Electrolyte infiltration studies of supercapacitors by neutron scattering

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EFree Neutron Day, Dec 10 2015

Outline

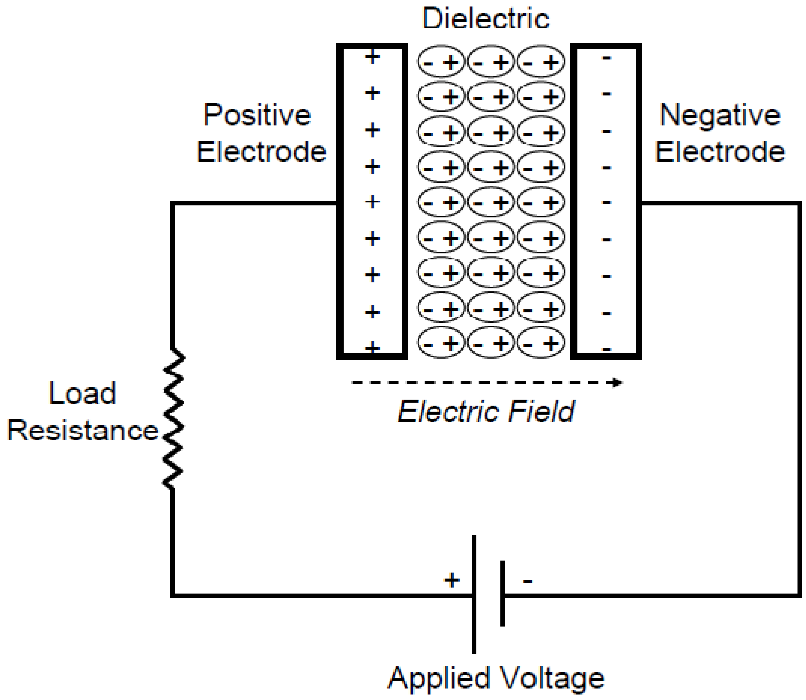
1 Introduction of supercapacitors

2 Concept of supercapacitive swing adsorption

3 Proposed neutron scattering experiments

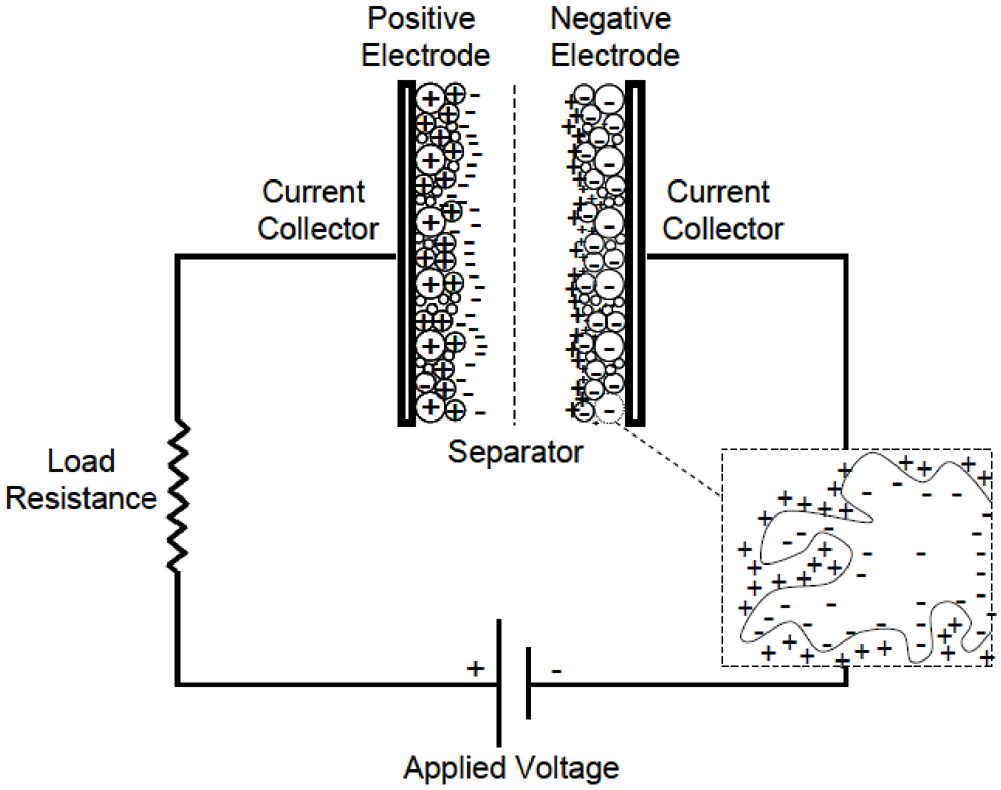
Supercapacitors

Parallel plate capacitor



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

Electric double layer capacitor



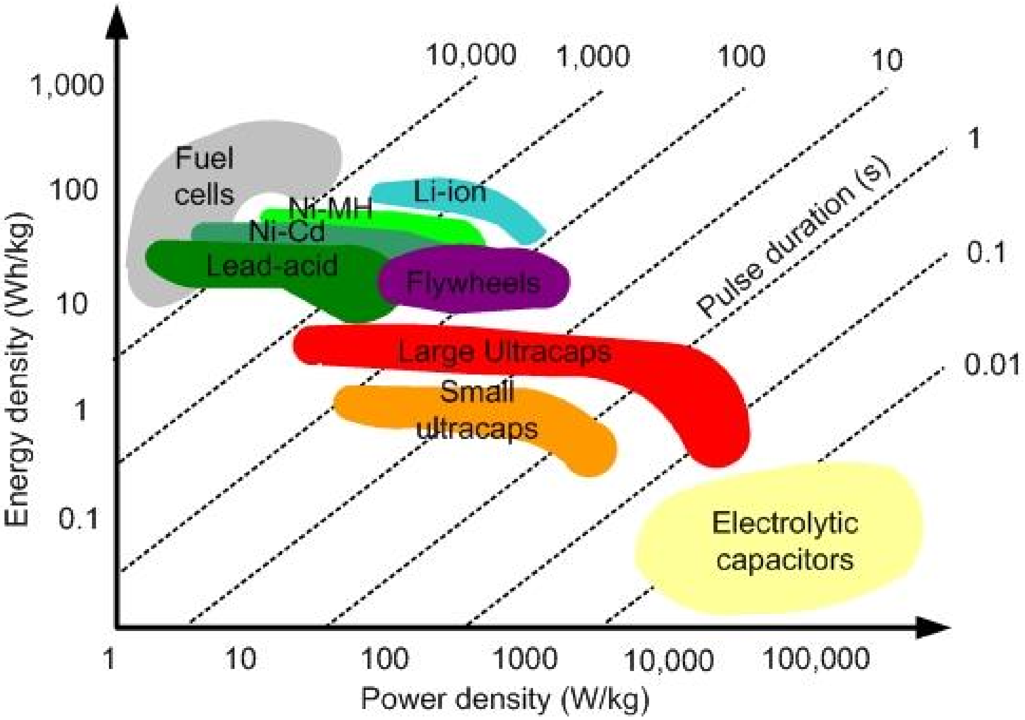
- Electrodes: Activated carbon (aerogels, porous carbon,)
- Electrolyte: KOH, organic solution, sulfuric acid, ionic liquid

Supercapacitors

Supercapacitors**:**

