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Enhancement of supercapacitors by mutually adapting electrolytes and nanoporous carbons

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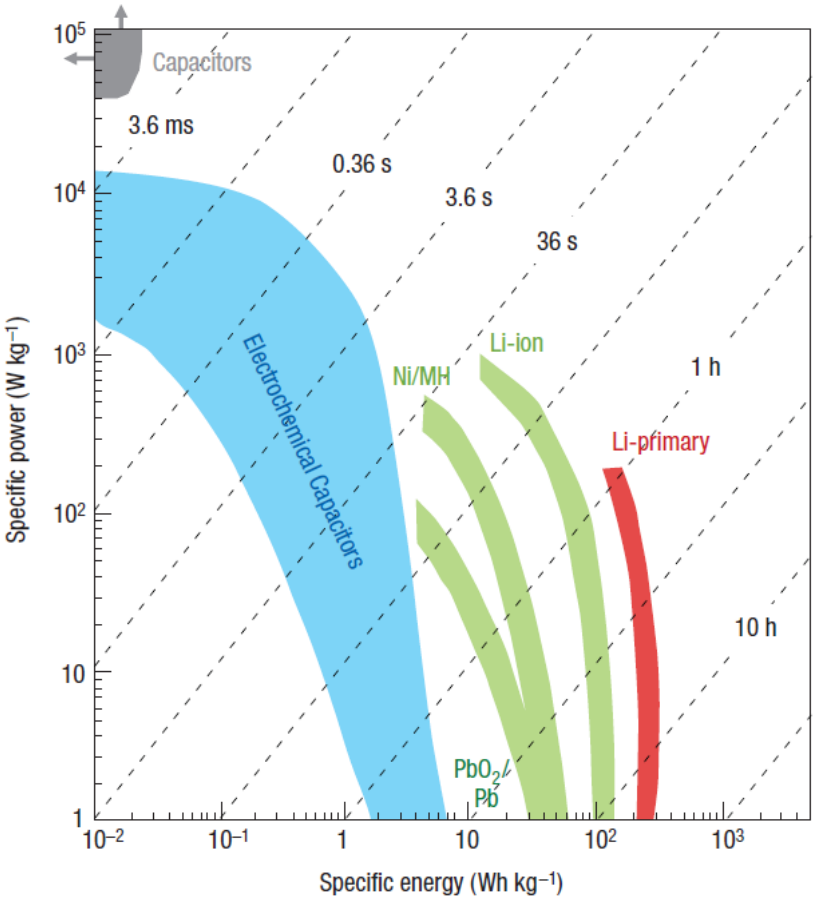
Outline

1. Background and state of the art
2. Objectives and approach
3. Methodology and working plan
4. Preliminary results
5. Conclusions

1. Background and state of the art

Supercapacitors among other electrochemical energy storage technologies[1]

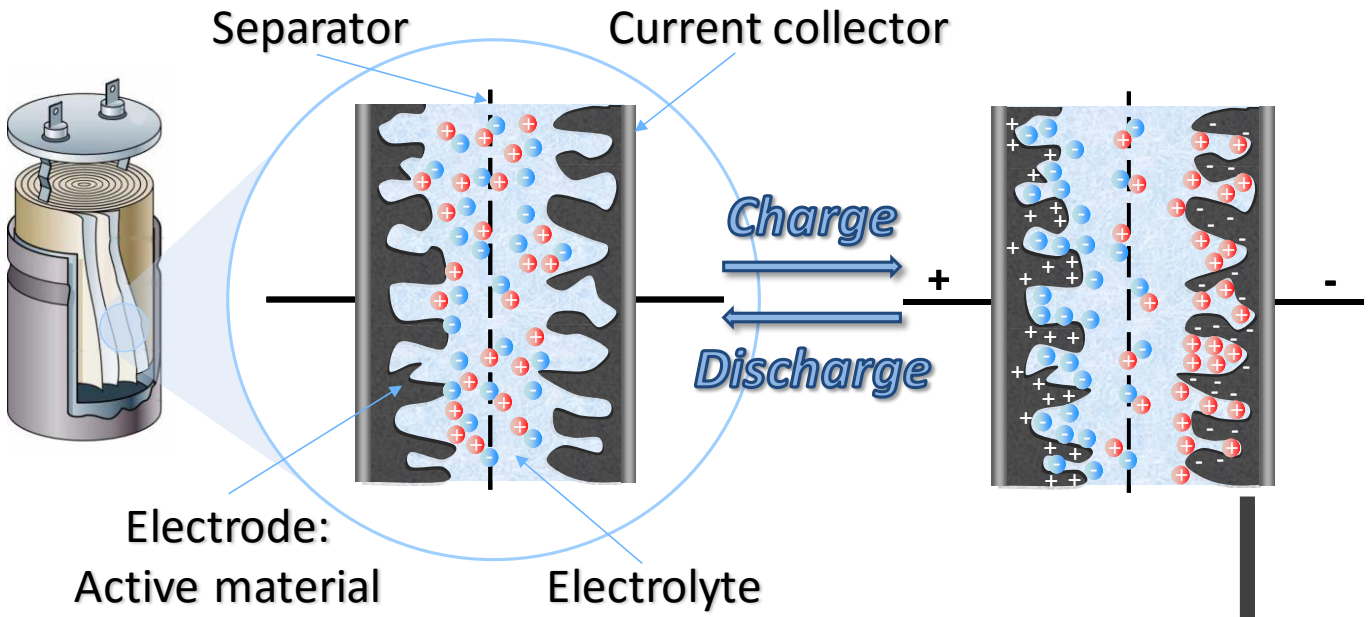


- Energy storage systems
- Performance between batteries and conventional electrolytic capacitors.
  - ✓Power density: 10 kW kg^{-1}
  - ✓Energy density: ~ 5 Wh kg^{-1}
  - ✓t_{charge} or $t_{discharge}$: 1-10s
- Other assets:
  - ✓Long cycle life
  - ✓Broad operational temperature range -45 +60 ^{0}C
  - ✓Lower cost per cycle
  - ✓Fast charge time
  - ✓Safety
  - ✓Maintenance-free operation

[1] P. Simon and Y. Gogotsi *Nature Materials* **2008**, 7, 845.

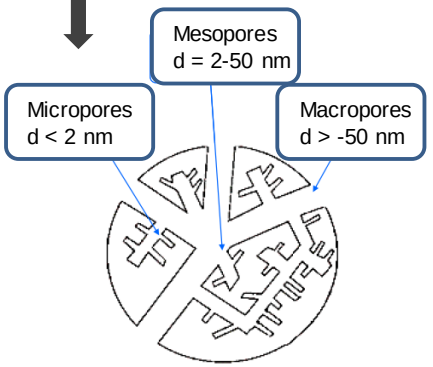
1. Background and state of the art

Principle of electrical double-layer capacitors (EDLCs) [2]



- Capacitor stores energy electrostatically.
- It is charged when a potential difference is applied: cations and anions concentrate in the negative and the positive electrodes, respectively.

$$E = \frac{CV^2}{2} \qquad P = \frac{E}{\Delta t} \qquad P_{max} = \frac{V^2}{4R}$$



$$S_{micro} >> (S_{meso} + S_{macro})$$

[2] F. Beguin and E. Frackowiak *Carbons for Electrochemical Energy Storage and Conversion Systems* **2010**, 329.

