*Ultracapacitors ● Microelectronics ● High-Voltage Capacitors*

# Abstract

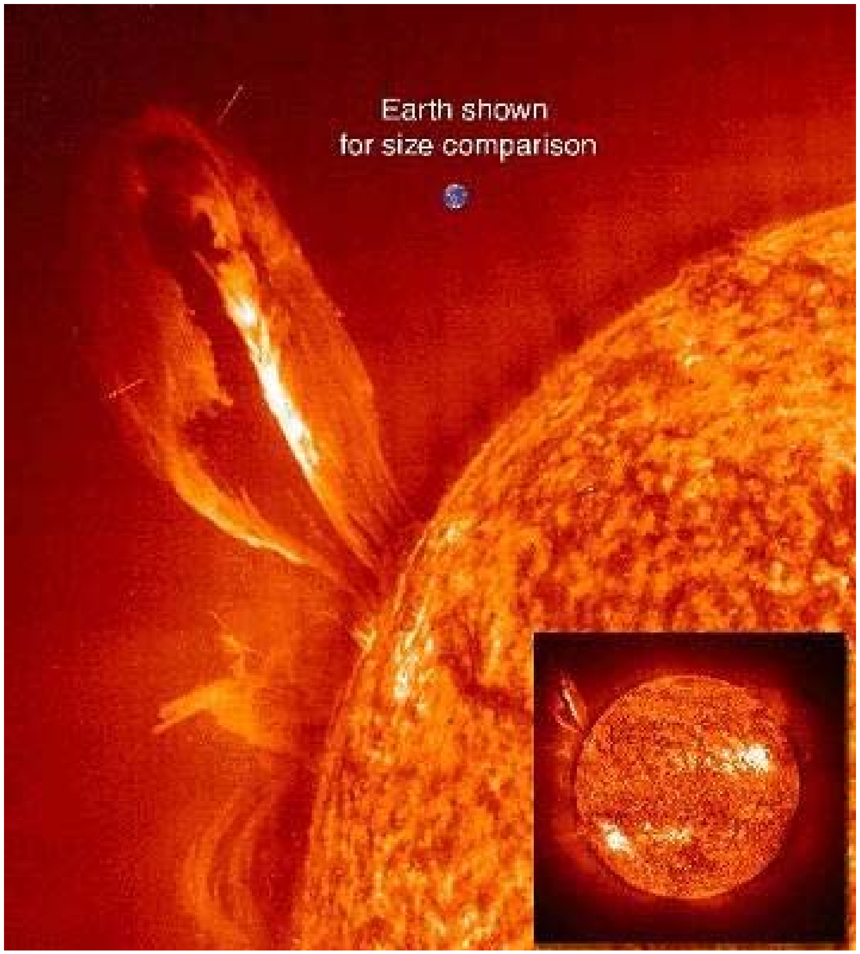
Ultracapacitors are becoming widely accepted in the energy storage industry in both standalone and in combination with batteries. Standalone applications, once niche, are now rapidly expanding as the technical and economic benefits of this power dense component become more widely understood. Combination examples continue to proliferate, primarily in battery electric and hybrid electric commercial transportation segments such as transit buses and trains. The ultracapacitor offers a fast energy buffer to advanced chemistry energy reservoirs such as nickel metal hydride and lithium batteries and offer an opportunity for truly energy optimized battery systems. This presentation will discuss trends in energy storage systems, advanced chemistry batteries such as nickel-hydrogen and lithium-ion and why such components would benefit from working in combination with carbon capacitors.

# Outline

- Primary Energy: Our Motivation
- Ultracapacitor Energy Storage Mechanism
  - Electrostatic vs. Electrochemical
- Markets for Energy Storage Systems and 2007 Outlook
  - Diverse, best applied where existing energy storage is low
- Challenges for Lithium that Ultracapacitors Benefit
  - Low temperature, high rates, long calendar & cycle life
- Application Examples:
  - Commercial,
  - Industrial,
  - Transportation
- Wrap-up

# Source of all Primary Energy

- Solar radiation intercepted by earth's disk is 178 PW
  (Tera = $10^{12}$, Peta = $10^{15}$, Exa = $10^{18}$)




Of 178 PW, only 40 TW is absorbed into plants Globally.
40 TW x 600 MYr => present fossil fuel supply

30% Albedo, or 52 PW reflected to space

3 TW tidal Sun-moon-Earth interact

178 PW

Solar

32TW from Terrestal (core)

# Where Does the Energy Go?

- Consider a 1 vehicle household in the U.S (equiv. gasoline)
  - Electricity consumption in average home = 1000 kWh/mo

$$Household \Rightarrow 1000\frac{kWh}{mo}\left(12\frac{mo}{yr}\right)\left(\frac{eff\_coal}{0.34}\right)\left(\frac{3600s}{h}\right)\left(\frac{kg\_gasoline}{43.2MJ}\right) = 2941kg$$

  - Vehicle having 25 mpg on average and 15,000mi/yr consumes:

$$Veh \Rightarrow \frac{15{,}000mi}{25mpg}\left(3.43\frac{kg}{gal}\right) = 2060kg$$

  - Total energy consumption of 1 vehicle household in U.S. in equivalent gasoline usage:
  - = (2.941 + 2.06)= 5.00 metric tons of gasoline per household/year!

