Carbon Materials for Today and Future
Turkish-Japanese Joint Carbon Symposium
18-19, March 2010, Istanbul

Nanocarbons as electrode materials for electrochemical capacitor

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National Institute of Advanced Industrial Science and Technology (AIST)
Energy Technology Research Institute
Energy Storage Materials Group

National Institute of Advanced Industrial Science and Technology (AIST) was established in 2001, by merging former 15 inst into one large Inst.

Number of Employees (as of April 1, 2004)

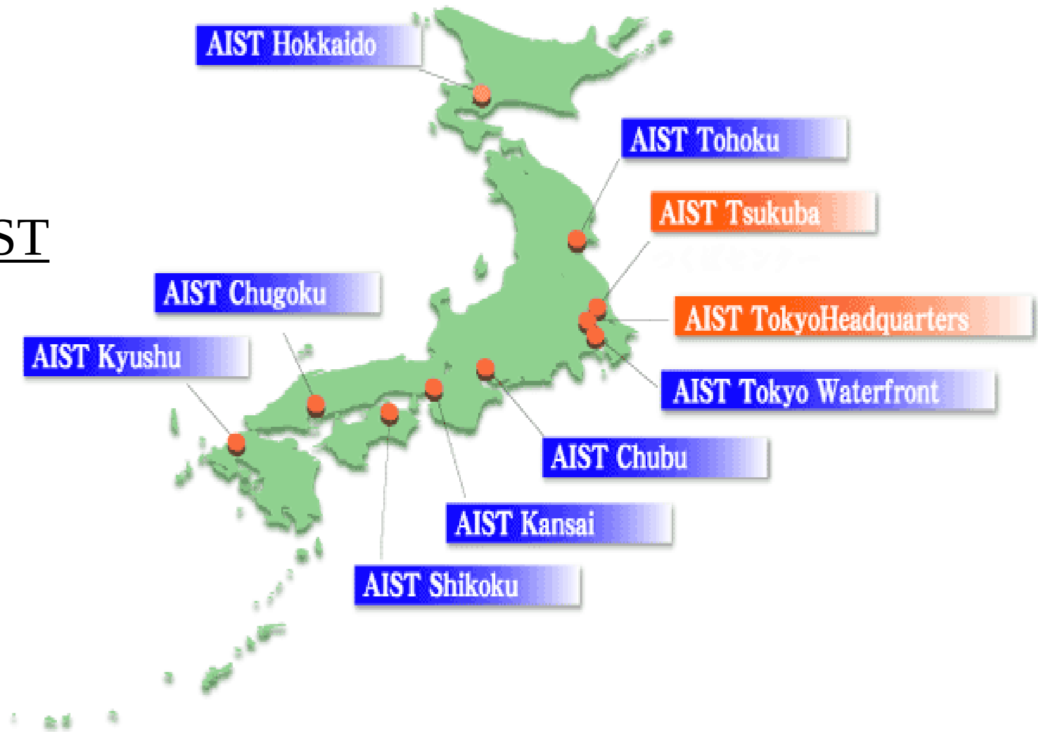
Researchers: 2,395 (including 55 foreign researchers)

Tenured researchers: 2,016

Fixed-term researchers: 379

Administrative staff: 719

Total number of employees: 3,114



Number of Visiting Researchers at AIST

Postdoctoral researchers: 800

From private companies: 800

From universities: 1,700

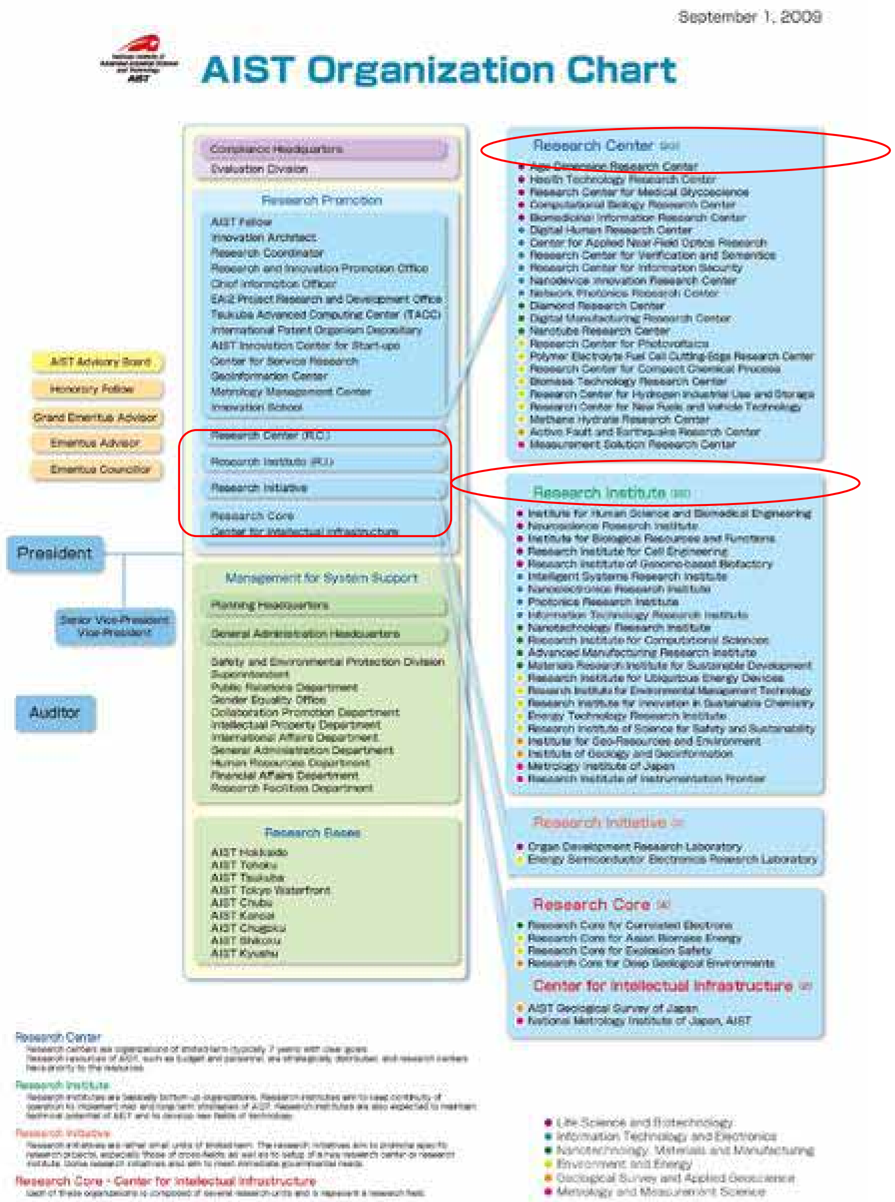
From overseas: 900

Total Number of

Visiting Researchers : > 4000

Research fields of AIST

- ✓ Life Science and Technology
- ✓ Information Technology
- ✓ **Environment and Energy**
- ✓ Nanotechnology, Materials and Manufacturing
- ✓ Standards and Measurement Technology
- ✓ Geological Survey and Geoscience, Marine Science and Technology

