InComEss

Innovative polymer-based composite systems
for high-efficient energy scavenging and storage

This project receives funding in the European Commission’s Horizon 2020 Research Programme under Grant Agreement Number 862597

Overview of supercapacitors, preparation of PANI/Carbon composites, and fabrication process of monolithic supercapacitor

Matti Mäntysalo, Jari Keskinen ,Timo Punkari ,Riikka Mikkonen -
Tampere University- Finland

Jürgen Pionteck, Ezgi Inci Yesilyurt –
Leibniz-Institut für Polymerforschung Dresden-Germany

This project receives funding in the European Commission’s Horizon 2020 Research Programme under Grant Agreement Number 862597

Tampere University

ipf

Content

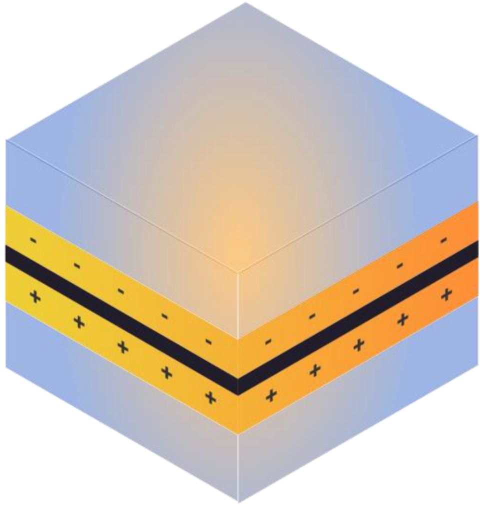
- Main objective of WP4 in the frame of the InComEss project
- Overview of supercapacitor from literature and lectures (types of supercapacitors, electrodes, advantages and limitations, structures, characterization, cyclic voltammetry, applications areas)
- Part 1- Preparation of PANI/Carbon composite and electrode ink
- Part 2- Monolithic supercapacitor fabrication process

IPF and TAU in the frame of the InComEss project

The InComEss project proposes a new green-and-cost-effective strategy for high efficient energy harvesting by combining new smart advanced polymer-based composite materials and structures into a single/multi-source concept.

Main objective:

Development of low-cost environmentally sustainable storage supercapacitors (SCs) with high energy density and power density together with extended operation window (temperature and voltage) to store the energy harvested by the PEG, TEG and hybrid TPEG devices.



IPF will develop new electrode materials

- → Development of printable high energy density and power density polymer/carbon-based composite electrode materials with increased capacitances (above 400 F/g) and high-energy densities (around 5 Wh/kg).
- → Development of monolithically fabricated supercapacitors by using printing technology to store the energy harvested by the energy harvester components of the PE-EHS, TE-EHS and TPE-EHS

(PE – piezoelectric, TE – thermoelectric, PEG - PE generator, TEG - TE generator, TPEG combined PE/TE generator, EHS – energy harvesting system, TPE-EHS – combined PE/TE EHS)

