Stable high-power density aqueous asymmetric supercapacitor using $NiCo_2O_4$ and superactivated carbon

presented by Roman Mysyk
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CIC energiGUNE

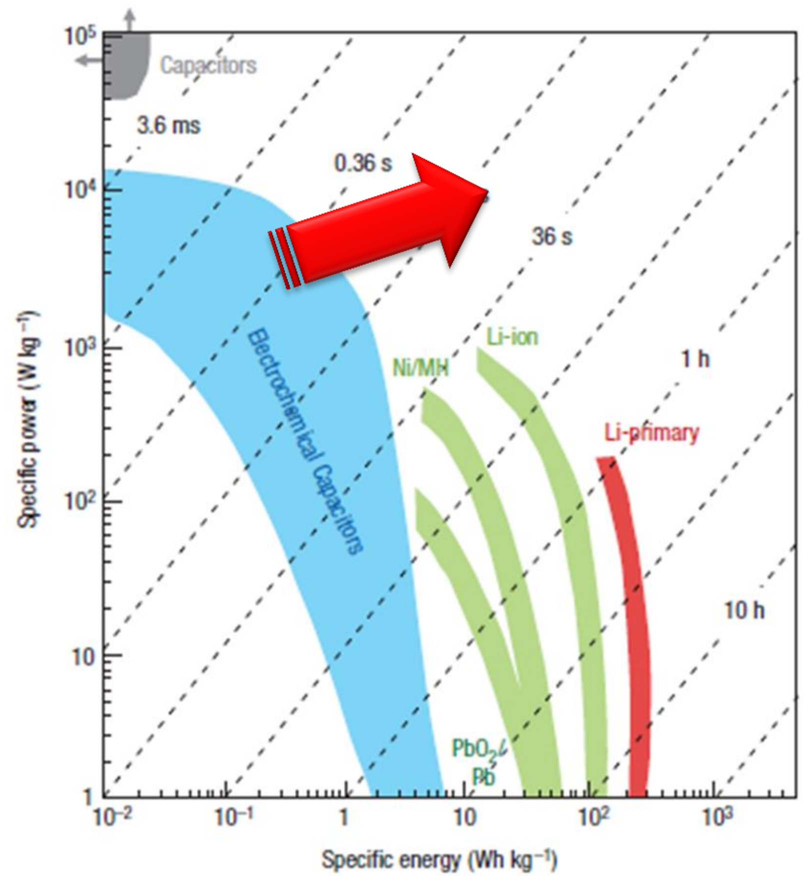
- Beginning of research activity in 2011.
- Two Research Areas: Electrochemical Energy Storage (EES) and Thermal Energy Storage (TES)
- >100 employees

Why supercapacitors?

- Energy storage system
- Performance between electrolytic capacitors and batteries.

✓ High power: 10-20 kW/kg
✓ Energy density: 5 Wh/kg
✓ Time constant: 1 – 5 s
✓ Rapid charge
✓ Symmetric charge and discharge
✓ Life time > 1M cycles
✓ Low temperature use (down to - 40˚C)
✓ Safety
✓ Maintenance-free operation

- Cost/Wh
- Energy density
- Voltage

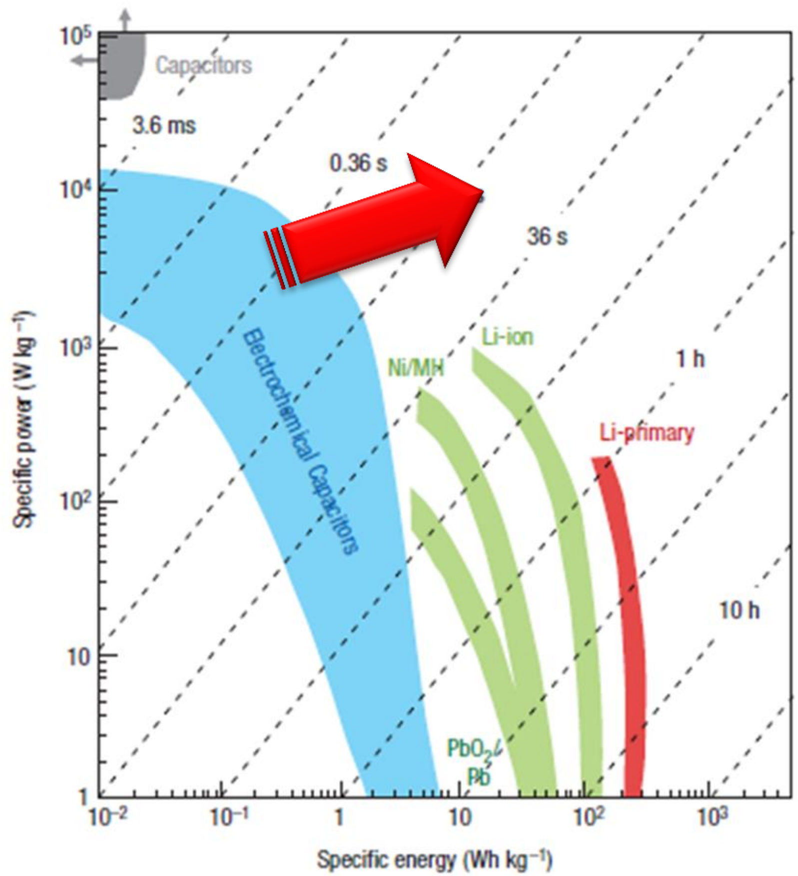


Simon P. and Gogotsi Y. *Nature Materials*, **2008**, *7,* 845.

Why aqueous supercapacitors?

- Inexpensive components and assembly
- High conductivity
- High power density
- Low viscosity
- Safety
- No strict requirements for porosity

➢ **Narrow voltage window ⇒ low energy density**



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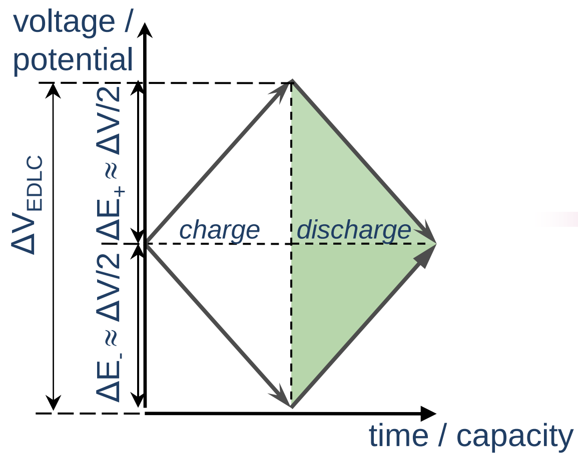
Why aqueous ASYMMETRIC supercapacitors?

