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ICTP Conference Graphene Week 2008

25 - 29 August 2008

GrapheneGraphene--based Material based Material.

R. Ruoff

The University of Texas at Austin
U.S.A.

Graphene-based Materials

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ICTP Graphene Week Trieste

Support by the The University of Texas, the Texas Nanotechnology Research Superiority Initiative (TNRSI)/SWAN, *iMINT-DARPA Center*, and prior support by the *NASA "BiMAT" URETI Institute* and the *NSF,* is appreciated

Tunable conductivity in a single graphene oxide sheet

I Jung, D. A. Dikin*, R. D. Piner, and R. S. Ruoff.* *Nano Letters* submitted. **Presented as poster #14 by Dima Dikin.**

Effect of Water Vapor on Electrical Properties of Reduced Graphene Oxide

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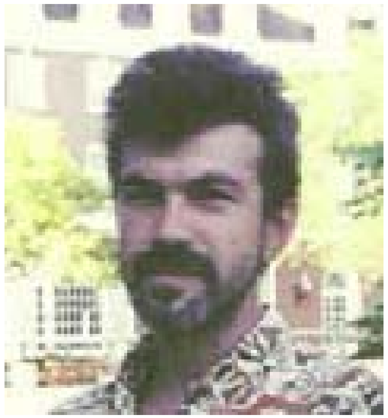
Journal of Physical Chemistry, submitted



Dima Dikin

Nature Nanotechnology "News and Views", entitled "Calling All Chemists" by Rod Ruoff

"Graphene has potentially useful electronic properties but it is difficult to produce and process on large scales. Working with chemically modified forms of graphene — such as graphene oxide — may provide an alternative."

nature nanotechnology | VOL 3 | JANUARY 2008 | www.nature.com/naturenanotechnology

Nanoelectronics: There is a perceived need to achieve *atomic-level control* of patterning in graphene for devices, and perhaps for interconnects

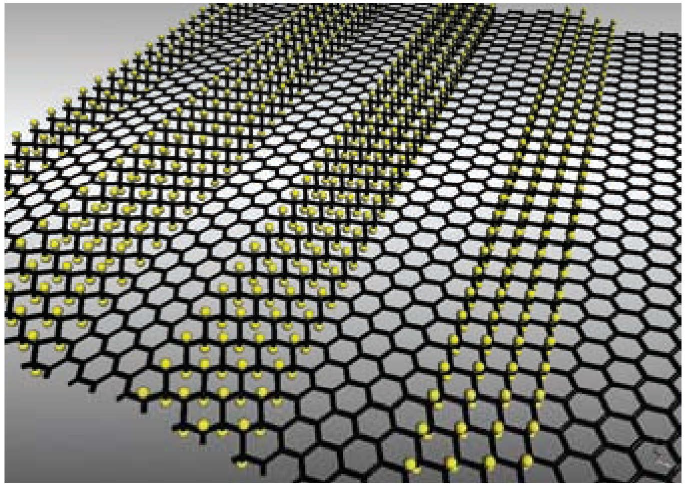


Figure by Jorge Sofo and colleagues, U Penn; in N&V article

Potential applications (among others)

• nanoelectronics (RF-mm, memory/logic, interconnects)
• ultracapacitors, fuel cells, batteries (EES)
• adsorbents
• composites (polymers, ceramics, perhaps metals)
• thin film materials (transparent conductive films etc)
• ‘paper-like’ materials (‘thicker’ thin films)

I. Micromechanical exfoliation: Inspiring the Physicists

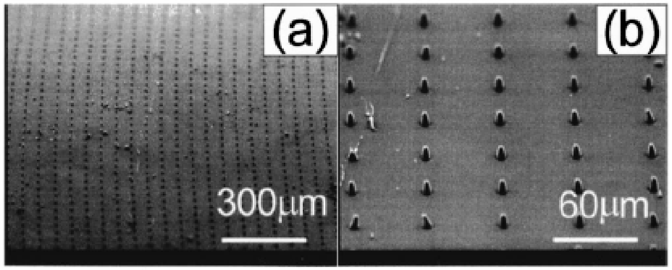


FIG. 1. SEM images of island arrays created on a HOPG surface. (a) and (b) are taken at different magnifications, as shown by the scale bars.

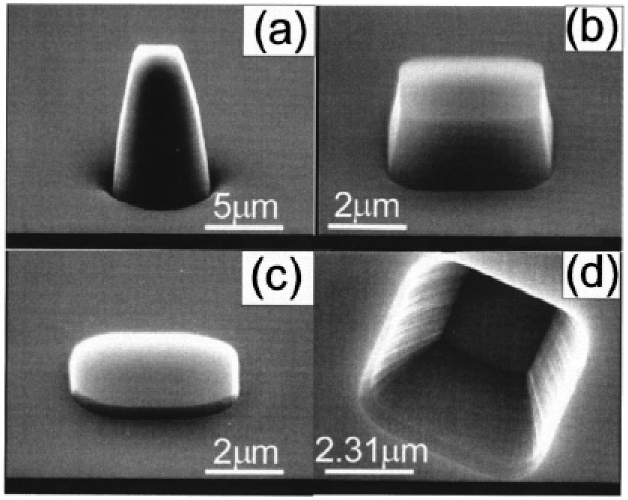


FIG. 2. (a)–(c) SEM images of individual HOPG islands on samples etched under different conditions. (d) SEM image of a hole etched in a HOPG substrate. This hole, if used as a container, could hold a liquid volume of $\sim 20\ \mu m^3$.

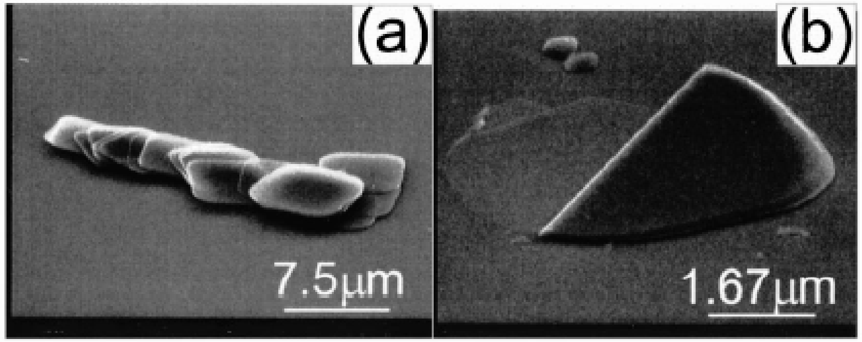


FIG. 5. SEM images of HOPG islands smeared on a Si(001) substrate. (a) Stacked thin platelets. (b) Example of a very thin layer left on the substrate while the platelet folds over.

X. K. Lu, H. Huang, N. Nemchuk and R. S. Ruoff, *Patterning of highly oriented pyrolytic graphite by oxygen plasma etching,* Appl. Phys. Lett., 75, 193-195 (1999).

Lu, Xuekun; Yu, Minfeng; Huang, Hui; Ruoff, Rodney S.. Nanotechnology (1999), 10(3), 269-272. *Tailoring graphite with the goal of achieving single sheets.*

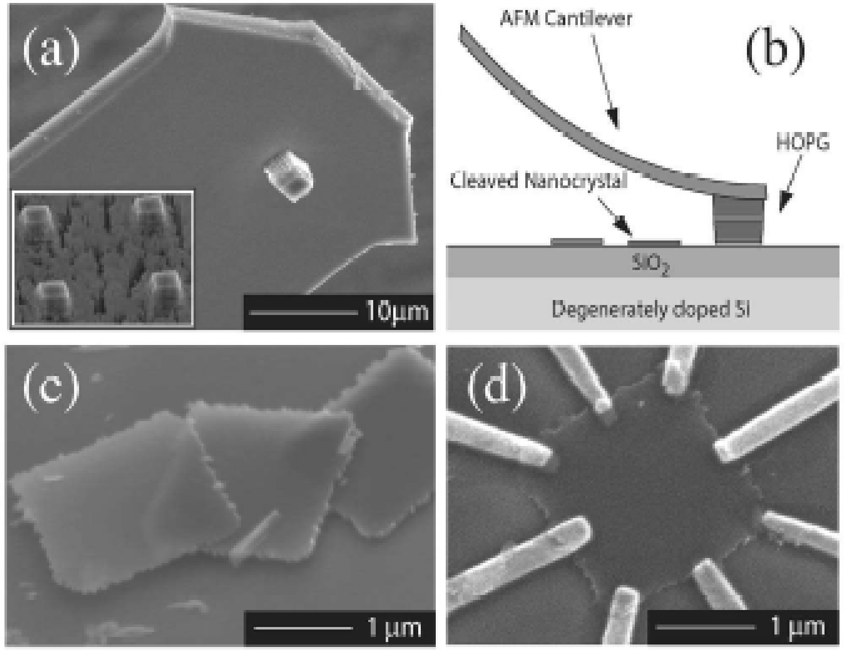


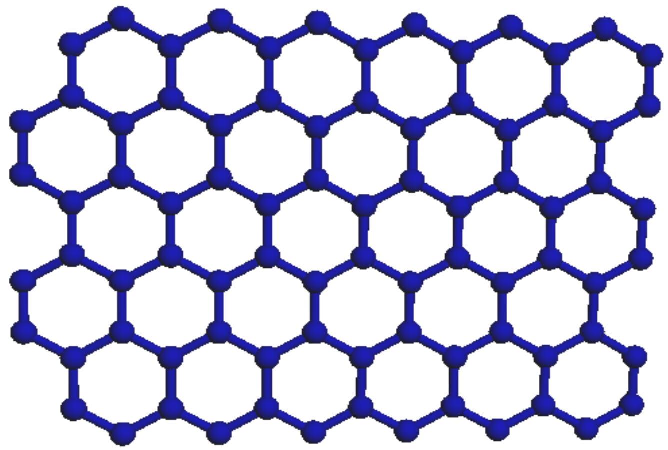
FIG. 1: (a) scanning electron microscope image of an HOPG crystallite mounted on a microcantilever. Inset: Bulk HOPG surface patterned by masked anisotropic oxygen plasma etching. (b) Schematic drawing of the micro-cleaving process. (c) Thin graphite samples cleaved onto the SiO_2/Si substrate. (d) A typical mesoscopic device fabricated from a cleaved graphite sample.

Zhang, Yuanbo; Small, Joshua P.; Pontius, William V.; Kim, Philip. ***Fabrication and electric-field-dependent transport measurements of mesoscopic graphite devices*****.** **Applied Physics Letters (2005), 86(7), 073104/1-073104/3.**

Why Graphene Sheets?

Outstanding properties:

- ~1100 GPa modulus (stiffer than steel); 125 Gpa (much stronger than steel—Hone and coworkers)
- Density ~2.2 g/cm^3 (lightweight yet stiff/strong)
- Thermal conductivity graphite in-plane: 3000 W/m-K
- Electrical conductivity (ballistic electron transfer; high mobility)
- Open to the full repertoire of synthetic organic chemistry for 'chemical tuning'

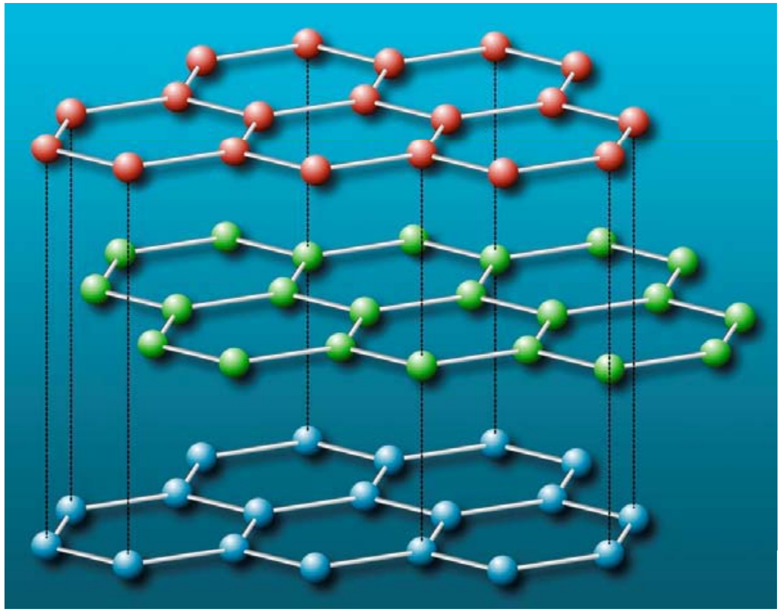


Graphene sheet

All of the above make graphene sheets an attractive material.

Graphite: Inexpensive and Available

- **2004 USGS survey: 100,000,000 metric tons of natural graphite exist***
- **750,000 metric tons of natural graphite mined, processed, and used in 2004**
  250,000 metric tons of synthetic graphite made and used in 2004
- **Graphite sells for a few Euros per kilogram**



How to "disassemble" graphite into individual sheets?