2. Objectives and Approach

- Develop a series of carbons out of an inexpensive, abundant and locally available material (olive pits) [4].
  - Surface area accessible to the electrolyte.
  - Narrow pore size distribution, adapted to ions of various electrolytes.
  - Good conductivity.

- Utilization of carbons to maximize the performance of supercapacitors.
  - Targeted performance: Capacitance: at least 60 F cm^{-3} and 120 F g^{-1} in organic electrolyte and > 100 Fcm^{-3} and 200 F g^{-1} in aqueous electrolyte.
  - <10 % capacitance loss after 10000 cycles.

- Understand the capacitive electrosorption in the nanopores on each electrode, by combining electroanalytical techniques with gas adsorption. Determining:
  - Solvatation level.
  - Relationship between coions and counterions.
  - Pore size distriburtion.

- Maximize the energy and power of the supercapacitor device by disigning asymmetric cells.

[3] M. Molina-Sabio and F. Rodriguez-Reinoso, *Colloids and Surfaces A: Physicochem. Eng. Aspects* **2004**, 241, 15.

Optimization of electrode/electrolyte interface

$$C = S_a \frac{\varepsilon_0 \varepsilon_r}{b - a_0}$$

Capacitance in a slit-shaped micropore

C α S_a

Capacitance vs accessible SSA

$$d_{eff} = b - a_0$$

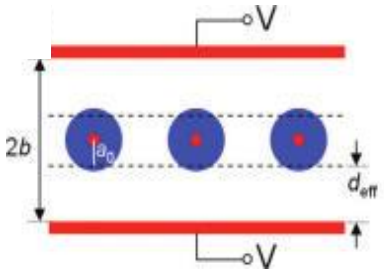
C α $1/d_{eff}$

Capacitance vs pore size

C α ε_r

Capacitance vs solvation

Slit-shaped micropore

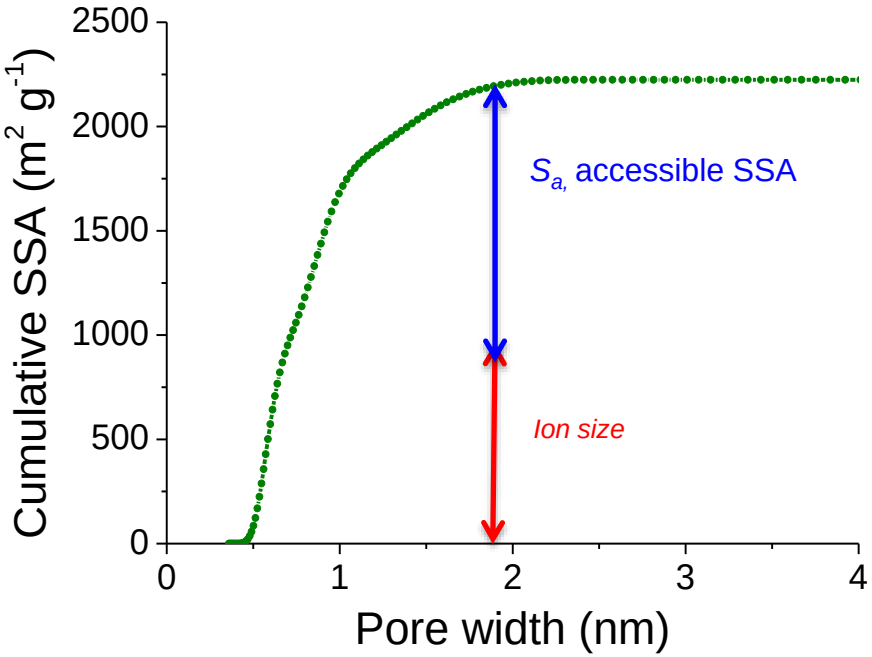


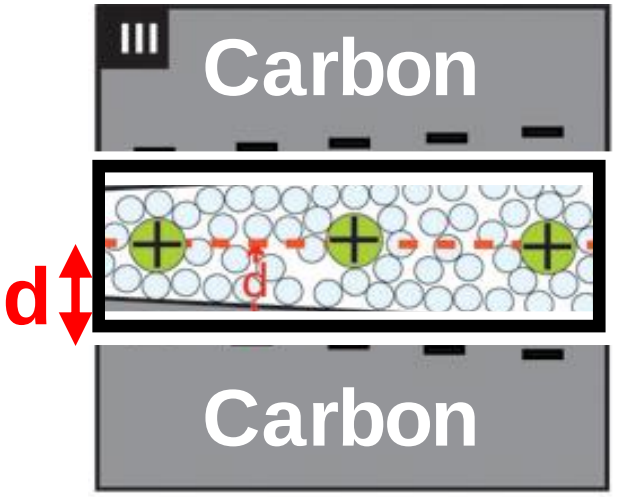
2. Objectives and Approach

Optimization of electrode/electrolyte interface

➢ Typical pore size distribution of microporous carbons (0.5 to 2 nm)

$$C = S_a \frac{\varepsilon_0 \varepsilon_r}{b - a_0}$$





- Need to control the pore size distribution to maximize **S_a**

- Pore size distribution may influence solvation **(ε_r)** and **d_{eff}**

3. Methodology and Work Plan

Expected impact

- ✓ Better understanding the electrode/electrolyte interface in supercapacitors - one of the priority topics established by the European Commission (C(2012)4536 of July 2012).
- ✓ Improved power response by mutually adapting electrolytes and electrode materials
- ✓ Using alternative abundant inexpensive and local raw material - olive pits

3. Methodology and Work Plan

- Task 1. Preparing microporous and micro/mesoporous carbons with variable porosity optimized for specific electrolytes.
- Task 2. Physicochemical characterization of the microporous carbons.
- Task 3. Electrochemical characterization in various electrolytes:
  - Task 3.1 Aqueous alkali electrolyte
  - Task 3.2 Organic electrolyte
  - Task 3.3 Neutral aqueous electrolyte
  - Task 3.4 Ionic liquid electrolyte
- Task 4. Study of the electrode-electrolyte interactions
- Task 5. Maximizing the electrochemical performance of supercapacitors
- Task 6. Writing of the doctoral thesis.