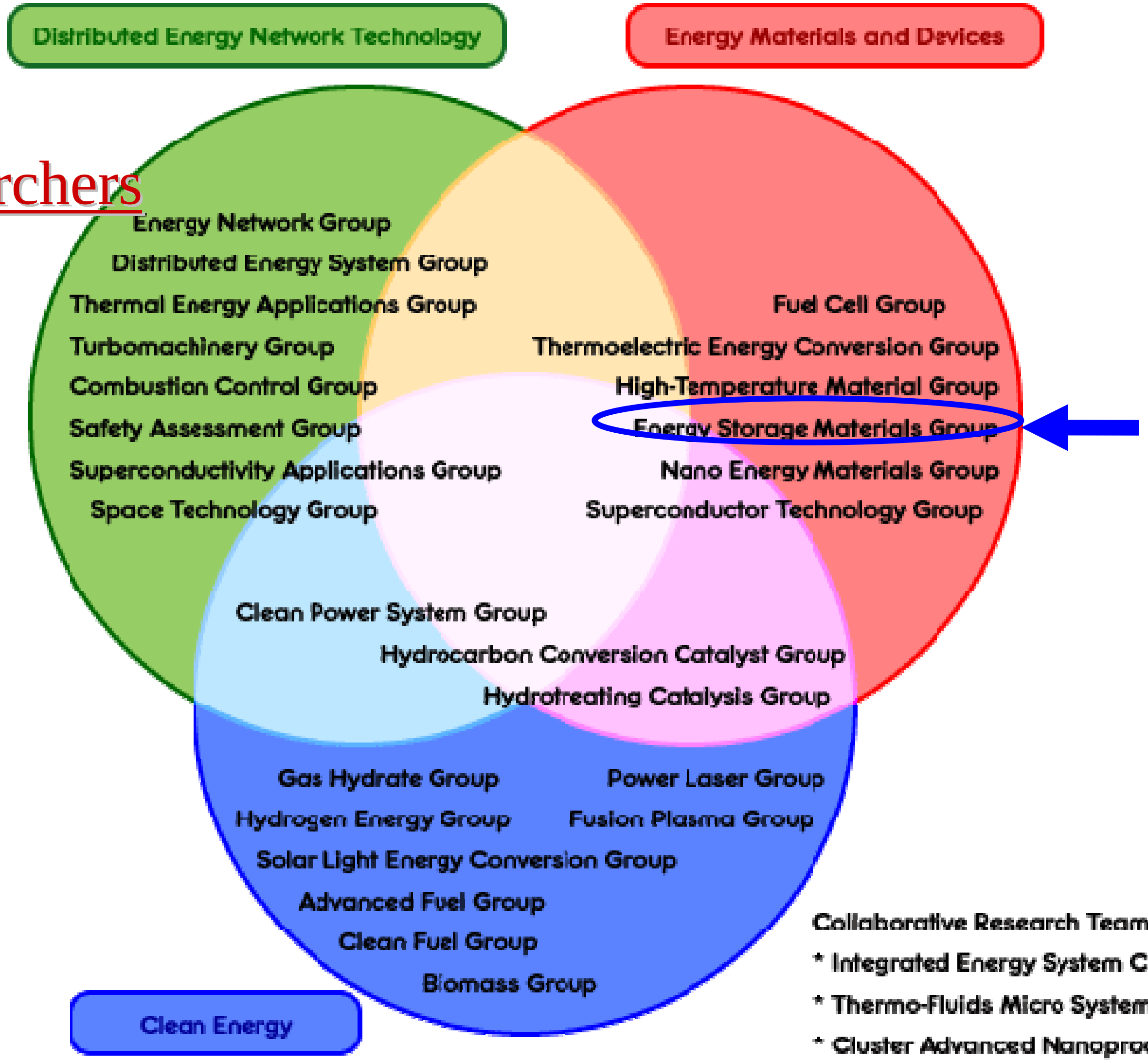


23 Research Center
22 Research Institute
3 Research Initiative

- Research centers are limited-term (typically 7 years) organizations with clear goals. Research resources of AIST, such as budget and personnel, are strategically distributed, and research centers have priority to the resources.
- Research institutes are basically bottom-up organizations. Research institutes aim to keep continuity of operation to implement mid- and long-term strategies of AIST. Research institutes are also expected to maintain technical potential of AIST and to develop new fields of technology.
- Research initiatives are rather small units of limited terms. The purposes of research initiatives are to promote specific research projects, especially those of cross-fields. Some research initiatives also aim to meet immediate governmental needs.

Energy Technology Research Institute

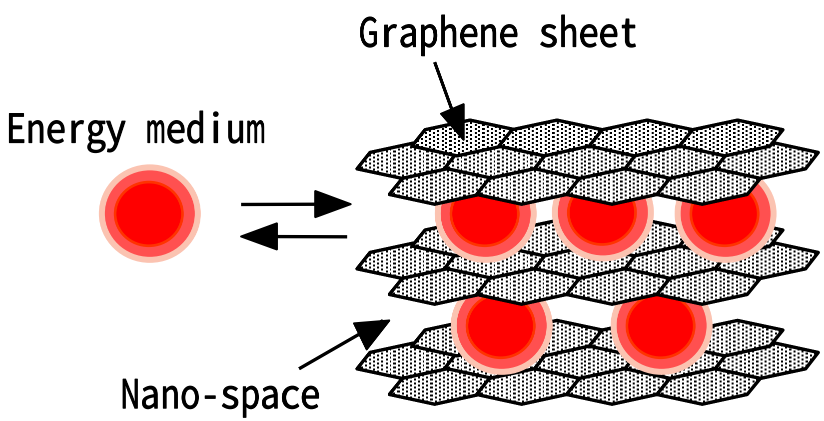
~180 Employees
~140 Visiting researchers
24 Research Groups



Collaborative Research Teams (CRT)
* Integrated Energy System CRT
* Thermo-Fluids Micro Systems CRT
* Cluster Advanced Nanoprocesses CRT

Energy Storage Materials Group

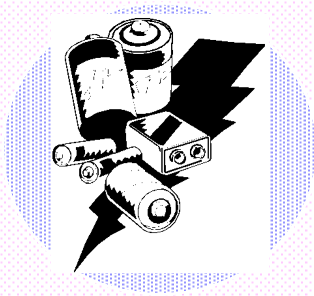
Energy Storage Materials Group



Energy Storage Materials Group conducts research and development on carbon materials for energy storage, which contributes to energy system in commercial and residential use. Our group, having great potentials for synthesis and characterization of carbon materials, aims at development of innovative **nanocarbons used for electric double layer capacitors,** hydrogen storage and fuel cell applications.

Application of Electric Double Layer Capacitor (EDLC)

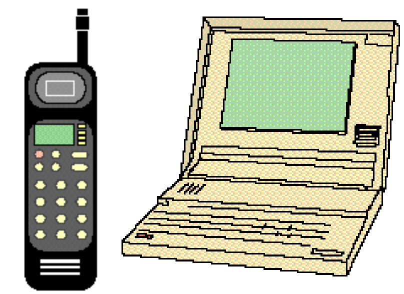
EDLC



● **High power density**
immediate charge-discharge

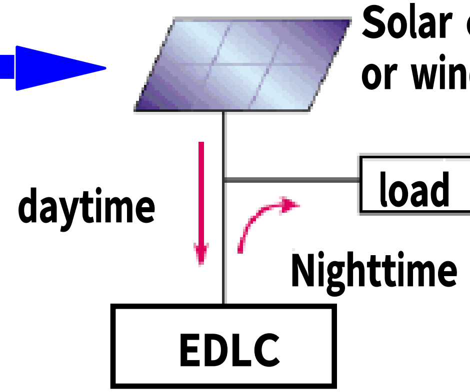
● **Long life**
maintenance free, reliable

Fuel Cell Vehicles
Electric Vehicles
Hybrid Vehicles



Power supply for memory backup

Solar cell
or wind power station



Leveling of power demand

Small scale distributed energy system

needs storage of electricity, but different way from battery

Energy storage devices

Battery

Primary

Electrochemical reaction:
Large capacity, slow reaction

Secondary (rechargeble)