*ignoring its actual fractal geometry I calculate that there is thus enough graphene to coat the entire surface of the Earth with at least a monolayer—perhaps a comforting thought to some, and a wholly disturbing one to others

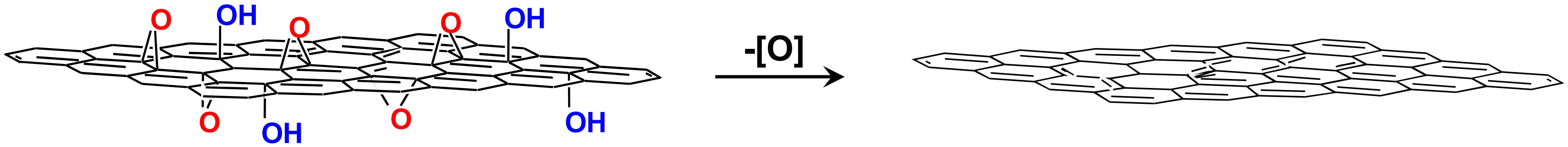
II. Alternative Approach: Graphite Oxide
'Chemical exfoliation'

$$\text{Graphite} \xrightarrow{\text{Oxidant}} \text{Graphite oxide (GO)}$$

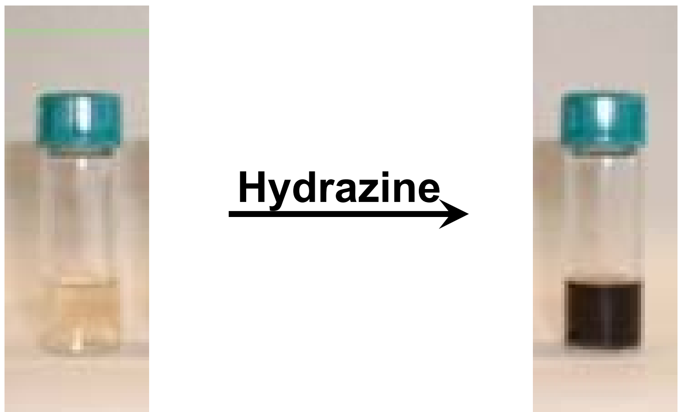
Graphite oxide suspended in water

Exfoliation/Reduction Approach

- **Graphene oxide sheets are not conductive**
- **Reduction (de-oxygenation) can be employed to partially restore the graphene network**

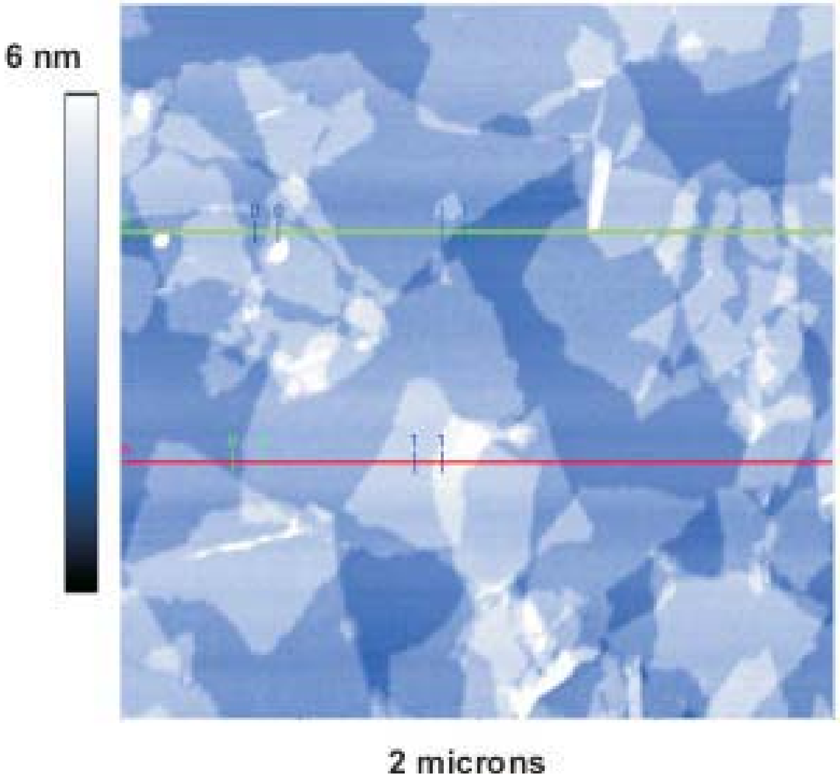


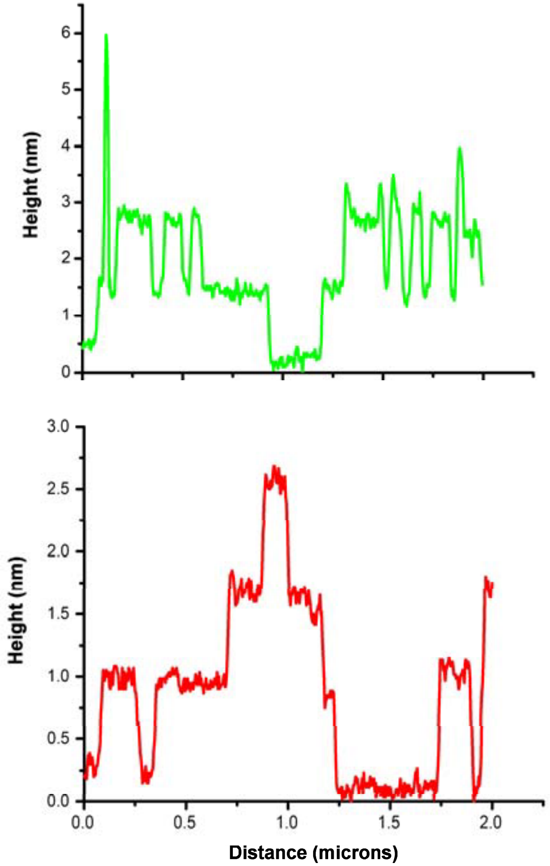
Graphene oxide **'Graphene'**



Reduction of graphite oxide with hydrazine

AFM Images of Exfoliated GO





Sheets ~ 1 nm thick deposited on a mica surface.

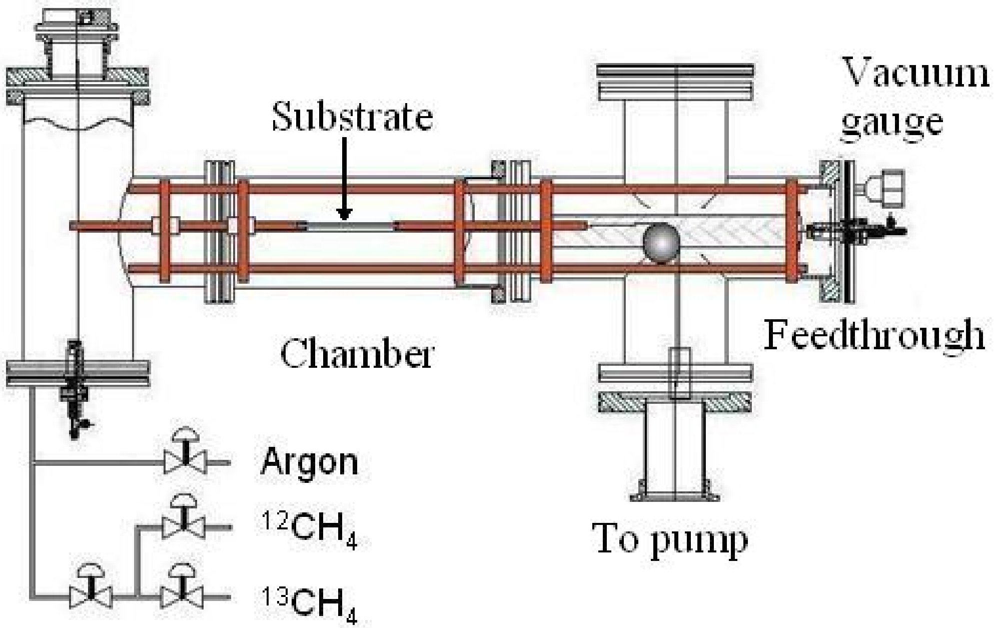
Individual 'graphene oxide' sheets

A. Production of ^{13}C-labeled synthetic graphite

Please also see:

Cai, Weiwei; Piner, Richard D.; Stadermann, Frank J.; Park, Sungjin; Shaibat, Medhat A.; Ishii, Yoshitaka; Yang, Dongxing; Velamakanni, Aruna; An, Sung Jin; Stoller, Meryl; An, Jinho; Chen, Dongmin; Ruoff, Rodney S.. **Synthesis and Solid-State NMR Structural Characterization of 13C-Labeled Graphite Oxide. Science (2008), 321(5897), 1815-1817.**

Production of ^{13}C-labeled synthetic graphite

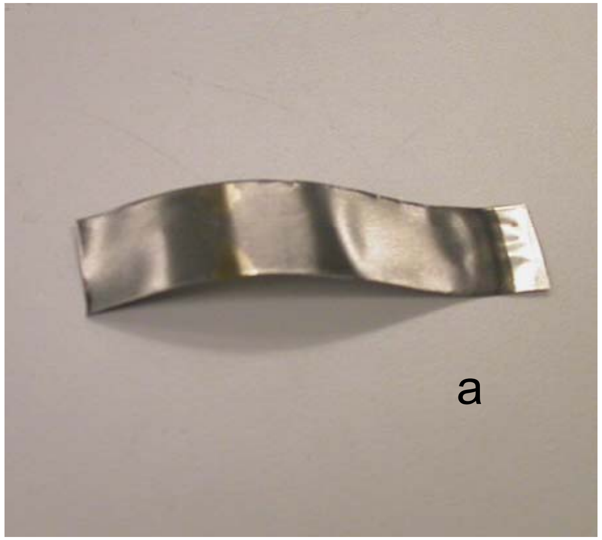


Schematic diagram of the CVD apparatus
(Richard Piner, Weiwei Cai, RSR)

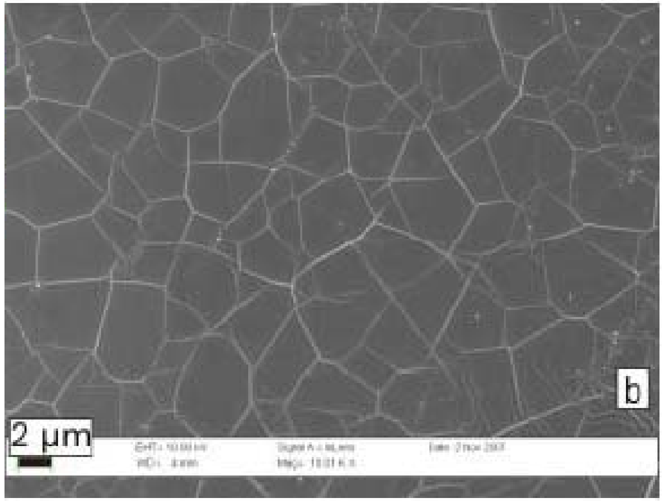
Some experimental parameters:

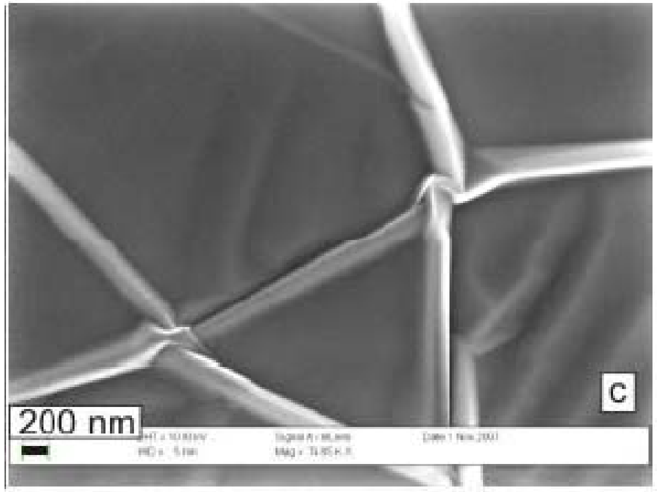
1. **10% methane ($^{13}CH_4$+$^{12}CH_4$) and 90% Ar**
2. **Temperature range of Ni substrate was from 1100-1200 ºC measured by pyrometer.**

B. Results of ^{13}C-labeled synthetic graphite

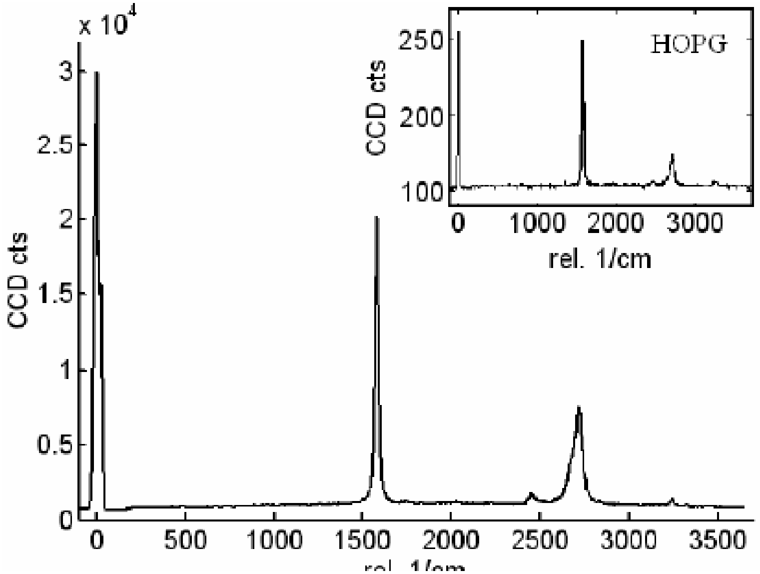


^{13}C-labeled synthetic graphite film deposited on Ni foil (a)

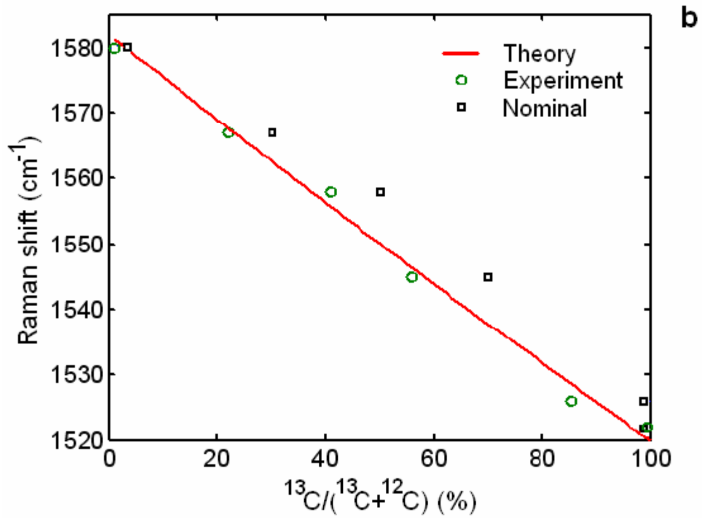




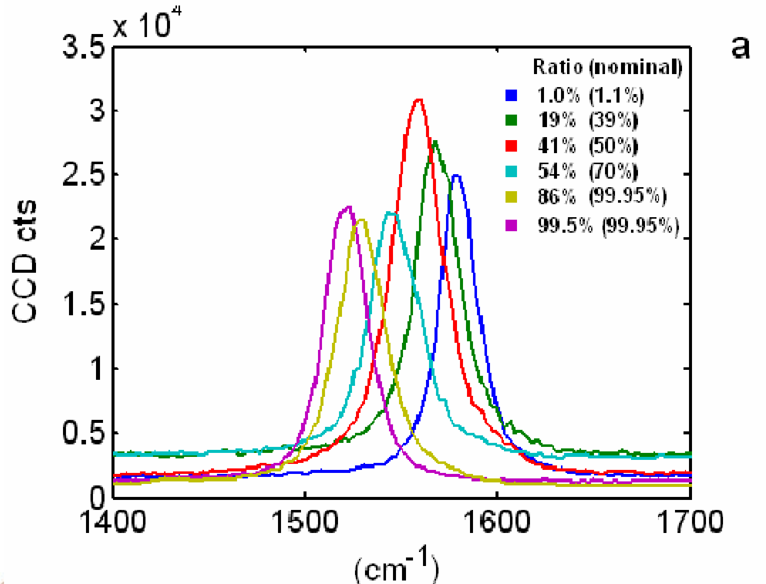
SEM picture of synthetic graphite (b) and the wrinkles (c).