Task/Month	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
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Task/Month	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
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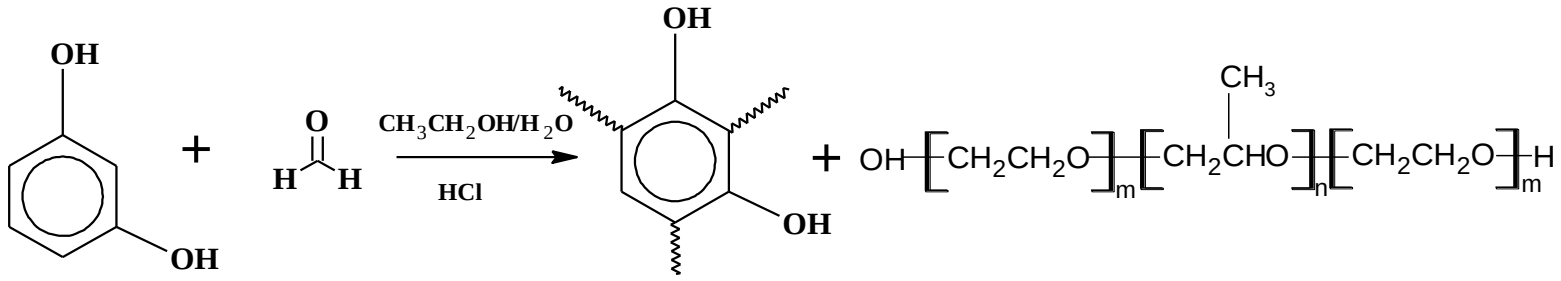
4. Results – Synthesis of micro/mesoporous carbons

Micro/mesoporous carbons with ordered or disordered mesopores[4]

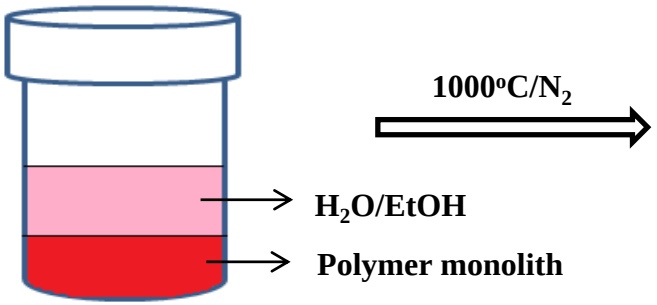


Resorcinol **Formaldehyde** **RF resin** **F127-Triblock copolymer**

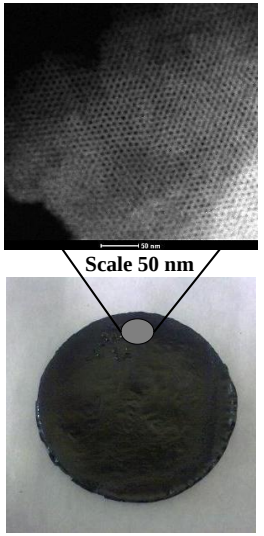
Order/disorder is regulated by the resorcinol/formaldehyde (R/F) ratio

i) R/F = 1 ordered and straight mesopores

ii) R/F= 2 disordered and tortuous mesopores



Hydrothermal treatment 50ºC

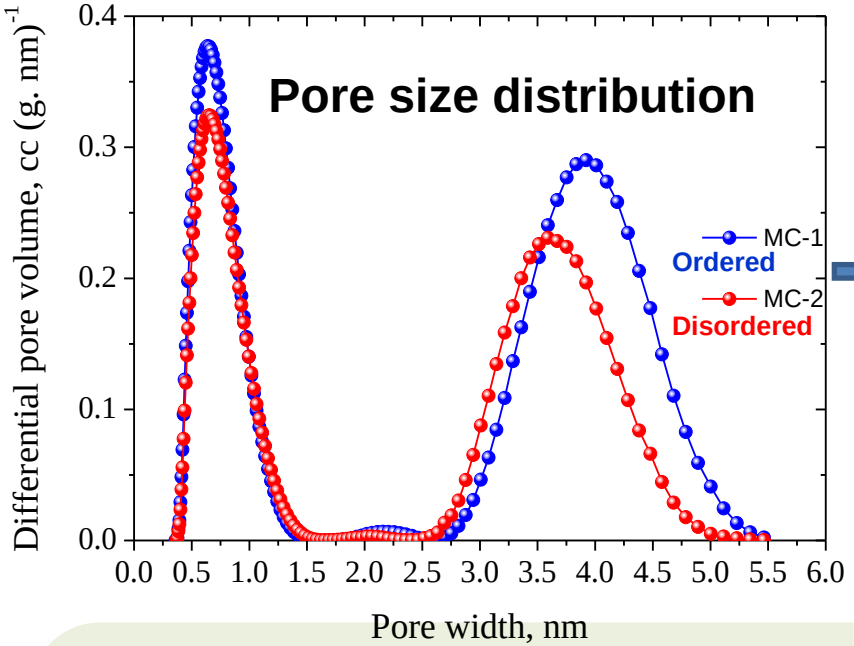


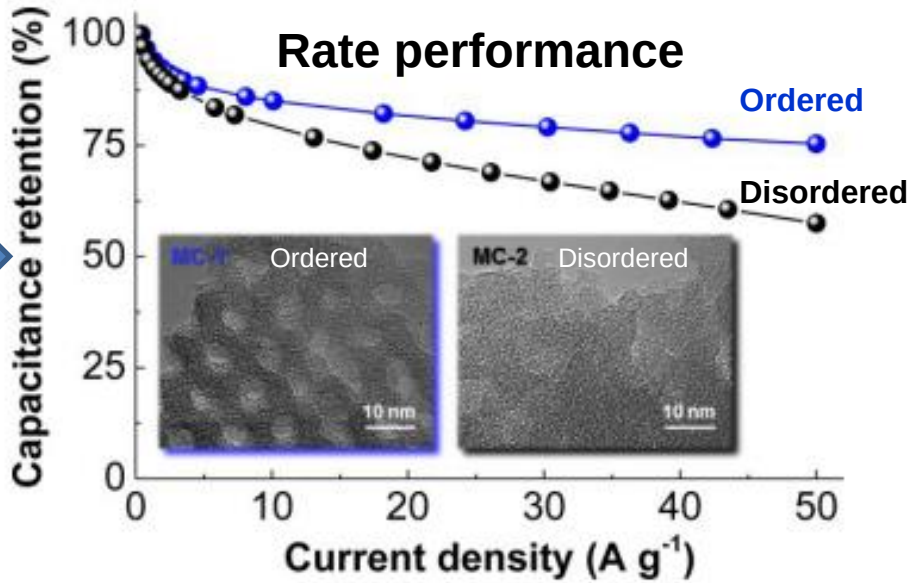
Mesoporous carbon monolith

[4] M. Karthik, E Redondo et al., *Energy Env Focus*, 2015, 3, 201.