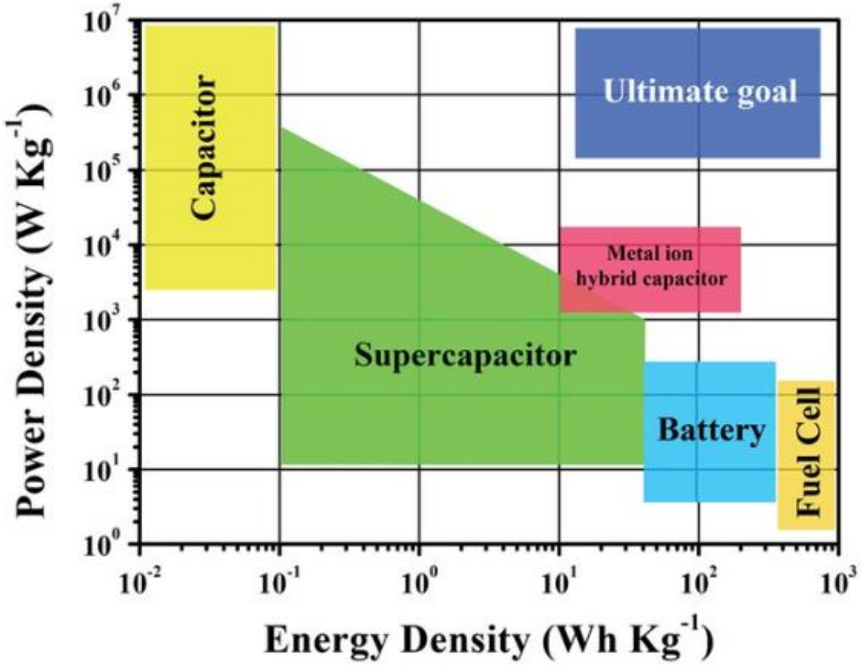
Tampere University

ipf

SUPERCAPACITOR

Comparison with conventional capacitors and batteries supercapacitors possesses;

- High specific power
- High specific energy
- Capacitance values between 0.1 - 5000 F (several decades higher than in conventional capacitors)
- Maximum voltage in one cell about 3 V
- $E = 1/2\ CU^2$



F : farad, unit of capacitance
E: Amount of energy stored (joule, J)
C: capacitance, (farad, F)
U: potential difference (voltage, V)

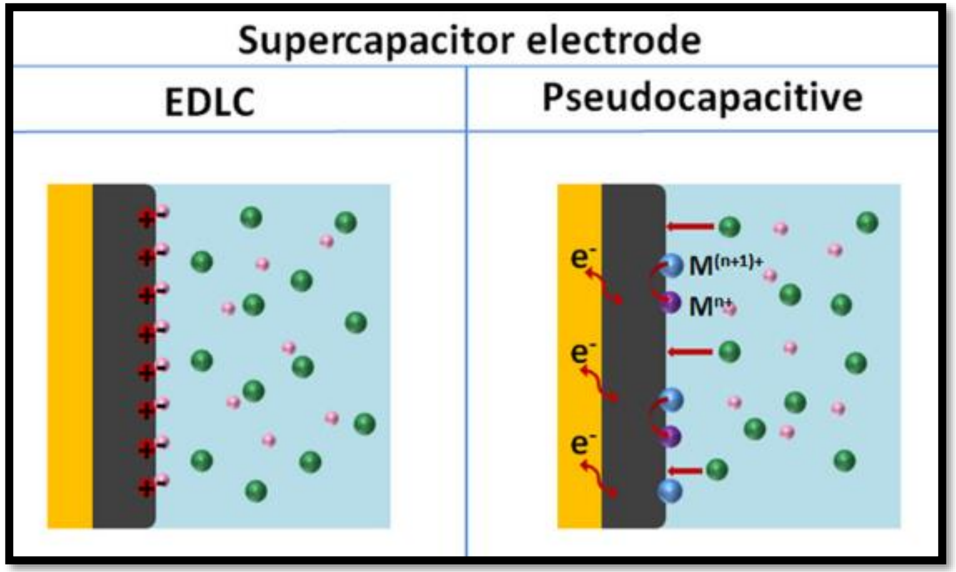
Tampere University

TYPES of SUPERCAPACITOR

EDLC

Charge storage - *Electrostatically (Helmholtz layer) - rapid ion adsorption and desorption.*

- ❖ *High power density & long-term cycle stability but low energy density.*



Pseudocapacitive

Charge storage - *Electrochemically (Faradaic charge transfer) - rapid & reversible redox reactions.*

- ❖ *High specific capacitance & energy density*

Jiang, Yuqi, and Jinping Liu. "Definitions of pseudocapacitive materials: a brief review." Energy & Environmental Materials 2.1 (2019): 30-37.