Lead acid
NiCd, MH
Li ion

Capacitor
(condenser)

Electrochemical capacitors

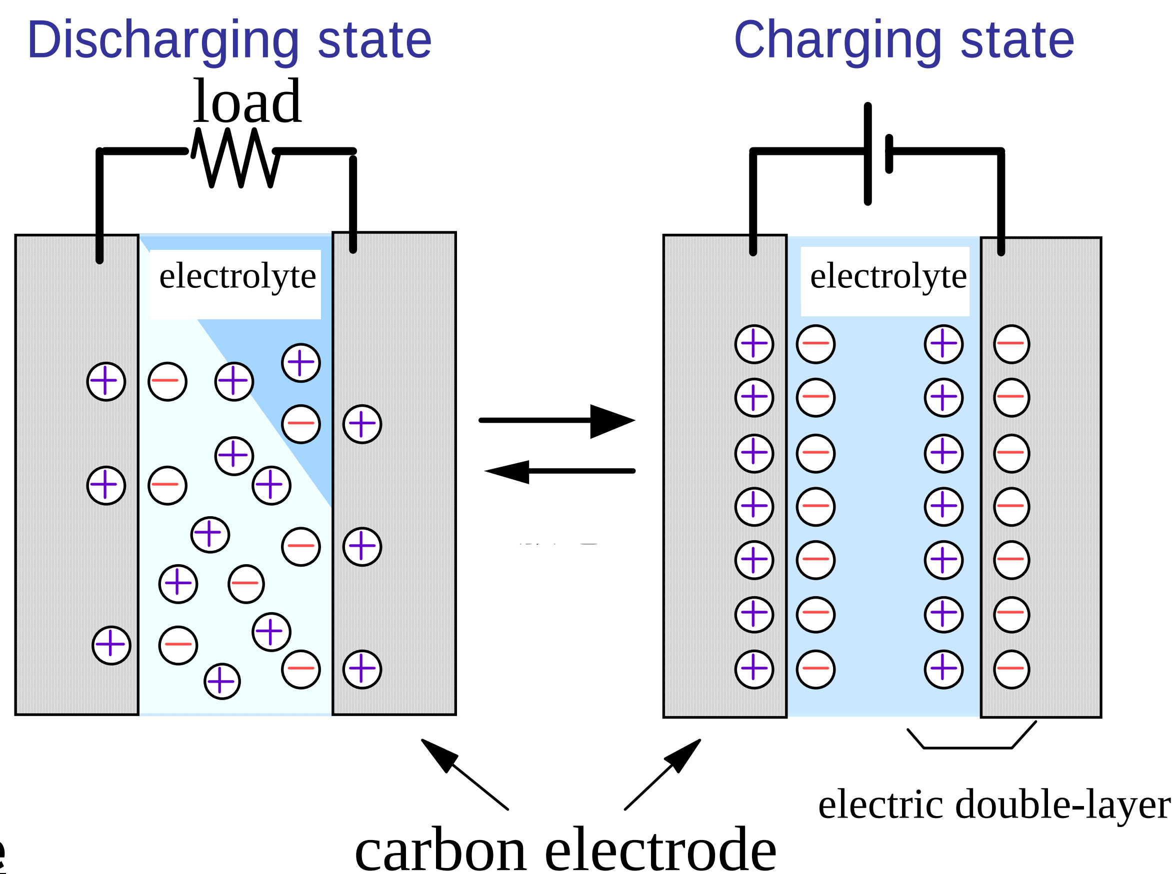
Nanocarbon, metal oxide, polymer

Charge accumulation at the interface:
Fast phenomenon, small capacity

Electric double layer capacitors
Ceramic capacitors
Aluminum electrolytic capacitors