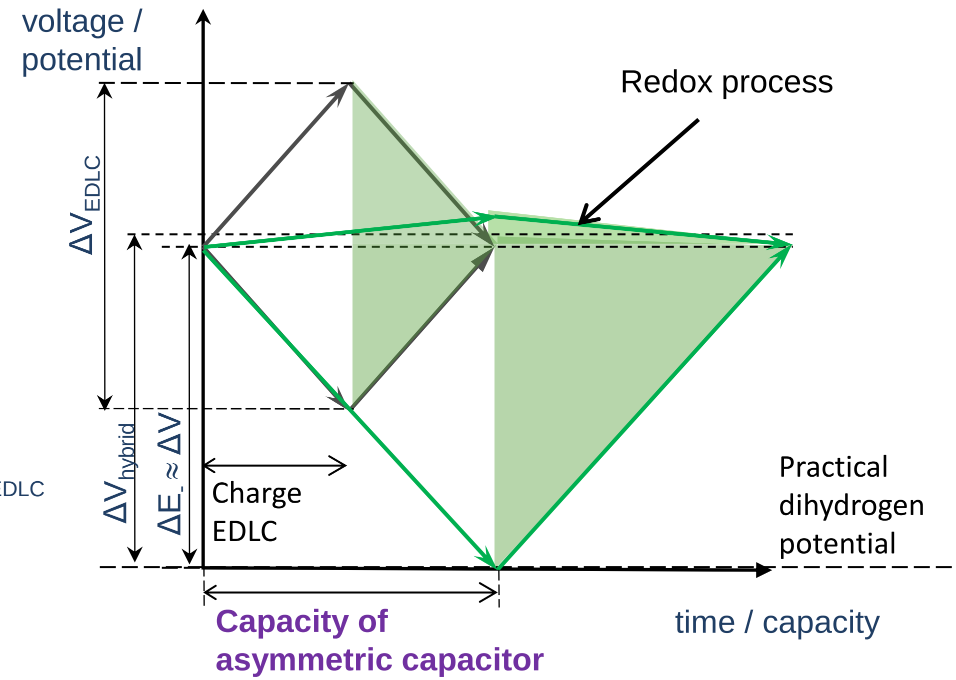
Symmetric EDLC



$\Delta V_{hybrid} \approx \Delta V_{EDLC}$

Capacity of symmetric capacitor

Aqueous ASYMMETRIC capacitor



Advantages:

I) ↑Stability

II) ↑Rate response

Drawbacks:

I) ↓Charge storage capacity

II) ↓ Cell potential

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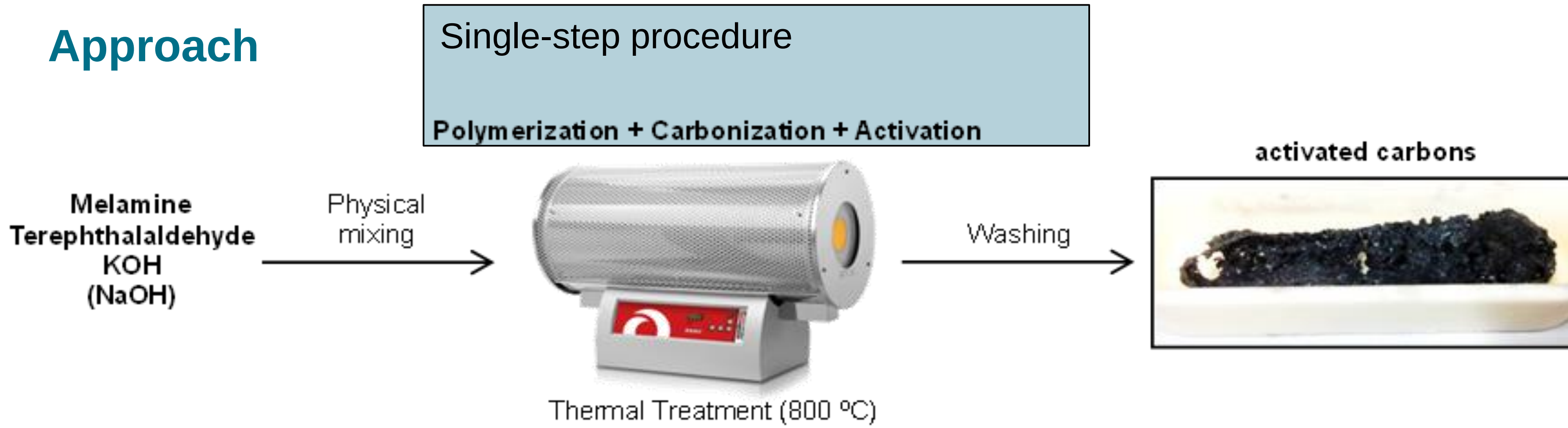
II) ↓Rate response

Materials – superactivated carbon - Negative electrode

Motivation

Simple procedure for high specific surface area carbons with porosity adapted to high-rate supercapacitors with specific aqueous electrolytes

