Centre de Recherche sur la Matière Divisée

Institut de Science des Matériaux de Mulhouse

HIPASCAP

High Power Asymmetric SuperCAPacitor in organic electrolyte

Supercondensateur asymétrique de haute puissance en milieu organique

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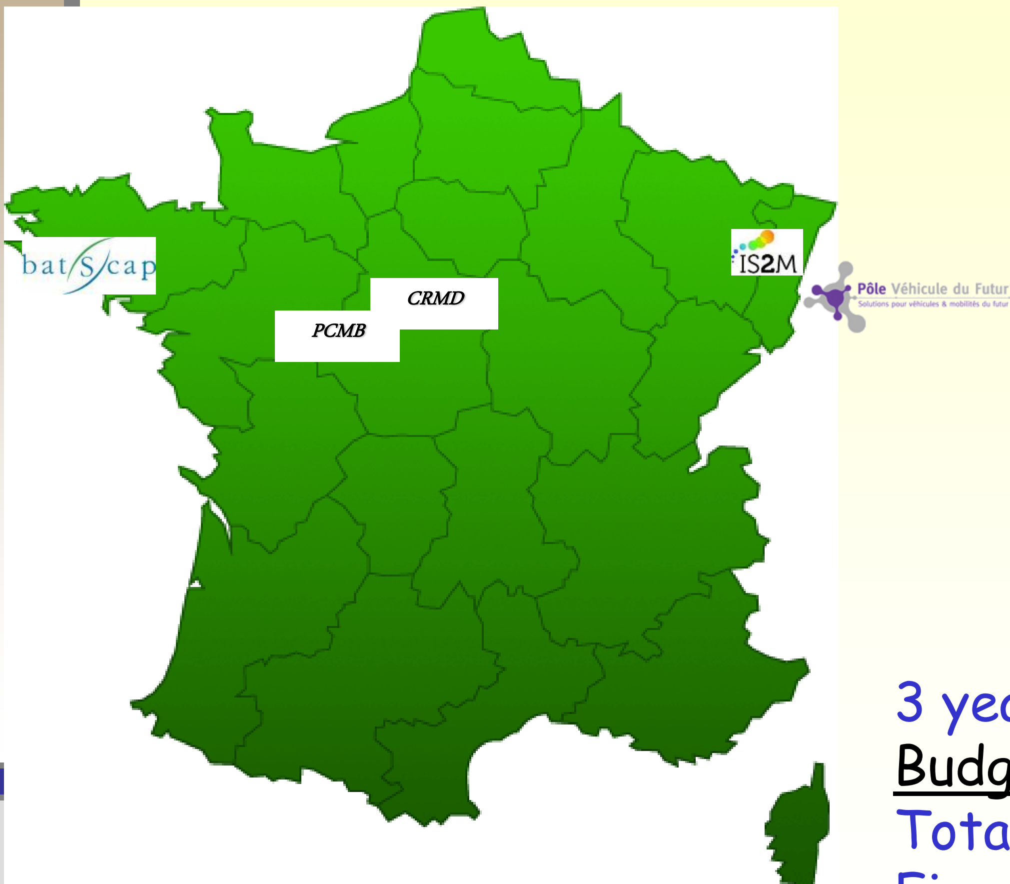
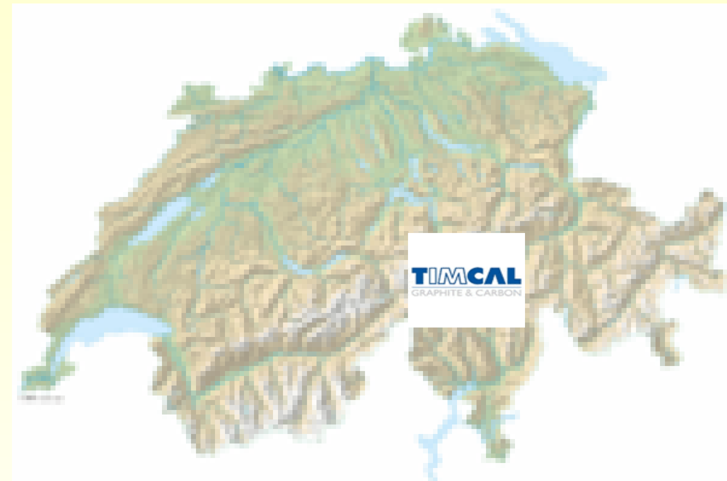
Chimie-Physique des Interfaces et des Milieux Electrolytiques

HIPASCAP Project:

3 Academic Laboratories – 2 Industrial Partners – 1 Competitivity center (Future Vehicle)





Suisse

3 years 2009/2012

<u>Budget</u>

Total 1.781 M€

Financial aid 0.761 M€ (34%)

Objective of the HIPASCAP Project:

Stock-E :
Electrochemical energy storage – Supercapacitors

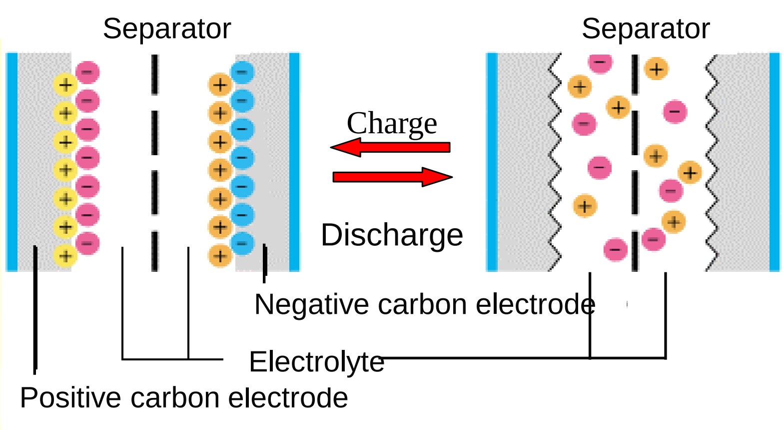
Develop a new and optimized asymmetric capacitor involving two different carbon electrodes (graphite for the negative electrode, activated carbon for the positive electrode).

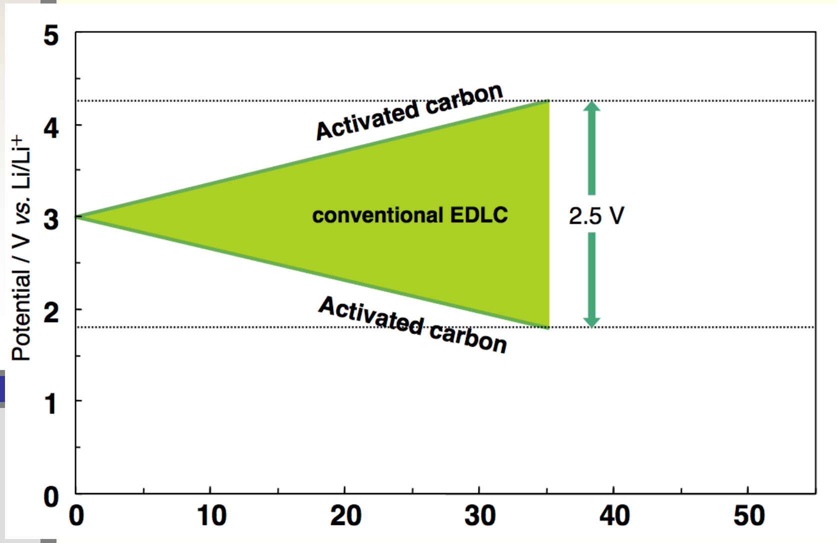
Scientific challenges
Realize asymmetric systems in organic electrolyte having a better energy density than symmetric EDLCs (good power density and cyclability)
High performance asymmetric capacitor with all security requisites