- Gasoline combusted generates ~3.14 kg CO2/kg
  - => 15.7 metric tons of CO2/household/year !

# Primary Energy Summary

- A single household with one vehicle consumes the equivalent of 5,000 kg of gasoline/year.
  - = 216 GJ of energy/household/year
  - 100M households consume 21.6 EJ

- U.S. energy supply breakdown (in Quad ~=EJ)
  - Coal…………22.6
  - Gas…………23.1
  - Oil……………40.6
  - Nuclear………8.2
  - Hydro…………2.7
  - Alternative……3.6

  Total…………100 Quad = 104.5 EJ

## What is going on ? Mega-trends

- Rising global awareness that we need more carbon free energy sources:
  - No viable non-carbon alternative can meet the energy demands of $10^{10}$ people in the near future, 2050.
  - Globally, 6.3B people, 12.8 TW (U.S. @ 25% =3.3 TW) now → 28 TW in 2050
  - The right people are working on this, but have not been heard.
- Climate change is now positively linked to anthropogenic activities with very high confidence.
  - Net effect of human activity since 1750 has been one of warming.
- Hydrogen economy is a myth, will never happen! Yes, for niche applications.
  - Electricity from fuel cell costs 4x grid delivered electricity
  - It would take 400 Gen IV nuclear plants to equal hybridizing trans.
- Electricity is the energy carrier of the future.

# What is an Ultracapacitor?

- Invented in U.S. by Robert A. Rightmire of SOHIO company.
  - U.S. Patent 3,288,641 *"ELECTRICAL ENERGY STORAGE APPARATUS: This invention relates generally to the utilization of an electrostatic field across the interphase boundary between an electron conductor and an ion conductor to promote the storage of energy by ionic adsorption at the interphase boundary." Nov. 29, 1966*
- Electrochemical storage batteries and capacitors have been in existence for over 200 years (Baghdad battery BC), Volta "pile" 1800, to Ben Franklin 1848 who coined the term "battery".
  - Battery stores energy in chemical bonds that follow reduction-oxidation (REDOX) reactions. Mass transfer is involved.
  - Capacitors store energy in electrostatic fields between ions in solution and a material. No mass transfer involved – hence no electrochemcial wearout.

Source: Joel Schindall, "Concept and Status of Nano-sculpted Capacitor Battery," Presented at 16th Annual Seminar on Double Layer Capacitors and Hybrid Energy Storage Devices December 4-6, Deerfield Beach, Florida

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# Ultracapacitor Material and Electrode

- **On cost of ultracapacitors** is dominated by carbon.
  - Raw material – coconut shells =>
- **Carbon is the cost driver**
  - Resin based – high purity, high mat'l costs
  - Natural product based – (coconut, wood, coal, peat, etc.) lower cost, higher impurities