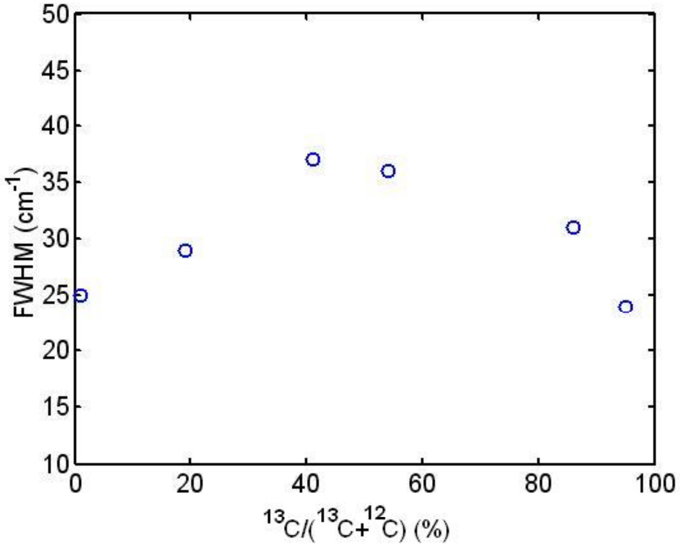
Raman spectra of synthetic graphite and HOPG



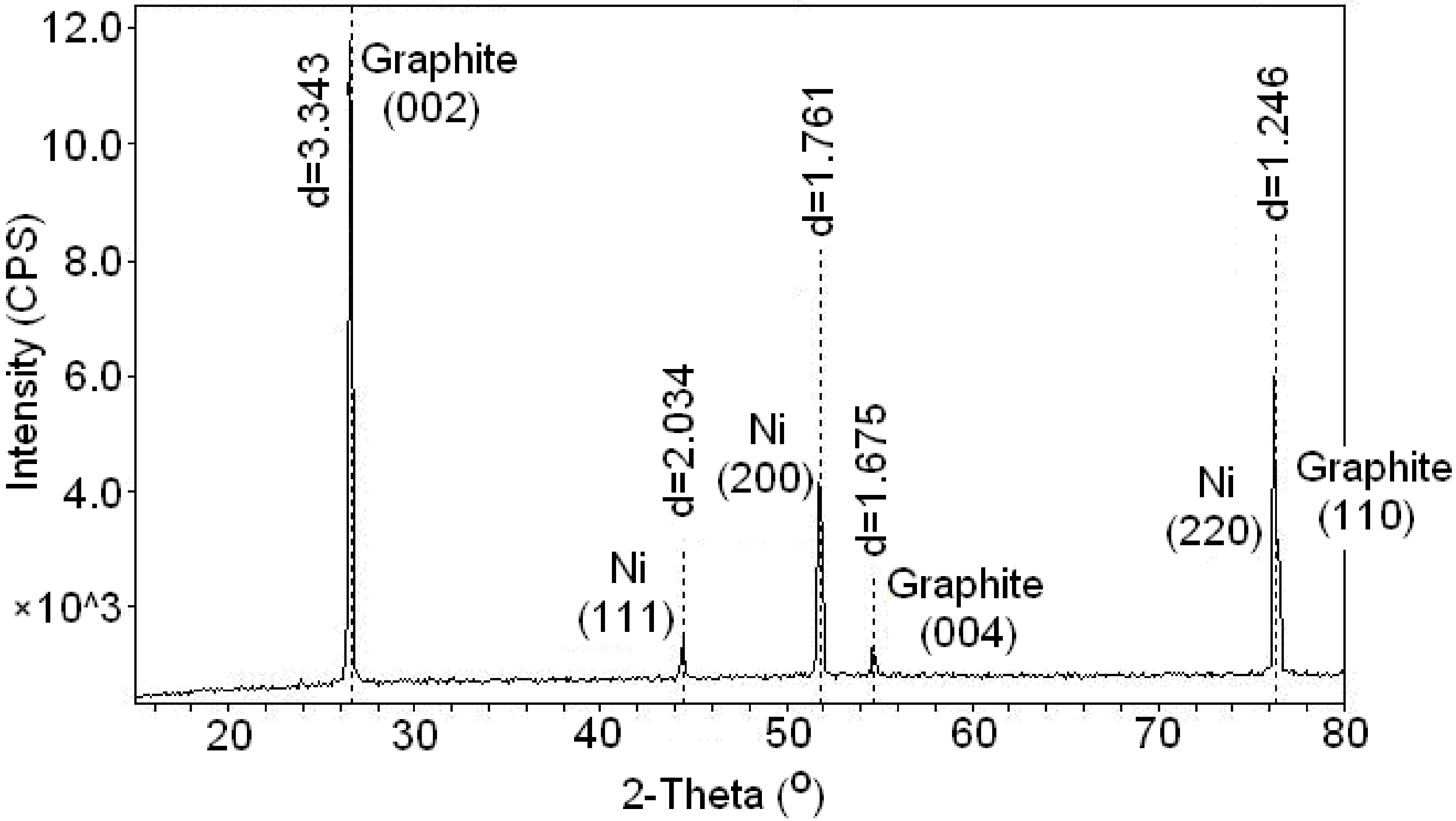
Shift of the G band frequency as a function of increasing of ^{13}C



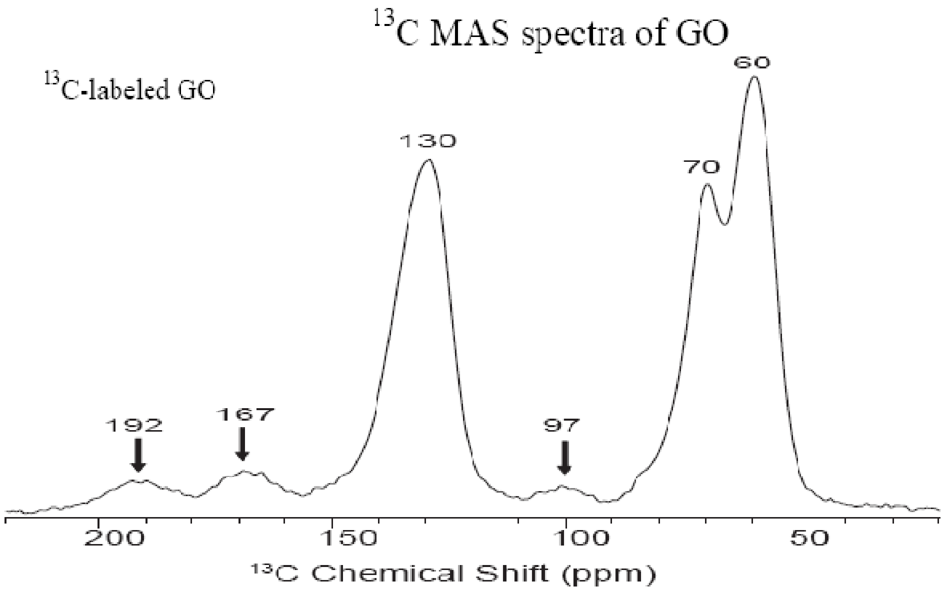
The G band of ^{13}C-labeled synthetic graphite



FWHM of G band as a function of increasing of ^{13}C


Graphite
(002)
d=3.343
d=2.034
Ni
(111)
Ni
(200)
d=1.761
d=1.675
Graphite
(004)
Ni
(220)
d=1.246
Graphite
(110)
12.0
10.0
8.0
6.0
4.0
×10^3
Intensity (CPS)
20
30
40
50
60
70
80
2-Theta (°)

C. Characterizing ^{13}C-labeled synthetic *graphite oxide* by solid-state NMR



1D ^{13}C MAS SSNMR spectrum of 12.2 mg 100% ^{13}C-enriched graphite oxide obtain at an NMR frequency of 100.643 MHz.

Three major peaks (integral intensity):

60ppm (104%) → epoxide ^{13}C

70ppm (100%) → ^{13}C-OH

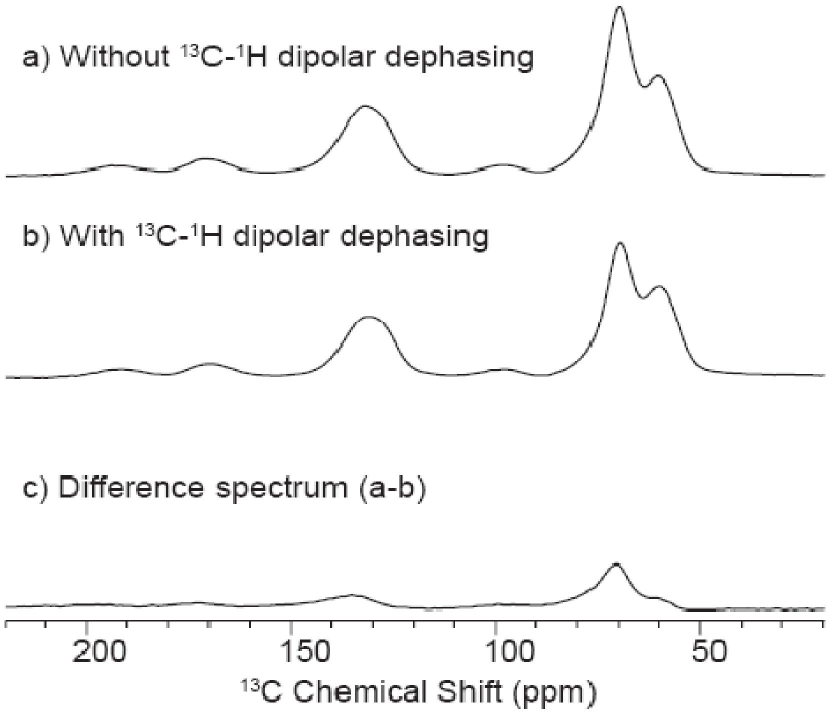
130ppm (150%) → unoxidized sp2 carbon

Three weaker peaks:

97ppm → ?

167ppm → ^{13}COOH

192ppm → carbonyl ^{13}C



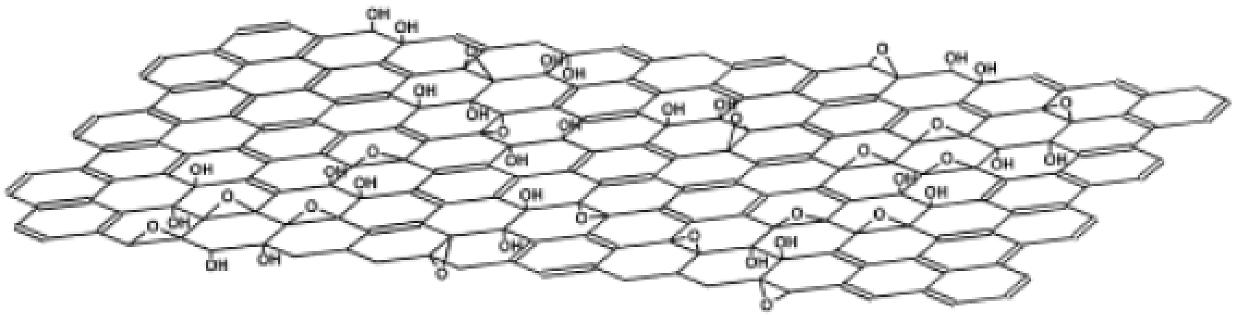
^{13}C CPMAS SSNMR spectra (a) without and (b) with ^{13}C-^{1}H dipolar dephasing, together with (c) the difference spectrum

The peaks at 60,70,130 ppm were dephased only by 11%,21%,11% respectively.