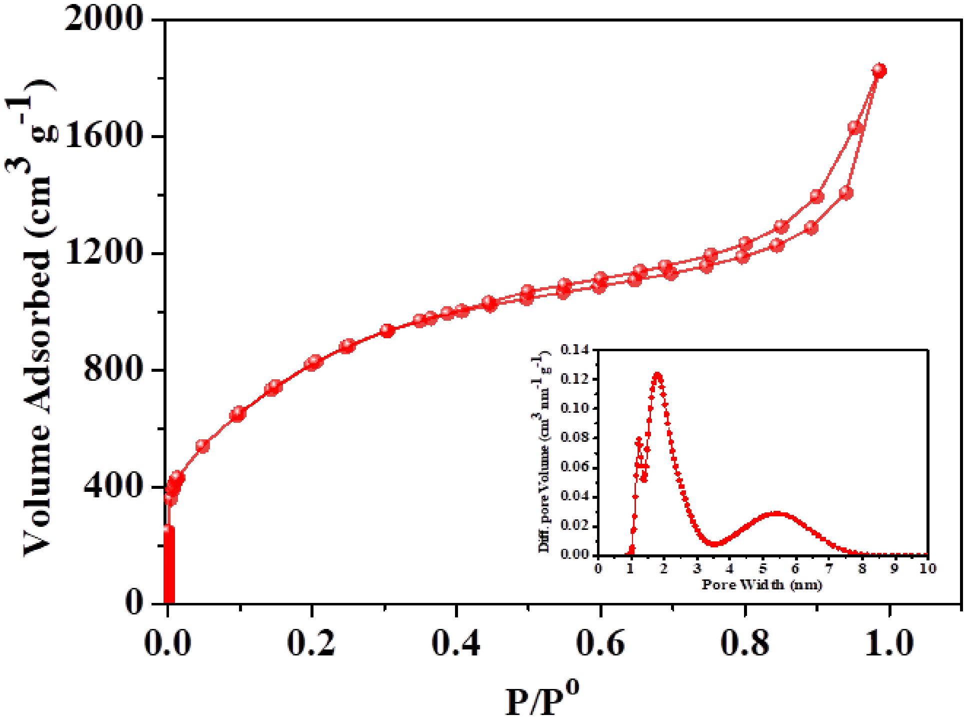
Approach



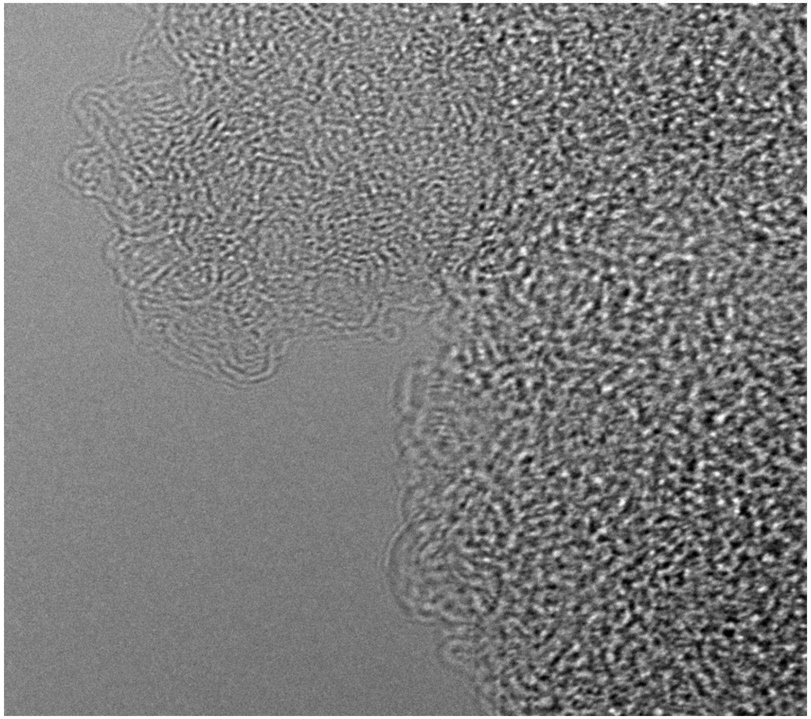
- Superactivated carbon, BET SSA = 3000 $m^2.g^{-1}$
- **Electrode composition 90 wt % SAC, 5 wt% CB, 5 wt% PTFE**

Properties – Superactivated carbon

Adsorption



TEM



S_{BET} ($m^2\ g^{-1}$)	S_{DFT} ($m^2\ g^{-1}$)	V_T ($cm^3\ g^{-1}$)	V_{DR} ($cm^3\ g^{-1}$)	V_{me} ($cm^3\ g^{-1}$)
3071	1730	2.82	1.00	1.82