Technological challenges
Build asymmetric laboratory cells - engineer demonstration cells

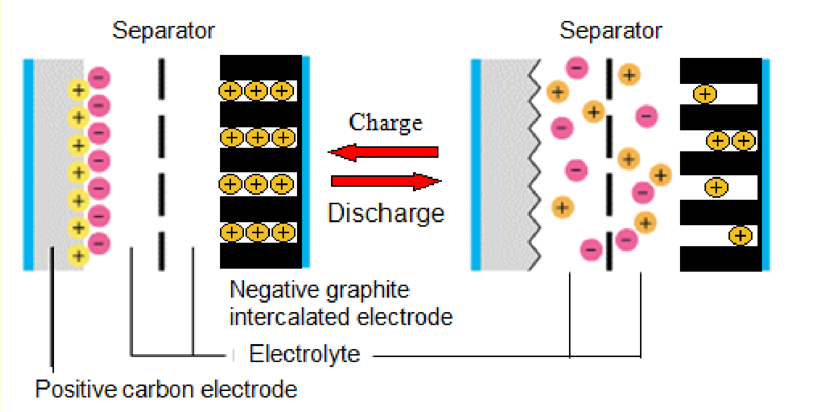
Asymmetric capacitor vs. EDLC

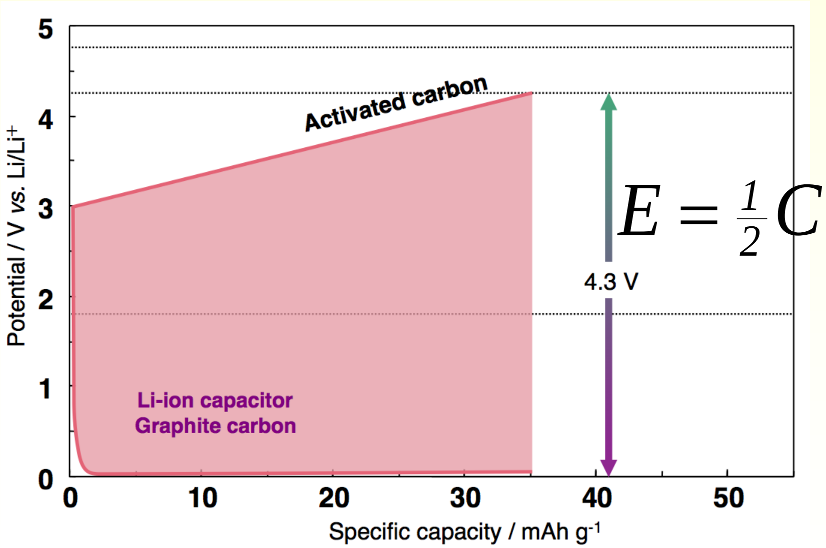
EDLC





Hybrid capacitor





$$E = \frac{1}{2} C U^2$$

K. Naoi in "Electrochemical capacitors: materials, systems and applications", F. Béguin & E. Frackowiak eds, John Wiley (in press)

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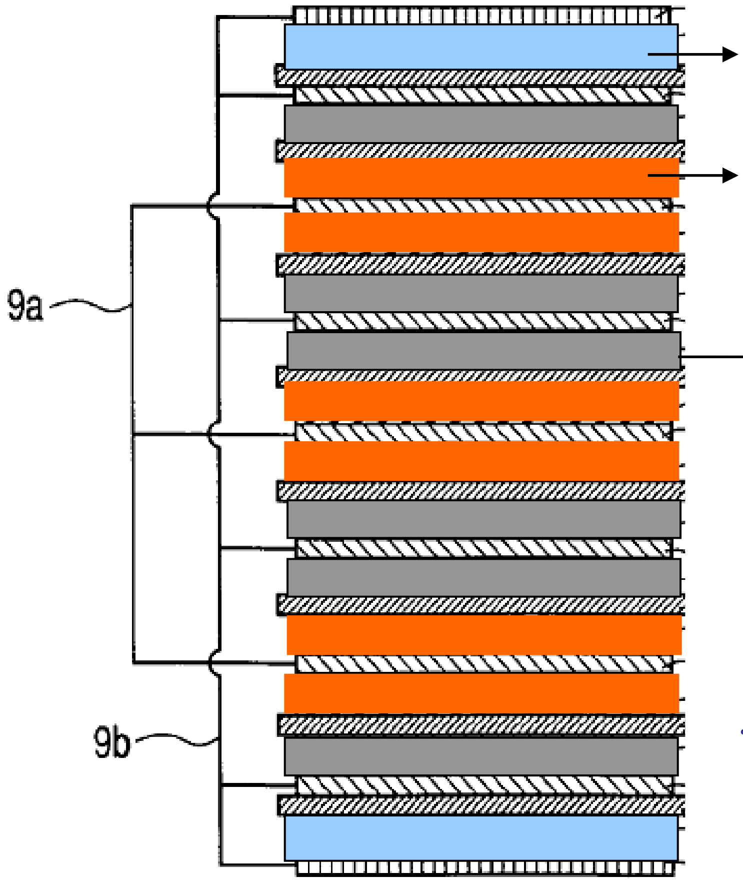
The Li-ion capacitor*