Grind

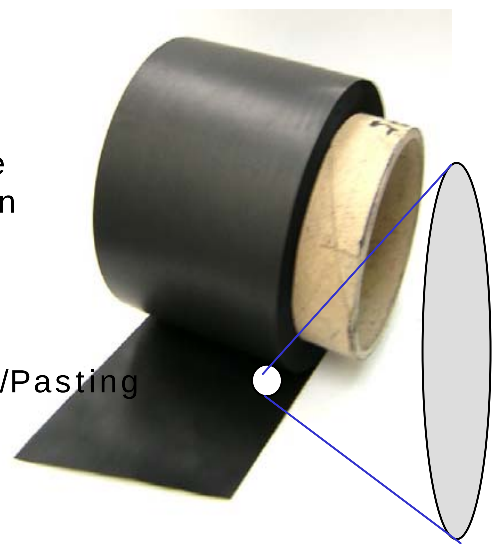
Activation

Activated carbon powder

Electrode fabrication

Coating

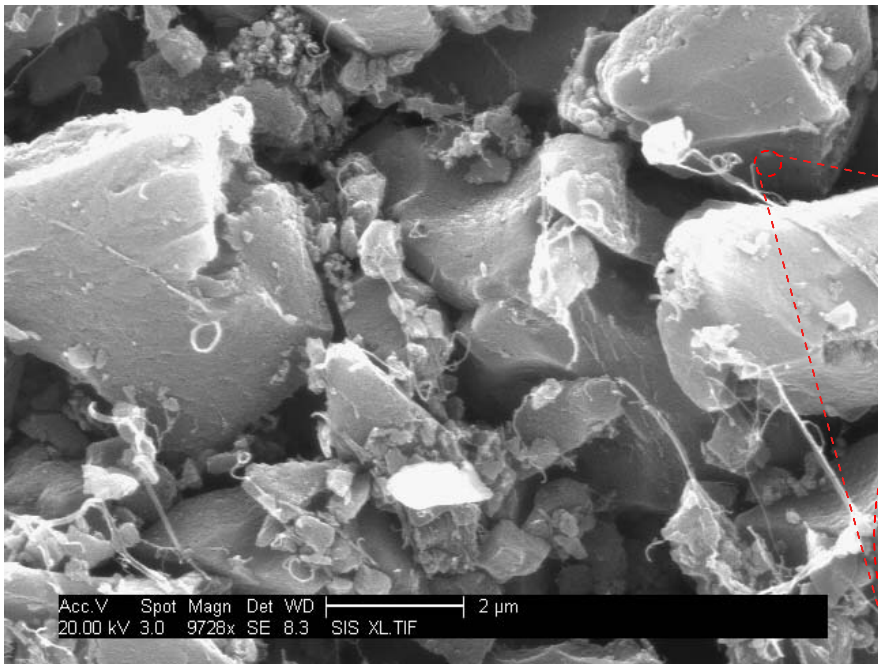
Rolling/Kneading/Pasting



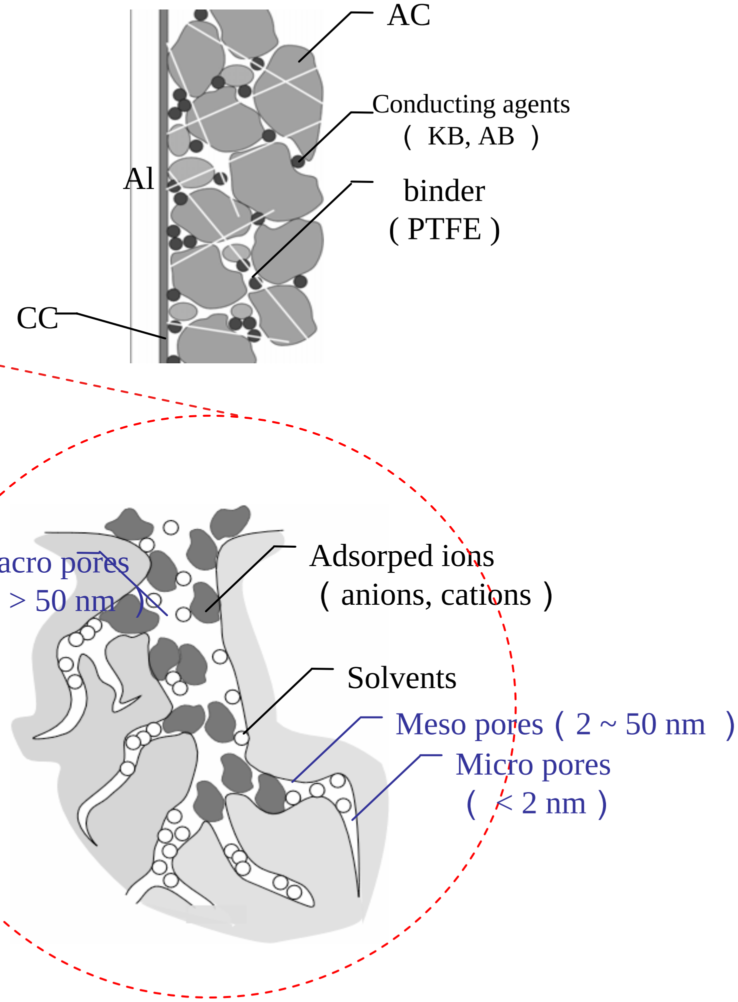
Source: Prof. Katsuhiko Naoi, Institute of Symbiotic Science and Technology, Tokyo University of Agriculture and Technology, Recent Advances in Capacitors and Hybrid Power Sources in Japan, presented to DOE Basic Energy Sciences Wkshp, 3-4 March 2007

# Ions and Pores Model

- Pore sizes must be controlled to provide access for both ion species.