Tampere University

Electrodes

- PANI electrode

Polyaniline (PANI)

- Multi-redox reactions
- High conductivity
- High flexibility
- Low cost
- High thermal stability

- Hybrid electrode

PANI/Carbon composites

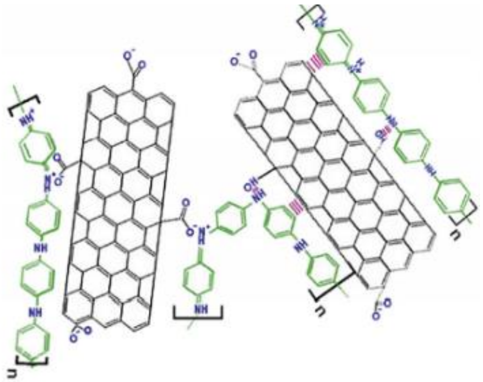
Charge storage

Electrochemically

- Polyaniline

Electrostatically

- Carbon materials



- Carbon electrode

Carbon structures

- Large surface area
- Good chemical stability
- High electrical conductivity

Wang, Huanhuan, Jianyi Lin, and Ze Xiang Shen. "Polyaniline (PANi) based electrode materials for energy storage and conversion." Journal of science: Advanced materials and devices 1.3 (2016): 225-255.

Advantages and limitations of supercapacitors

Compared to commercial capacitors and batteries

Advantages

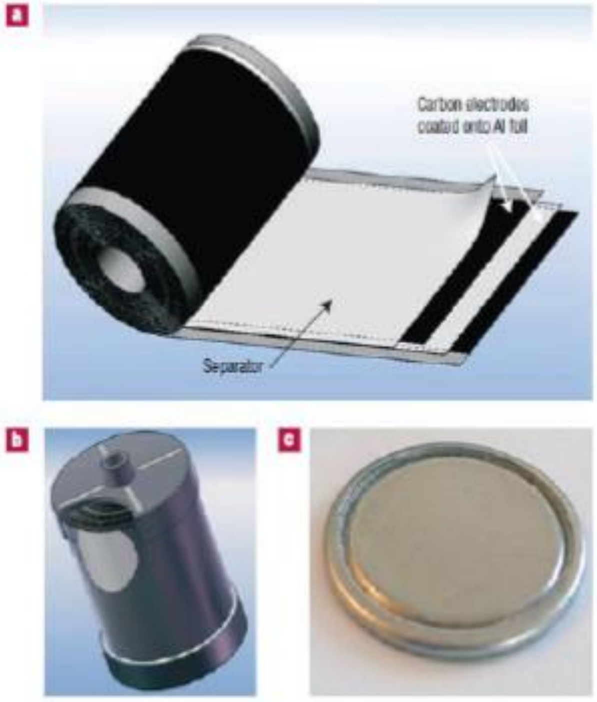
- Virtually unlimited cycle life - can be cycled millions of times.
- Low impedance - enhances load handling when put in parallel with a battery.
- Rapid charging -supercapacitors charge in seconds.
- Simple charge methods - no full-charge detection is needed; no danger of overcharge.

Limitations

- Linear discharge voltage prevents use of the full energy spectrum.
- Low energy density - typically holds one-fifth to one-tenth the energy of an electrochemical battery.
- Cells have low voltages - serial connections are needed to obtain higher voltages.
- Voltage balancing is required if more than three capacitors are connected in series.

Source: https://www.maxwell.com/products/ultracapacitors

Structure of practical supercapacitors



Batscap:

a- Schematic of a commercial spirally wound double layer capacitor.
b- Assembled device weighing 500 g and rated for 2,600 F

Y-Carbon, USA:

c- A small button cell, which is just 1.6 mm in height and stores 5 F

- Both devices operate at 2.7 V

Simon, Gogotsi, Nature Materials, 7(11) 2008, 845-854

Characterization of supercapacitors

Capacitance

- Constant voltage e.g. 2.5V, then discharging with constant current

Equivalent series resistance (ESR)