Li foil → To pre-dope graphite

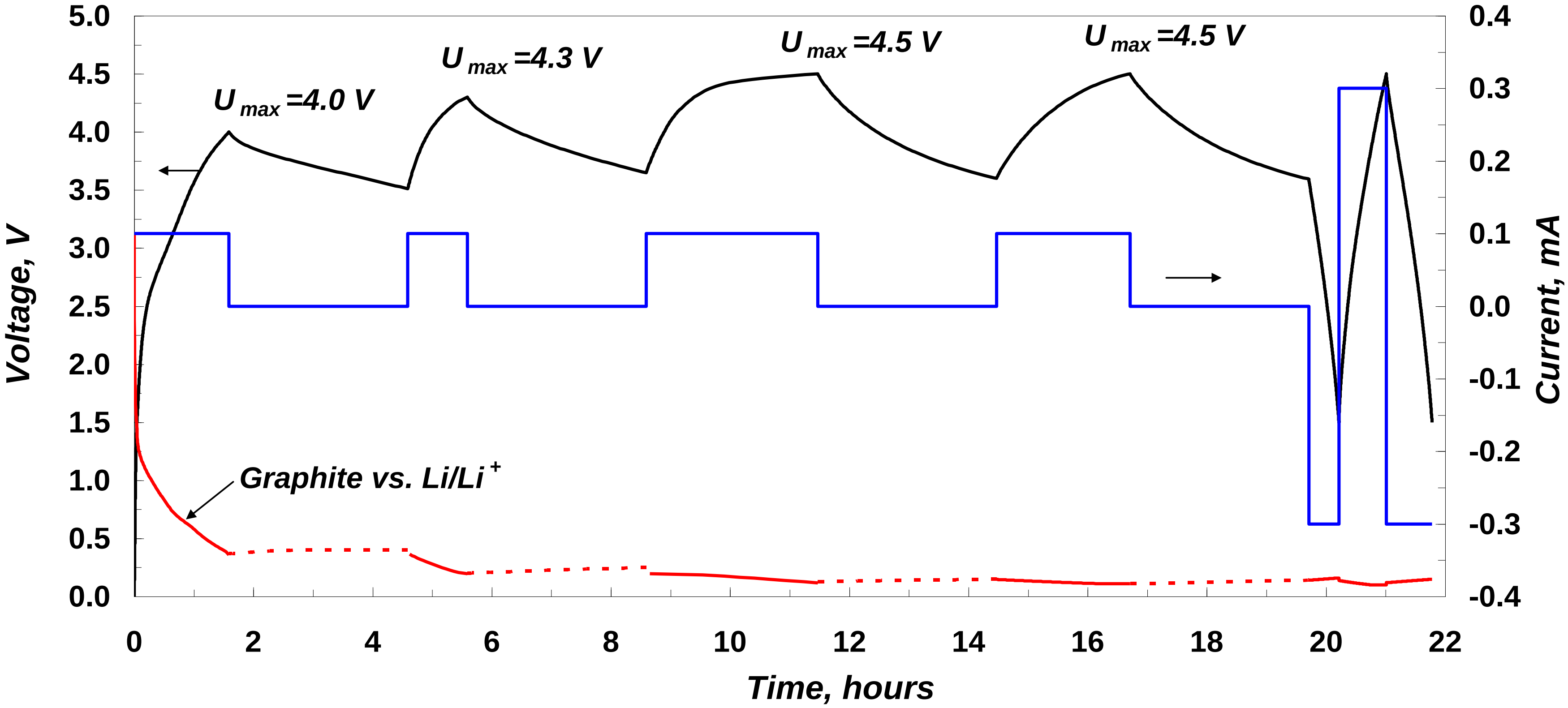
Positive electrode (Porous Carbon)

Negative electrode (Graphite)

HIPASCAP Objective:
To develop a safe Li-metal **FREE** hybrid capacitor

*Fuji Heavy Industry patents: EP1400996A1 (2002); WO2006112068A1 (2006); US2007/0002524A1 (2007) ; EP1914764A1 (2007); etc

Li-metal free hybrid AC/graphite system*



Li from the electrolyte (1 mol.L^{-1} $LiPF_6$ in EC/DMC) is progressively intercalated in the graphite electrode through formation cycles, allowing a further linear charge/discharge profile

*V. Khomenko, E. Raymundo-Pinero, F.Béguin, J. Power Sources 177 (2008) 643

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Objectives

Up-scaling the high energy AC/graphite capacitor from laboratory to industrial type cells

Technological and scientific difficulties to overcome:

- Designing an appropriate electrolyte compatible with both types of electrodes/current collectors, and having enough high amount of Li ions
- Designing of activated carbon and graphite for high power operation and long cycle life
- Conditioning of the cells by adapted “formation cycles”

Outline

1- Choice of the electrolyte

2- Electrochemical characterisation of the positive electrode

3- Electrochemical characterisation of the negative electrode

4- Development and performance of the hybrid AC/graphite supercapacitors

1- Choice of the electrolyte

Lithium salt

$LiPF_6$:
High conductivity
Low solubility
LiTFSI :
Good thermal stability
Better solubility

Non Toxic Solvent

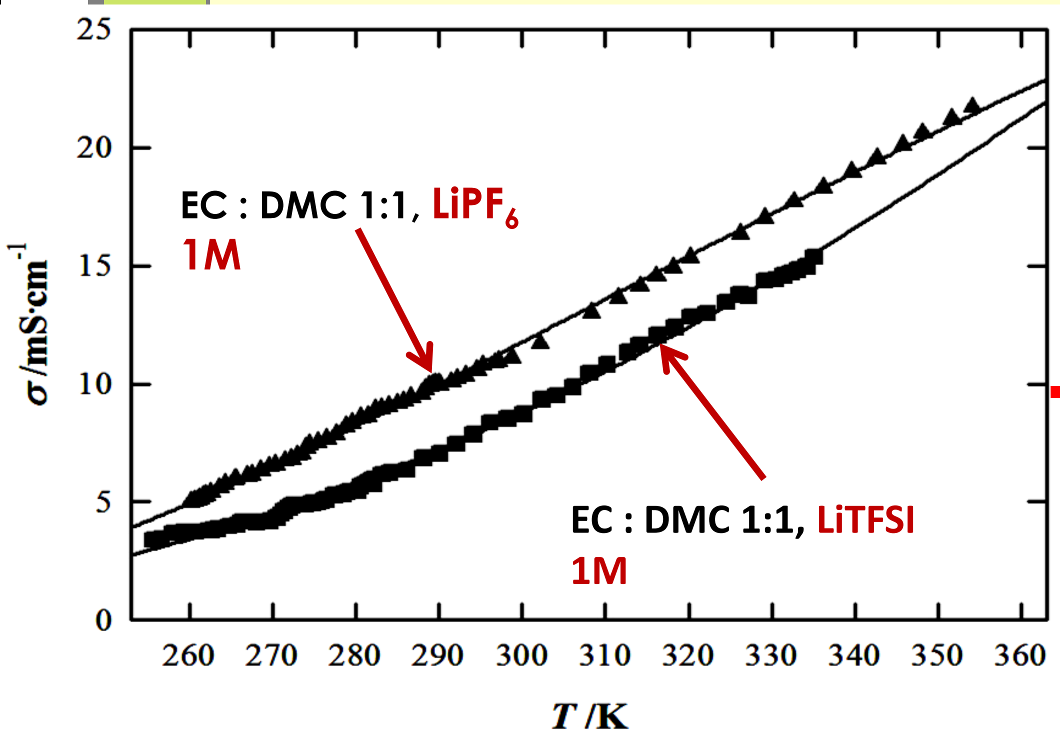
alkyl carbonates

EC :
Good Solid Electrolyte Interface (SEI) formation
DMC :
Low viscosity

Usual Current Collectors

Cu for the negative electrode
Al for the positive electrode

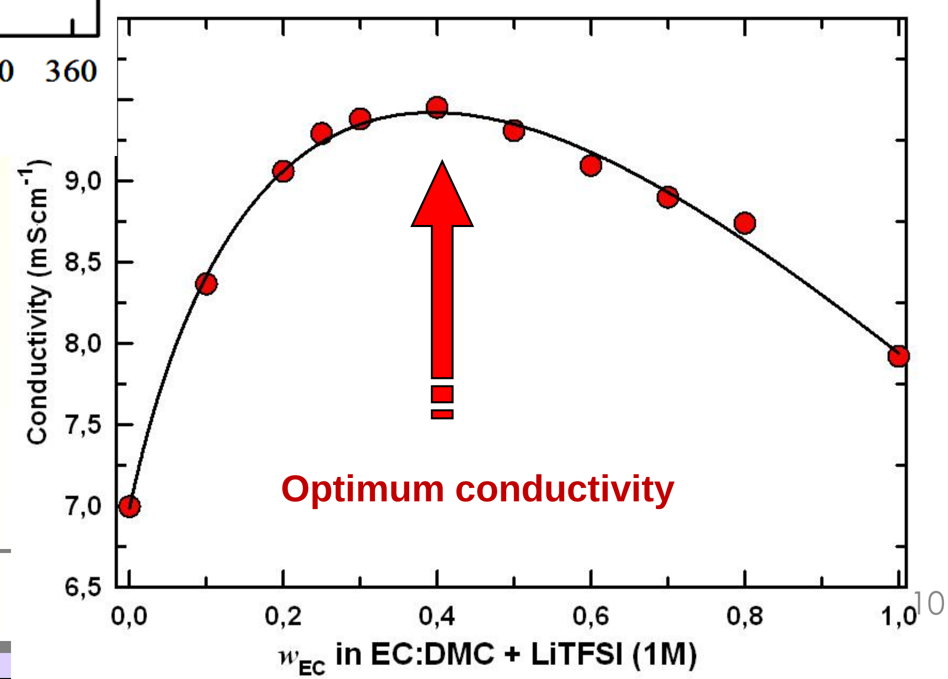
Electrolyte concentration and conductivity