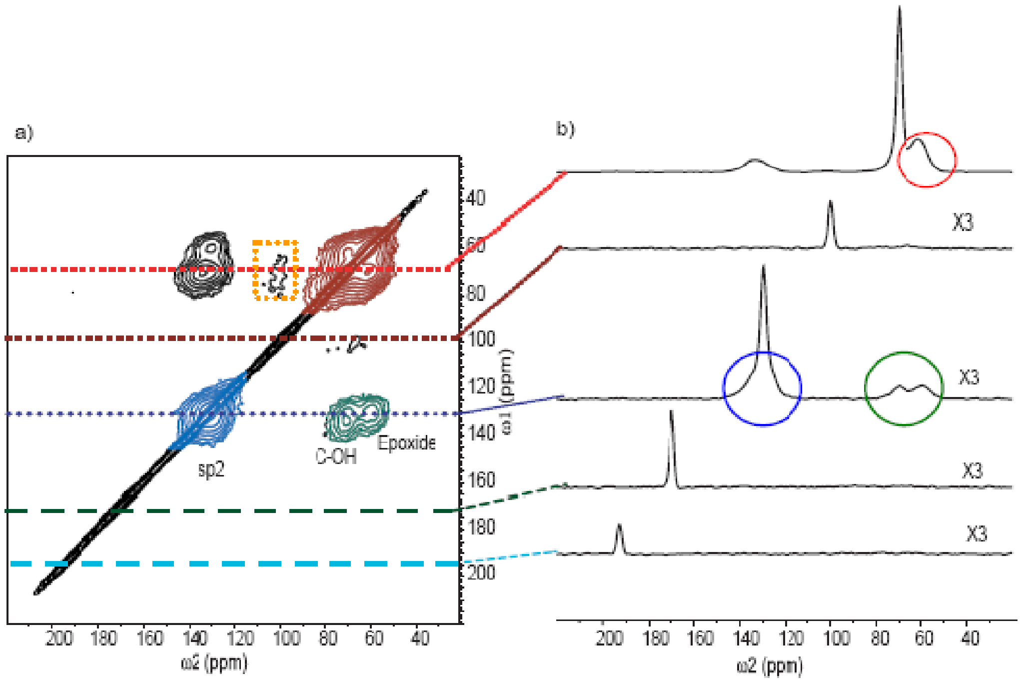
Result:

1) The GO system is rigid, the experiment clearly demonstrates that all the six signals are attributed to non-protonated carbons.
2) the ^{13}C-^{1}H distance should be shortest for the 13C observed at 70 ppm

graphite oxide



The integral intensity for the peak at 60, 70, 130 ppm and the results of 13C-1H dipolar dephasing experiments are consistent with the model by Heyong He et al (figure above)



(a) 2D $^{13}C/^{13}C$ correlation SSNMR spectrum. (b) shows slices from the 2D $^{13}C/^{13}C$ correlation spectrum along the ω_2 dimension at the position indicated by dotted lines

Cross peaks:

(130 ppm, 60 ppm)

(133 ppm, 70 ppm)

(60 ppm, 70 ppm)

Result:

sp^2 ^{13}C -- ^{13}C-OH ;

sp^2 ^{13}C -- ^{13}C-epoxide

OH-^{13}C -- ^{13}C-epoxide

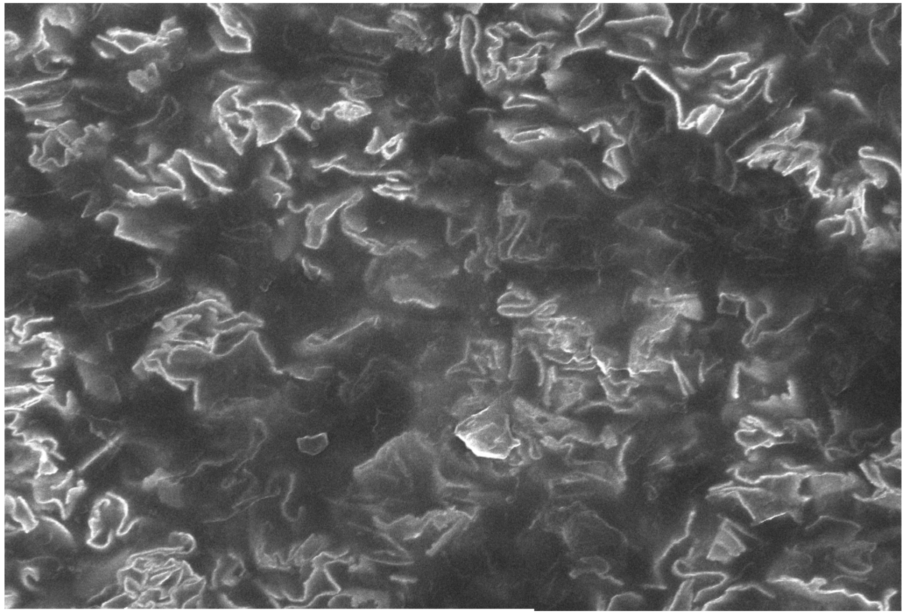
"13C-13C bonds exist only at 0.01 % abundance without labeling; thus, obtaining an equivalent 2D spectrum for an unlabeled sample would require about 10^8-fold more time."

For Physics: 13C-labeled graphite and graphenes

- fundamental properties measurements (mechanical properties; thermal, electrical conductivity, electron-phonon coupling, measurements related to spintronics for 12C-pure material vs 13C-labeled,etc.)

- Skyrmion physics (Allan MacDonald)

IV. Graphene in EES—*E*lectrical *E*nergy *S*torage



If we think of the polymer at the left being replaced with electrolyte, the very high surface area of graphene should be considered as an electrode material for ultracaps. (light weight, high surface area, electrically conductive)

Ultracaps: $300-400M market circa 2008 could be a $20B market in 5 years with improvements of specific capacitance to about 200 F/gram*. Energy densities could be above 10 W-h/kg, perhaps as high as lead acid batteries (24-25 W-h/kg).

Electrical Energy Storage (EES) is targeted by USA DOE as *the most critical area for technological advances* for large scale implementation of renewable energy.

AWEA notes that in 2007 5.1 GW power production installed in 2007 in USA (48 TW-h energy), & growth was 45%. *For fun:* 84/45=1.87 yrs doubling time: 20 years, about 11 doublings; 2^11=2048. ~100,000 TW-h wind energy generated in 2028? Worldwide <u>total</u> energy production in 2005 was 139,000 TW-h! *But: We cannot move forward at the pace we need to with wind and solar without better EES!*

Stoller, Meryl D.; Park, Sungjin; Zhu, Yanwu; An, Jinho; Ruoff, Rodney S.. **Graphene-Based Ultracapacitors. Nano Letters ACS ASAP.**

ABSTRACT

The surface area of a single graphene sheet is **2630 m^2/g**, substantially higher than values derived from BET surface area measurements of activated carbons used in current electric double layer capacitors. Our group has pioneered a new carbon material that we call **chemically modified graphene (CMG)**. CMG materials are made from 1-atom thick sheets of carbon, functionalized as needed, and here we demonstrate in an ultracapacitor cell their performance. **Specific capacitances of 135 F/g and 99 F/g in aqueous and organic electrolytes, respectively, have been measured. In addition, high electrical conductivity gives these materials consistently good performance over a wide range of voltage scan rates.** These encouraging results illustrate the exciting potential for high performance, electrical energy storage devices based on this new class of carbon material.

Outline

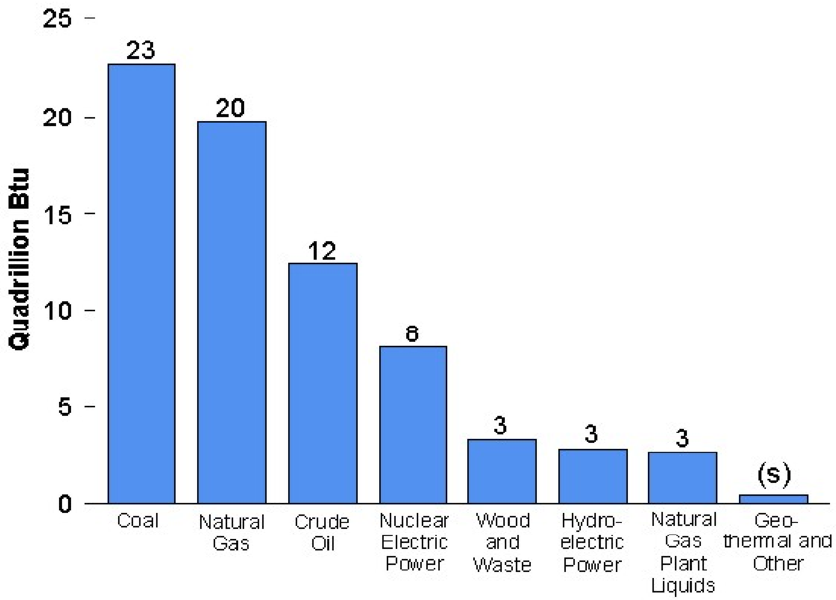
- Renewable and alternative forms of energy depend on electrical energy storage
- Energy efficiency requires increased system component specialization (hybrids)
- EES + increased specialization = ultracapacitors
- Ultracapacitor technology
- Examples of ultracapacitor applications
- Graphene-based ultracapacitors

Domestic Energy Sources and Supply

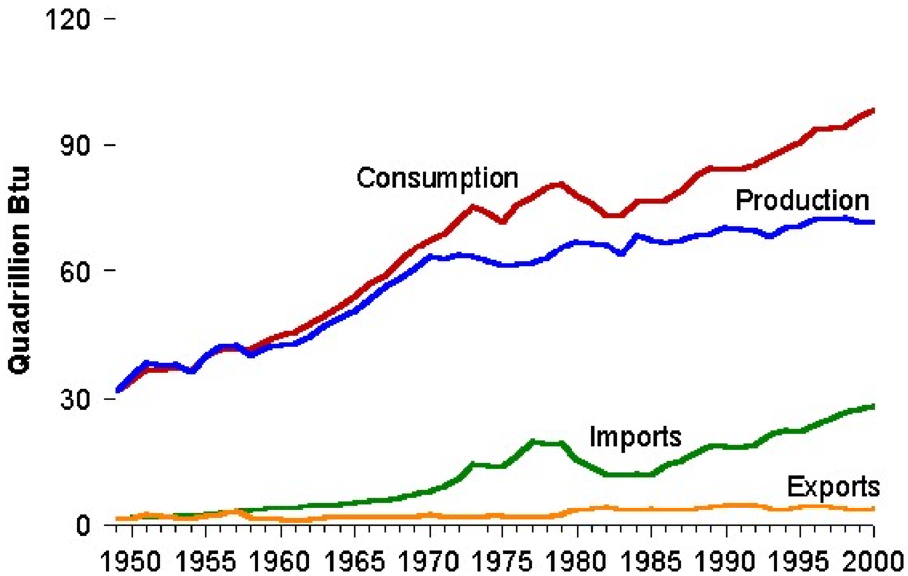
- Primary energy usage non-renewable carbon based
- Consumption outpacing production
- Imports increasing

BOTTOM LINE:

- Need increased usage of domestic energy sources
- Need renewable energy sources
- Need increased energy efficiency and conservation



Energy production by source for 2000



Energy consumption and demand

DOE. Energy in the United States. Adapted from:http://wwweiadoegov/emeu/aer/eh/totalhtml. 2000.

Electrical Energy is the Fastest Growing Form of Energy by Usage

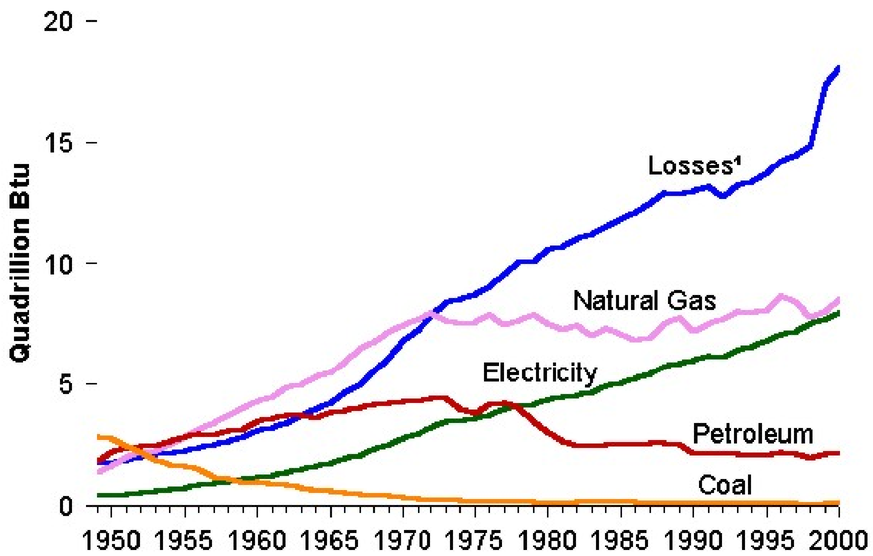
Energy Usage Segments:

Residential, Commercial

Transportation: limited by electrical energy storage technologies

Energy storage methods:

- **Pumped Hydro**
- **Heat reservoirs (thermal gradients)**
- **Compressed air**
- **Hydrogen**
- **Flywheel**
- **Superconducting magnetic (SMES)**
- **Batteries**
- **Ultracapacitors**



Residential and commercial energy consumption

DOE. Energy in the United States. Adapted from:http://wwweiadoegov/emeu/aer/eh/totalhtml. 2000.

Energy Sources and Requirements

Long Term Energy Sources:

- Coal, nuclear, hydroelectric: abundant and domestic, but the energy is generated at central locations requiring transport to point of use.
- Hydrogen: must be converted to an energy form that can be easily used (fuel cells have low power output requiring storage that builds up the energy for rapid release when needed).
- Solar, wind: not generated in sync with the time/location that the energy is used.
- In the case of transportation, all of the above must be made available to mobile vehicles.

Energy conservation / efficiency trends:

- Optimizing systems will increasingly involve adopting hybrid schemes – specialized components where each excels at a given task (ie: hybrid vehicles – IC engine optimized for energy density, battery/capacitors/traction motor for power density)
- Hybrid system strategies will be favored when:

  Value of energy savings from specializing > cost of extra components/integration

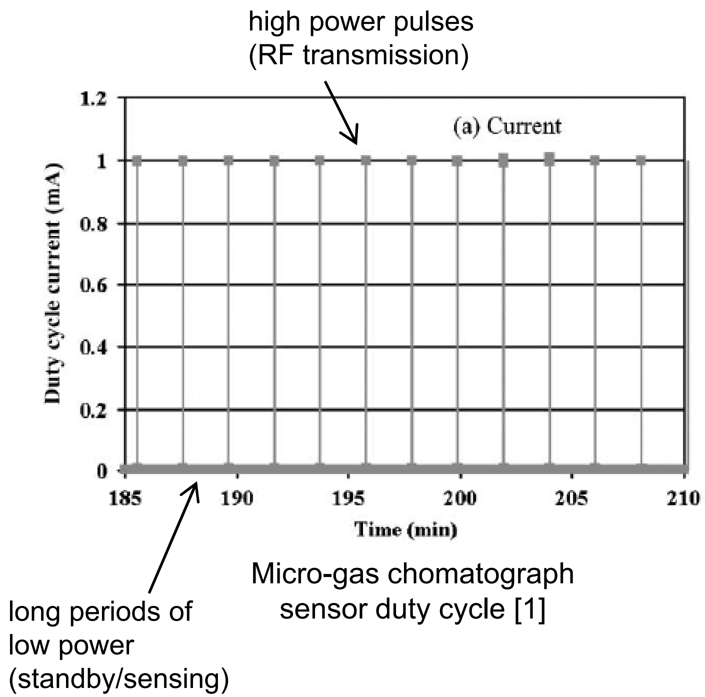
Energy Requirements:

- Increased need to temporarily store and reshape the delivery characteristics before any new sources can be feasible (for electrical storage: batteries and ultracapacitors)
- Increased requirement for specialized energy storage / delivery components (power vs energy density)

Why Ultracapacitors

For applications with duty cycles consisting of low power periods interspersed with high pulses, a hybrid power supply will have the smallest volume / weight and give the longest lifetimes.[1,2,3]