Activated carbon

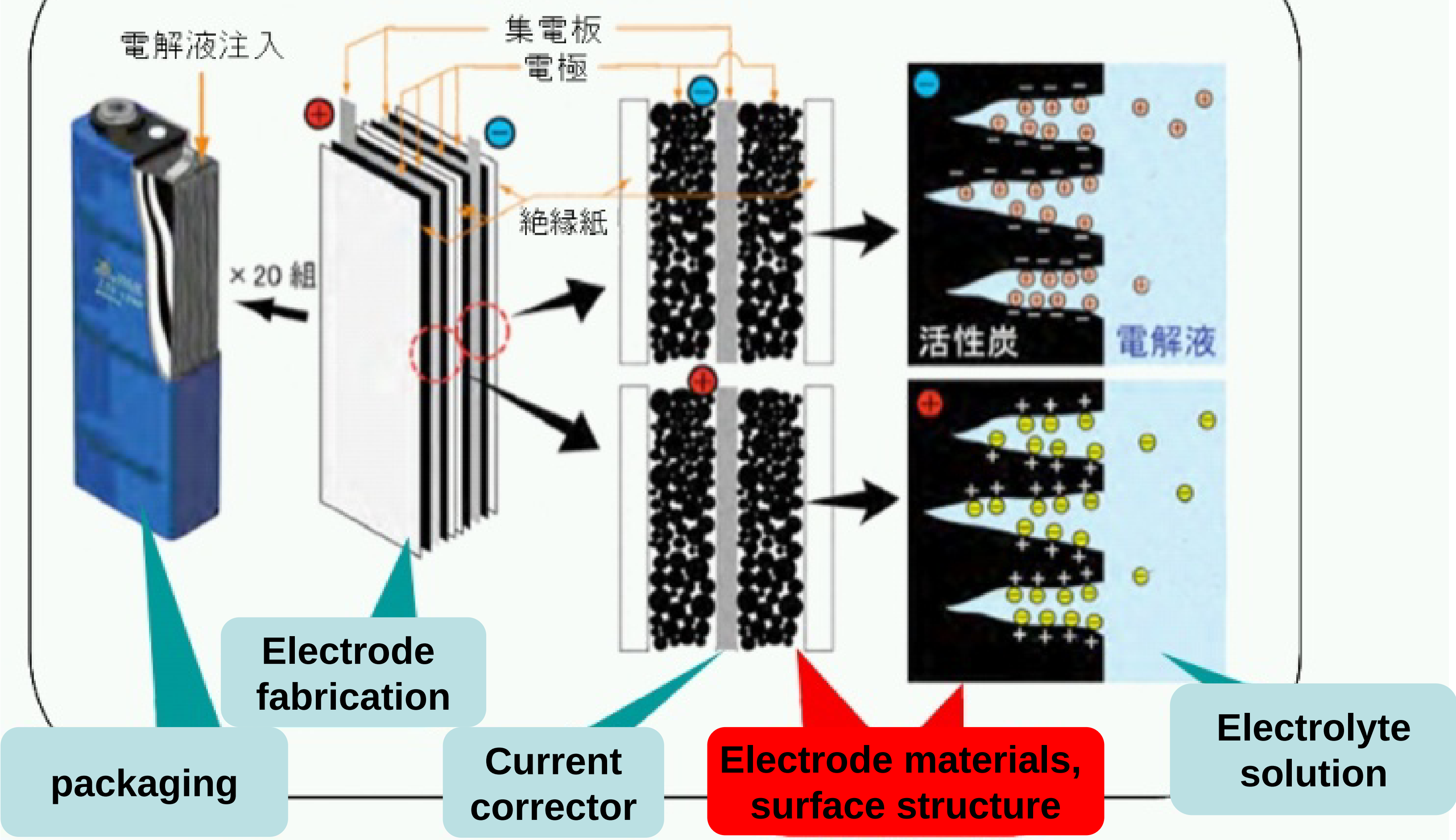
Charge-Discharge Mechanism of EDLC



Capacitance

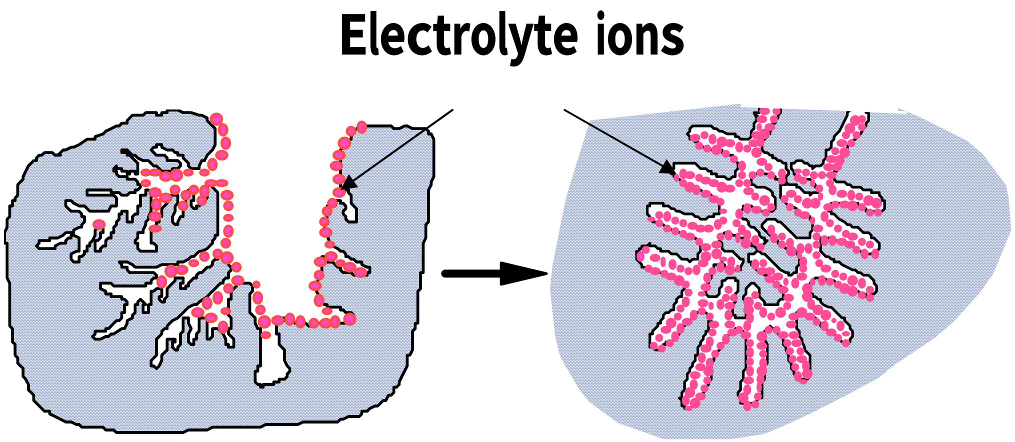
$$C = \int \frac{\varepsilon}{4\pi l} dS$$ = **(Capacitance per Unit Area)** × **(Surface Area)**

Structure and materials in Electric Double Layer Capacitor



Design of Carbon Nanostructure

$$C_{\text{(Capacitance)}} = \int \frac{\varepsilon}{4\pi l} dS$$



Conventional Activated carbons

Nanocarbons with Uniform pore size

Optimum structure with maximized effective-surface-area

Electrolyte

	Aqueous (0.8-1.2V)	Non-aqueous (2-3V)
Advantage	• High conductivity (**high power density**) • Stable • Wide temperature range • Impedance • **Low cost, safety**	• High energy density • Variety of components
Disadvantage	• Low energy density	• Long-term stability • High cost (material and moisture control) • Flammability
Application	• Small device for power usage	• Large device for energy storage

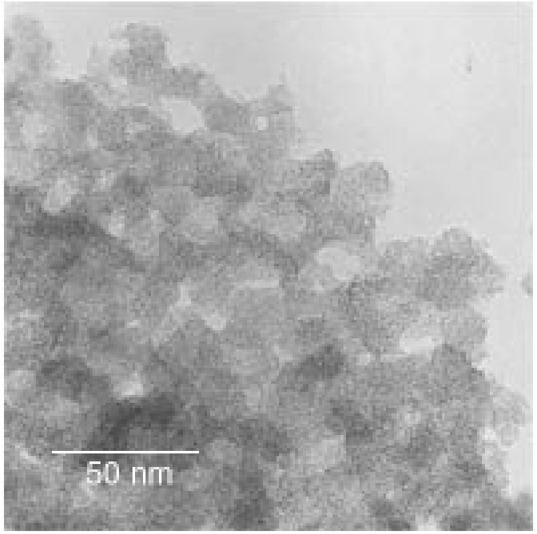
Pseudo capacitance in electrochemical capacitor

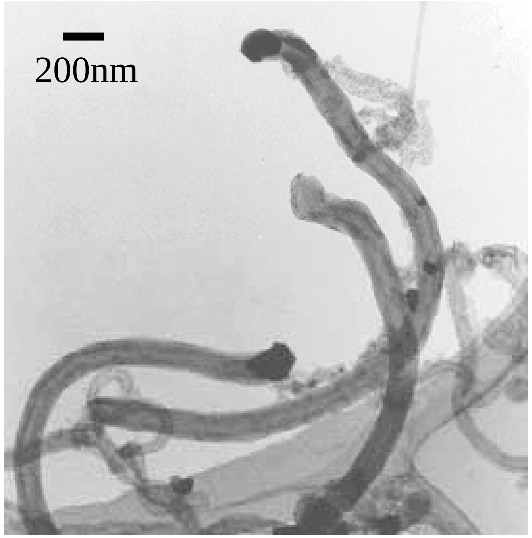
$$RuO_2 + H^+ + 2e^- \rightleftharpoons RuOOH$$

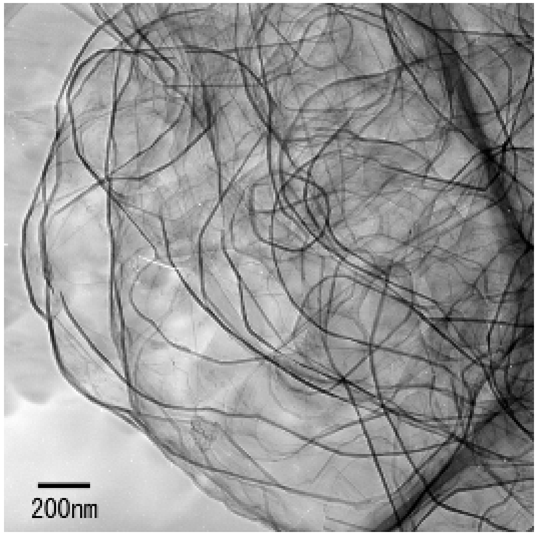
Charge-discharge response is similar to EDLC
Activated carbon: ca.200F/g, RuO_2: ca.800F/g

Candidates: transition metal oxides (compounds)
conducting polymers
intercalation reactions
carbon surface functional groups
hetero atom substitution in carbon structure