EC : DMC 1:1, **$LiPF_6$ 1M**
Conductivity = **10.4 mS.cm^{-1}**
EC : DMC 1:1, **LiTFSI 1M**
Conductivity = **9.3 mS.cm-1**

$\sigma_{(LiTFSI)} \sim \sigma_{(LiPF_6)}$

Optimum conductivity for 1 mol L^{-1} concentration and 0.4:0.6 EC:DMC



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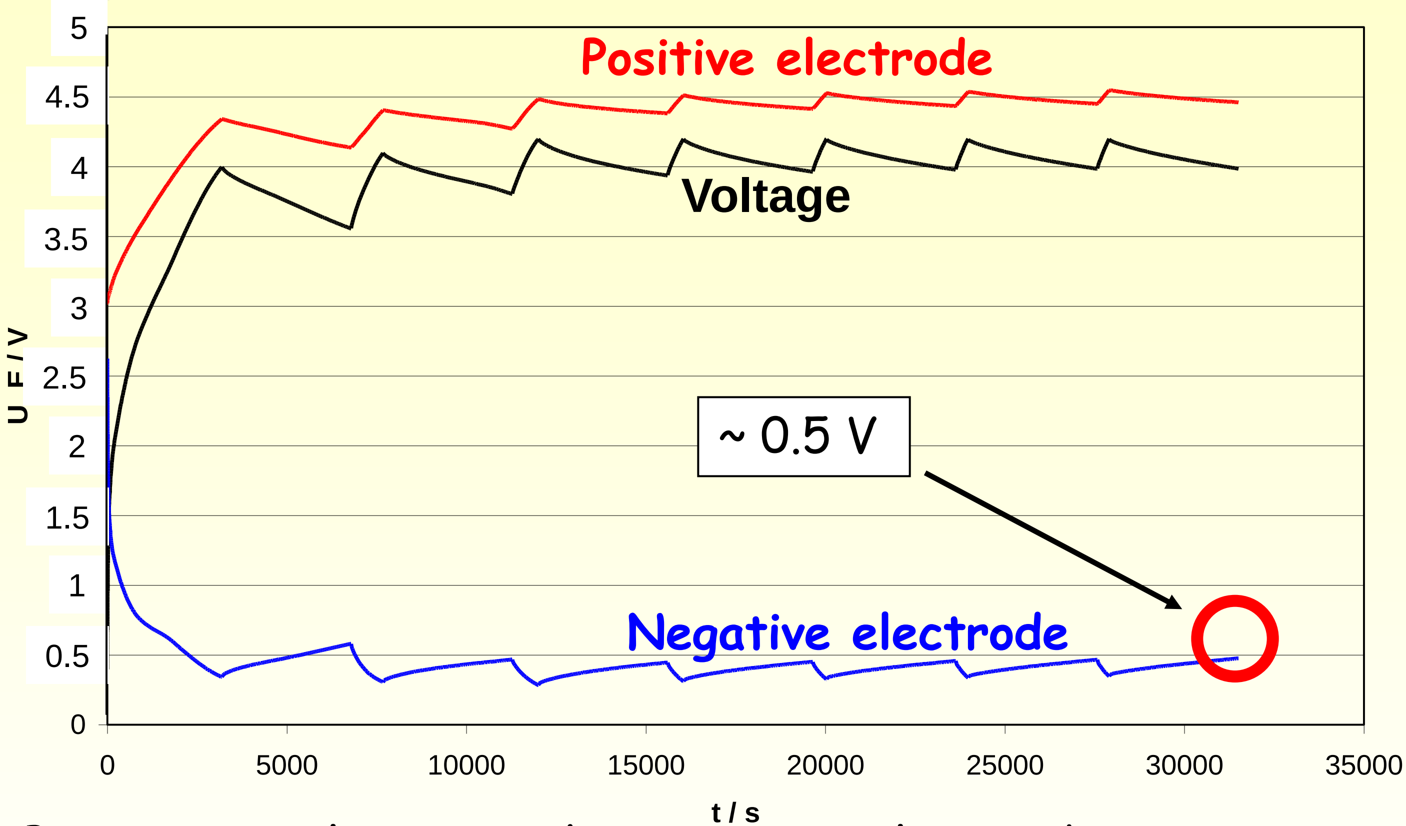
Graphite lithiation: ACref/SLP30 in 1 mol.L^{-1} $LiPF_6$