Typically, a hybrid power supply combines a high-power density / low energy density power element to support high pulses, and high-energy density / low-power density element to provide low, sustained power.[1]



Micro-gas chomatograph sensor duty cycle [1]

Two main types of electrical energy storage devices:

- ➔ **Chemical energy storage (batteries)**
- ➔ **Electrochemical Dual Layer Capacitors (ultracapacitors)**

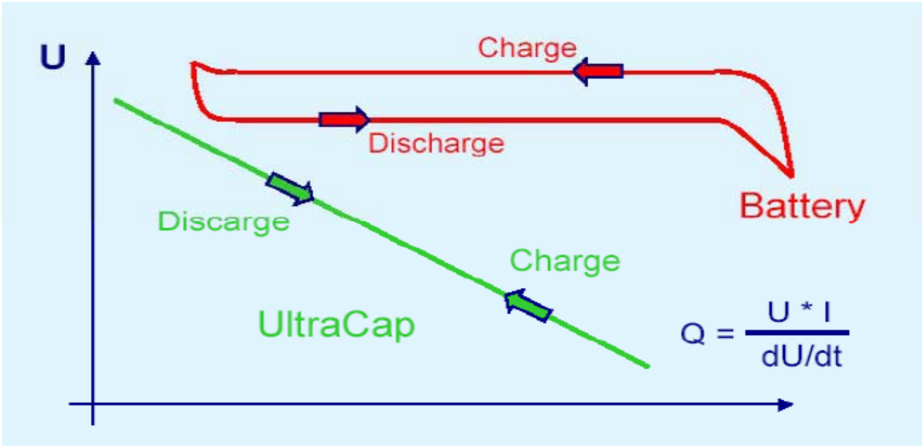
Ultracapacitors: excellent cycle lifetimes, high-power densities, high efficiencies, tolerant to deep discharge / overcharging, wider temperature tolerance, lower-energy densities [3]

➔ **Ultracapacitors rapidly being adopted for macro-sized electrical mechanical systems ($400 million plus market)**

1. Cook KA, Sastry AM. An algorithm for selection and design of hybrid power supplies for MEMS with a case study of a micro-gas chromatograph system. J Power Sources. 2005 Jan 10;140(1):18
2. Harb JN, LaFollette RM, Selfridge RH, Howell LL. Microbatteries for self-sustained hybrid micropower supplies. J Power Sources. 2002 Jan 15;104(1):46-51.
3. La O' GJ, In HJ, Crumlin E, Barbastathis G, Shao-Horn Y. Recent advances in microdevices for electrochemical energy conversion and storage. Int J Energ Res. 2007 May;31(6-7):548-75.

Technology Comparison (Maxwell)

Available Performance	Lead Acid Battery	Ultracapacitor	Conventional Capacitor
Charge Time	1 to 5 hrs	0.3 to 30 s	10^{-3} to 10^{-6} s
Discharge Time	0.3 to 3 hrs	0.3 to 30 s	10^{-3} to 10^{-6} s
Energy (Wh/kg)	10 to 100	1 to 10	< 0.1
Cycle Life	1,000	>500,000	>500,000
Specific Power (W/kg)	<1000	<10,000	<100,000
Charge/discharge efficiency	0.7 to 0.85	0.85 to 0.98	>0.95



Adapted from Maxwell ppt ieee.scv Jan2005

Commercial EDLC/Lead Acid Battery Energy Densities

Measured performance of commercially available EDLCs

Device	V rated	C (F)	R (mOhm)	RC (sec)	Wh/kg (1)	W/kg (95%) (2)	W/kg Match. Imped.	Wgt. (kg)	Vol. lit.
Maxwell**	2.7	2800	.48	1.4	4.45	900	8000	.475	.320
Ness	2.7	10	25.0	.25	2.5	3040	27000	.0025	.0015
Ness	2.7	1800	.55	1.00	3.6	975	8674	.38	.277
Ness	2.7	3640	.30	1.10	4.2	928	8010	.65	.514
Ness	2.7	5085	.24	1.22	4.3	958	8532	.89	.712
Asahi Glass (propylene carbonate)	2.7	1375	2.5	3.4	4.9	390	3471	.210 (estimated)	.151
Panasonic (propylene carbonate)	2.5	1200	1.0	1.2	2.3	514	4596	.34	.245
Panasonic	2.5	1791	.30	.54	3.44	1890	16800	.310	.245
Panasonic	2.5	2500	.43	1.1	3.70	1035	9200	.395	.328
EPCOS	2.7	3400	.45	1.5	4.3	760	6750	.60	.48
Okamura Power Sys.	2.7	1350	1.5	2.0	4.9	650	5785	.21	.151
ESMA	1.3	10000	.275	2.75	1.1	156	1400	1.1	.547

Measured performance of commercially available lead acid batteries

Battery Technology	Applic. type	Ah	V	Wh/kg At C/3	Resist mOhm	W/kg Match. Imped.	W/kg 95%eff.	Useable SOC,
Lead-acid								
Panasonic	HEV	25	12	26.3	7.8	389	77	28%
Panasonic	EV	60	12	34.2	6.9	250	47	----

Burke AF. Batteries and ultracapacitors for electric, hybrid, and fuel cell vehicles. P Ieee. 2007 Apr;95(4):806-20.

Commercial Ultracapacitor Performance

Device	V rated	C (F)	R (mOhm)	RC (sec)	Wh/kg (1)	W/kg (95%) (2)	W/kg Match. Imped.	Wgt. (kg)	Vol. lit.
Maxwell**	2.7	2800	.48	1.4	4.45	900	8000	.475	.320
Ness	2.7	10	25.0	.25	2.5	3040	27000	.0025	.0015
Ness	2.7	1800	.55	1.00	3.6	975	8674	.38	.277
Ness	2.7	3640	.30	1.10	4.2	928	8010	.65	.514
Ness	2.7	5085	.24	1.22	4.3	958	8532	.89	.712
Asahi Glass (propylene carbonate)	2.7	1375	2.5	3.4	4.9	390	3471	.210 (estimated)	.151
Panasonic (propylene carbonate)	2.5	1200	1.0	1.2	2.3	514	4596	.34	.245
Panasonic	2.5	1791	.30	.54	3.44	1890	16800	.310	.245
Panasonic	2.5	2500	.43	1.1	3.70	1035	9200	.395	.328
EPCOS	2.7	3400	.45	1.5	4.3	760	6750	.60	.48
Okamura Power Sys.	2.7	1350	1.5	2.0	4.9	650	5785	.21	.151
ESMA	1.3	10000	.275	2.75	1.1	156	1400	1.1	.547

(1) Energy density at 400 W/kg constant power, Vrated - 1/2 Vrated
(2) Power based on P=9/16*(1-EF)*V2/R, EF=efficiency of discharge
** Except where noted, all the devices use acetonitrile as the electrolyte

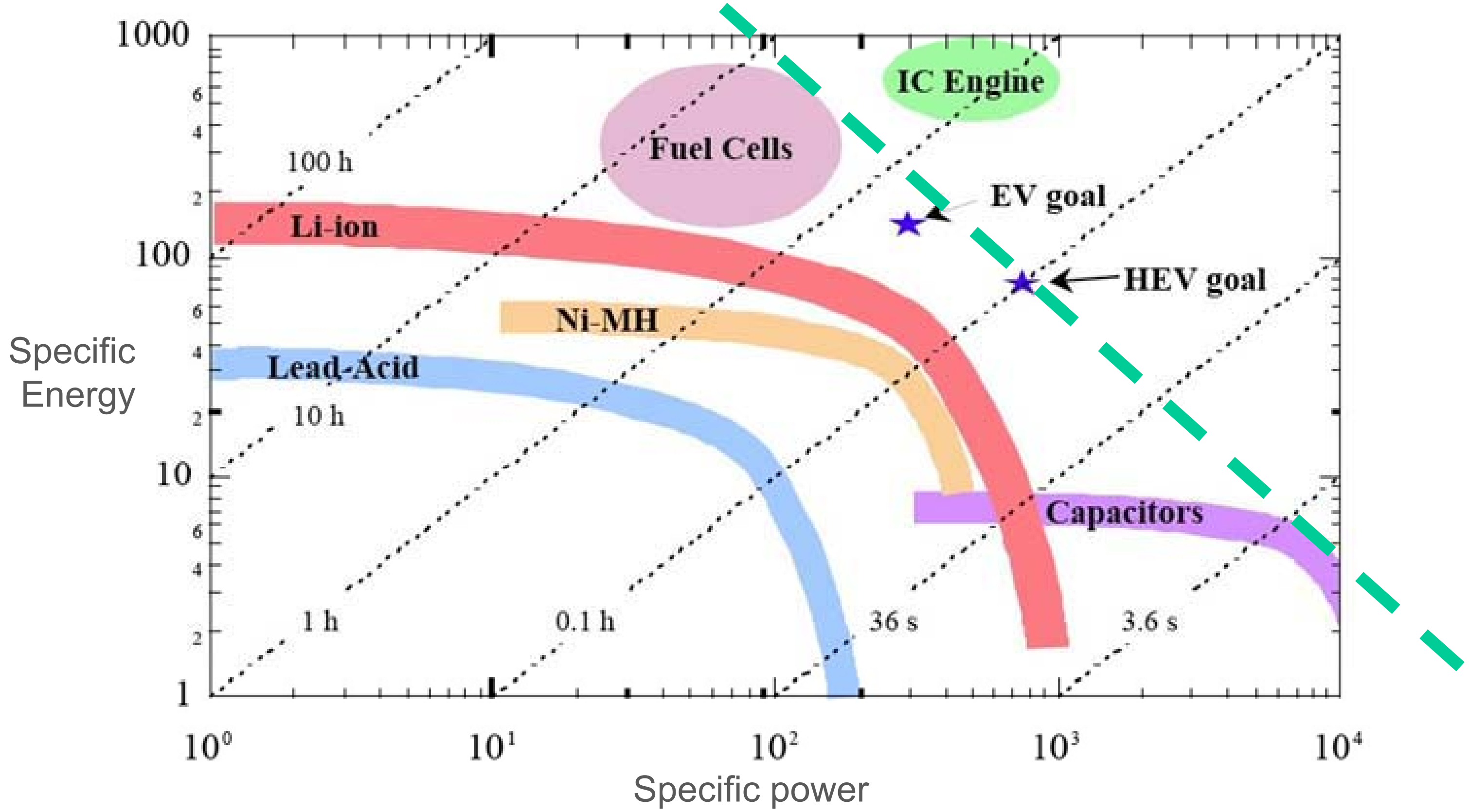
Burke AF. Batteries and ultracapacitors for electric, hybrid, and fuel cell vehicles. P Ieee. 2007 Apr;95(4):806-20.

Commercial Battery Performance

Battery Technology	Applic. type	Ah	V	Wh/kg At C/3	Resist mOhm	W/kg Match. Imped.	W/kg 95%eff.	Useable SOC,
Lead-acid								
Panasonic	HEV	25	12	26.3	7.8	389	77	28%
Panasonic	EV	60	12	34.2	6.9	250	47	----
Nickel Metal Hydride								
Panasonic EV	EV	65	12	68	8.7	240	46	----
Panasonic EV	HEV	6.5	7.2	46	11.4	1093	207	40%
Ovonic	EV	85	13	68	10	200	40	----
Ovonic	HEV	12	12	45	10	1000	195	30%
Saft	HEV	14	1.2	47	1.1	900	172	30%
Lithium-ion								
Saft	HEV	12	4	77	7.0	1550	256	20%
Saft	EV	41	4	140	8.0	476	90	----
Shin-Kobe	EV	90	4	105	.93	1344	255	------
Shin-Kobe	HEV	4	4	56	3.4	3920	745	18%

Burke AF. Batteries and ultracapacitors for electric, hybrid, and fuel cell vehicles. P Ieee. 2007 Apr;95(4):806-20.

Specialization / Hybridization Improves Performance



Capacitors / fuel cells currently occupy the extremes of the Ragone diagram.

All other things equal, the most efficient combination will be a hybrid composed of components located the greatest distance from each other on the diagram.

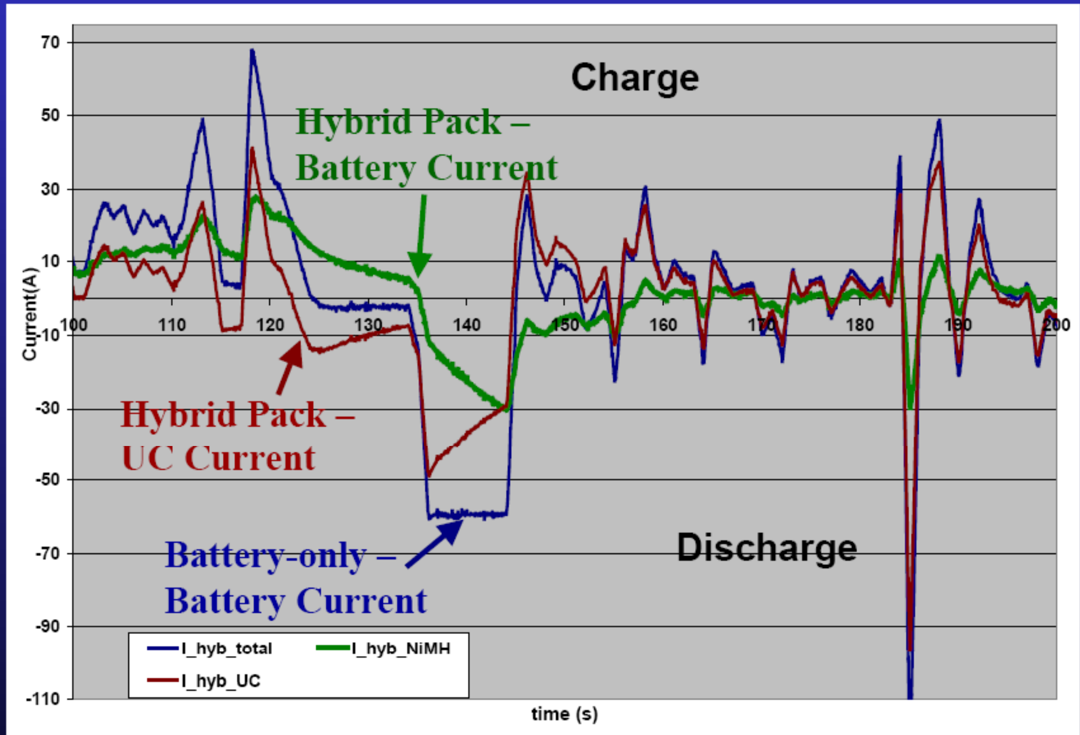
Ultracapacitors are alone at the high power end of the spectrum.