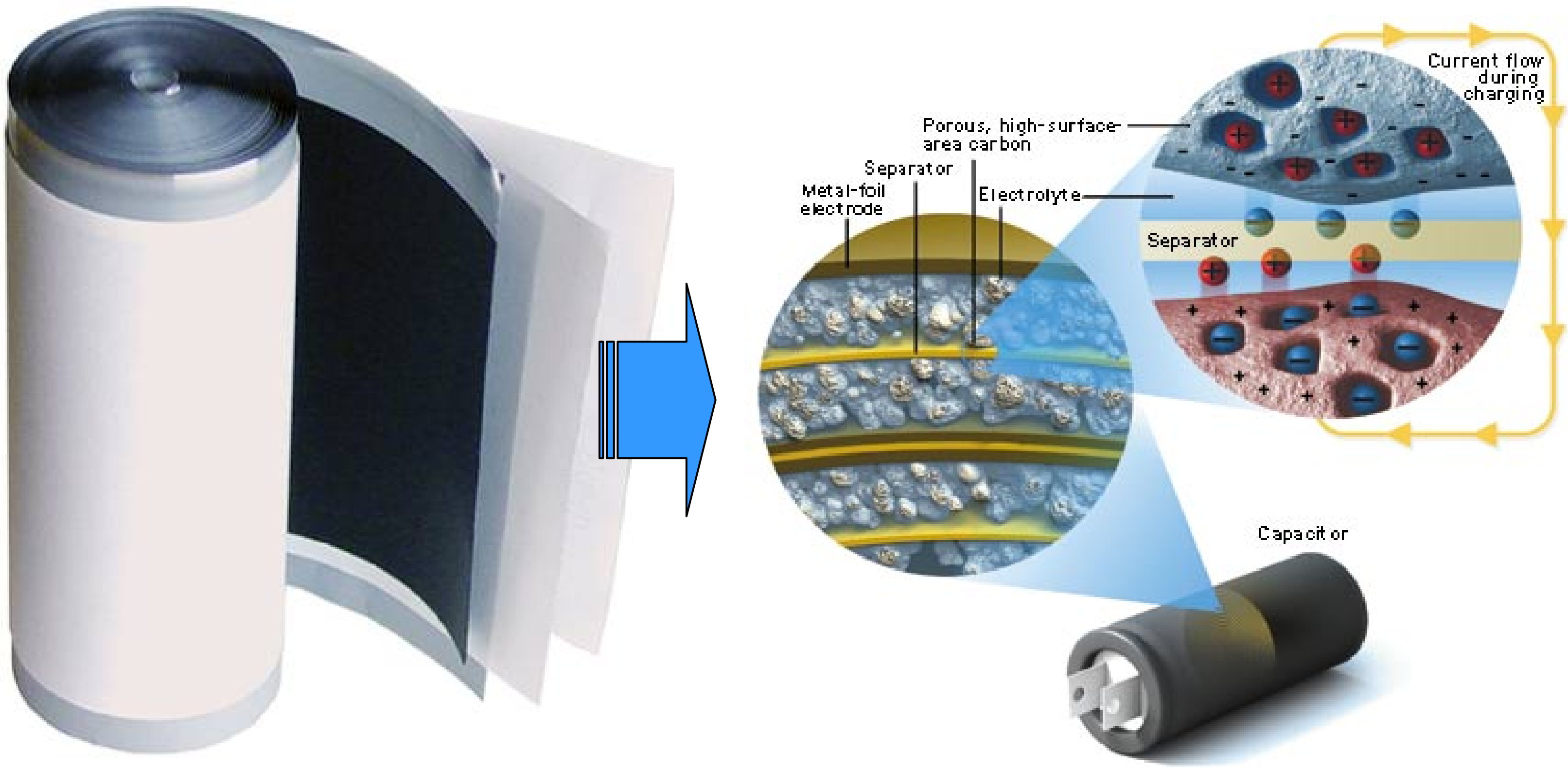

### Electrode for EDLC




Inset from: Prof. Katsuhiko Naoi, Institute of Symbiotic Science and Technology, Tokyo University of Agriculture and Technology, Recent Advances in Capacitors and Hybrid Power Sources in Japan, presented to DOE Basic Energy Sciences Wkshp, 3-4 March 2007

# The Fundamentals

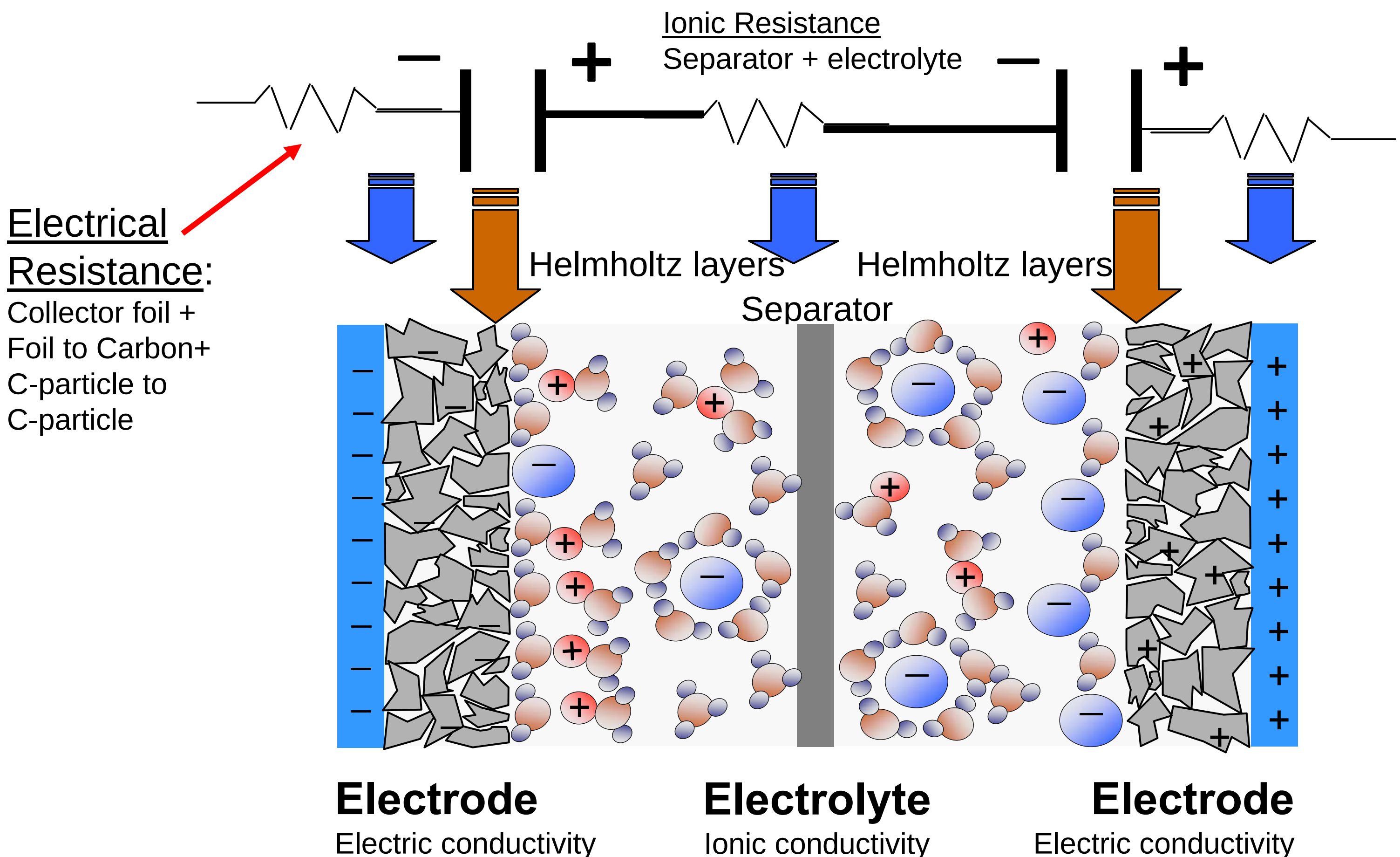
- Basics of the electronic double layer, i.e., ultracapacitor
  - An electronic charge accumulator having extreme capacitor plate specific area and atomic scale charge separation distance.