4. Results – Textural properties & Morphology – Phenolic resin carbon

Mesopore Order vs High-Rate Performance of Electric Double-Layer Capacitors[5]





- The same precursors
- Similar electrical conductivity, S cm^{-1} : 21.03 (ordered) and 17.96 (disordered),
- The same micropore size distribution
- Similar mesopore size distribution
- **Rigorous conditions provided to study the effect of mesopore shape**

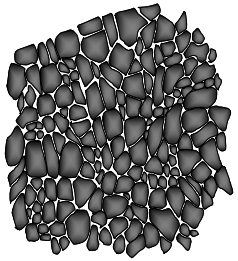
- **Increasing the rate capability in straight mesopores despite their size >> the size of ions**

[5] **M. Karthik, E.Redondo *et al.*, *J.PhysChem C,* 2014, 118, 27715.**

4. Results – Textural properties & Morphology – Olive pits carbons

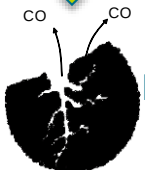
Precursor:
olive pits

Carbonization
(600 - 900ºC)



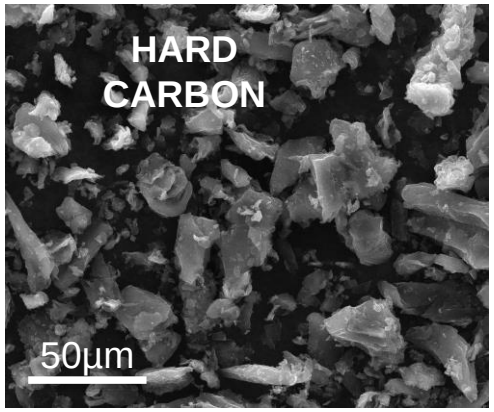
HARD CARBON

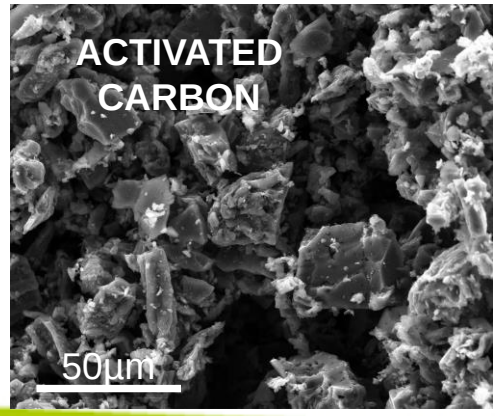
KOH activation
(600 - 900ºC)



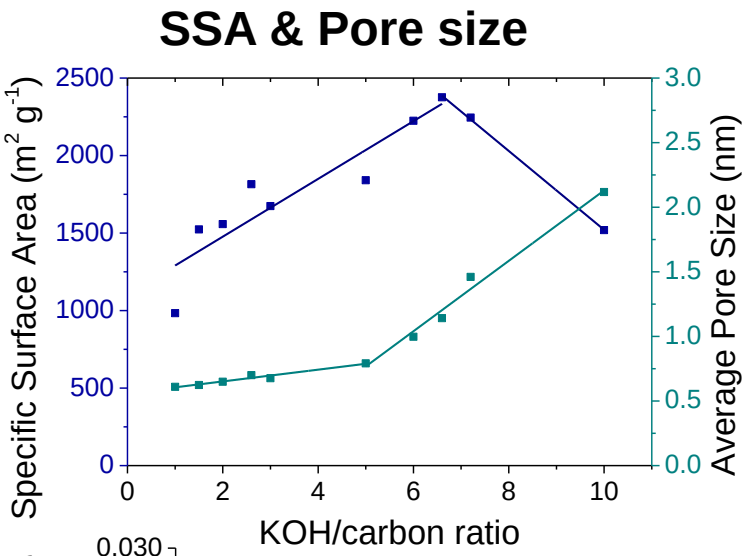
MICROPOROUS CARBON

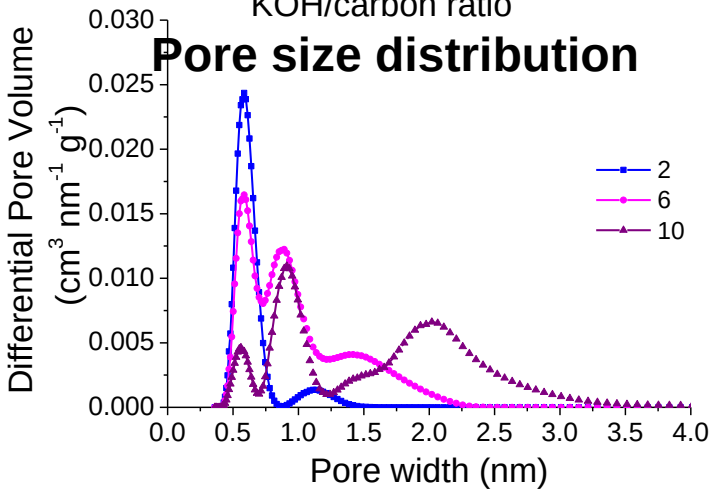
Morphology: carbon char & porous carbon





Textural properties vs KOH/C ratio

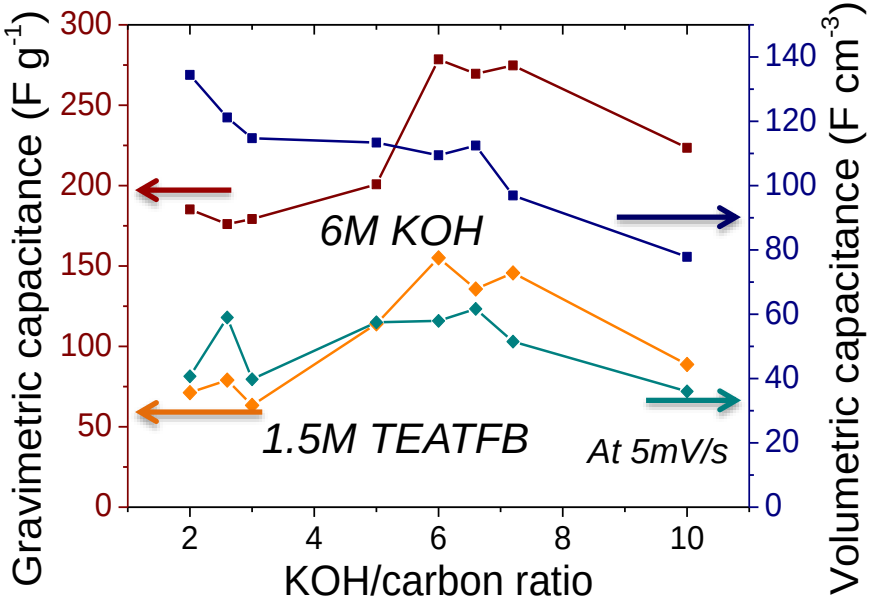




[6]E. Redondo *et al., Electrochimica Acta,* 2015, 160, 178.