- ESR= Rs

Efficiency

- Energy or charge

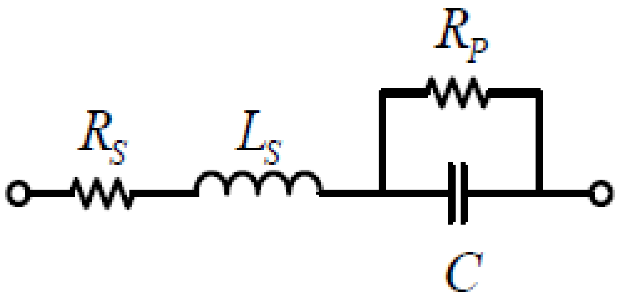
Leakage current, e.g. 1 hour at 2.5 V

- I_{leak}= current at 1 hour

Impedance spectroscopy

- Properties as a function of frequency

General capacitor model



I_{leak} = leakage current
C = capacitance
Rs= the internal resistance
L_S = the equivalent series inductance
Rp= the leakage resistance

Cyclic voltammetry measurements

- CV (cyclic voltammetry) experiments can be run with two-electrode or three-electrode cell connections
- Three-electrode configurations are common in fundamental research where it allows one electrode to be studied in isolation, without complications from the electrochemistry of the other electrodes.

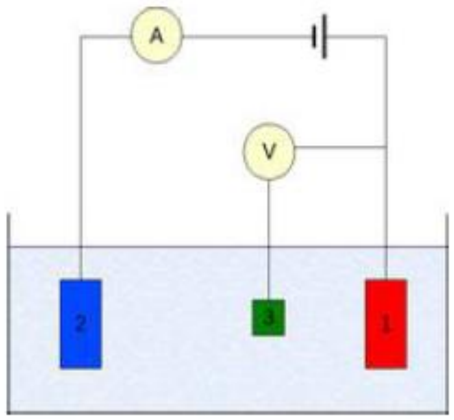
The three electrodes are:

Working Electrode –the electrode being tested.

Reference Electrode –an electrode with a constant electrochemical potential.

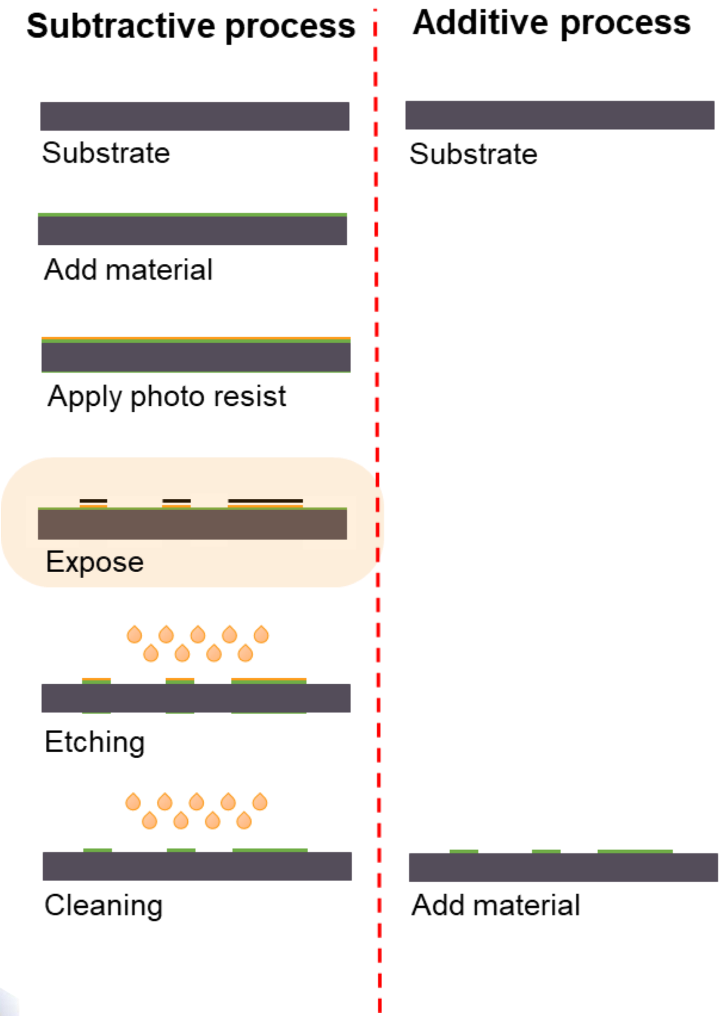
Counter Electrode –generally an inert electrode, present in the cell to complete the electric circuit.