Nanocarbons

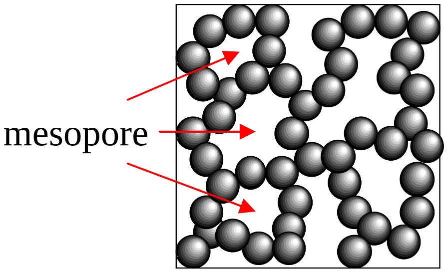






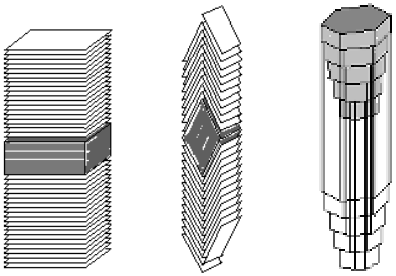
Carbon Aerogels

Surface area 〜2000 m²/g
Mesoporosity



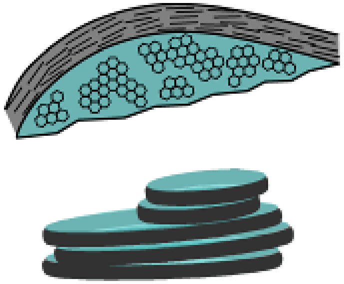
Carbon Nanofibers

Diameter 〜100nm
Various nanotexture

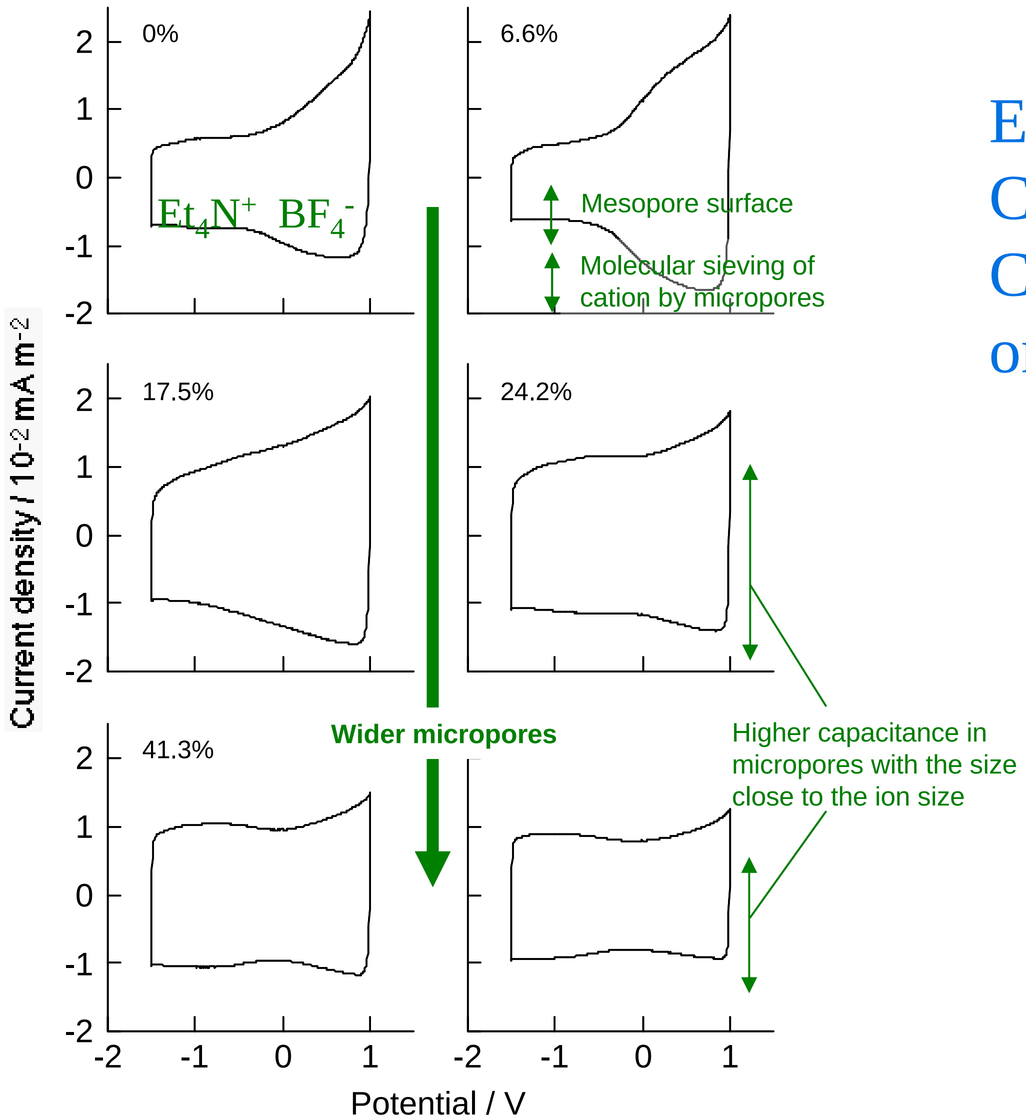


Mesoscopic Carbons

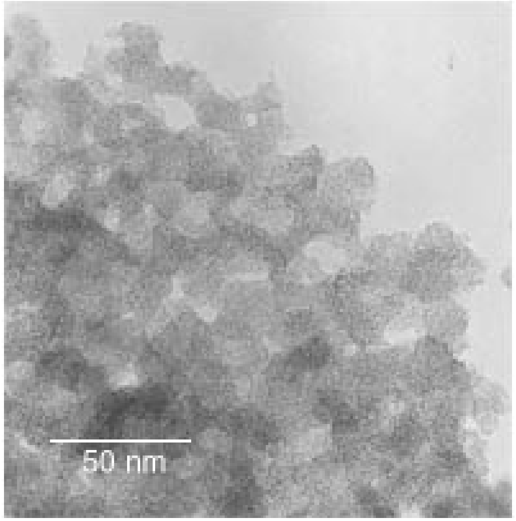
Thickness 〜 2 nm
Unique structure



Dependence of Capacitance on micropore size

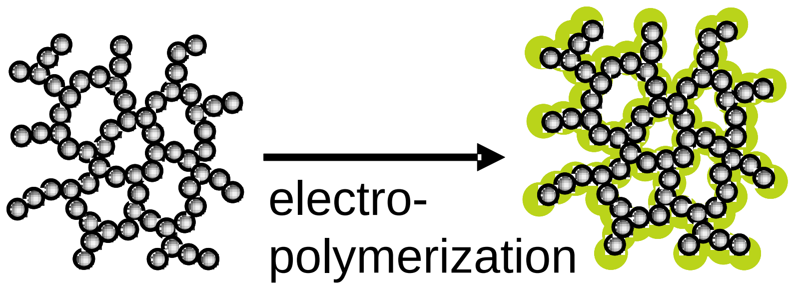


Electric Double-layer Capacitance of Activated Carbon Aerogels depends on the micropore size.

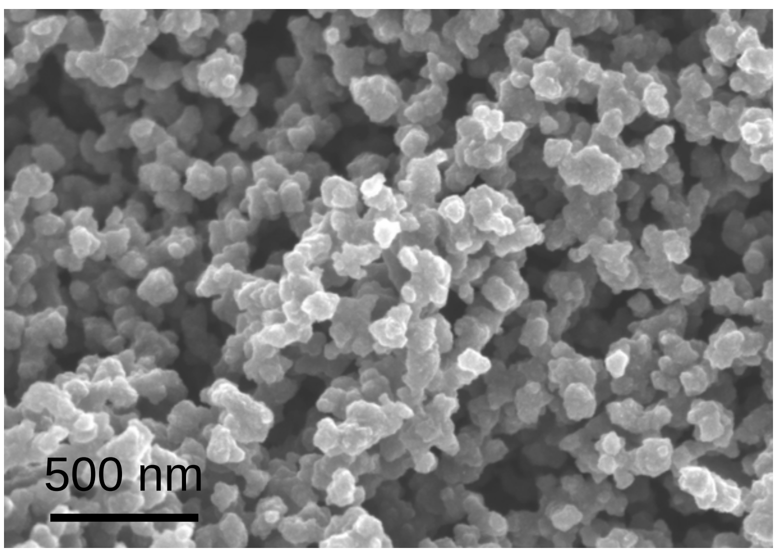


Carbon Aerogels

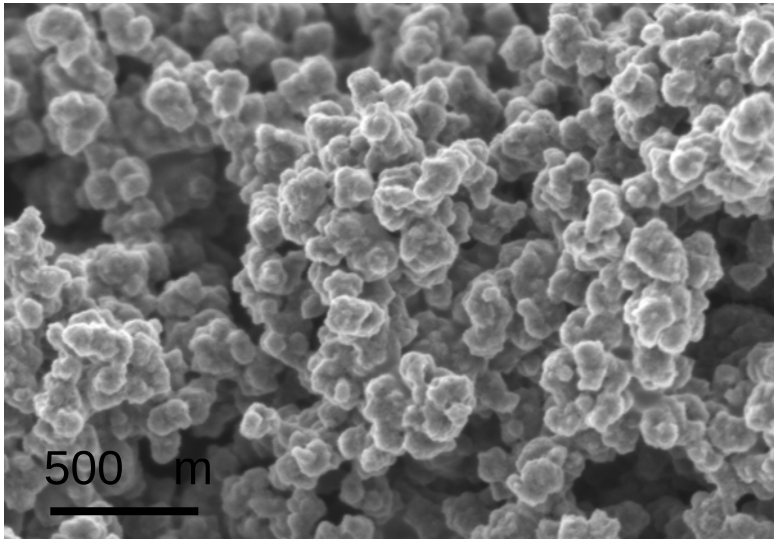
Electrochemical properties of carbon xerogels coated with poly(p-fluorophenylthiophene)