Materials - $NiCo_2O_4$ - Positive electrode

Synthesis

- $Ni(NO_3)_2.6H_2O$
- $Co(NO_3)_2.6H_2O$
- Urea
- DI Water

Continuous Stirring

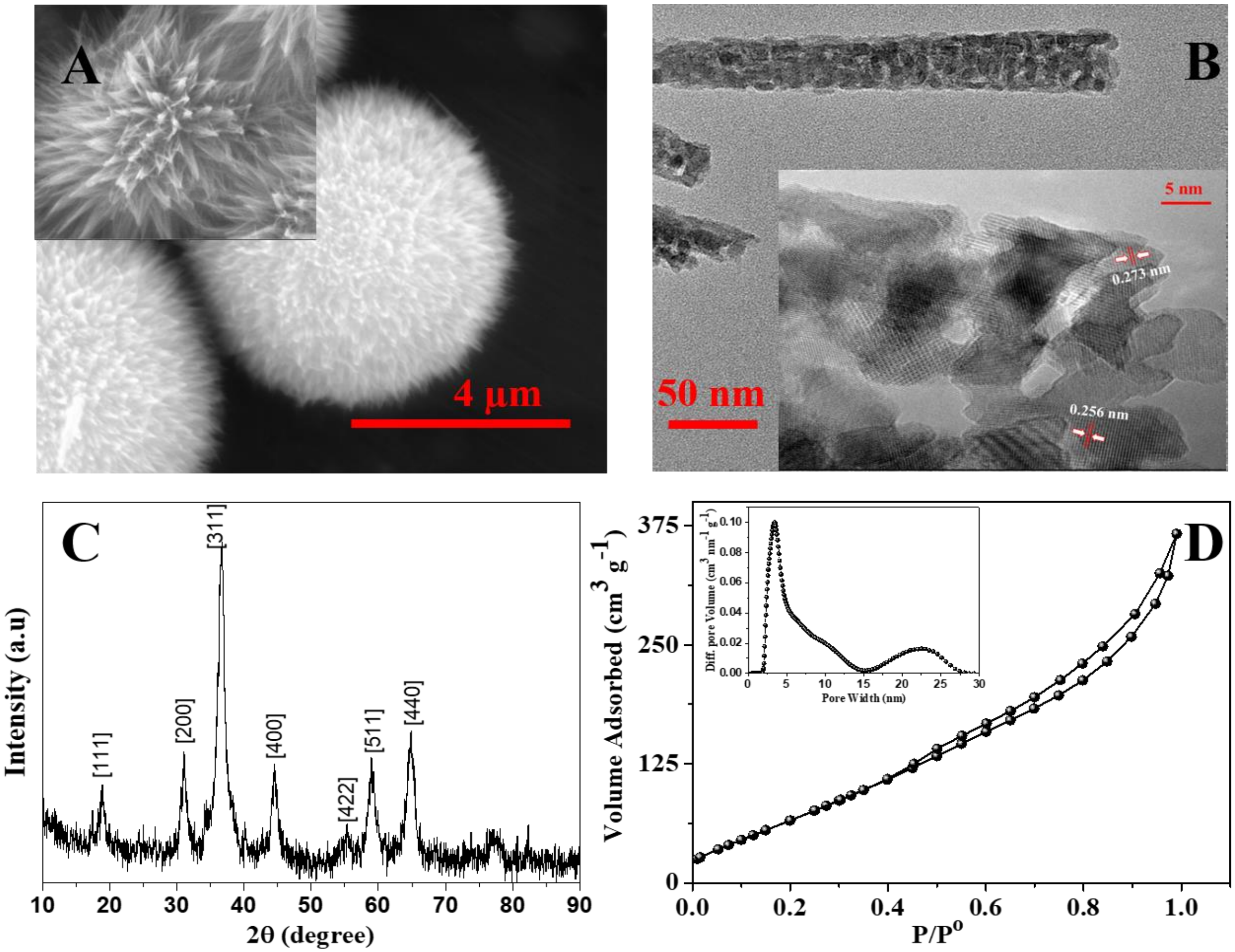
180^{o}C for 2 hr

Centrifugation and drying

Calcination at 300^{o}C for 3 h

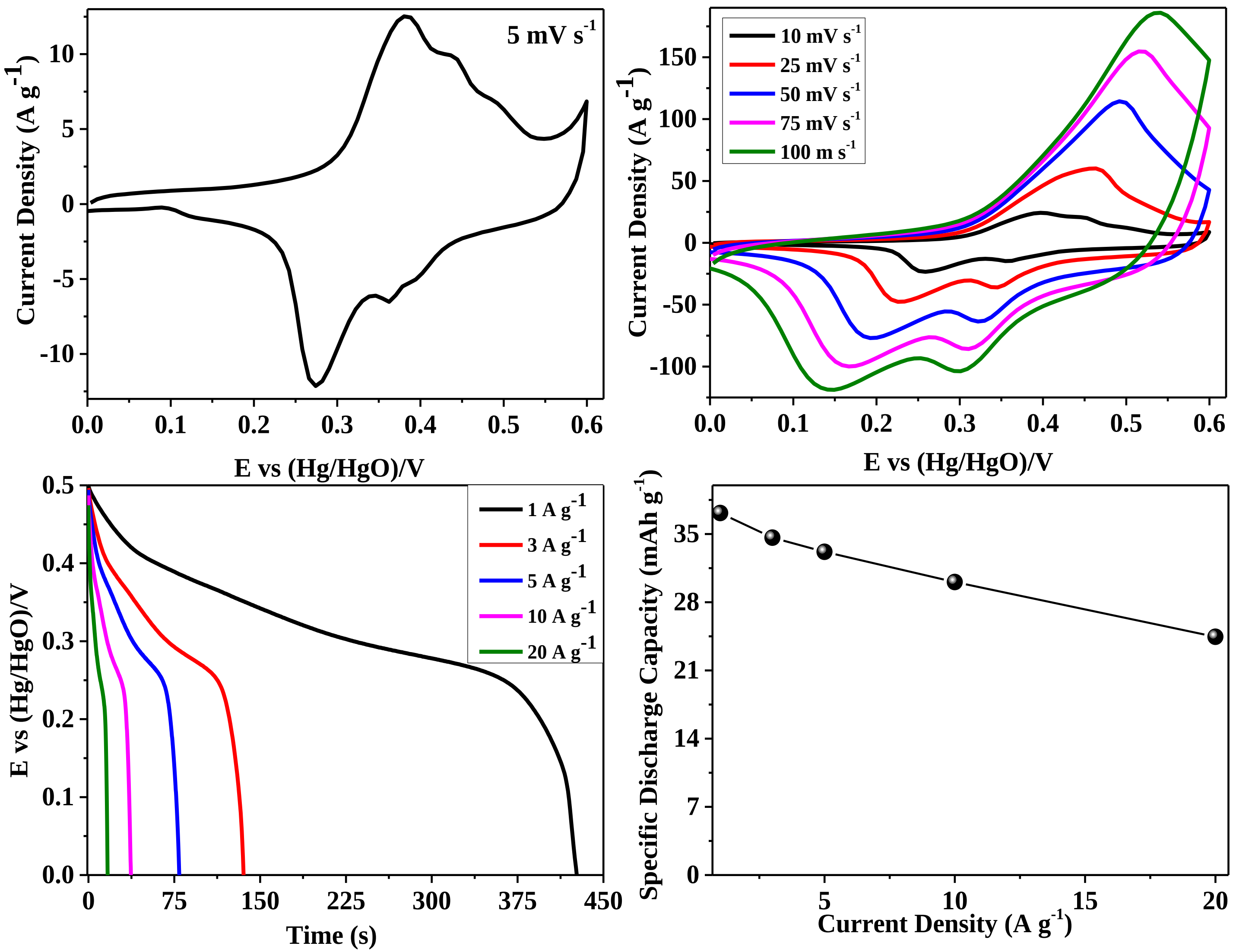
- **Electrode composition 60 wt % $NiCo_2O_4$, 30 wt% CB, 10 wt% PTFE**

$NiCo_2O_4$ nanothorns



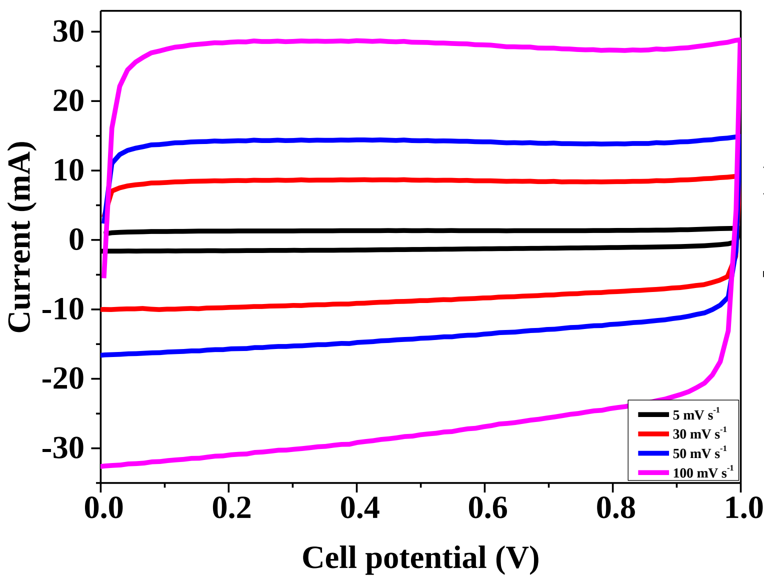
- Microspheres formed by the assembly of $NiCo_2O_4$ nanothorns
- SSA 255 m^2/g

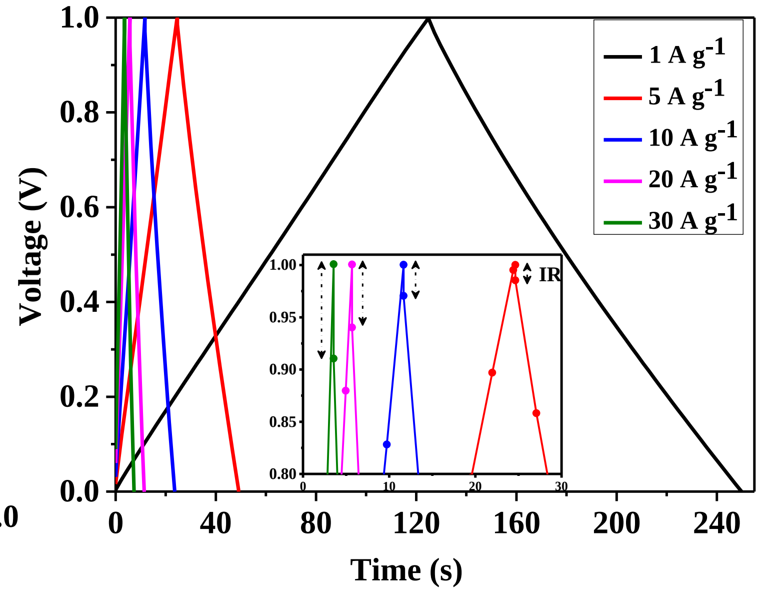
$NiCo_2O_4$ nanothorns - 3 electrode characterization