- Testing of packaged capacitor requires two electrode connections.

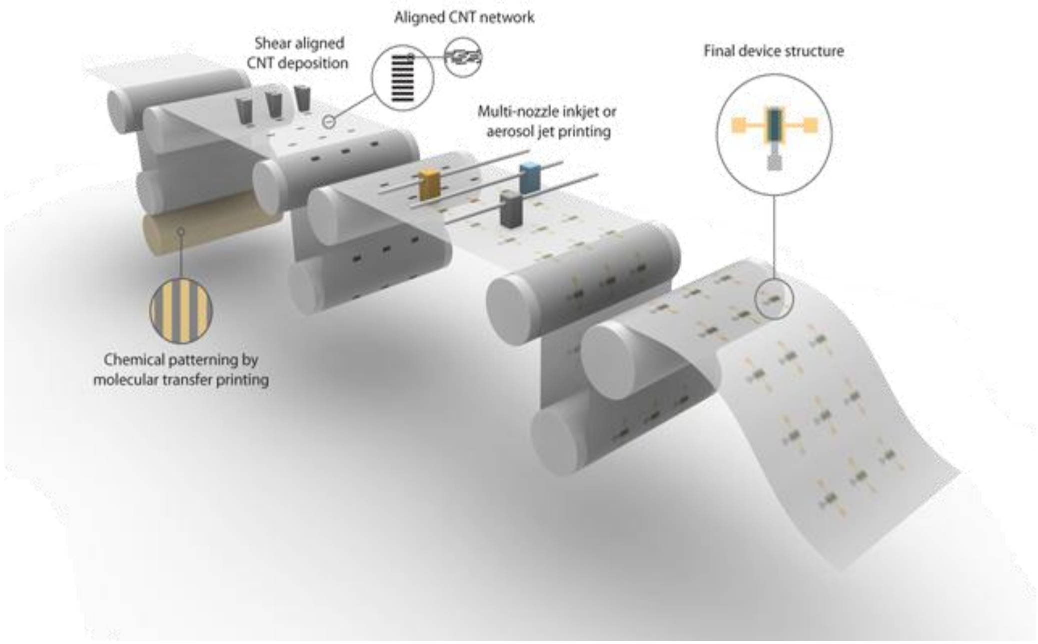


Three-electrode setup: (1) working electrode; (2) auxiliary (=counter) electrode; (3) reference electrode

Printed electronics - low-cost environmentally sustainable manufacturing



- Additive => *less material waste*
- No etching => less harsh chemicals
- Less process steps => *simplified process*



Source: Printed Electronics Processing Concept (Grant Illustration)
From Dr. C. Daniel Frisbie at the University of Minnesota.

Supercapacitor applications, examples

Applications as (hybrid)energy source

- Power supplies, peak power, recovery of braking energy
- Batteries
- Fuel cells
- Communications technology
- Rapid reserve power
- Power for starting motor
- Small size supercapacitors
- Back-up energy
- Autonomous systems
- Electronics
- Digital camera flash
- Toys
- Price of one supercapacitor < 1 € , several hundreds €

Emergency system for wind turbine

Starter device

ultracapacitors

Sinautecbus, Shanghai

Source: https://maxwell.com/products/ultracapacitors/cells/

PART-1

Preparation of PANI/Carbon Composite and Electrode Ink

Synthesis of PANI/Carbon composite

- *Pure PANI and PANI/Carbon composites were synthesized by in-situ chemical oxidative polymerization of aniline.*

aniline+carbon added to 600 mL HCl solution

APS dissolved in 200mL HCl

2h sonication
(%50 amplitude, Cycle 1)

The reaction is carried out for 24 hours with vigorous stirring.