Graphic: IEEE Spectrum, Jan 2005

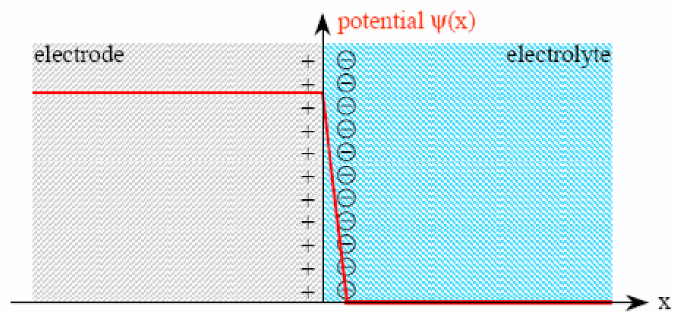
# Ultracapacitor Basics

- The ultracapacitor model commonly applied is that of the series combination of two DLC's at the electrode - solvent compact layer.
- The compact layer interface between the carbon particles and electrolyte ions, the Helmholtz layer, is on the order of 1 atom thickness.

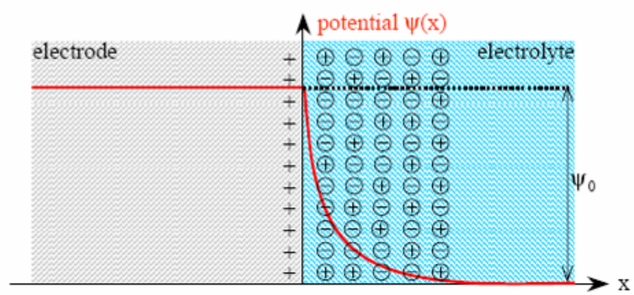


# The Compact Layer

- Evolution of electrochemical capacitor modeling theory:
  - Helmholtz
  - Gouy-Chapman
  - Stern's model

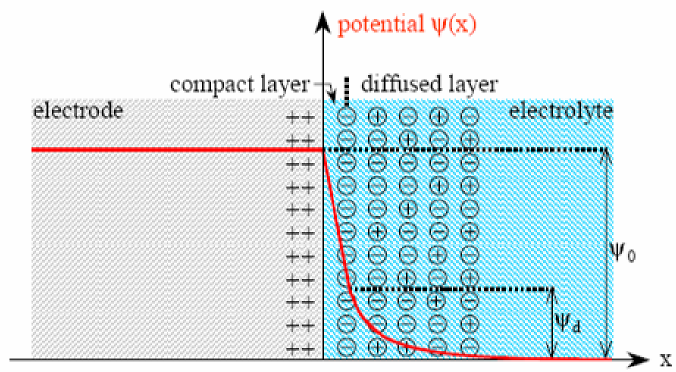



Helmholtz model:
ε~78 for organic electrolyte
d~ 0.2nm for solvent molecule
C→ 340 uF/cm2, is 10x experiment
C is not voltage dependent.



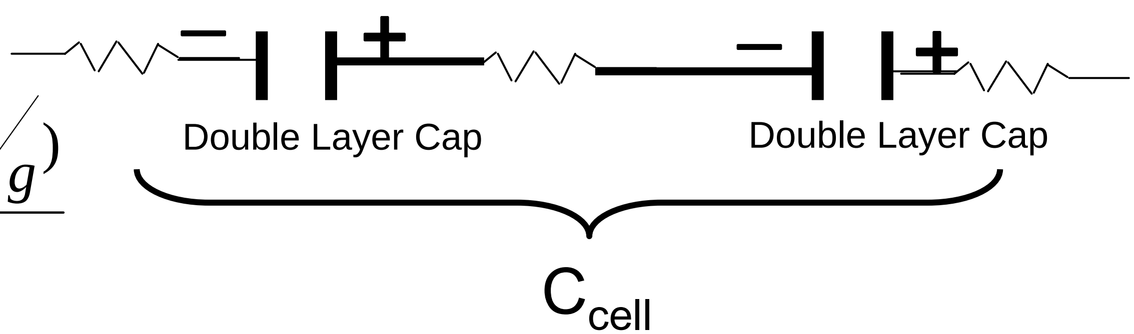

Known as the diffuse Model. Works well at low potential, over estimates C for higher potentials.