"Capacitors and fuel cells are made for each other" Andrew Burke, UC, Davis

http://india.cchem.berkeley.edu/~reimer/topics/images/ragone.jpg

Ultracaps Coupled with Batteries Extend Battery Range and Lifetimes

Battery Currents in the Hybrid-Pack Are Reduced Compared to the Battery-Only Pack



Components in hybrid pack share currents – ultracapacitor clearly has lower impedance than high-power NiMH batteries.

www.ctts.nrel.gov/BTM

Ultracapacitor Markets

Electric Rail Pack
Braking Energy Recapture
Diesel engine starting

TRACTION

Wind power plant pitch systems
Burst power

INDUSTRY

Small cell applications
Digital cameras, AMR,
Actuators, Memory boards

CONSUMER

Adapted from Maxwell ppt ieee.scv Jan2005

Honda FCX Clarity

The FCX Clarity is a next-generation, zero-emissions, hydrogen-powered fuel cell vehicle.

The FCX Clarity's fuel economy is approximate equivalent of 68 mpg combined fuel economy (about 2-3 times the fuel economy of a gasoline-powered car, and 1.5 times that of a gasoline-electric hybrid vehicle)

Honda ultra-capacitor (system module)

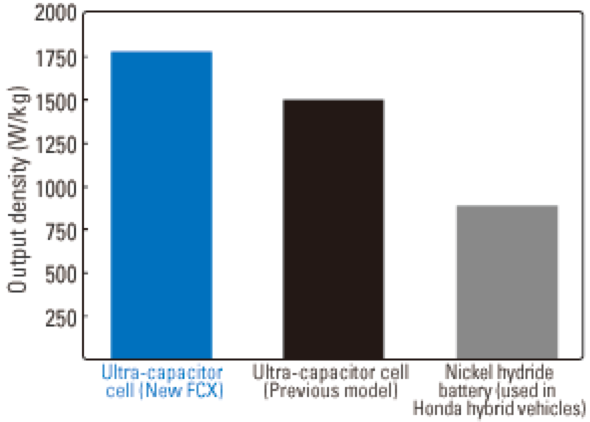
Honda has independently developed a high-performance ultra-capacitor (electrical two-layered condenser) to serve as a supplementary power source to the FCX's main power source - the fuel cell stack - for more powerful performance under various driving conditions. The ultra-capacitor combines the electrical storage capacity needed for high output and high responsiveness with solid reliability. It stores energy produced during deceleration and braking and provides powerful drive assist during startup, acceleration and at other times when an extra boost is required. The ultra-capacitor's internal resistance is lower than that of a battery, and moreover, because it stores and discharges electricity in response to fluctuations in the fuel cell stack, it doesn't require a converter for voltage regulation as in a battery system, so it delivers higher output. The result is improved drive-power performance and higher system efficiency.

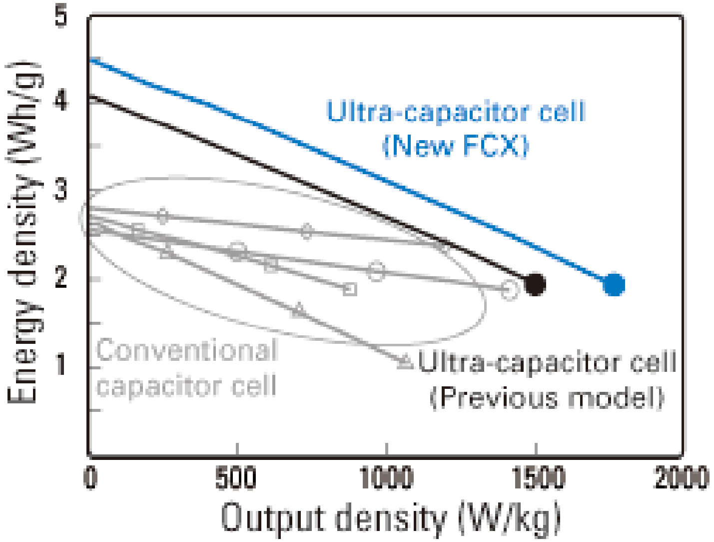
More powerful drive assistance, more efficient energy recovery during braking

http://world.honda.com/FuelCell/FCX/ultracapacitor/

Honda FCX Ultracapacitor

Output density
The output of the nickel hydride battery is limited to around 900W/kg due to the effect of heat loss, but the ultra-capacitor's low resistance enables it to handle much higher output. The ultra-capacitor further improves on the performance of the previous model, achieving an output density of 1750W/kg or more.



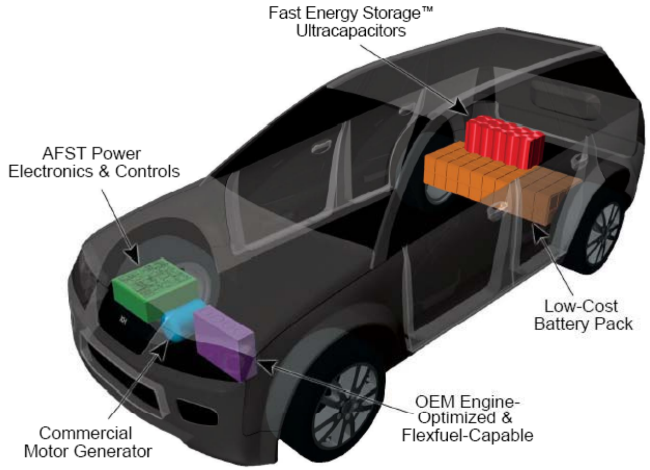


Capacitor charging and discharge performance (cell unit)
The Honda ultra-capacitor's high-performance electrodes and electrolyte deliver outstanding energy density and output density that surpass those of conventional capacitors. In particular, the low resistance reduction effect of the electrodes and collectors enable a high level of output normally considered difficult to obtain in a capacitor. The ultra-capacitor boasts a further 10% improvement in charging and discharge performance over the previous model.

http://world.honda.com/FuelCell/FCX/ultracapacitor/

AFS TRINITY
POWER CORPORATION

This is not a concept car. It is running now.



The low-cost lithium batteries—protected from excessive resistive heating by the ultracapacitors—will make the XH-150™ much less expensive to purchase.

80% Electricity + 20% Hybrid = >150 MPG*
(∞ MPG) (30 MPG*)

Power Grid

Engine + Batteries

gasoline or flexfuel

78% of Americans drive less than 40 miles/day**

AFS TRINITY XH-150™ PERFORMANCE COMPARISON TABLE

	AFS Trinity XH-150™	*2008 Lexus RX400h*	*2007 Saturn Vue Greenline*	*2008 Chevrolet Tahoe Hybrid*
Combined City/Hwy Mileage	150 MPG	25 MPG	26 MPG	20 MPG
0-60 time • Full Hybrid mode	6.9 secs	7.5 secs	12.5 secs	8.1 secs
• All-electric mode	11.5 secs			
• Mild Hybrid mode	12.5 secs			
Top Highway Speed	87 MPH	116 MPH	106 MPH	112 MPH
Weekly Gasoline Cost	$7.93	$47.60	$45.77	$59.50
Weekly Electricity Cost	$7.56	$0.00	$0.00	$0.00
Total Weekly Fuel Cost	$15.49	$47.60	$45.77	$59.50

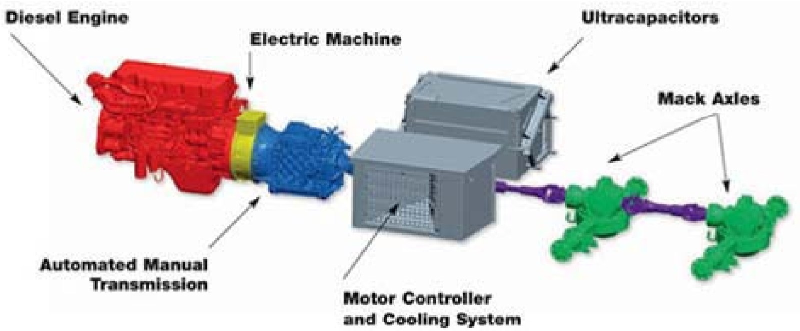
http://www.afstrinity.com/

Mack Ultracapacitor / Diesel Hybrid Truck Developed for US Air Force

A Mack Granite diesel-electric hybrid truck was on display at the Hybrid Truck Users Forum in Seattle. The hybrid Mack Granite was built for the U.S. Air Force Advanced Power Technology Office and is stationed at Nellis AFB in Nevada.

This technology provides the maximum fuel savings on routes with frequent braking and accelerations, particularly refuse collection and urban delivery, as well as certain construction applications.

The Mack hybrid electric powertrain features an integrated starter, alternator and motor referred to collectively as an electric machine. The electric machine assists the Granite vehicle's Mack MP7 diesel engine in providing torque to the wheels and regenerates energy during braking. This energy (stored in ultracapacitors) is then used in place of diesel fuel.



Specifications for Mack Granite Hybrid Diesel Electric Truck

Engine:
Type: Mack Model: MP7 - 365M, 11-liter turbocharged diesel 365 hp @ 1500-1900 RPM

Electric Machine
Type: Permanent Magnet; Synchronous Motor
Power: 161 hp peak; 94 hp continuous
Torque: 590 lb-ft. peak; 295 lb-ft continuous

Energy Storage
Type: Ultracapacitors
Usable Energy: 582 watts
Voltage: 300-725 volts DC

Transmission
Type: 12-speed automated manual

http://www.forconstructionpros.com/online/Equipment-News/US-Air-Force-to-Display-Mack-Hybrid-Electric-Vehicle-/38FCP8588

HYDROGENICS FUEL CELL BUS

- System Installed in Modern New Flyer Invero Bus
- Uses ISE-Siemens Hybrid Drive System with Maxwell Ultracapacitors (First Fuel Cell Ultracapacitor Bus)
- Hydrogenics Fuel Cell System Comprised of 3 60kW PEM Fuel Cells
- Goal is Very High Efficiency Bus
- Fuel Cell Output Voltage is Matched to Drive System (No DC-DC's)
- Ultracapacitor Energy Storage Yields 10-15% Better Fuel Economy
- Bus will be Demonstrated in Canada and the US

http://www.hydrail.org/docs/present3/bartley.pdf

Cell Phone Applications (CAP-XX)

Picture without flash (top)
and with flash (bottom)

Application:

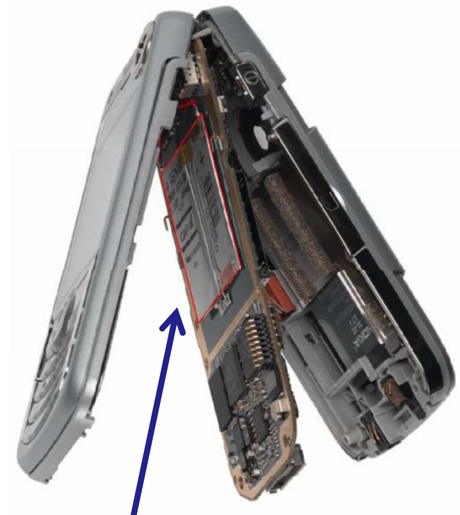
Nokia cell phone camera flash and speakers
(replace current capacitor - longer battery life,
improved flash & sound, smaller phone)

Requirement:

High power and energy density
dense packaging

Cell Configuration:

Single cell rated at 2.5 V (layers in pairs)
Dual cells rated at 4.5V and 5.5V (stacked)



	Standard mobile phone setup without supercapacitor	Mobile phone setup with Supercapacitor
Peak Battery Current	0.56A	0.261A
Average Battery Current	0.084A	0.253A
Peak Speaker Power	**1.65W**	**5.2W**
Average Speaker Power	0.211W	0.67W
Crest Factor	7.82	7.76
RMS Battery Power	0.64W	0.96W
RMS Speaker Power	0.50W	1.60W
Battery energy in 1 period	0.160J	0.48J
Speaker energy in 1 period	0.105J	0.34J
Efficiency	65%	70%

P. Aitchison, Supercapacitors for Portable Electronics, 2007
Adapted from CAP-XX at www.cap-ss.com

Other Applications That Leverage the Unique Strengths of Ultracapacitors

Military: Requires low volume, low weight, high reliability

- **"Soldier power requirements have gone off the charts" Jim Stone, Dir, Army Infantry Center [1]**
- **An infantry platoon of 40 soldiers on a 72-hour mission requires about 65 batteries per man.**
- **Outfitting a brigade on a five-day mission costs taxpayers $1.5 million in batteries.**
- **Individual soldiers currently carry 20-40 lbs of batteries on standard 4 day missions to power personal portable electronics (GPS, night vision goggles, radio packs, Sure Fire lights, etc).[2]**

Satellite Power: Requires high cycle lifetime, low weight

- **LEO (Low Earth Orbit) 100 minute orbit duration, 30-40 min eclipse duration, 12-16 cycles per day, requires 5,000 cycles per year [3]**
- **Battery lifetime 40,000 cycles = 8 years; Ultracapacitor lifetimes > 500,000 cycles.**

Oil / Gas, Geothermal Exploration MWD: Requires high temperature tolerance

- **Measurement while drilling (MWD) "keep alive" power for downhole instrumentation**

  Oil/gas boreholes 180^{o}C; geothermal boreholes 300 ^{o}C [4]