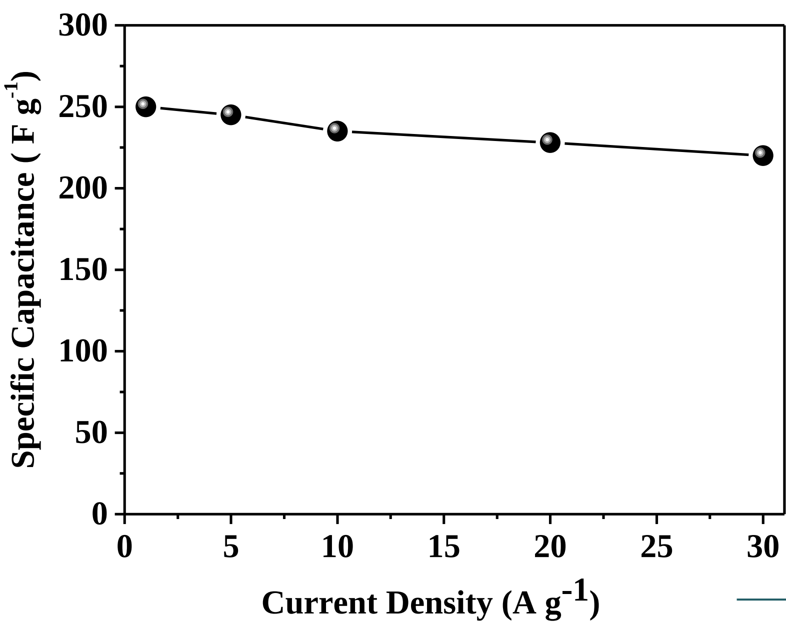


- High-rate performance with high rate of capacity retention

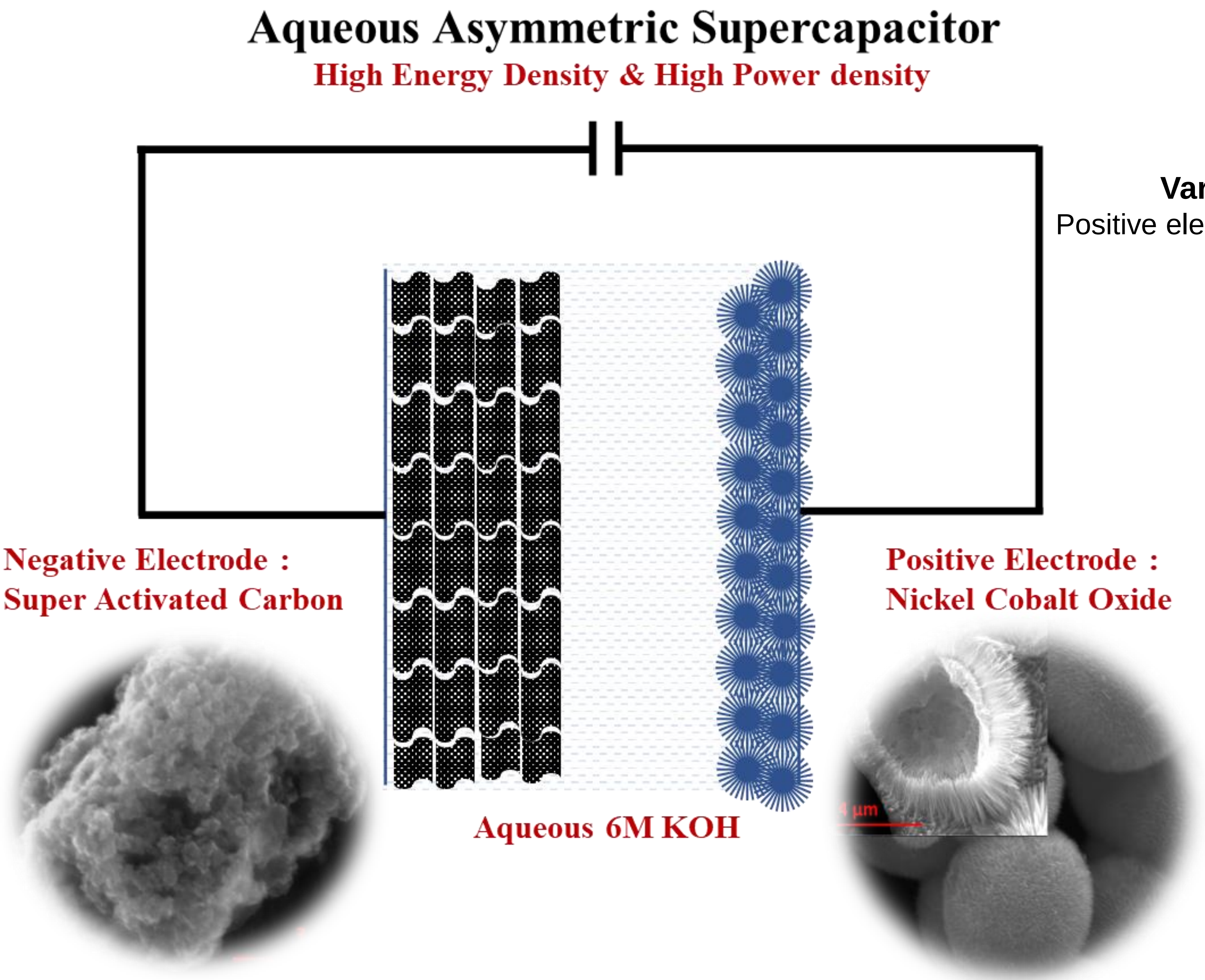
Superactivated carbon – Symmetric 2-electrode cell