Carbon xerogel



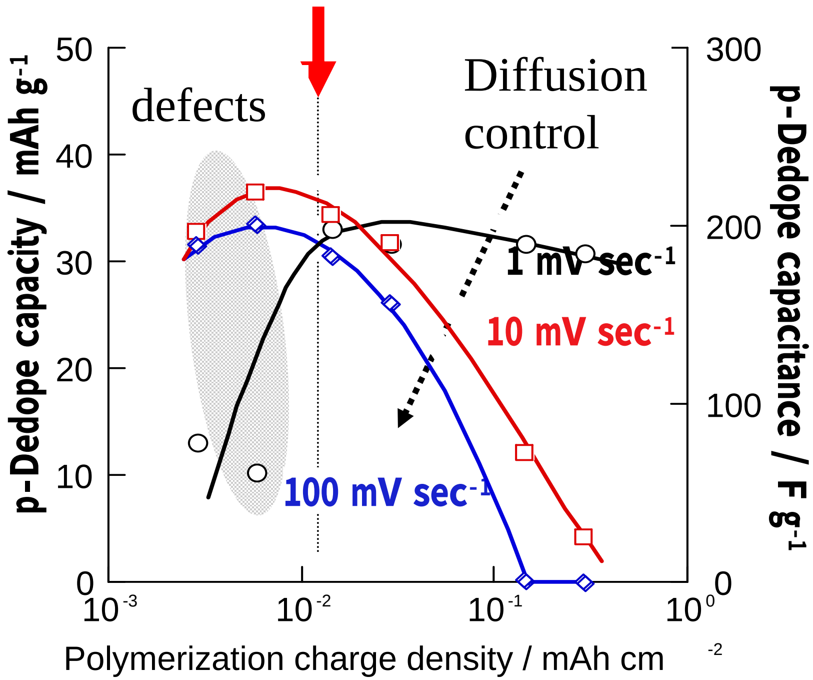
PFPT-coated carbon xerogel

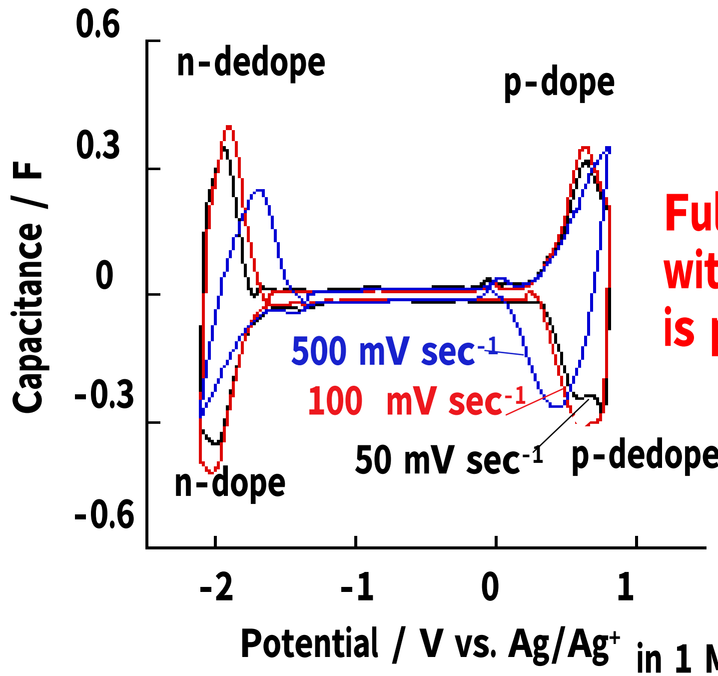


➢Conductive polymer/Carbon Nano-Composite

Rate performance of PFPT coated on carbon xerogels

Optimum thickness 200 nm (PFPT content in electrodes >90%)





in 1 M Et4NBF4/PC

Full charge within 6sec is possible

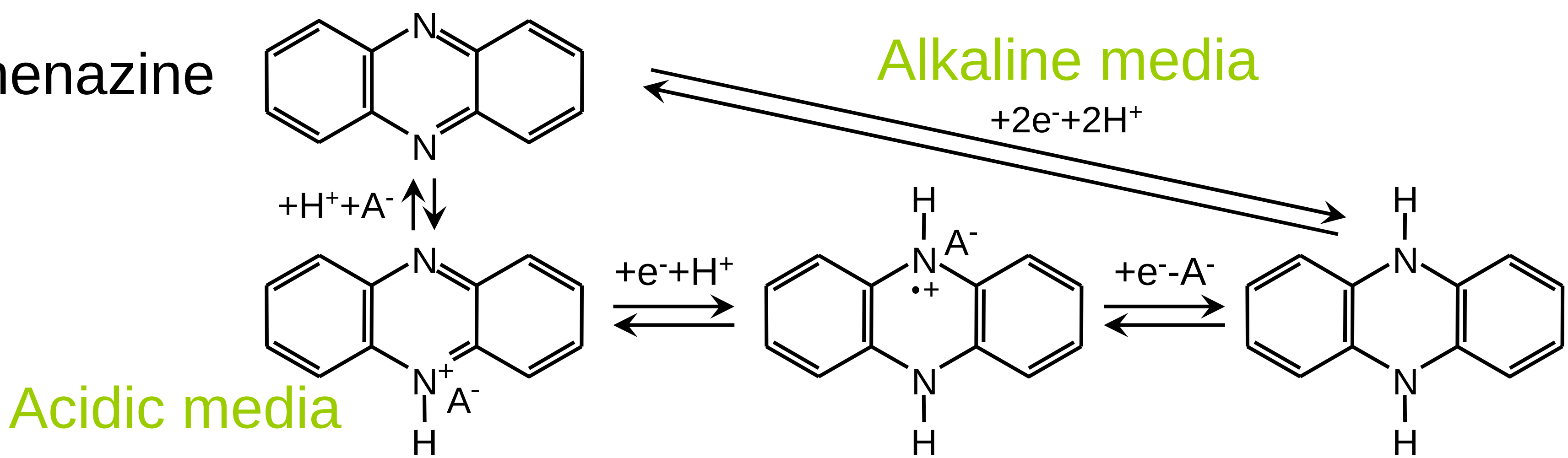
Cyclic voltammograms of PFPT coated carbon xerogels