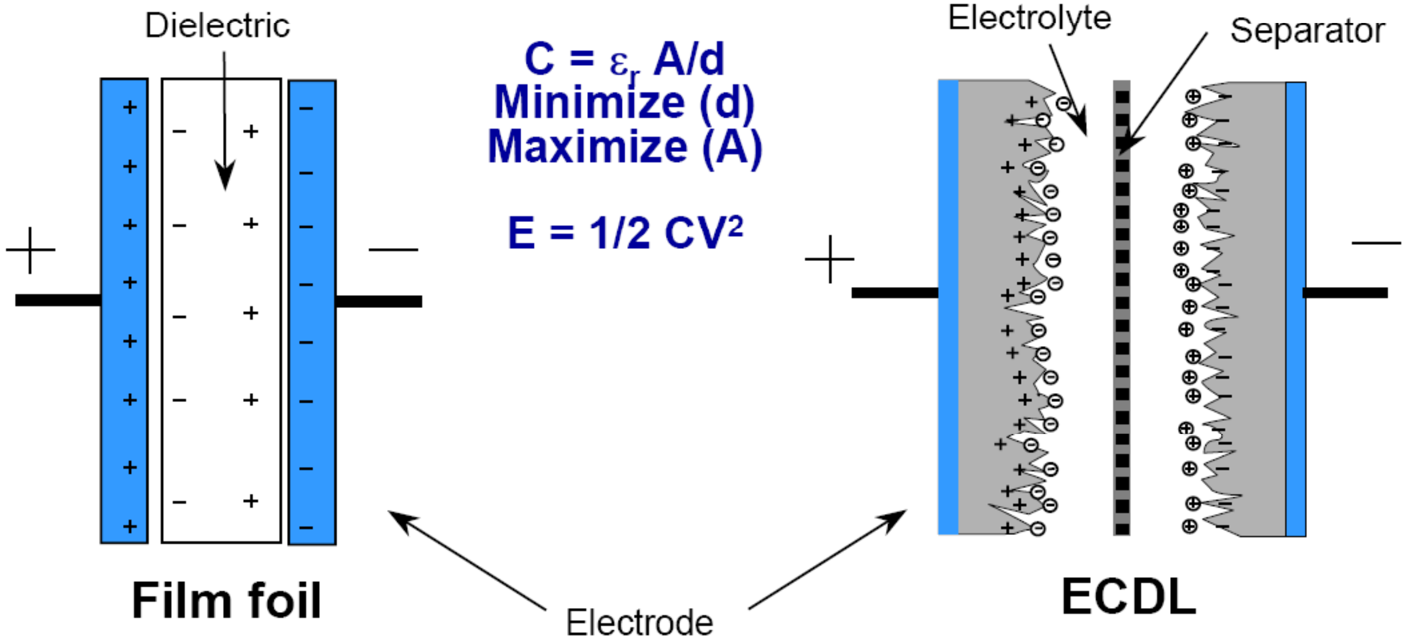
  Current AN / PC electrolyte based ultracapacitors are rated for -40 ^{o}C to 70 ^{o}C

1. Jim Stone, Deputy director of combat developments, Army Infantry Center, Adapted from feature article, National Defense Magazine, April 2007
2. Missouri University of Science and Technology, Nano News, Physorg.com, March 27, 2008.
3. Satellite battery systems, Saft, www.saftbatteries.com
4. Guidotti RA, Reinhardt FW, Odinek J. Overview of high-temperature batteries for geothermal and oil/gas borehole power sources. J Power Sources. 2004 Oct 1;1

Ultracapacitor Technology

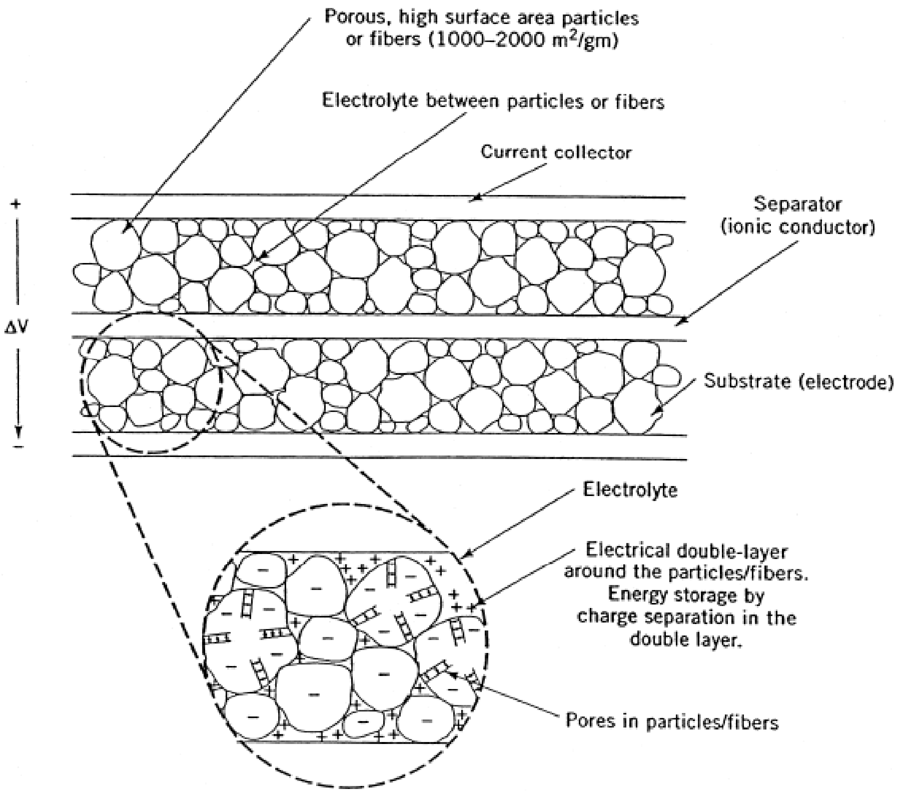
Ultracapacitors are:

- A 100-year-old technology, enhanced by modern materials
- Based on polarization of an electrolyte, high surface area electrodes and extremely small charge separation
- Known as Electrochemical Double Layer Capacitors and Supercapacitors

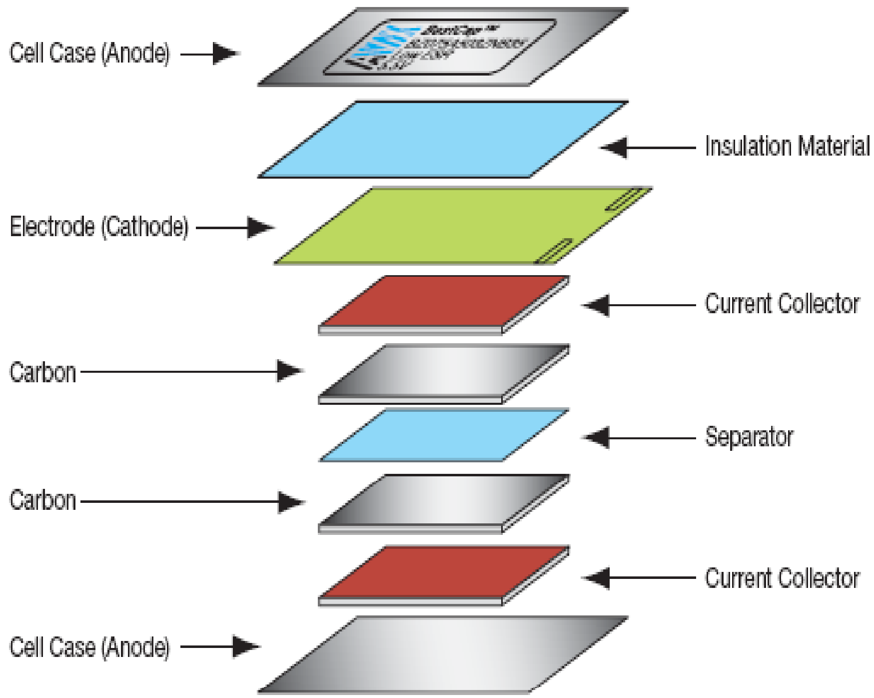


Adapted from Maxwell ppt ieee.scv Jan2005

Ultracapacitor Operation / Construction



Schematic of a double-layer ultracapacitor [1]



Ultracapacitor construction [2]

1 Burke A. Ultracapacitors: why, how, and where is the technology. J Power Sources. 2000 Nov;91(1):37-50.
2 BestCap product specs , http://www.avx.com

2007 DOE Workshop:
Basic Research Needs of Electrical Energy Storage

- "EDLCs with specific capacitances in excess of 200 F/g, cycle life > 1 x 10^6 are especially noteworthy"
- "Increasing energy density of EDLCs to the level of lead-acid batteries will have enormous impact"

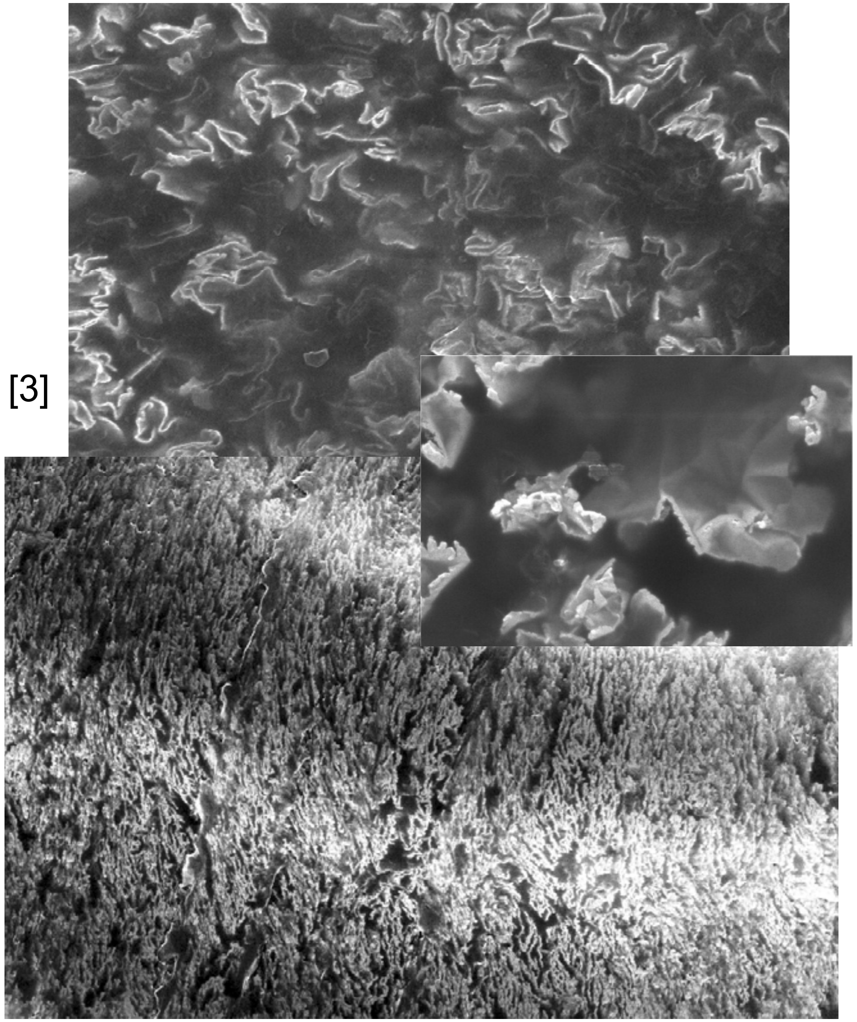
Major cross cutting themes (both batteries and ultracapacitors):

- Need for developing novel materials tailored for optimal EES performance. (This also requires that the fundamental principles that govern capacitive charge storage be understood.)
- Need for new characterization tools that will provide insight into charge and mass transfer within electro-active particles as well as across electrode-electrolyte interfaces.
- Need for innovations in electrolytes (the interaction of electrolytes with pores in ECs may have vastly different capacitive performance as a function of pore size).

Goodenough J. Basic Research Needs for Electrical Energy Storage. Report of the Basic Energy Sciences Workshop on Electrical Energy Storage, 2007.

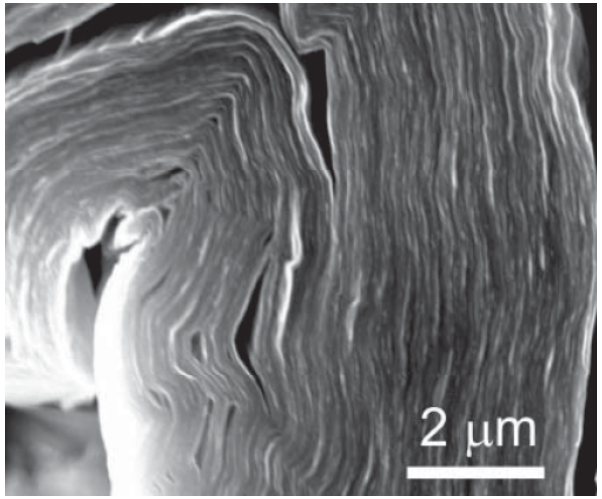
Why Graphene Materials for Ultracapacitors

[3]



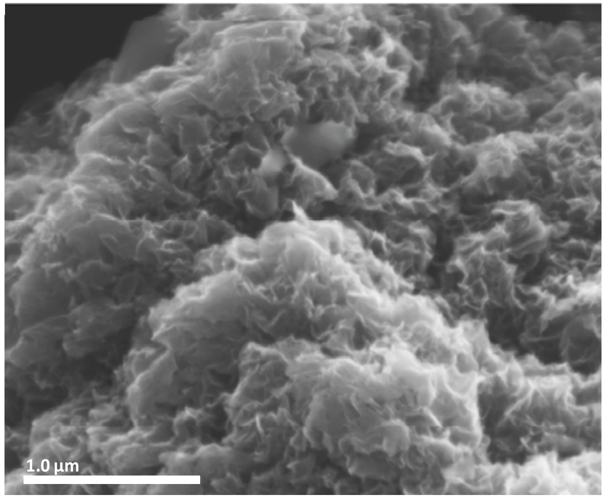
- ➔ **Very high surface areas - modeling indicates large potential gains in energy density [1]**
- ➔ **Can be assembled with wide range of morphologies / chemical functionalities [2,3] (compatibility with high voltage electrolytes)**
- ➔ **Conductive - no need for additional additives (low ESR / high power densities)**
- ➔ **Recent advancements: process-able aqueous dispersions of 'graphene' possible [4]**

[4]

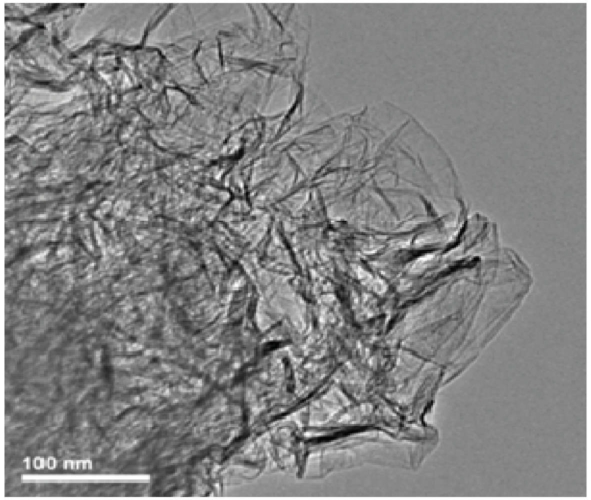


1. Lewandowski AG, Maciej. Practical and theoretical limits for electrochemical double-layer capacitors. J Power Sources. 2007.
2. Sasha Stankovich, Dmitriy A. Dikin, Geoffrey H. B. Dommett, Kevin M. Kohlhaas, Eric J. Zimney, Eric A. Stach, Richard D. Piner, SonBinh T. Nguyen and Rodney S. Ruoff, Graphene-based composite materials, Nature 42 (2006) 282-285 .
3. Dikin DA, Stankovich S, Zimney EJ, et al. Preparation and characterization of graphene oxide paper. Nature. 2007 Jul 26;448(7152):457-60.
4. Li D, Muller M, Gilje S, Kaner R, Wallace G. Processable aqueous dispersions of graphene nanosheets. Nat Nanotechnol. 2008.