Improves on Gouy-Chapman by retaining Helmholtz compact layer of adsorbed ions and Gouy-Chapman diffuse layer of point charges, but modifies situation to include physical size to the ions.



# Ultracapacitor Example

- The model looks simple – but it could be tricky.
- Consider:
  - Carbon at 75 F/g (i.e., Farads of capacity per gram of carbon)
  - Total mass of carbon per device = 187g (as example)
  - Therefore: 75 (F/g)x 187g = 14,025 F (this is a huge number!)
- However:
  - Each unit consists of a pair of electrodes (1/2 total mass each)
  - AND 2 each electrode Double Layer Capacitors are in series.

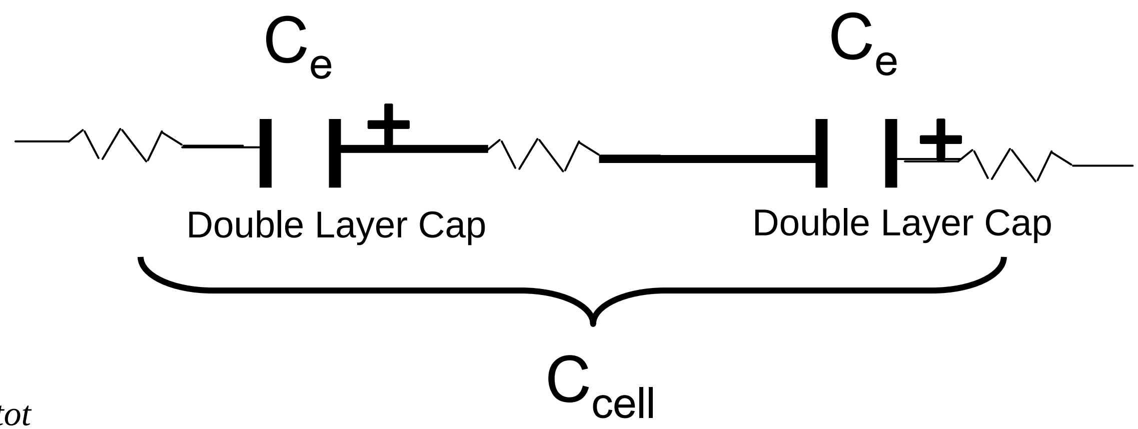



$$C = \frac{\varepsilon S}{d} = \frac{3\varepsilon 10^{3}(m^{2}/g)}{10^{-9}}$$

Ultra = $Scale * \left(10^{12}\right)$

# Ultracapacitor Example

- Completing the example.
  - Given that total Farads, $F_{tot}$ = 14,025



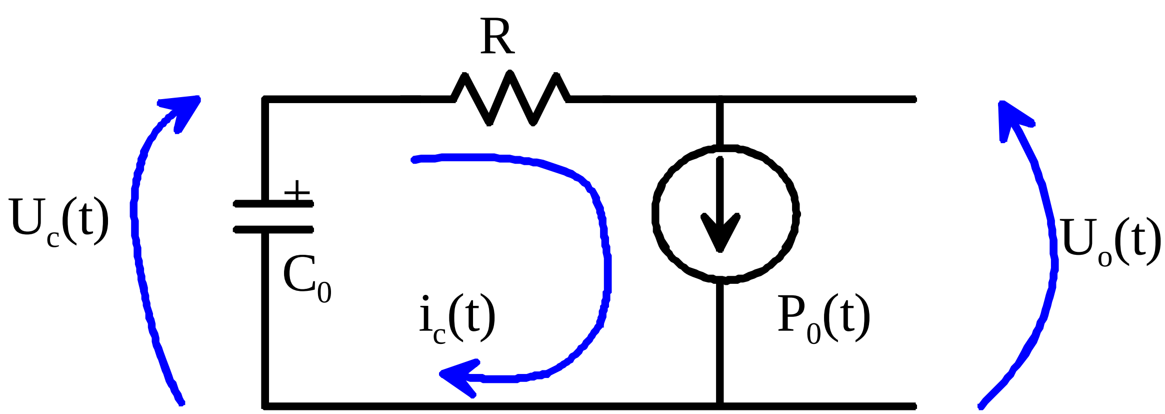

$$C_e = \frac{F_{tot}}{2}$$

$$C_{cell} = \left.\frac{C_1 C_2}{C_1 + C_2}\right|_{C_1 = C_2 = C_e} = \frac{C_e}{2}$$

$$\therefore C_{cell} = \frac{F_{tot}}{4} = \frac{14{,}025}{4} = 3506F$$

# Constant Power Model

- Analytical model and result
  - The result: 1st order, 2nd degree, nonlinear differential equation.