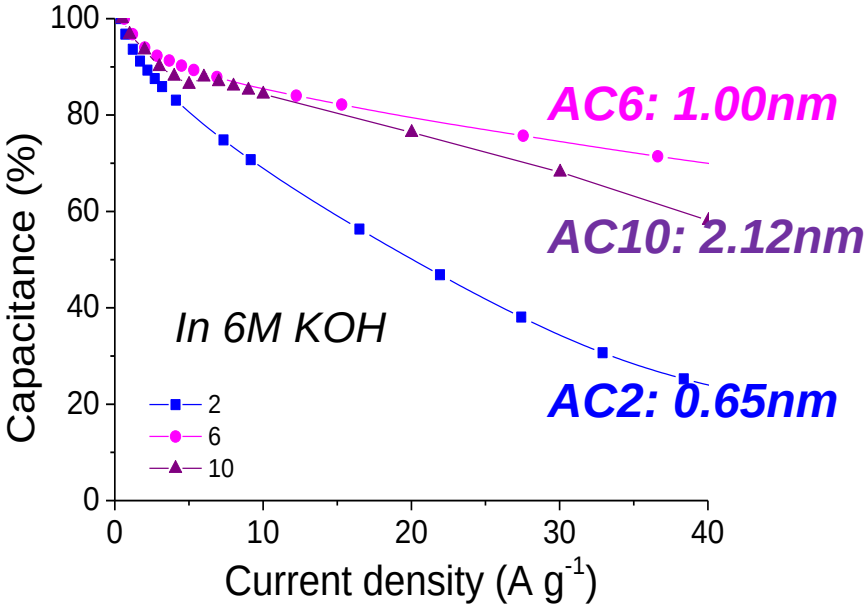
4. Results – Summary of supercapacitor performance

Capacitance vs KOH/C ratio



- High SSA → High gravimetric capacitance
- Low KOH loading → Higher volumetric capacitance

Capacitance vs current



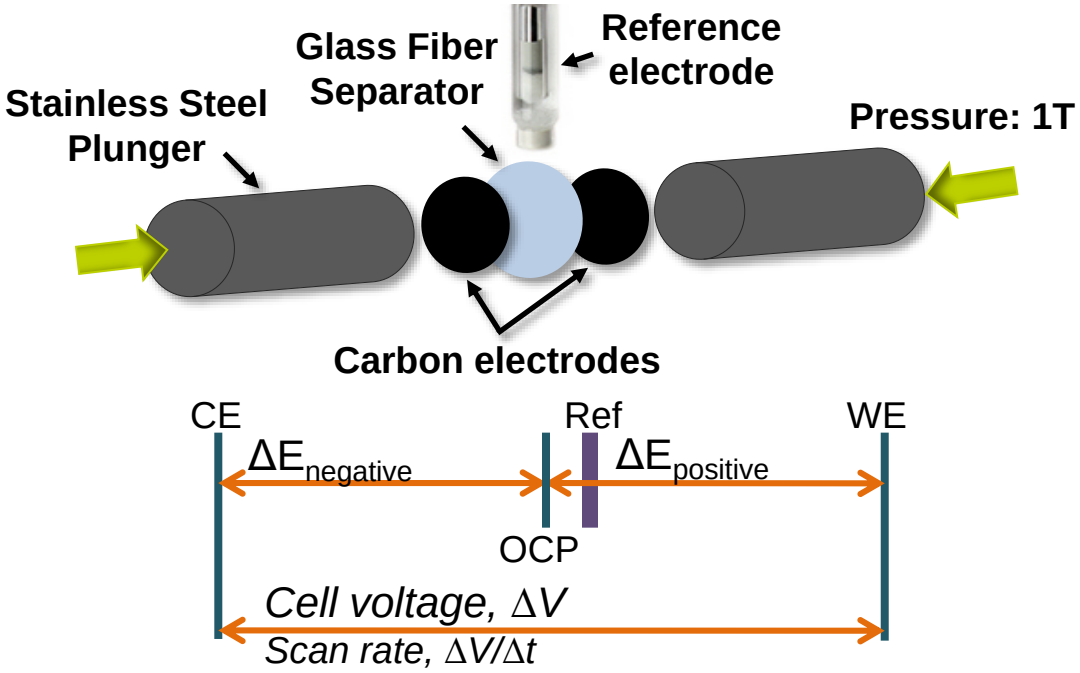
- Adjusting the pores to the electrolyte improves capacitance retention.

[6]E. Redondo *et al., Electrochimica Acta,* 2015, 160, 178.

4. Results – Study of each separate electrode in a full symmetric cell

Electrochemical performance by each electrode

Symmetric two-electrode cell with reference



i) Cell voltage is controlled, not the potential difference between the positive and Ref

ii) Potential evolution of each electrode can be monitored with a reference electrode

[6]E. Redondo *et al., Electrochimica Acta,* 2015, 160, 178.

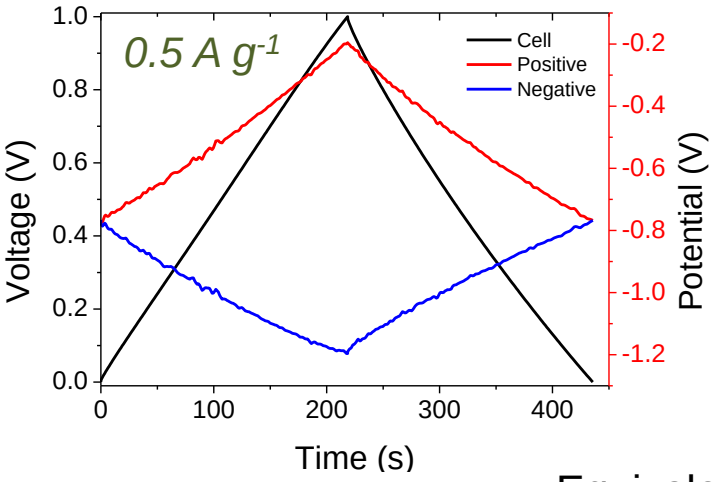
4. Results – Aqueous electrolyte 6M KOH

Charge dynamics by each electrode in KOH (6M)

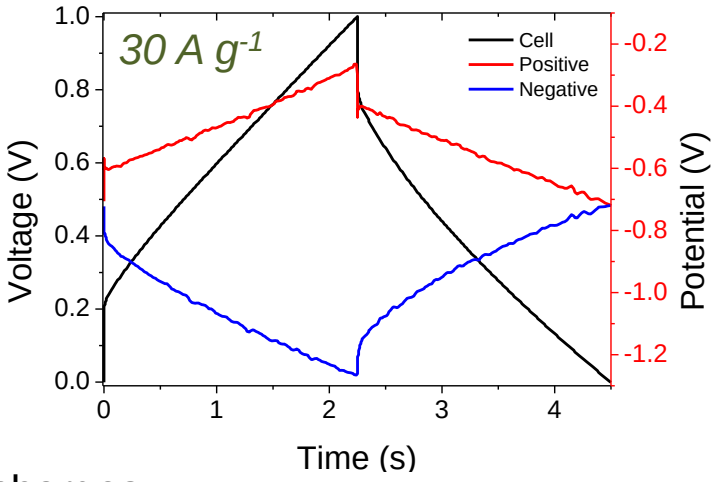
Wide pore size distribution - Unrestricted accessibility