- No redox reactions
- Fast charge/discharge rate
- Low internal resistance
- Long cycle life
- High efficiency

Ragone chart



Simon, P.; Gogotsi, Y. *Nat. Mater.* 2008, 7, 845ï 854

Surface area vs capacitance

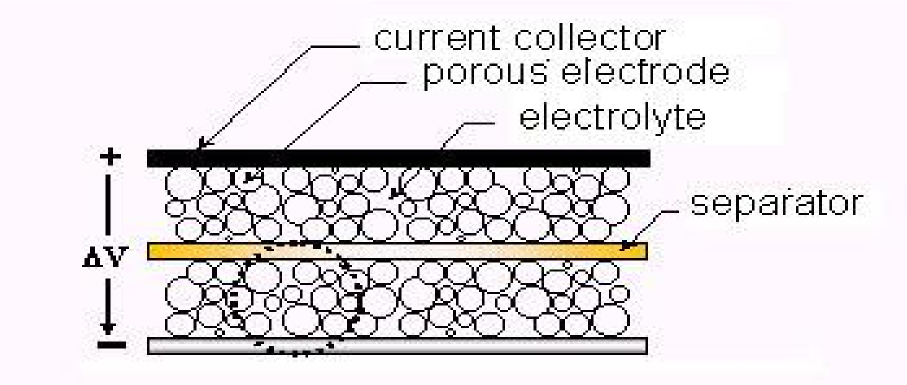
Carbon	Specific capacity (F/g)	Specific capacity (F/cm2)	BET surface area (m2/g)	Pore volume (cc/g)	Average pore size (Å)
M-10	55.95	0.041	1370	0.5	9.12
M-14	57.2	0.0047	1223	0.561	9.6
M-15A	78.1	0.043	1800	0.629	9.17
M-15B	55.8	0.034	1624	0.563	9.37
M-15C	63.34	0.042	1518	0.6	9.79
M-20	100	0.046	2130	0.709	14.73
M-30	62.9	0.024	2571	1.23	14.95
A-10	35.3	0.031	1150	0.424 –	
A-20	41.2	0.02	2012	0.902	14.23
SACF-20	48.8	0.027	1839	0.699	9.74
SACF-25	27.9	0.011	2371	0.977	11.93