- Apply KVL and substitution ic = -CdU/dt yields for discharge case:

$$\dot{U}_c^2 + \frac{1}{\tau} U_c \dot{U}_c + \frac{P_0}{\tau C_0} = 0$$

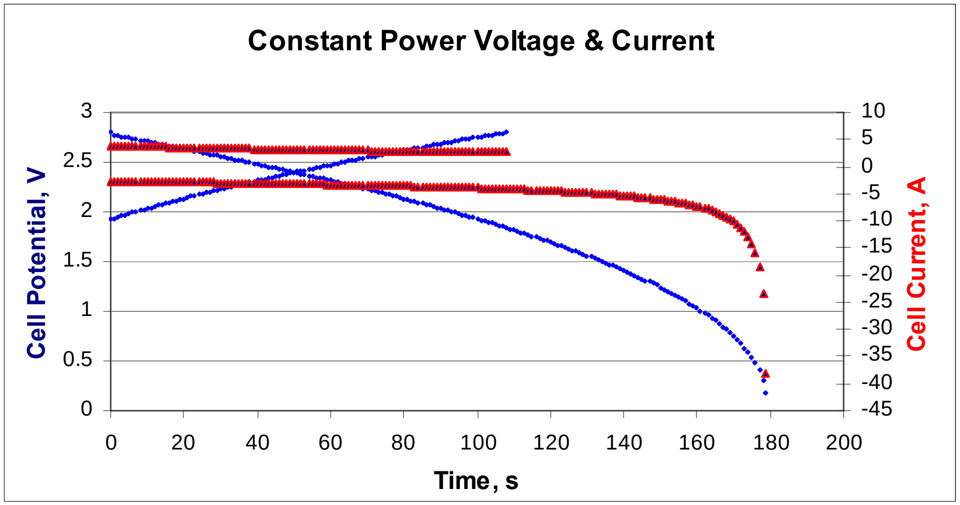
# Analytical Solution for CP Loading

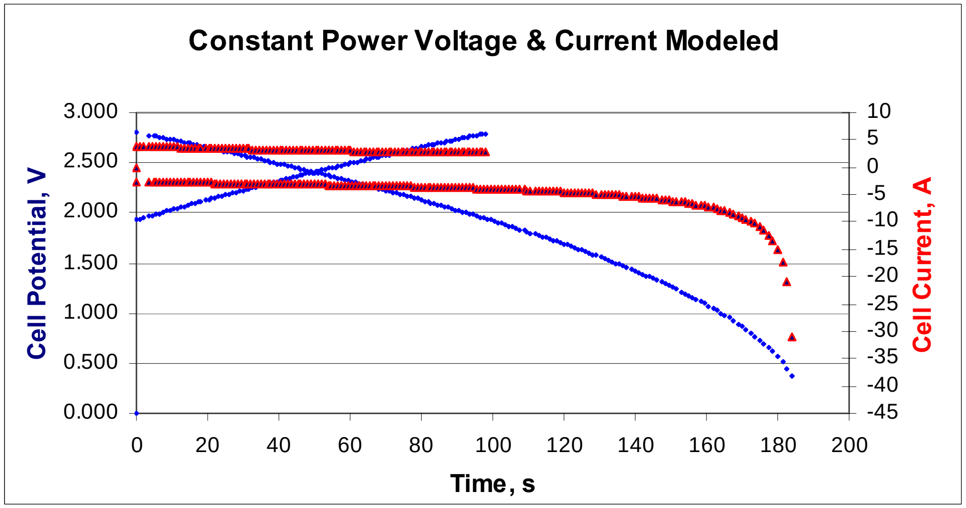
- Illustration of constant power voltage and current
  - Measured
    - Tf = 178.8s