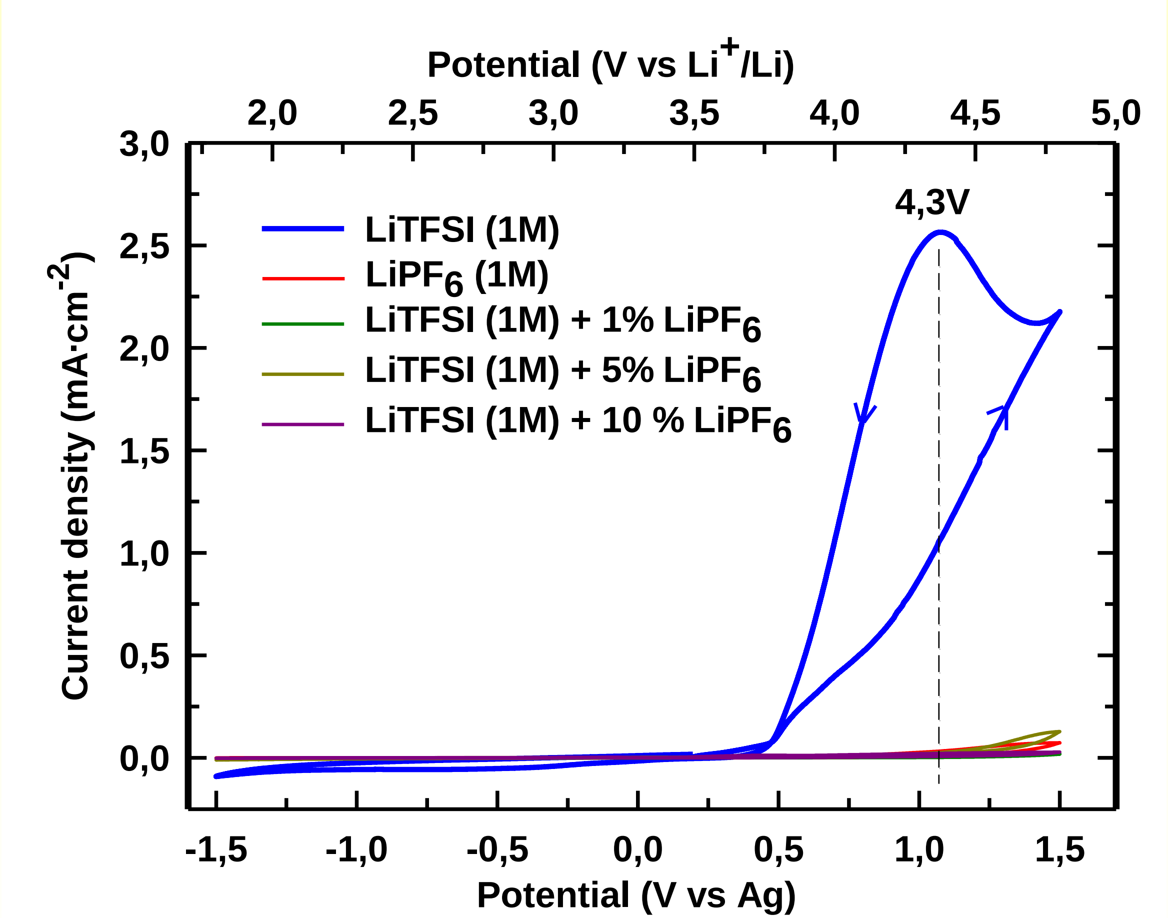


Poor intercalation in the negative electrode

Considering the mass of graphite and the electrolyte volume introduced, 80% of available Li^+ would be needed to reach LiC_{12}

➡ To use an electrolyte containing 2 mol.L^{-1} of LiTFSI

Electrochemical stability of aluminium

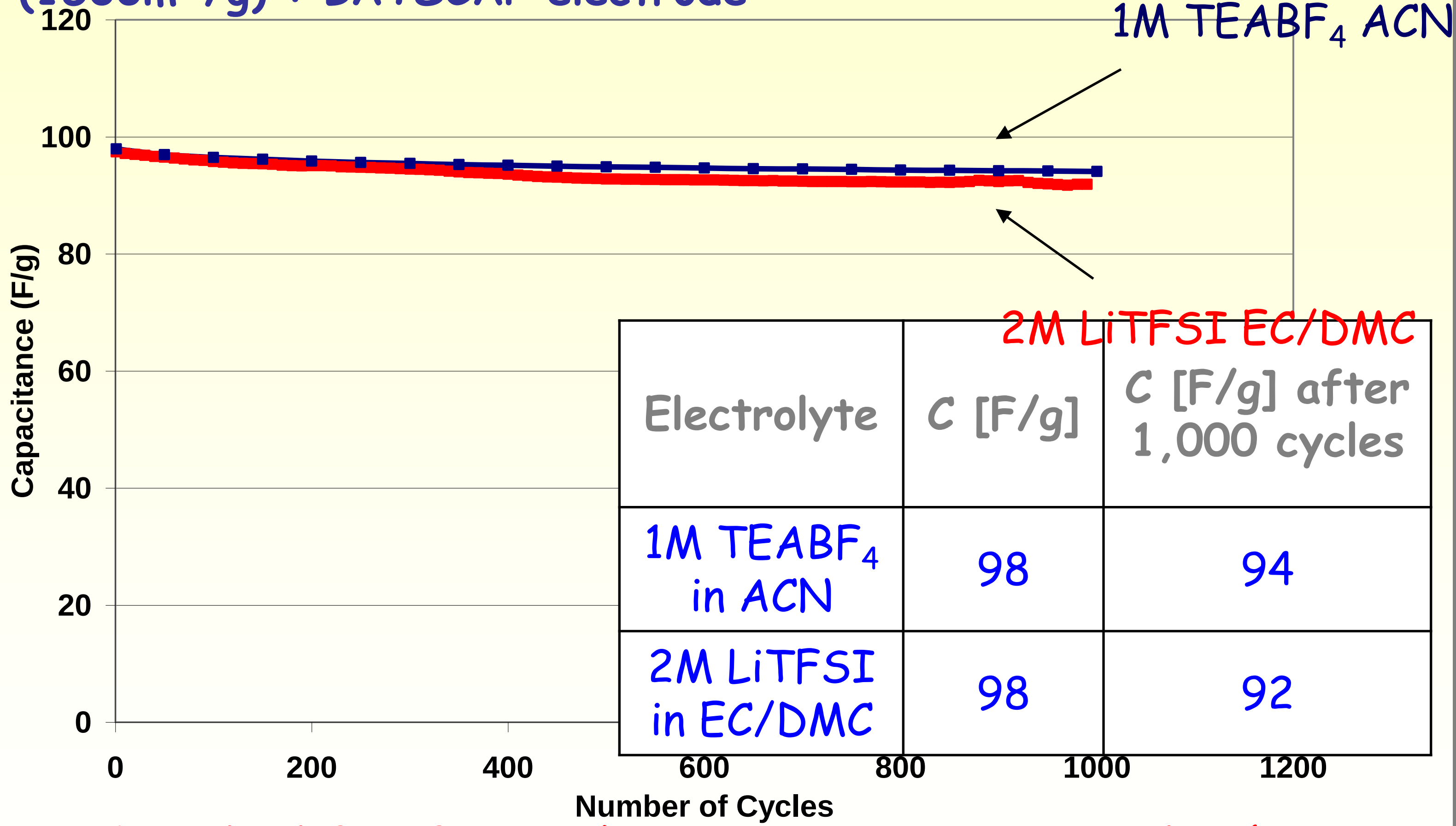


Maximum potential with Al current collector and LiTFSI: 4.2 V

2- Electrochemical characterisation of the positive electrode in AC/AC capacitor

Galvanostatic cycling: I = 0.65 A/g up to 2.5V

ACref (1500m²/g) : BATSCAP electrode



Electrolyte	C [F/g]	C [F/g] after 1,000 cycles
1M $TEABF_4$ in ACN	98	94
2M LiTFSI in EC/DMC	98	92

Good cycle-life of AC_{ref}/AC_{ref} capacitor in 2 $mol.L^{-1}$ LiTFSI EC/DMC

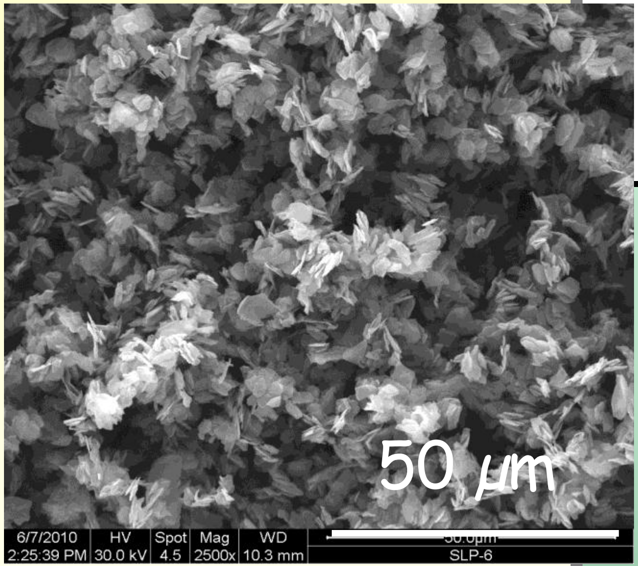
3- Electrochemical characterisation of the negative electrode