- Specific capacity doesn’t have a linear relationship with surface area
- Pore geometry, pore size and electrolyte infiltration have strong impact on specific capacity

Qu, D. & Shi, H. Studies of activated carbons used in double-layer capacitors. *J. Power Sources* **74**, 99–107 (1998)

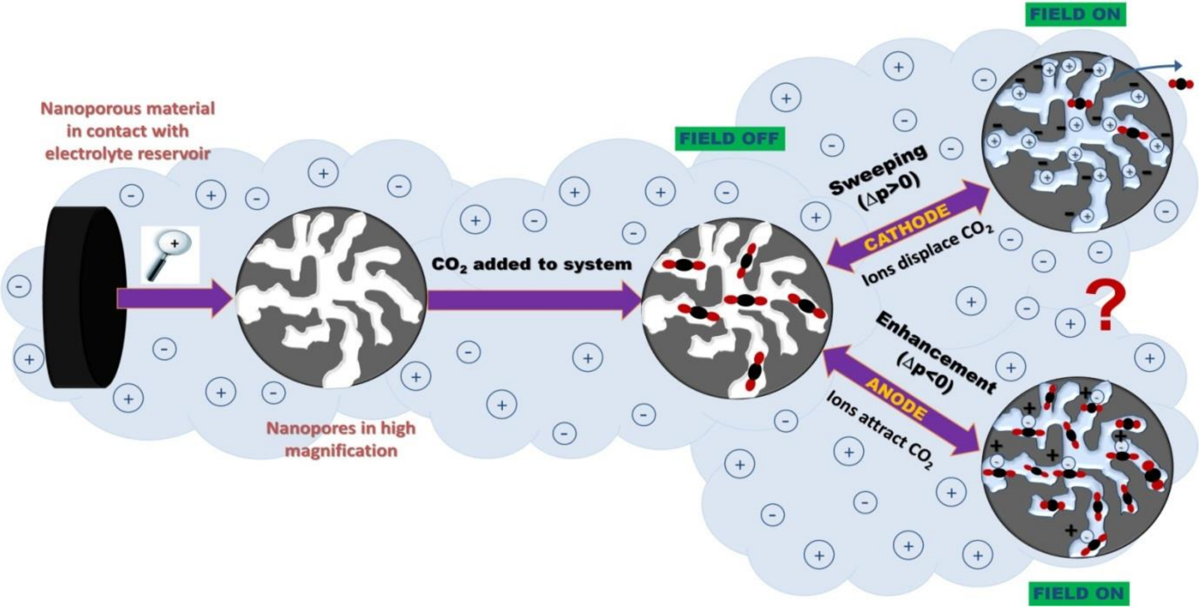
Supercapacitive swing adsorption

- SSA technique for CO_2 adsorption;
- Based on low-voltage and high-capacitance supercapacitor
- SSA uses mobile ions to reversibly change interaction of CO_2 molecules with sorbent
- SSA utilizes high capacitances seen in the electric double layer capacitors (EDLC’s) to provide a driving force for ion sweeping in and out of electrodes



- High surface area network of mesopores and micropores throughout electrically conducting high-surface area carbon (HSAC)
- HSAC material combined with liquid or solid electrolyte form electric double layer capacitor with about 100 F/g capacitance

SSA mechanism



- In discharged (field off) state, HSAC nanopores yield high adsorption capacity for CO_2 (~40 std. cm^3/g at room temp.)
- In charged (field on) state, ions move from electrolyte into nanopores to form electric double layer
- Two effects possible in principle:
  - ions displace CO_2 from pores (sweeping)
  - electrostatic ion-molecule interaction with surface ions increases adsorption (enhancement, dominant)
- Direction of effect may depend on electrode character (anode vs. cathode)