$$P_0 t_f \cong \frac{CU_{mx}^2}{2}$$

$$t_f = \frac{CU_{mx}^2}{2P_0} = \frac{340(2.8)^2}{2(7.5)} = 177.7$$

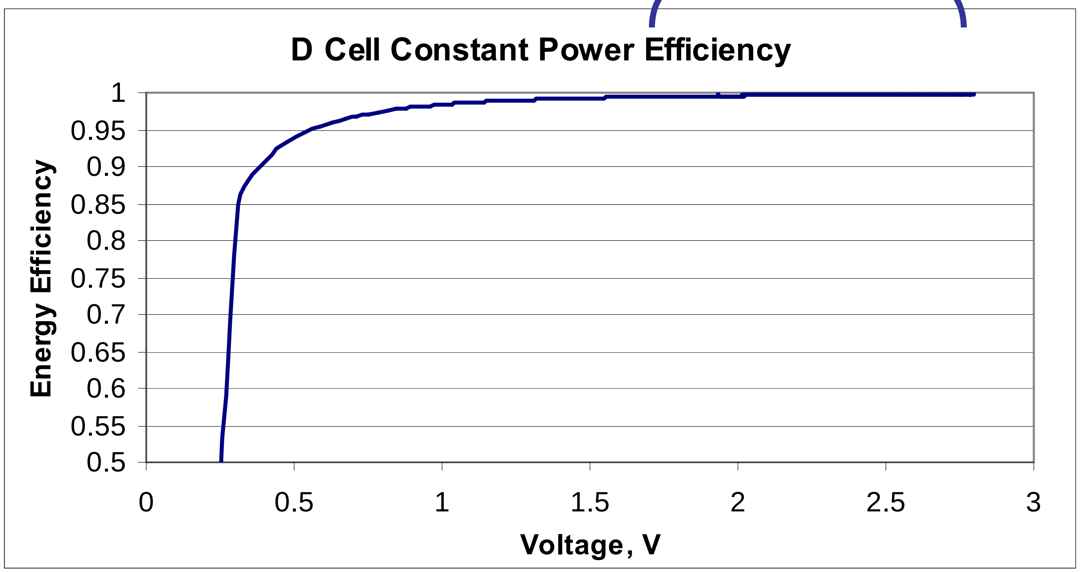
  - Analytical Result
    - Approx => time error!
    - ESR = Ro
    - C(U) = Co
    - $t_f$ = 184.4s
    - => small error!



# Constant Power Efficiency

- Results for D Cell




$$\eta_c = 1 - \frac{E_d}{E_0}$$

$$E_d = R_0 i_c^2 t_c$$

$$E_0 = P_0 t_c$$

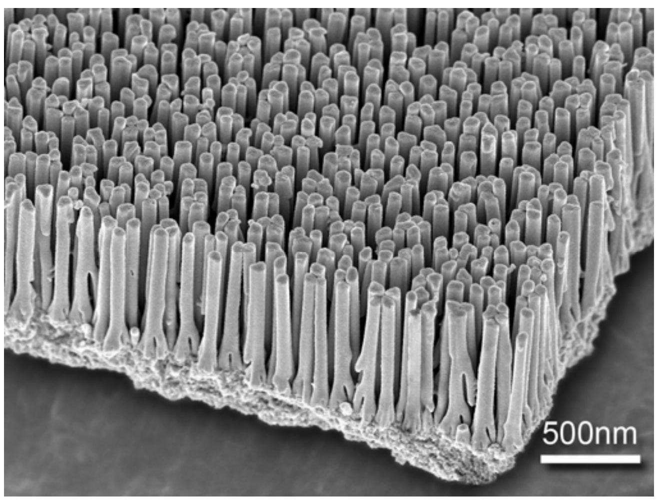
$$\eta_d = \frac{1}{1 + \frac{E_d}{E_0}}$$

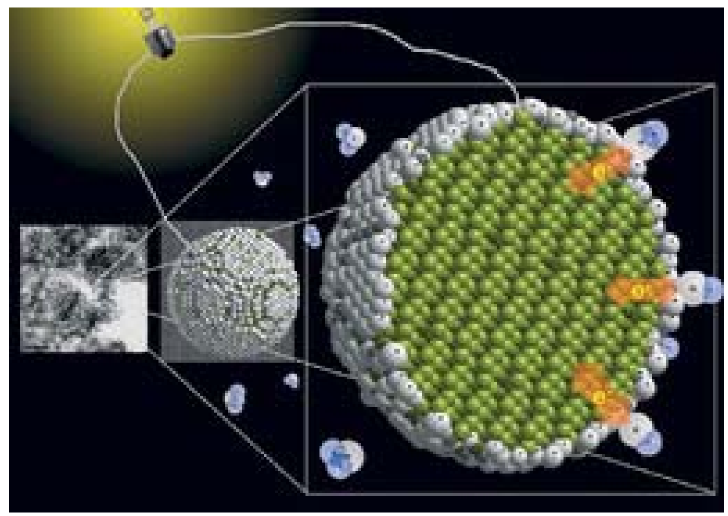
$$E_d = R_0 i_d^2 t_d$$

$$E_0 = P_0 t_d$$

# Ultracapacitors: Where to Next?

- Fundamental need - understand solvent-salt structure and physical properties.
- Performance - create a fundamental understanding of link between device performance and bulk/interfacial molecular interactions.
- Develop new EDLC materials and architectures that will dramatically boost energy and power.
- Electrode materials with controlled pore size and surface area deposited in ordered geometries with intimate contact to current collectors



Excerpted from: Bruce Dunn, Yury Gogotri, Plenary Closing Session Remarks, DOE Basic Research Needs Workshop on Electrical Energy Storage, Washington, D.C., 4 April 2007

# Markets for Energy Storage Systems

- Very diverse range of markets
  - Aerospace, industrial, transportation, utility, consumer electronics
- Energy Storage System (ESS) attributes
  - Regenerative braking and energy recuperation in bus, train, subway, etc.
  - Cold engine starting aide for standby power, UPS, truck, bus…
  - Burst power for wind turbine blade pitch systems, shipyard cranes, material handling trucks, etc.
  - Bridge power for telecommunications, medical office, etc.
  - Voltage sag compensators for utility interconnects to restore voltage and to smooth distribution voltage
  - Consumer applications in everything from camera's, car audio, and cell phones to fast heat coffee makers.
  - Virtually any application that demands high peak power.