Full cell – Asymmetric aqueous capacitor



Varied mass balance

Positive electrode : Negative electrode

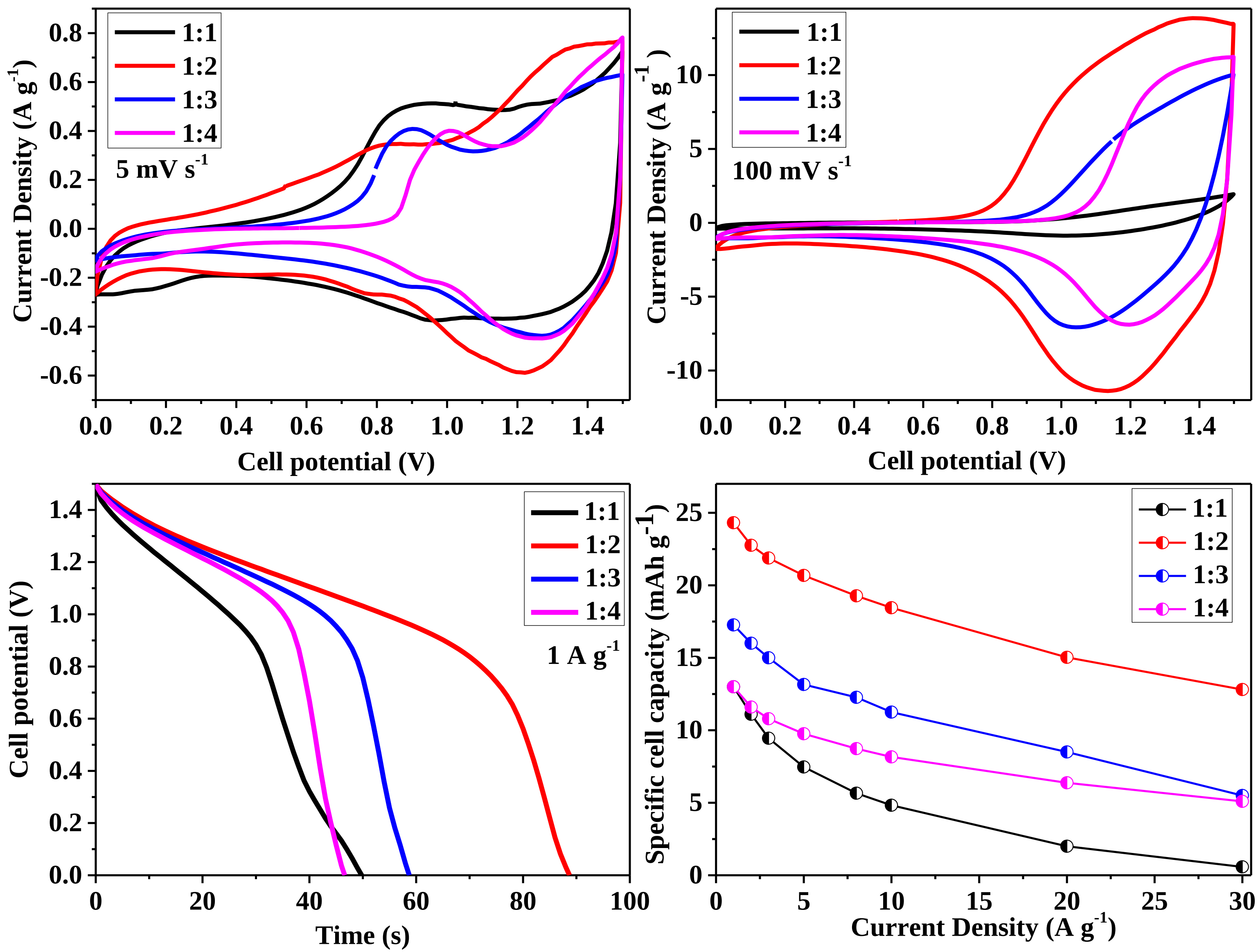
1:1

1:2

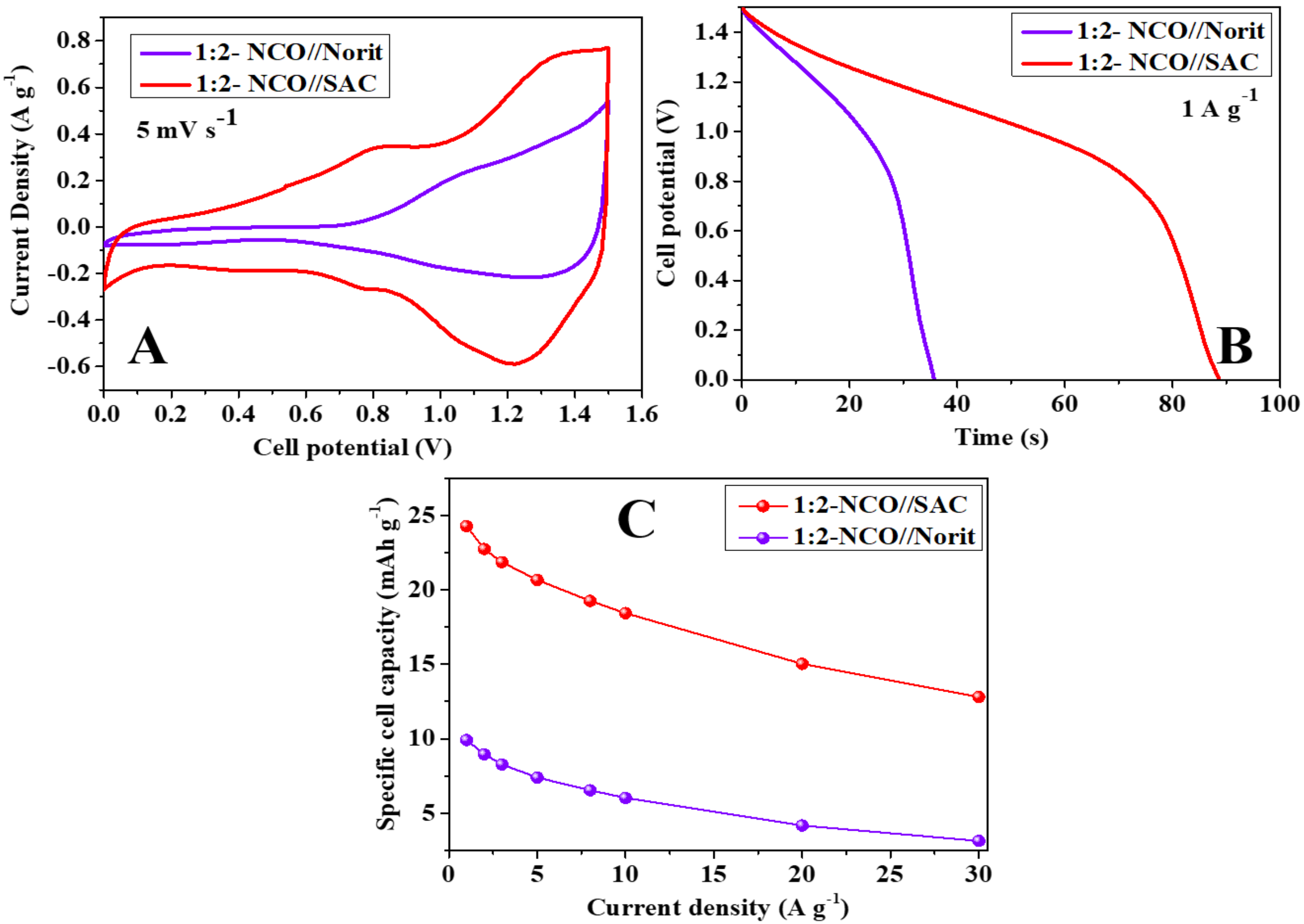
1:3

1:4

Full cell – Effect of mass ratio on electrochemical response

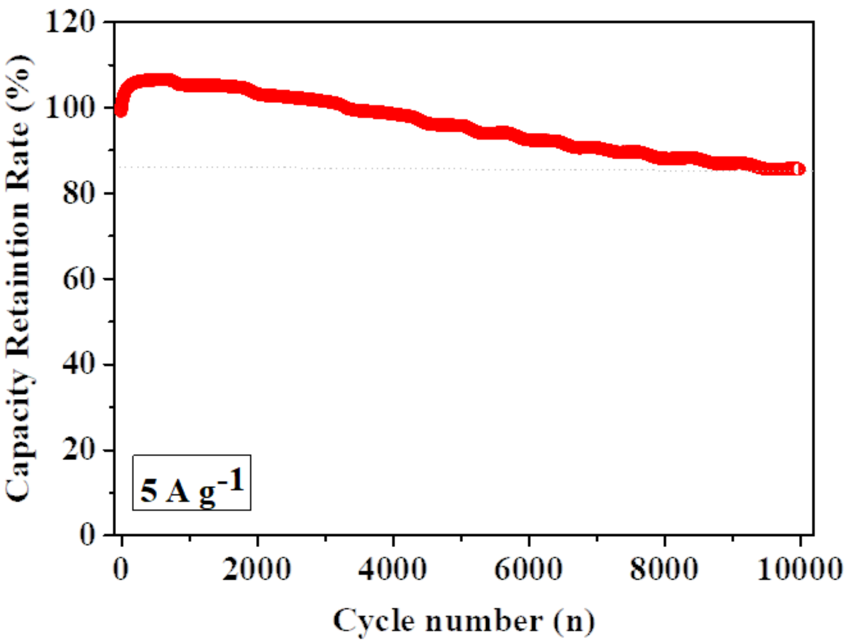


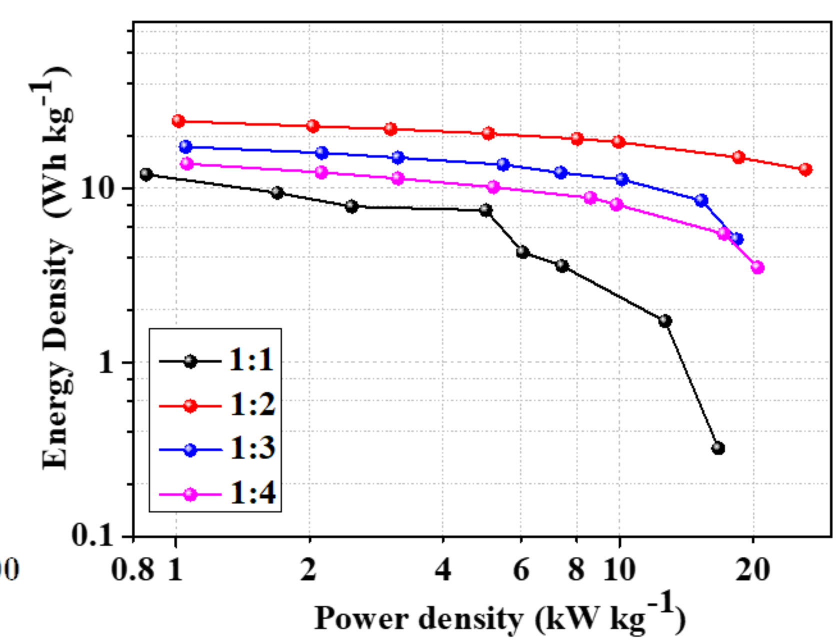
Full cell – Added value of superactivated carbons