Sample6
APS 1.00nm

Low current



High current



Equivalence of charges

$$\frac{C_-}{C_+} = \frac{\Delta E_+ m_+}{\Delta E_- m_-}$$

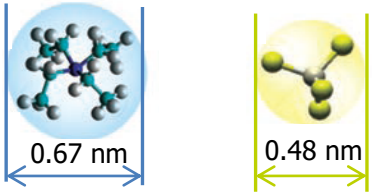
- ✓ At low current $\Delta E_- < \Delta E_+ \Rightarrow C_- < C_+$
- ✓ At high current $\Delta E_+ < \Delta E_- \Rightarrow C_- > C_+$

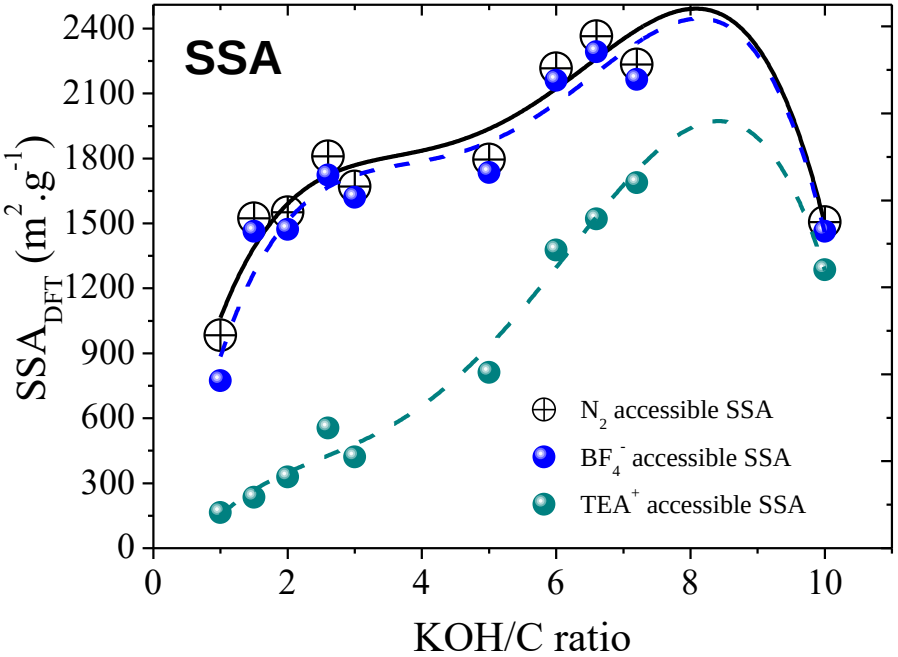
- *The positive electrode has the higher capacitance at the high current density.*

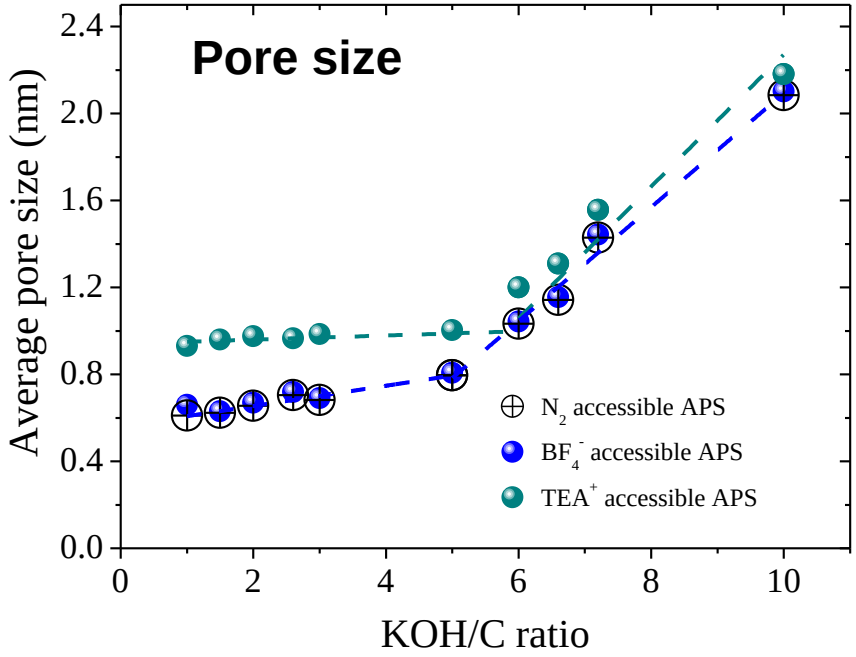
[6] **E. Redondo *et al.*, *Electrochimica Acta*, 2015, 160, 178.**

4. Results – Texture vs accessibility to organic electrolyte

SSA and pore size in Et_4NBF_4 (1.5ᴍ)