SSA experiment setup

Monolithic electrodes: BPL carbon with 5% binder

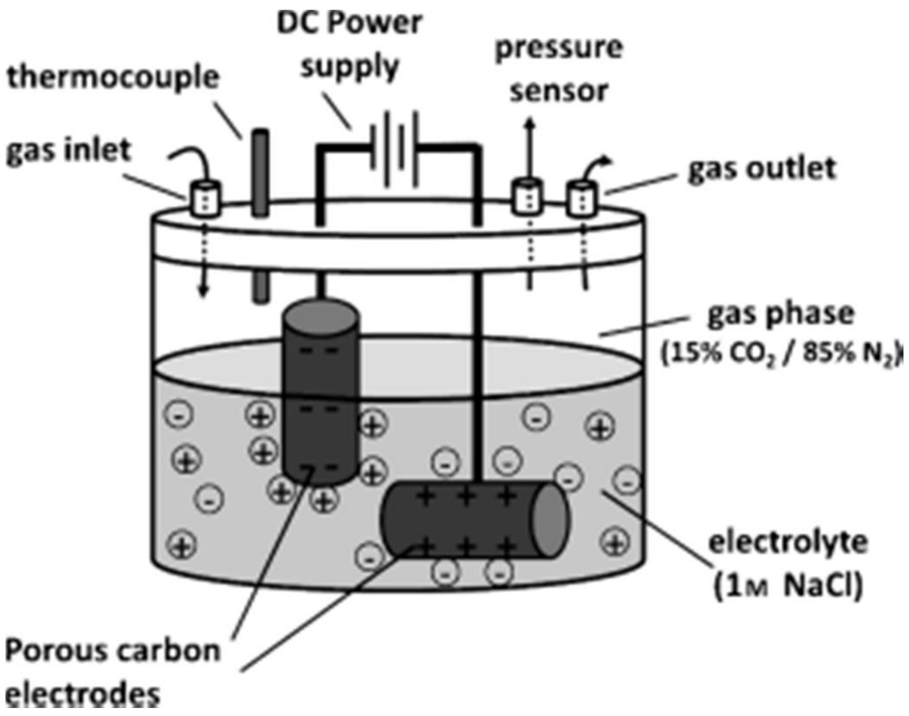
Electrolyte: 1M NaCl

Applied voltage: 1 volt

Void volume of the glass cell: 135mL

Electrode mass: 3.7g

Gas composition: 85% N_2, 15% CO_2

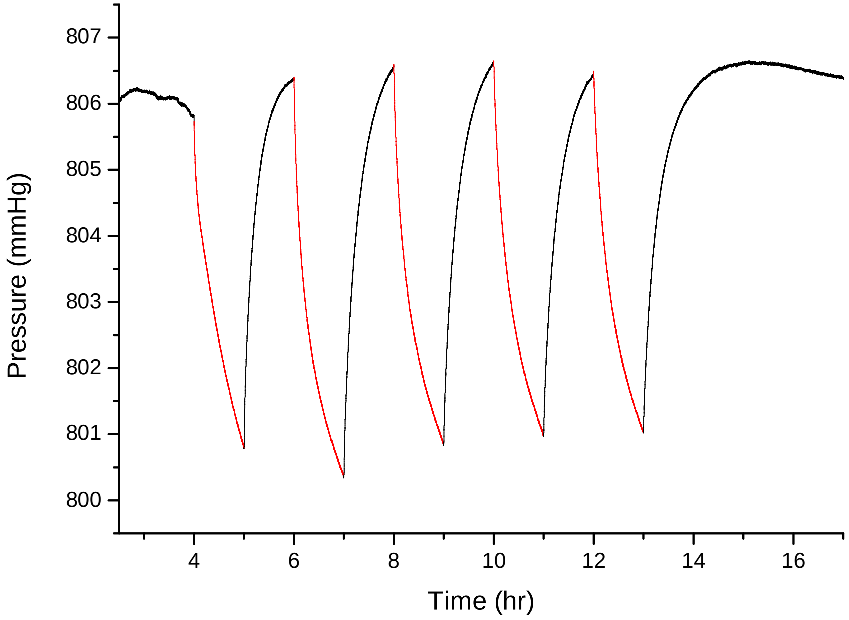


B. Kokoszka, et, al., Angew. Chem. Int. Ed., 53, **3698–3701**

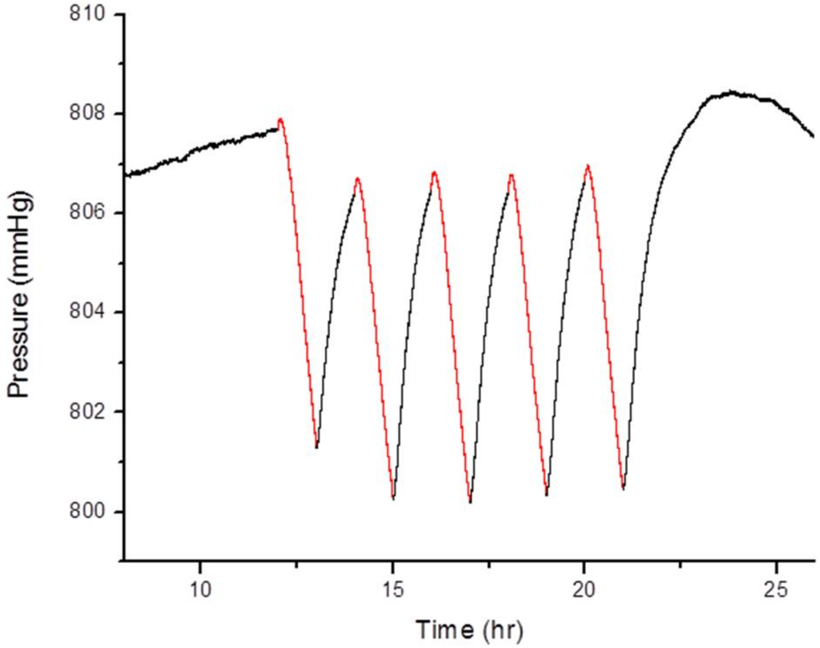
SSA effect

Electrodes with different soaking time

Red: charging cycle (1V)
Black: discharging cycle



Left : Electroldes soaked overnight
average φP 5.60 mmHg

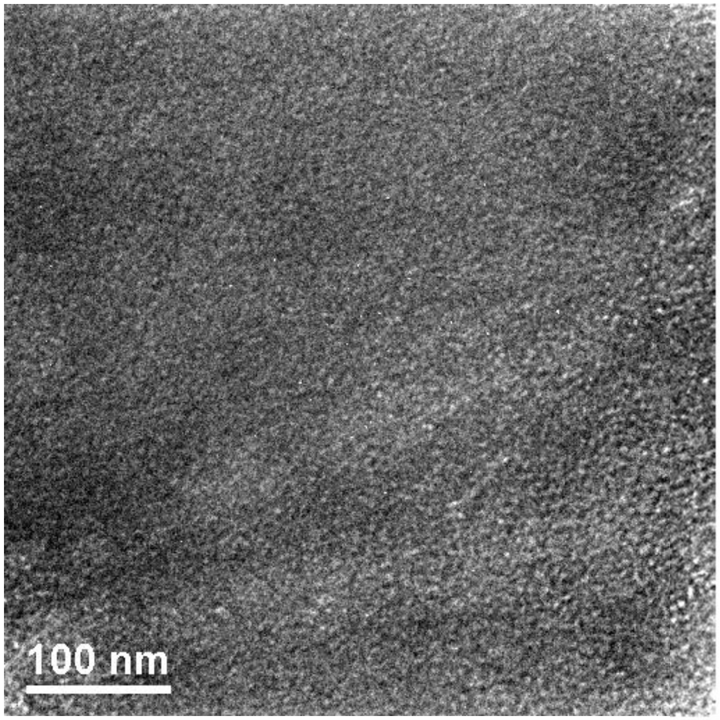


Left : Electrodes soaked for 1 week,