- Higher gravimetric charge storage capacity than commercial AC – Norit Supra 50

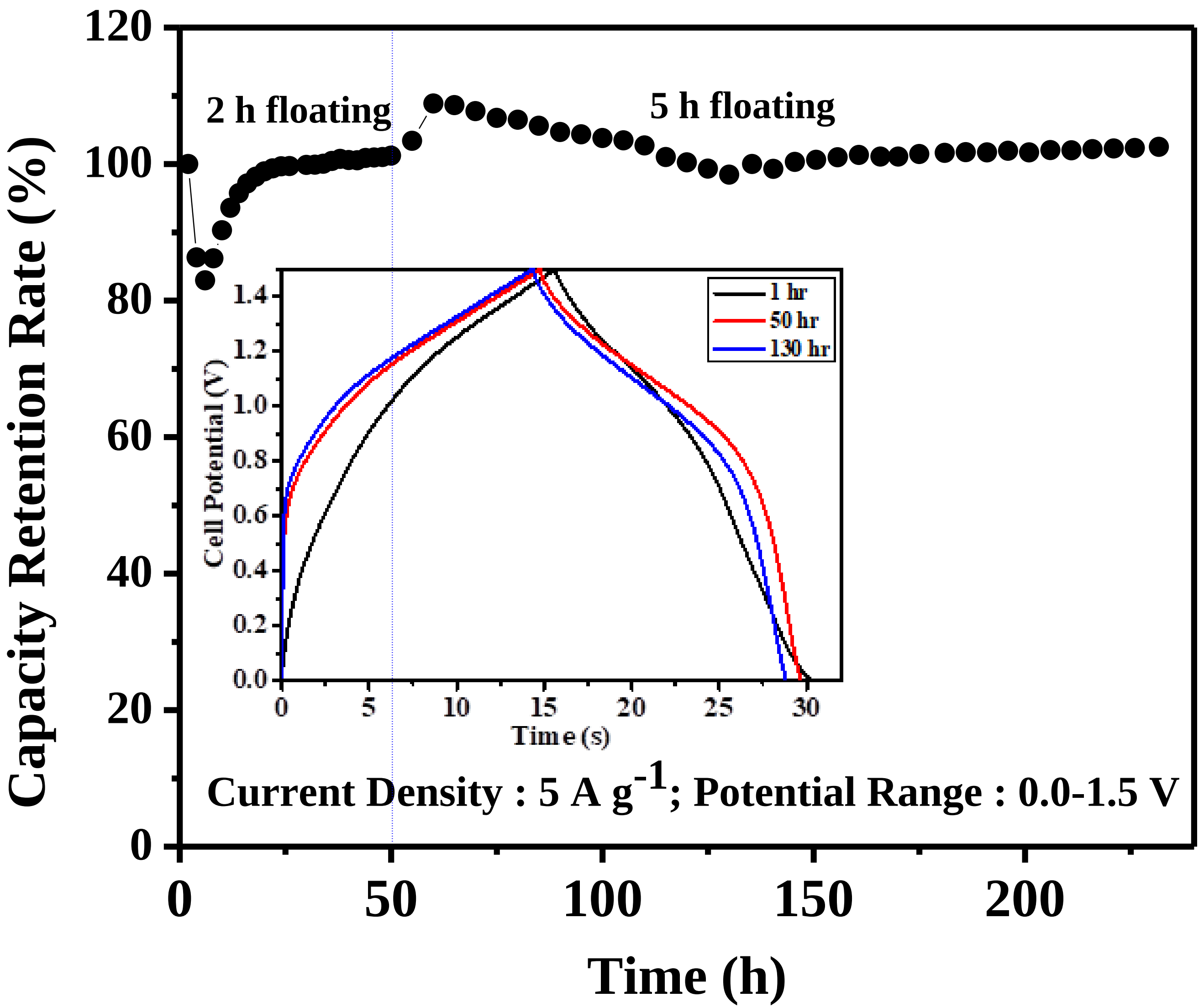
Full cell – Cycling stability & Ragone plot





- 87 % capacity retention after 10,000 cycles
- High power perfromance, 26.2 kW kg^{-1} @ 13 Wh kg^{-1}

Full cell – Floating stability test



➢ Stable float-voltage capacitance retention over 250 h floating

Full cell – Comparison with relevant research

AAS device electrode name(Positive//Negative)	Electrolyte	AAS capacitance F g^{-1} at 1 A g^{-1}	Cycling stability Retention
Ni-Co Oxide//APDC	2M KOH	188	89% up to 4000 cycles at 5 A g^{-1}
$NiCo_2O_4$//AC	2 M KOH	77.3	108.1% up to 10000 cycles at 3 A g^{-1}
NCH11/G/NF//AC	2 M KOH	108	84.4% up to 2000 cycles at 4 A g^{-1}
Ni-Co-Oxide//AC	1 M KOH	60	85% up to 2000 cycles at 8 mA
$NiCo_2O_4$-rGO//AC	2 M KOH	96	83% up to 2500 cycles at 1 A g^{-1}
$NiCo_2O_4$//RGO	6 M KOH	101.7	93.5% up to 10000 cycles at 5 A g^{-1}
C7N3//AC	2 M KOH	82	86.4% up to 10000 cycles at 2 A g^{-1}
1: 2 AAS device [$NiCo_2O_4$//SAC]	6 M KOH	81	87% up to 10000 cycles at 5 A g^{-1}

Conclusions

- An all-in-one procedure is proposed for preparation of high specific surface area carbons with tailored textural properties

- The hierarchical structure of active materials is critical to maintain good capacity retention at high current densities

- The optimization of the electrode mass balance within the AAS devices leads not only to both excellent energy and power densities but also to outstanding stability with no capacitance decay for over 250h floating time

- The optimized positive:negative mass ratio in a full cell is the 1:2 ratio, which allows maximum gravimetric energy density of 24.3 Wh kg^{-1} @ 1.0 kW kg^{-1} and 13 Wh kg^{-1} @ 26.2 kW kg^{-1}