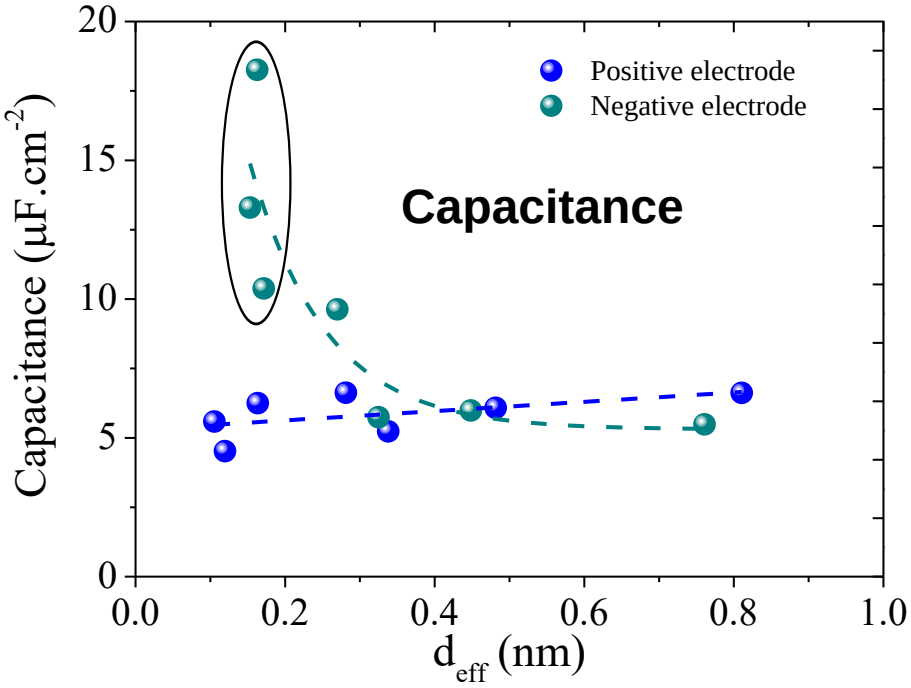


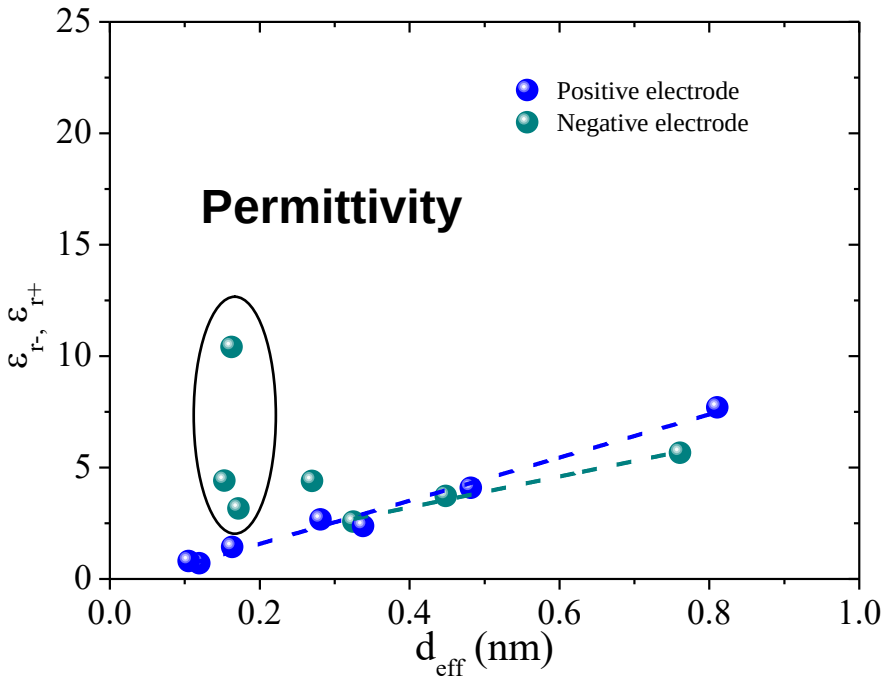
- N_2 and cation- accessible SSA and average pore size exhibit difference, especially for subnanometer pores.
- SSA and average pore size can be systematically underestimated in the subnanometer pore size region for cations if no correction for accessible porosity is applied

[7] **E. Redondo *et al.*, *under review in J Power Sources***

4. Results – Areal capacitance vs and permittivity in organic electrolyte

Capacitance and permittivity in pores of separate electrodes





- Areal capacitance is enhanced in the subnanometer pores for the negative electrode only
- Dielectric permittivity exhibits a linear trend with d_{eff} (like in aqueous electrolyte) except for the narrowest subnanometer pores in the negative electrode, leading to the capacitance increase

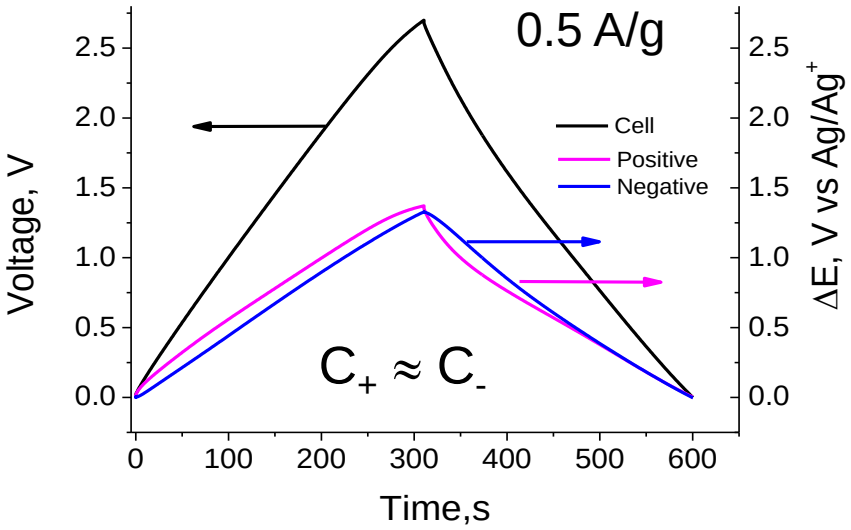
[7] E. Redondo *et al., under review in J Power Sources*

4. Results – Charge dynamics of separate electrodes

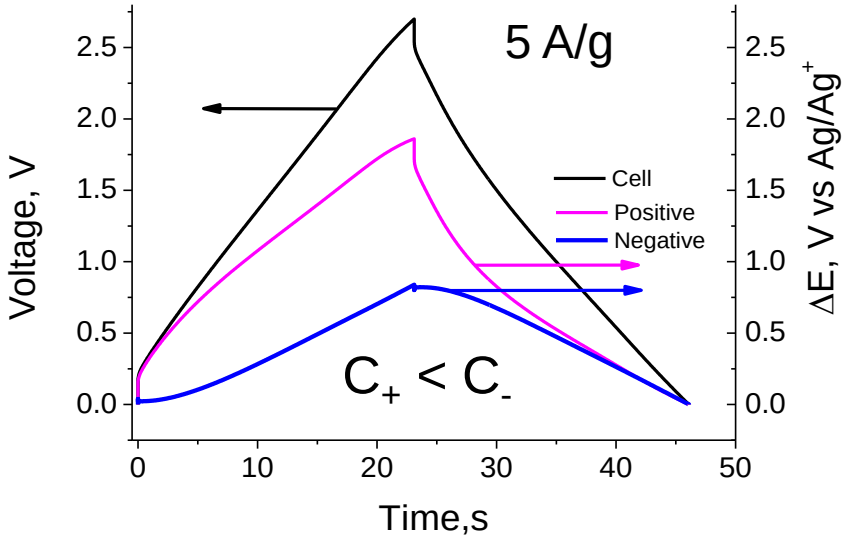
Electrochemical performance by each electrode for wide micropore size distribution