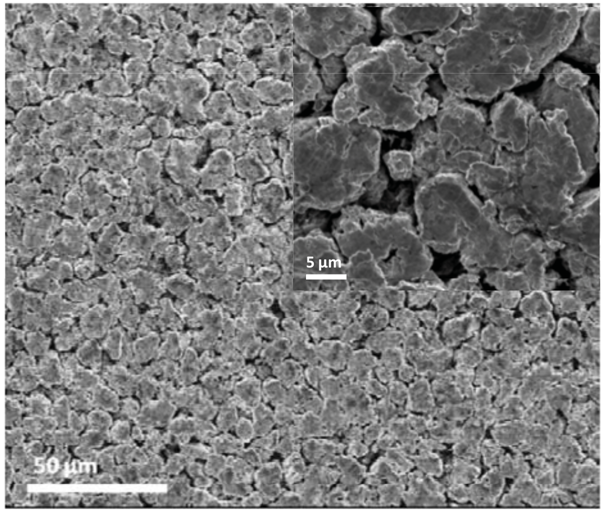
Graphene Material Used for Ultracapacitor Testing



SEM image of CMG particle surface



TEM image showing individual graphene sheets extending from particle surface

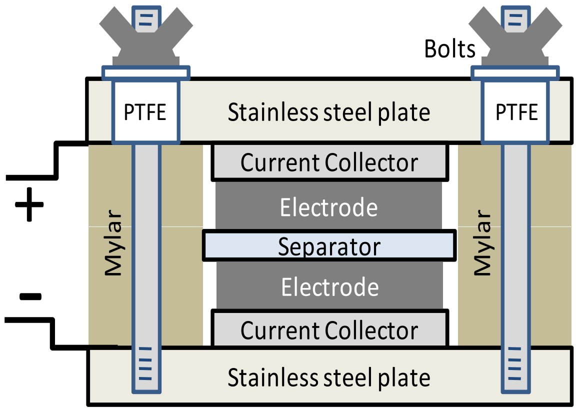


Low and high (inset) magnification SEM images of CMG electrode surface

- ➔ **CMG material used for electrodes consists of individual "graphene" sheets agglomerated into 15 - 25 um diameter particles.**
- ➔ **Measured powder conductivity (~2×10^2 S/m) approaches that of pristine (powdered) graphite.**
- ➔ **Surface area of the CMG agglomerate as measured by N_2 absorption Brunauer-Emmett-Teller (BET) method is 705 m^2/g .**
- ➔ **The C/O and C/N atomic ratios are 11.5 and 23.0 respectively.**

Graphene Based Ultracapacitor Testing

Two electrode cells provide a more accurate measure of an electrode materials performance for electrochemical capacitors than three electrode cells [1]



Two electrode cell construction

- Collectors (Intelicoat 4 mil conductive vinyl, 0.5 mil carbon-coated Al foil)
- Celgard 3501 porous separator
- CMG electrodes (3 wt% PTFE binder)
  (1.6 cm diameter x 75 um thick, 7.5 mg nominal wt)
- Electrolyte – aqueous: 5.5 M KOH; organic: TEA BF4 in PC and AN solvents.

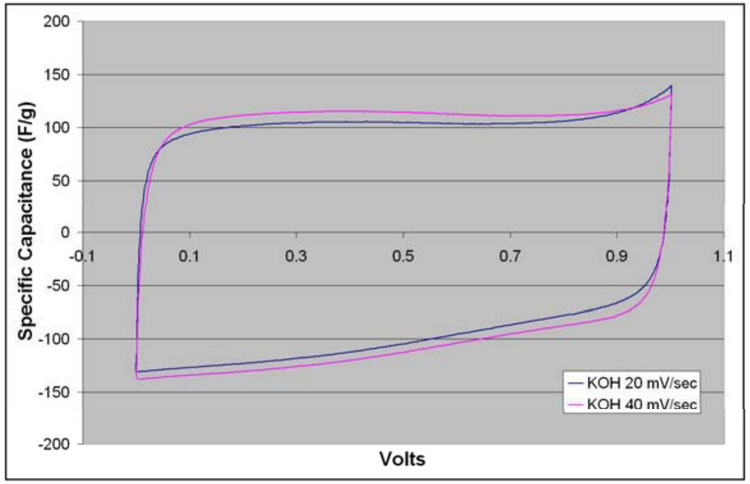
Electrochemical testing (Eco Chemie Autolab PGSTAT100 potentiostat / FRA2)

- Cyclic voltammograms
- Electrical impedance spectroscopy
- Galvanostatic charge/discharge

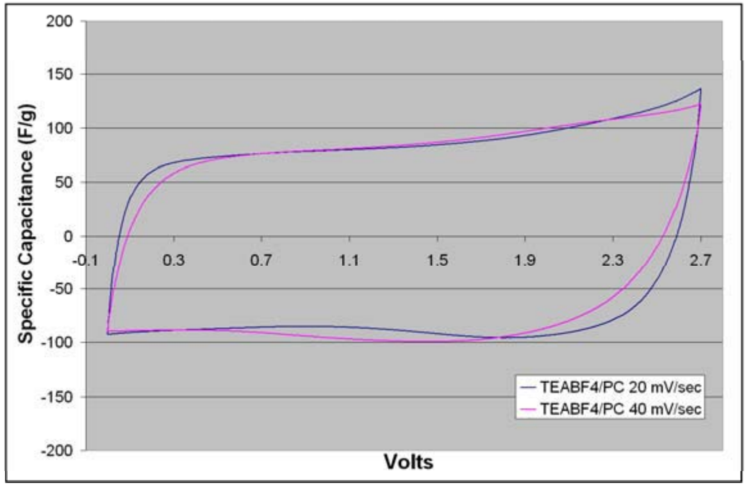
1. Khomenko, V., Frackowiak, E. & Beguin, F. Determination of the specific capacitance of conducting polymer/nanotubes composite electrodes using different cell configurations. *Electrochim Acta* **50**, 2499-2506 (2005).

Cyclic Voltammogram Results

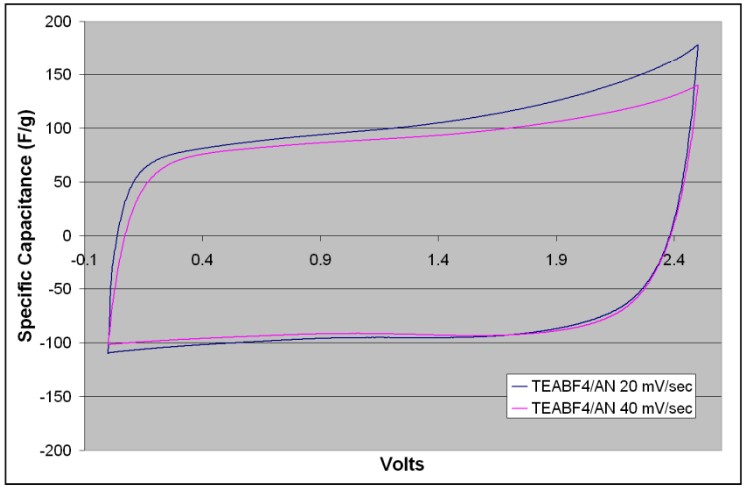
- ➔ Rectangular shape indicates good charge propagation within the electrodes and ideal capacitive behavior.
- ➔ Doubling the scan rate results in modest changes to the shape.
- ➔ Change in specific capacitance with respect to voltage remains relatively linear at the higher voltages indicating the charge is primarily faradic – there is only a small amount of pseudocapacitance and it can be attributed to the functional groups.



CV plot of CMG material with KOH electrolyte



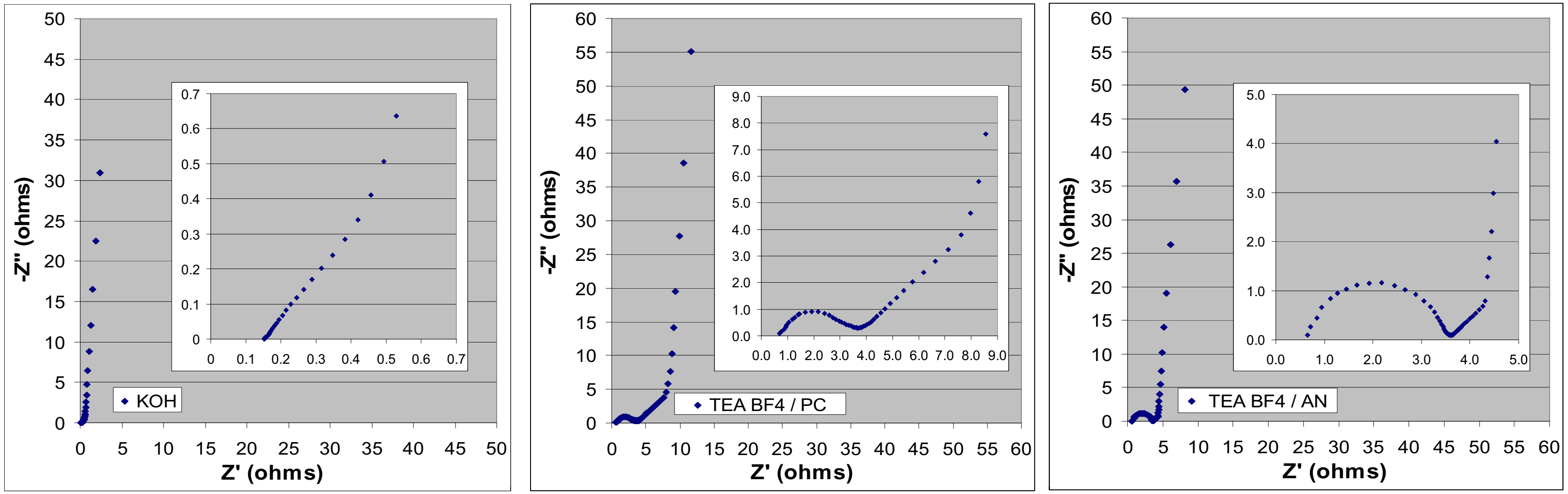
CV plot of CMG material with TEA BF4 in PC



CV plot of CMG material with TEA BF4 in AN

Electrical Impedance Spectroscopy

- Nyquist plots show frequency response of the CMG/electrode/electrolyte system.
- Vertical curves correspond to ideal capacitive behavior.
- The low equivalent series resistance, determined from the intersection of the curve with the X-axis, is due to the CMG materials' high conductivity. This allows the cell to quickly charge and discharge (high power density).
- The 45° linear portion of the curve is called the Warburg impedance and is a result of the frequency dependence of ion diffusion/transport in the electrolyte. The short Warburg region indicates short, unobstructed ion diffusion paths (absence of restrictions such as narrow pores typical in activated carbons).



Nyquist plots of CMG material with KOH electrolyte (left), TEA BF4 in PC (middle) and TEA BF4 in AN (right).

Specific Capacitance Calculation

The two methods commonly used to determine the specific capacitance of an electrode material are based on 1) the cyclic voltammogram curve and 2) the galvanostatic discharge rate.

Cyclic voltammogram calculation:

$$C_{sp} = (4 \times I) / (dV/dt \times mass)$$

Where:

I = integrated average current from the CV curve
dV/dt = voltage scan rate
mass = mass of CMG material in both electrodes

Galvanostatic discharge calculation:

$$C_{sp} = (4 \times I) / (dV/dt \times mass)$$

Where:

I = discharge current
dV/dt = slope of discharge curve
mass = mass of CMG material in both electrodes

CMG-Based Electrode Performance

- Results demonstrate that CMG materials are compatible with electrolytes commonly used in commercial ultracapacitors.
- Specific capacitance for CMG materials are comparable to current commercial activated carbons.

Electrolyte	Galvanostatic discharge		Cyclic Voltammogram average	
	mA		mV/sec	
	10	20	20	40
KOH	135	128	100	107
$TEABF_4$/PC	94	91	82	80
$TEABF_4$/AN	99	95	99	85

Csp (F/g) of CMG material

Scan Rate (mV/sec)	CV Average Specific Capacitance (F/g)
20	101
40	106
100	102
200	101
300	96
400	97

Csp (F/g) of CMG material in KOH by scan rate (mV/sec)

- Specific capacitance is very insensitive to a wide range of scan rates.
- Activated carbon-based electrodes degrade significantly at scan rates above 40 mV/sec.
- The wide operating range is due to the materials high conductivity and unrestricted access of the ions to/from the CMG surface.

Summary of ultracapacitors

Energy Trends:

- ➔ Migration to domestic / renewable energy sources will require increased energy storage capabilities.
- ➔ Electrical is fastest increasing form of energy by usage (direct storage of electrical energy has inherent efficiency advantage over other forms of storage)
- ➔ Increased focus on efficiency / conservation will increase hybrid systems and thus the need for specialized components.

Promise of graphene-based ultracapacitors:

- ➔ Electrochemical ultracapacitor technology occupies a unique position in the power/energy space.
- ➔ Graphene based materials have the potential to significantly improve EDLCs performance (energy density/volume).