Electrochemical reactions of N-hetero cyclic compounds

Reduction of pyridinic N

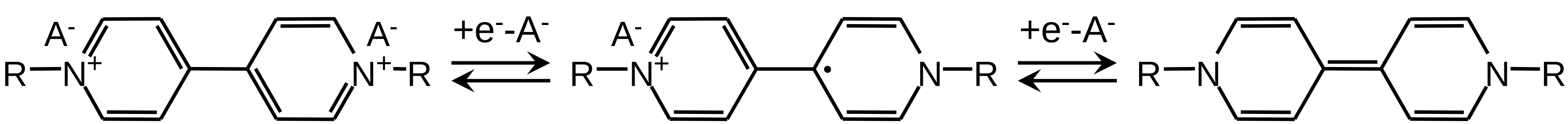
in aqueous solvent

Phenazine



Reduction of quaternary N

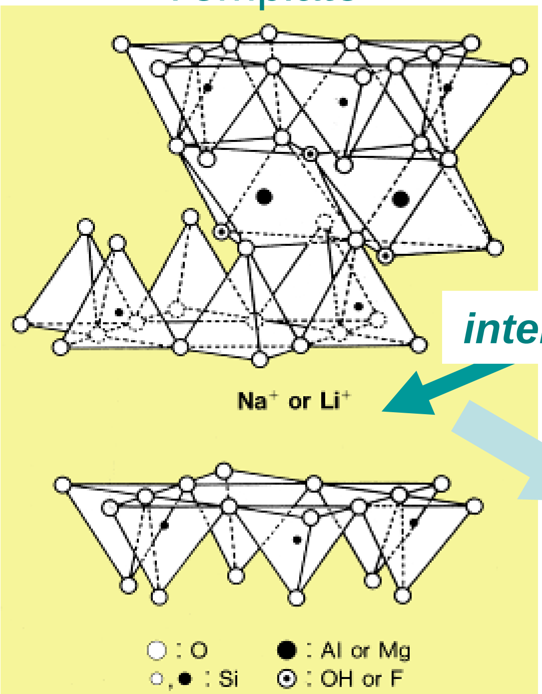
in aprotic solvent



Viologen

Template Carbons from Melamine Precursor

Template

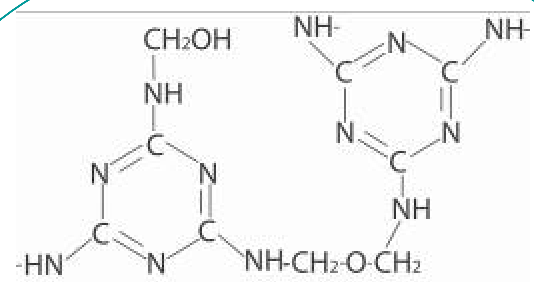


Expandable Fluorine Mica

$Na_{0.6\text{-}0.7}Mg_{2.8\text{-}2.85}Si_4O_{10}F_2$

Average particle size = 6μm
Specific surface area = 3.3m^2/g

Carbon source



melamine resin

intercalation

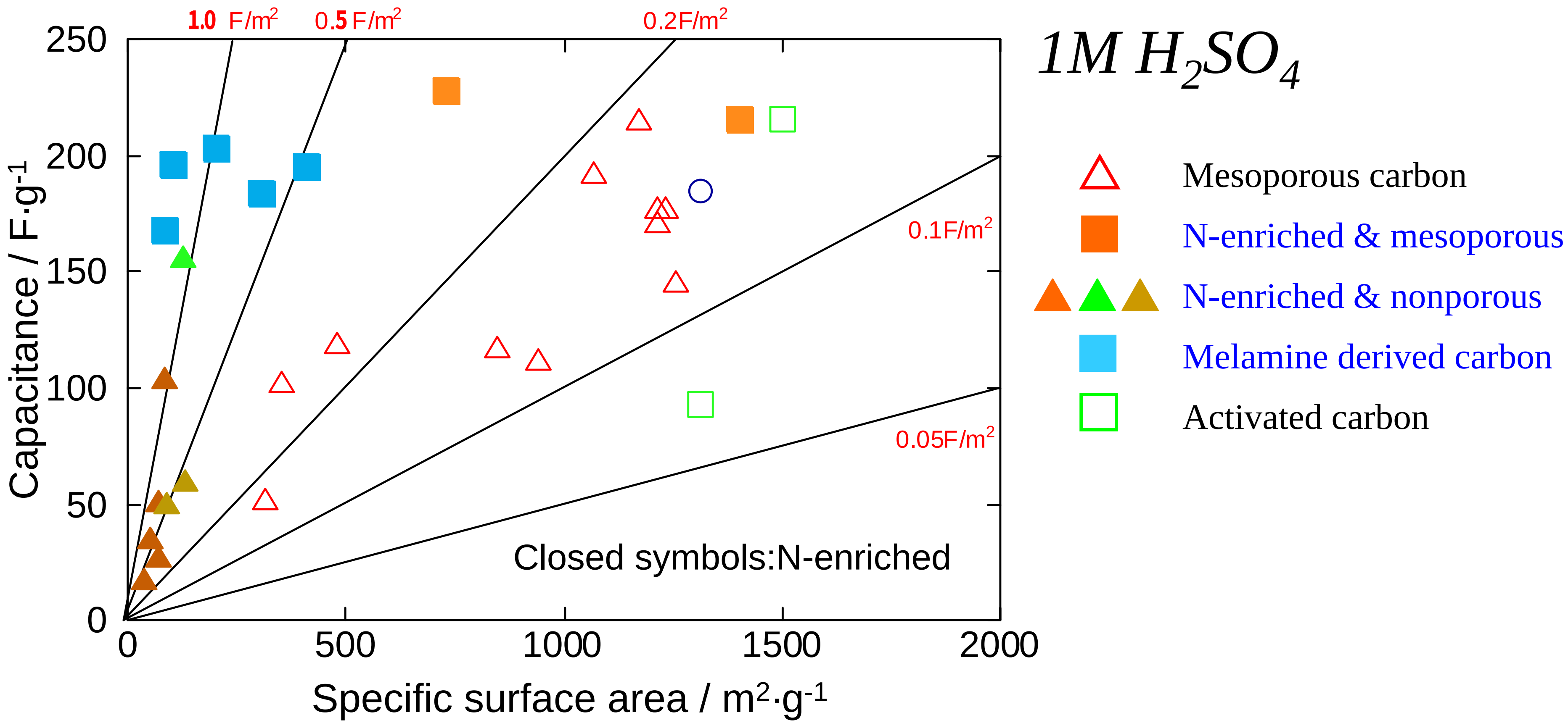
Melamine/Mica complex → Heat treatment in Ar → Carbon/Mica composite