❖ **Small particle size**

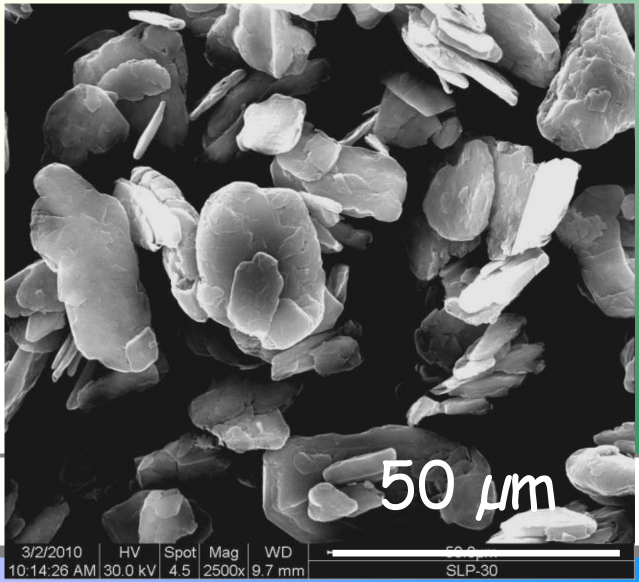
→ Coating thickness ~ 40µm

Graphite	S_{BET} (m^2/g)	Particle size D90 (µm)
SLP-6	15.5	6
SLP-30	6	31

SLP-6



SLP-30



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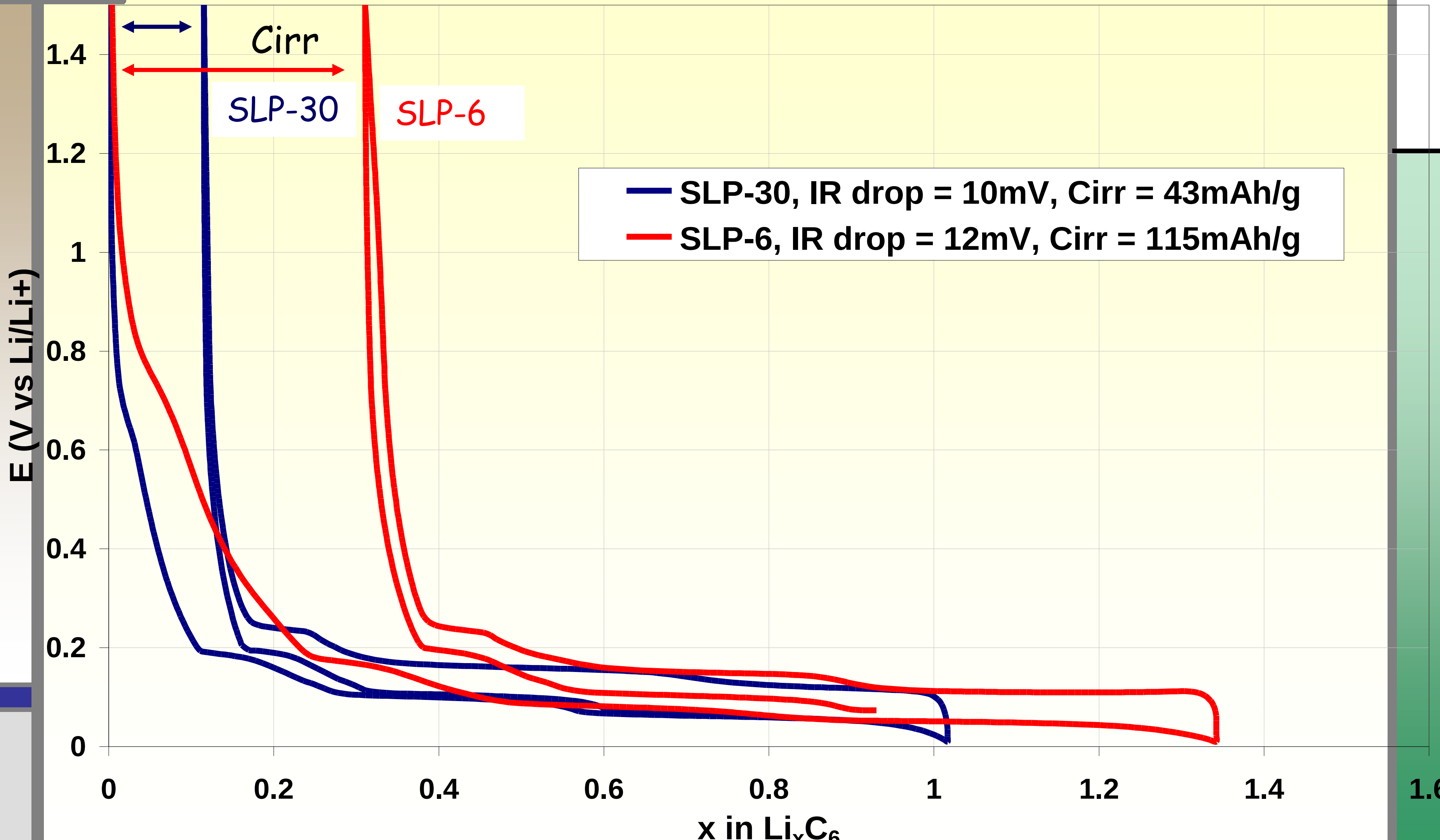
Galvanostatic profiles of graphites in 2 mol L^{-1} LiTFSI



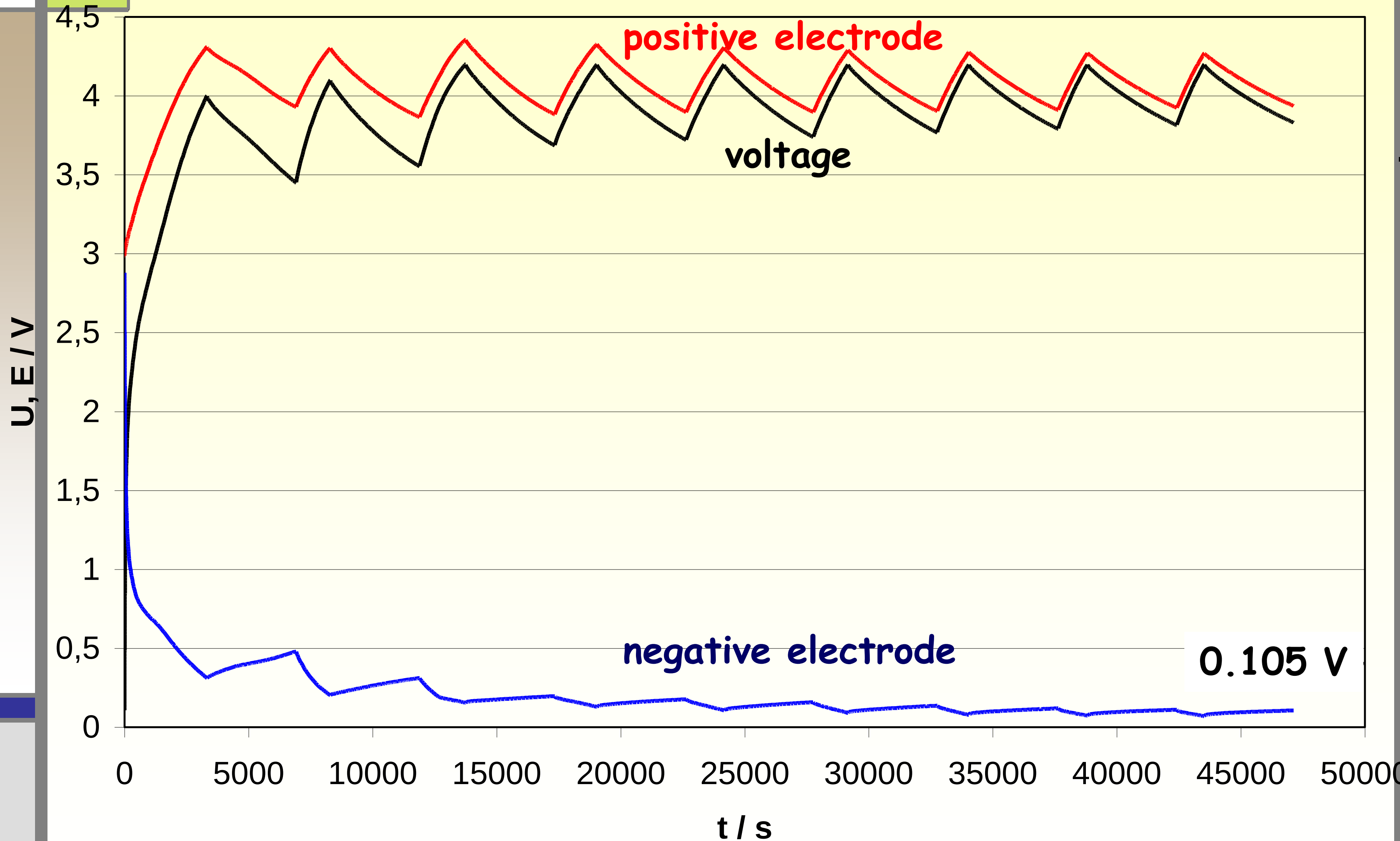
→ Smaller irreversible capacity for SLP-30