average φP: 6.65 mmHg

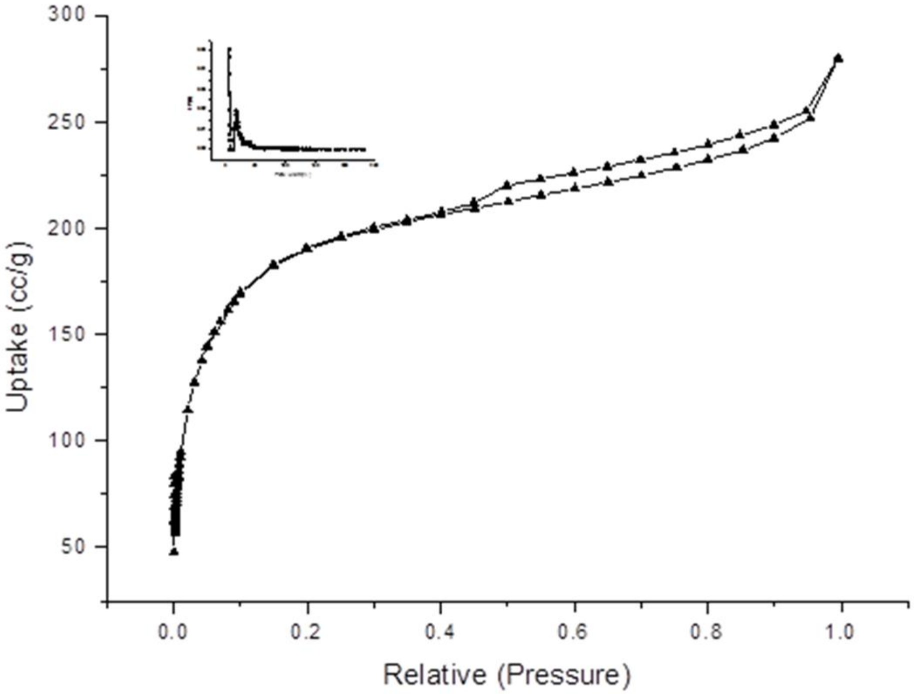
The SSA effect increased by 18%

Neutron scattering experiment

Electrode material



Transmission electron microscopy



Nitrogen adsorption isotherm

BET surface area: 640m^2/g
CO_2 uptake capacity: 38 cc/g at STP
Micropore: 0.4nm
Mesopore: 2-4nm
Natural selectivity for CO_2/N_2 : 9

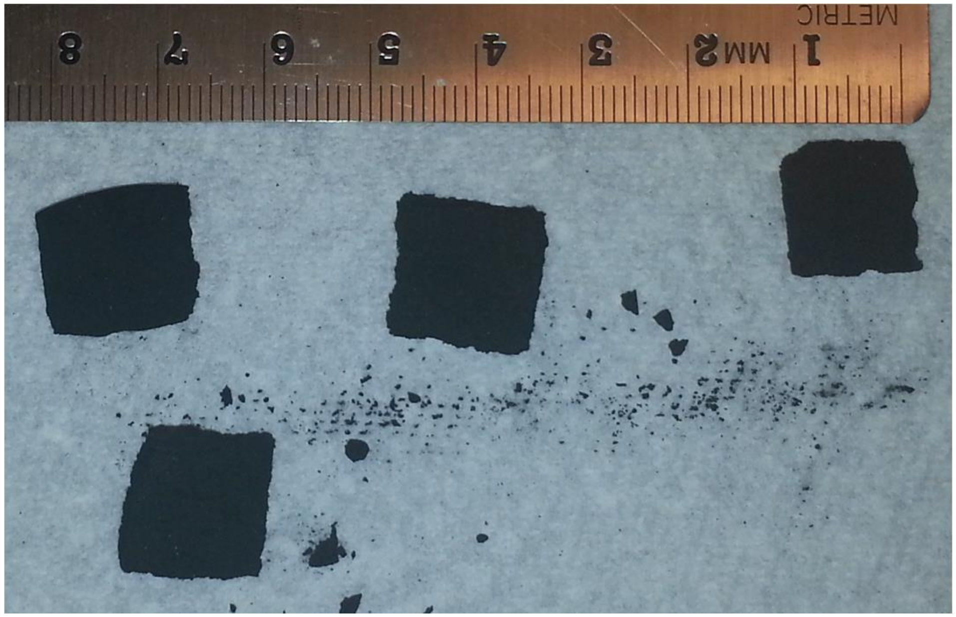
Neutron scattering experiment

- Carbon pellets prepared by mixing BPL carbon with 8% phenol resin, then carbonized at 900 °C

- 1 cm x 1 cm x 0.5 mm

- 1M NaCl solution in D_2O as the electrolyte

- One electrode un-infiltrated, one electrode completely infiltrated by vacuum infiltration and a series of electrodes soaked in electrode with different times, such as 1h, 8h, 24h, and so on.



Justification for using neutron scattering

Å Neutron contrast matching is a powerful tool to measure hydrogen concentration through neutron contrast and imaging

Å VULCAN diffractometer has the high flux and spatial resolution suitable for this measurement

Å Contrast matching neutron scattering to discover the degree of electrolyte infiltration with time

Å This measurement will help to design further in-situ experiments in working supercapacitors and SSA devices

Acknowledgement

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