- 750℃ for 3hr
- heating rate=20℃/min
- atmospheric pressure

→ Removing mica → Carbon

- HF washing
- HCl washing
- filtration

Pseudocapacitance on nitrogen-enriched carbon surface



Kodama M et al., ***Mat Sci Eng B-Solid*** **2004;108 (1-2):156-161.**

Melamine/MgO template method

Melamine

+

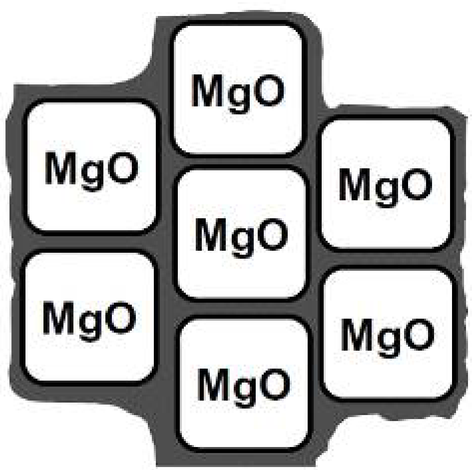
Mg citrate

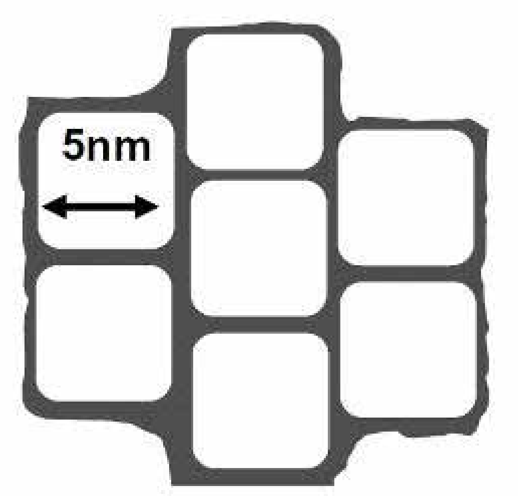
carbonization →

Carbon coated MgO

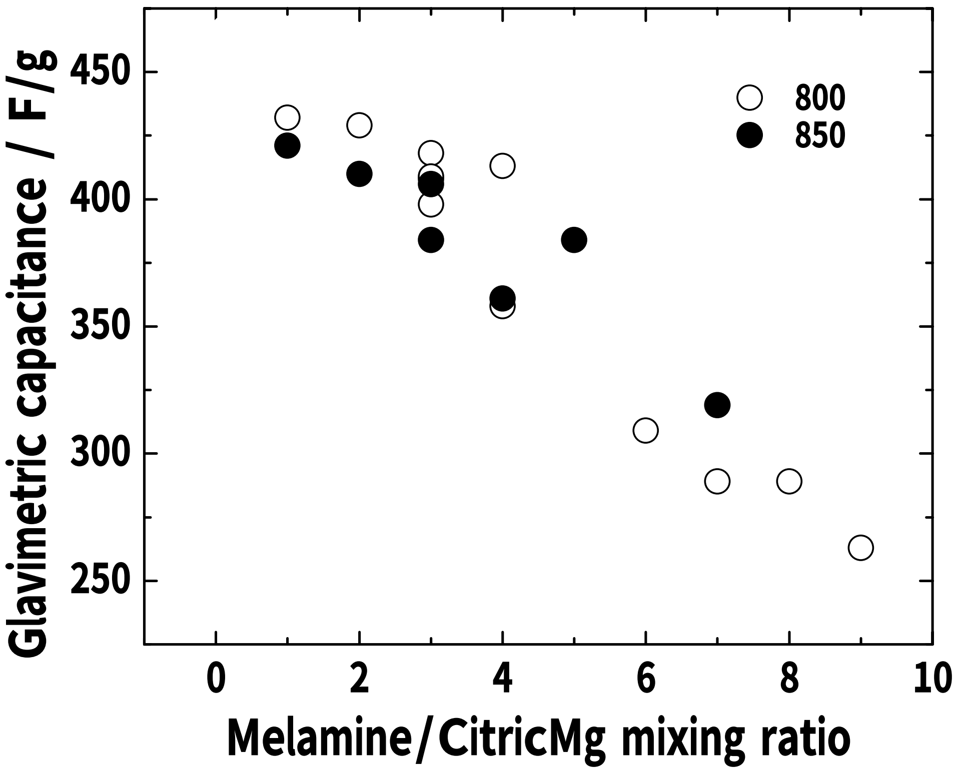
acid treatment →

Nitrogen enriched porous carbon





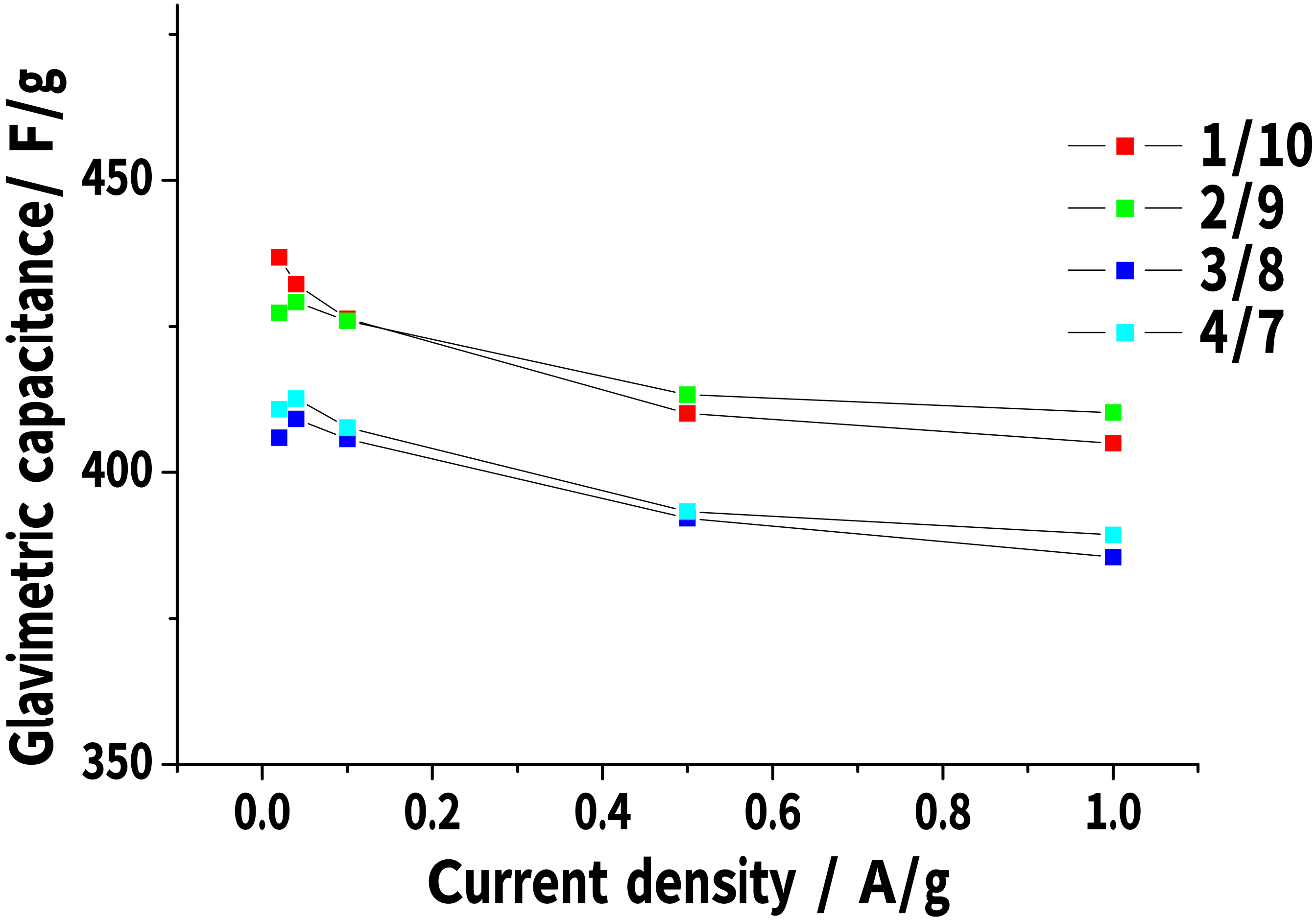
Specific capacitance (at 40mA/g) vs. melamine/MgO mixing ratio



- Huge glavimetric capacitance (ca. 400 F/g) were obtained in H_2SO_4 electrolyte.

40% H_2SO_4 RE:Ag/AgCl

Rate characteristics (high rate discharge)



Summary
~Nanocarbons for capacitor~

- Controlled pore structure
  - Carbon aerogels, carbon nanofibers & nanotubes, mesoscopic carbons, exfoliated carbon fibers
- Nitrogen substitution in carbon network
  - Nitrogen functionality, change in electronic structure
- Combining with pseudocapacitance materiasls
  - Polymer nano-coating on carbon aerogels, carbon coated W and Mo carbides,

Acknowledgement

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