Supercapacitor research line at CIC energiGUNE

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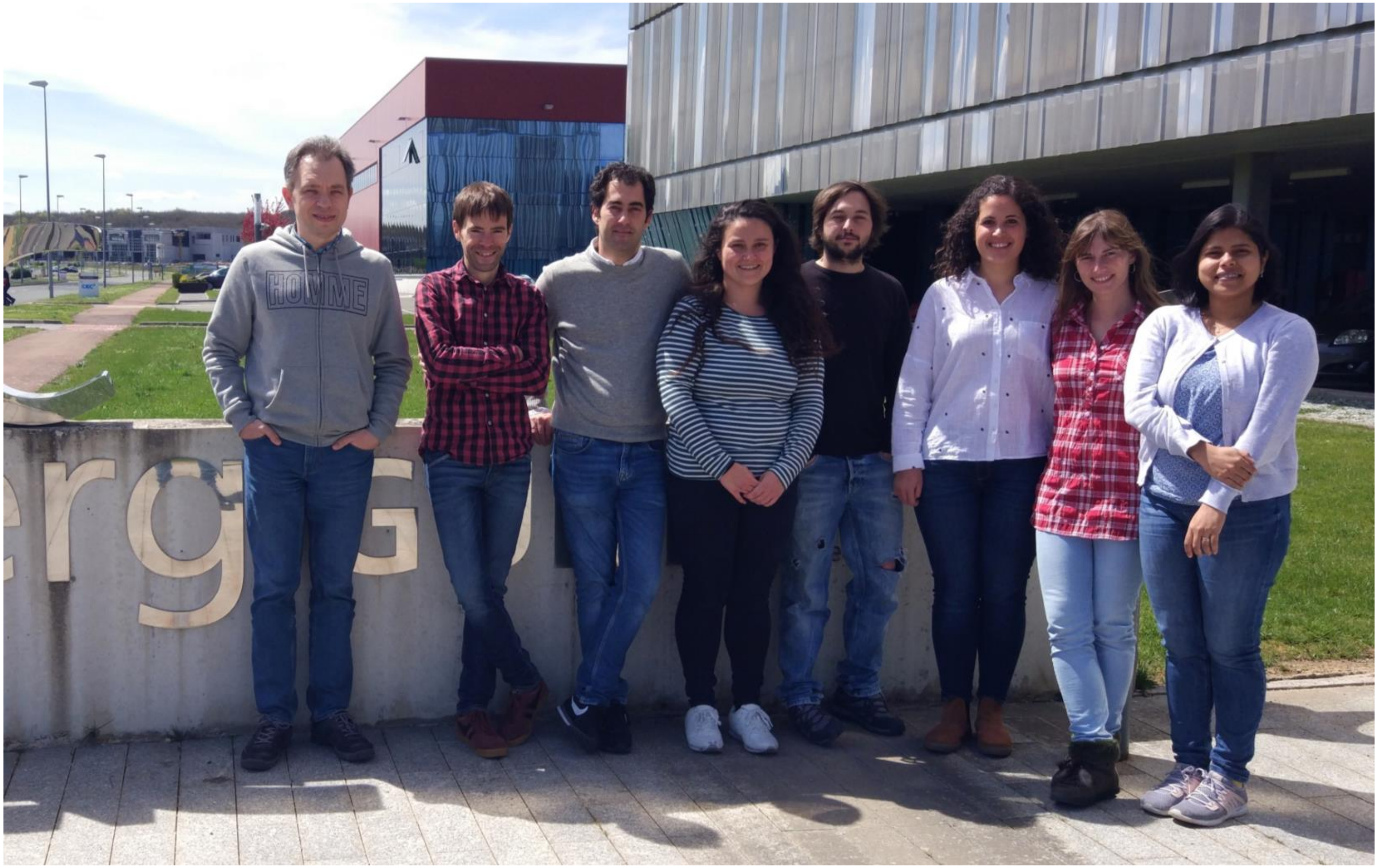

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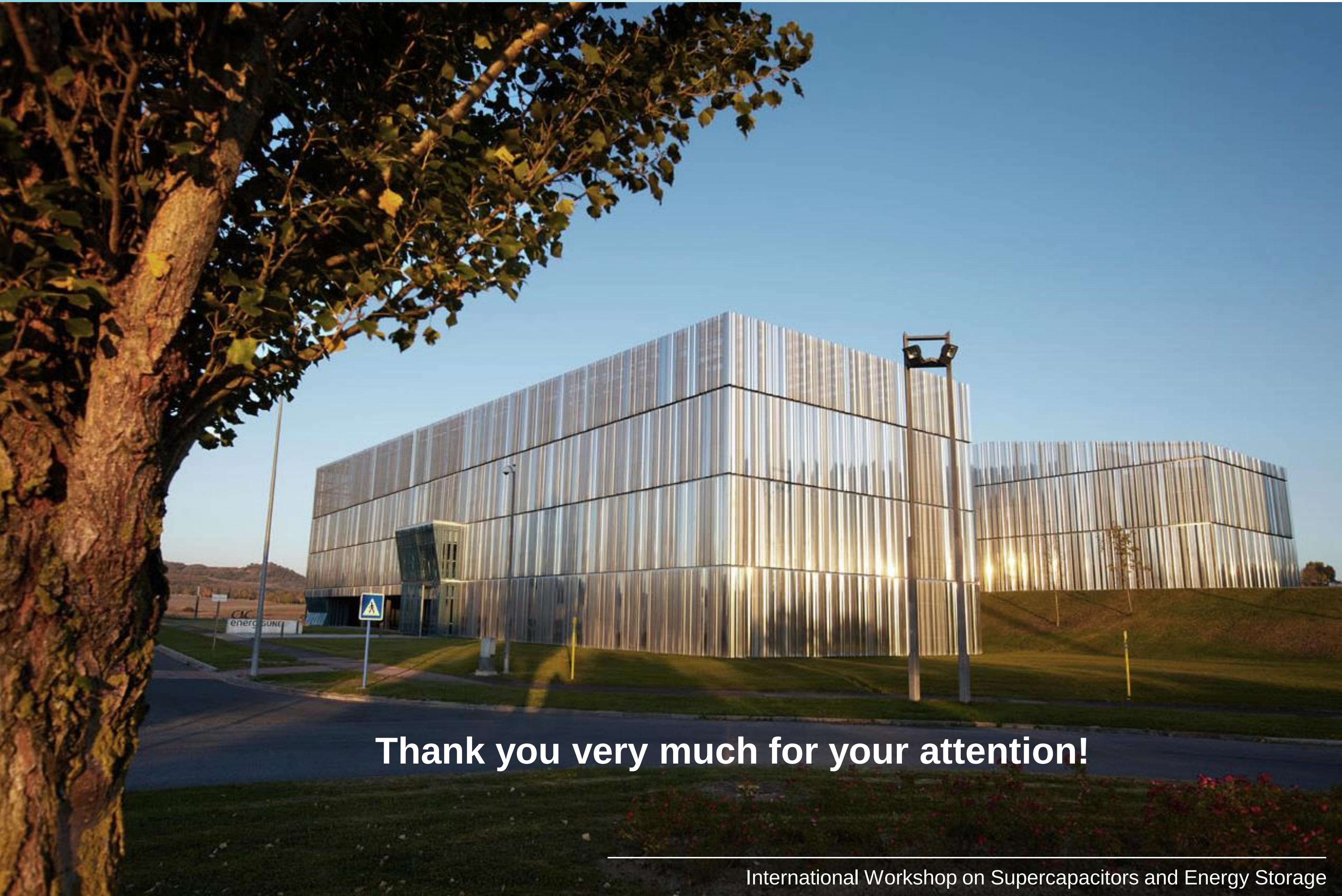

Thank you very much for your attention!