4 - Development and performance of hybrid supercapacitors

- Positive electrode : AC_{ref} BATSCAP electrode
- Negative electrode : SLP-30
- Reference for 3-electrode cell : Li metal
- Electrolyte : 2 mol L^{-1} LiTFSI in EC/DMC

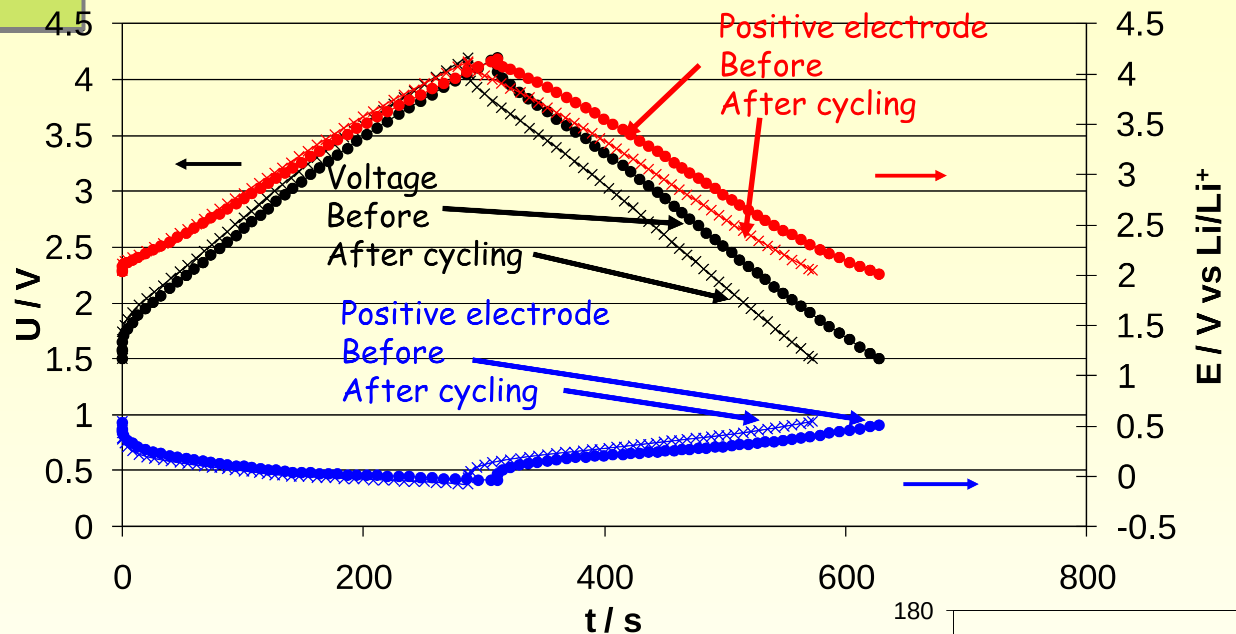
- GIC formation cycles : C/10 at stepwise increasing voltage
- Galvanostatic cycling at 650 mA/g from 1.5 to 4.2V

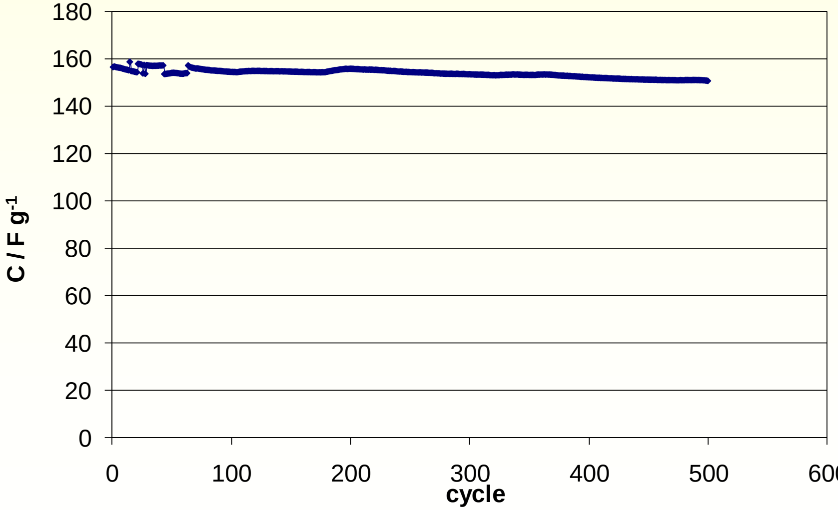
SLP-30 lithiation from LiTFSI in 3-electrode cell



Formation cycle is stopped when E^- ~ 0.100V (~ LiC_{12})