PORE SIZE
Et_4N^+ accessible/ BF^-_4 accessible
1.56 nm / 1.44 nm

Low current



High current

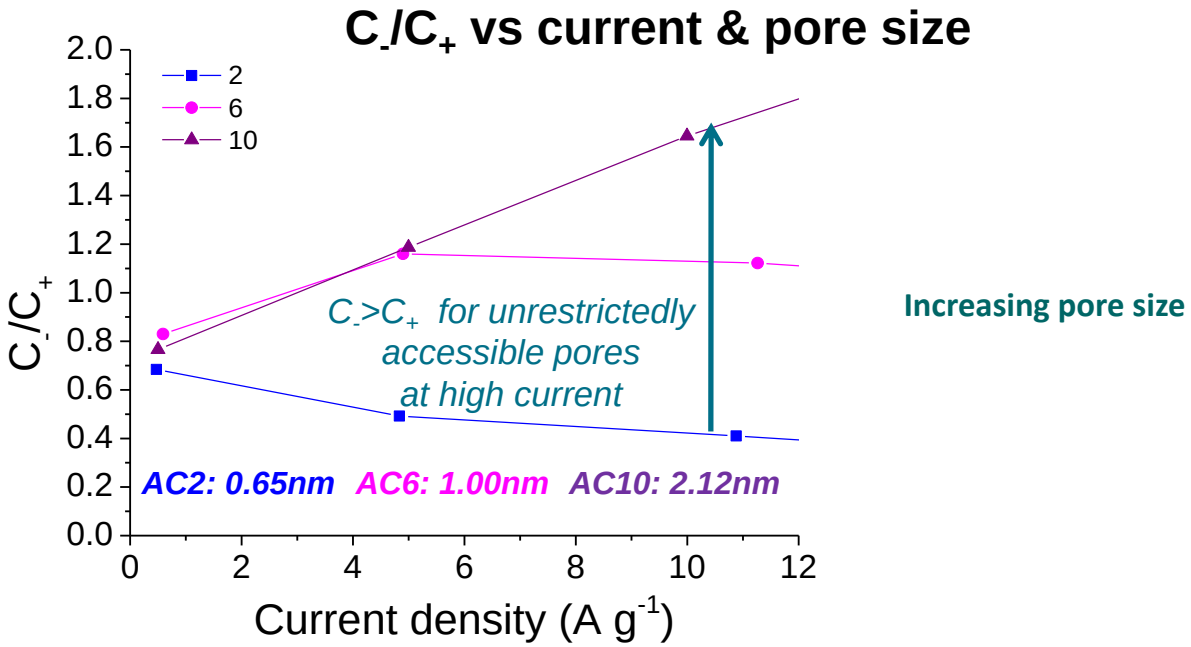


- Under unrestricted adsorption, the capacitance of the negative electrode exceeds that of the positive.

[7] E. Redondo *et al., under review in J Power Sources*

4. Results – Summary of rate response by separate electrodes

Electrochemical response by electrode in Et_4NBF_4 (1.5M)



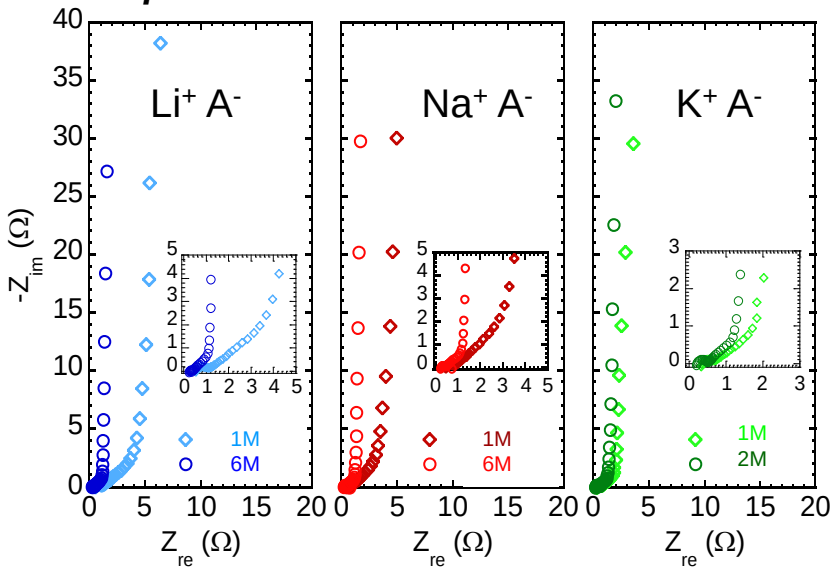
- In Et_4NBF_4(1.5M), $C_-/C_+<1$ at low rates → stable conditions for BF_4^-.
- At high rates C_-/C_+ depends on the porosity:
  - ✓ $C_- < C_+$ pores are too narrow to be fully accessible to cations
  - ✓ $C_- < C_+$ similar capacitance retention when pore size approaches solvated ion size
  - ✓ $C_- < C_+$ in wide pores, the negative electrode has higher high-current capacitance

[7] E. Redondo *et al., under review in J Power Sources*

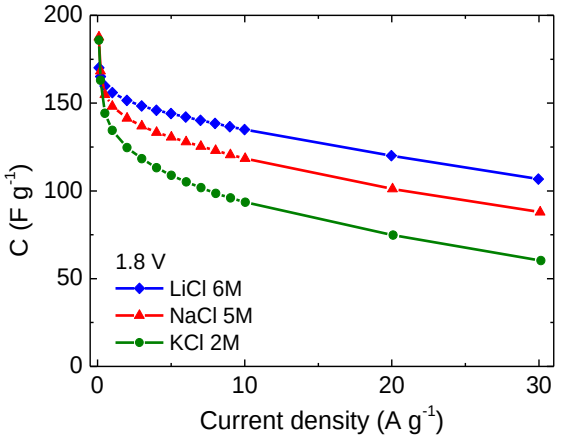
4. Results – Concentration of neutral salts electrolytes[8]

Electrochemical response in LiCl, NaCl and KCl (aq)

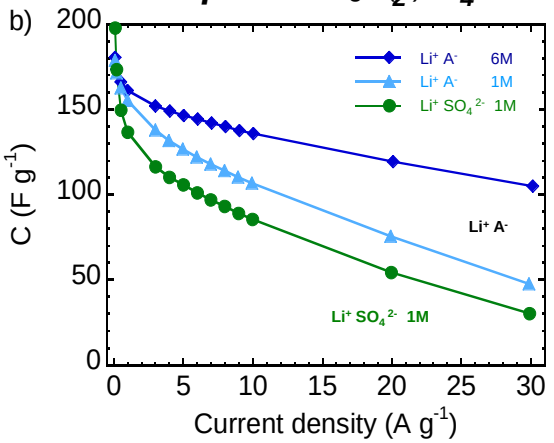
Optimum concentration



By cation



Compared to Li_2SO_4



- ✓The effect of electrolyte concentration is reflected on capacitance retention and cell resistance.
- ✓Stable operation of symmetric cells is evidenced at 1.6 V

[8] E. Redondo *et al., manuscript pending to be submitted*

5. Conclusion

- *Synthesis conditions optimized to produce nanoporous carbons for supercapacitors from inexpensive renewable material → allowing fine-tuning the porosity of carbons to specific electrolytes.*

- *The highest capacitance values are 280 F/g and 135 F/cm^3 in 6M KOH aqueous electrolyte and 155 F/g and 60 F/cm^3 in 1.5M Et_4NBF_4 /ACN organic electrolyte.*

- *For carbons providing the most unrestricted electrolyte access, the **negative** electrode limits the overall capacitance retention at high current **in 6M KOH (aq)** while the **positive** electrode is the limiting one in **1.5M Et_4NBF_4/AN***

- *Ions need to be almost fully **solvated** for rapid ion transport in the pores of this particular series of carbons **in 1.5M Et_4NBF_4/AN**, but an optimum pore size appears to exist with regard to rate response: too wide pores can deteriorate capacitance retention at the positive electrode.*

6. Acknowledgments

- Funding from the Basque Government under the Etortek Energigune'12 Program and Elkartek 2015.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research centre
Eskerrik asko zuen arretagatik!
¡Gracias por vuestra atención!
Thank you for your attention!