Cycling of the SLP30/ACref hybrid up to U = 4.2 V





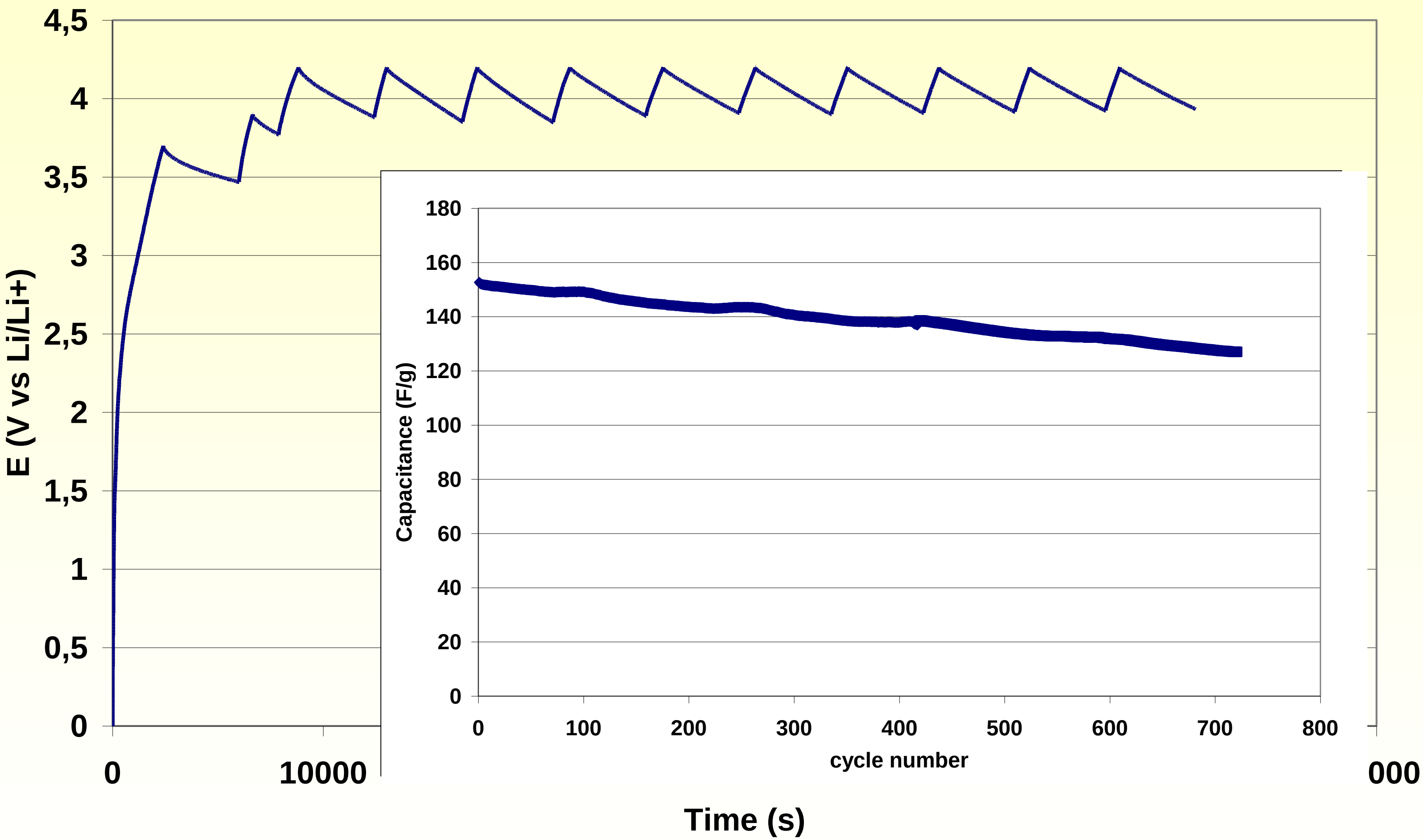
$$1/C = 1/C^{+} + 1/C^{-}$$

$$C^{+} \ll C^{-}$$

➡ $C \sim C^{+}$

➡ **Capacitance ~ 157 F/g**

SLP30 lithiation from LiTFSI in 2-electrode cell



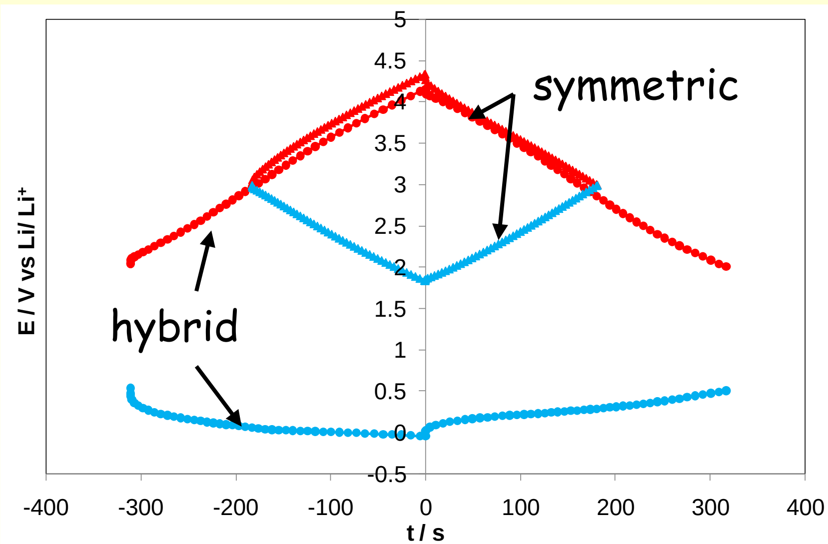
Initial Capacitance ~ 157 F/g

Compared profiles of symmetric and hybrid capacitors

Electrolyte 2 mol.L^{-1} LiTFSI in EC/DMC
Similar mass of electrodes

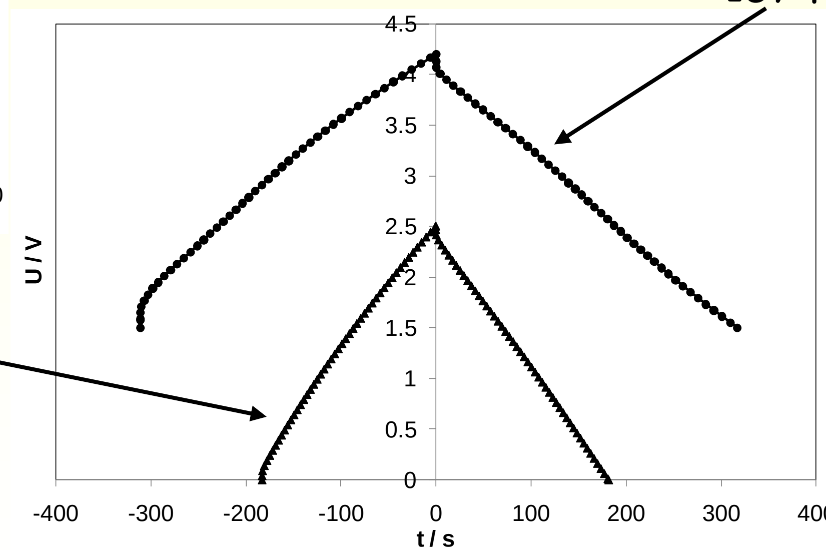
$$E = \frac{1}{2} C U^{2}$$

Hybrid 80 Wh/kg
Symmetric 20 Wh/kg
4 times higher



Hybrid capacitor 157 F/g

Symmetric capacitor 96 F/g



Conclusion

- Graphite and AC selection
- Graphite Intercalation Compound formation from 2 mol L^{-1} LiTFSI down to ~ 0.1 V vs Li/Li^{+}
- The hybrid AC/graphite supercapacitor operates up to 4.2V in 2 mol/L LiTFSI with aluminum current collector
- Specific capacitance : Cs ~ 160 F/g
- Energy density ~ 4 times higher than EDLC

Perspectives et Retombées Scientifiques

- Optimization of the electrolyte (Additive) to reduce aluminium corrosion and improve the SEI formation
- Optimization of the separator
- SEI formation
- Formation cycle mechanism
- Demonstration cells
- Effect of AC pore size distribution

- 4 Communications
- 3 Publications
- 1 Patent

Thank you for attention