The product washed with millipore water, ethanol,aceton and dried in a vacuum oven at 100°C ,24 h.

APS: Ammonium persulfate
HCl: Hydrochloric acid

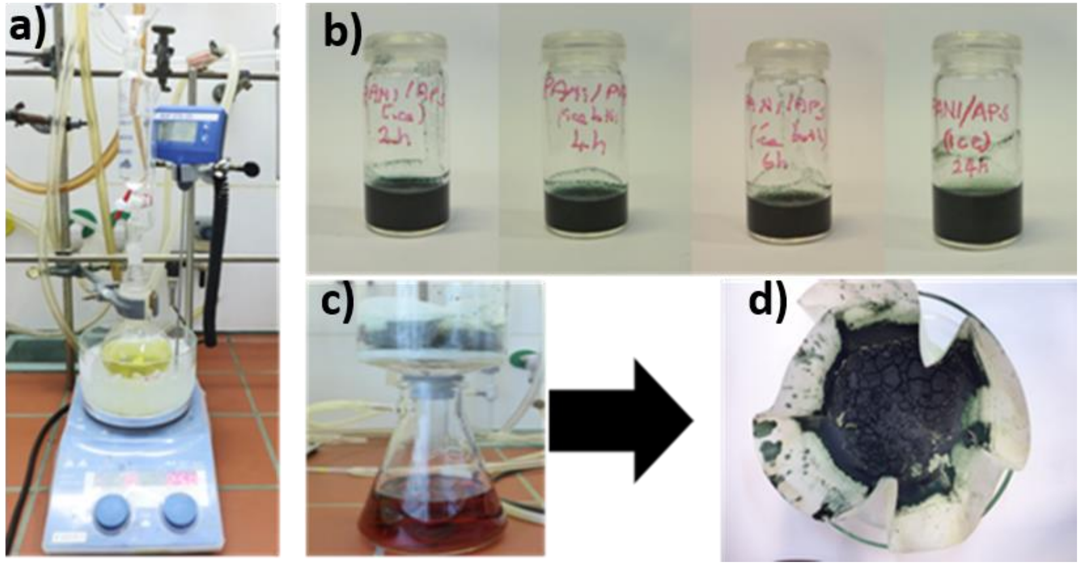


Figure 1. Method of producing PANI/carbon composites in 20 g scale:
a) oxidation of aniline, b) aliquots of PANI, c) filtration, and d) filter cake.

Preparation of ink material from PANI/Carbon composites

- Active material
- Binder
- Water
- 30 min sonication in ice bath

PTFE = Poly(tetrafluoroethylene)

Active material

- Pristine PANI, commercial carbons, PANI/Carbon composites

Binder

- PTFE, Chitosan

Medium

- Water

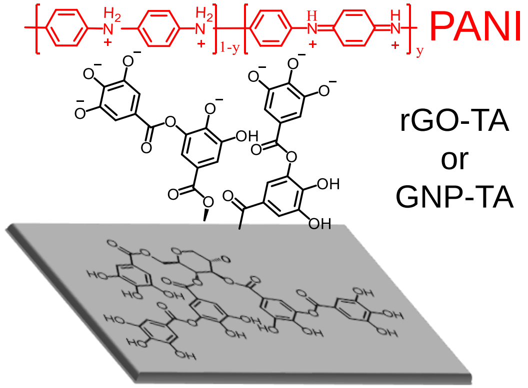
% weight ratio of active material/binder $\sim 90/10$

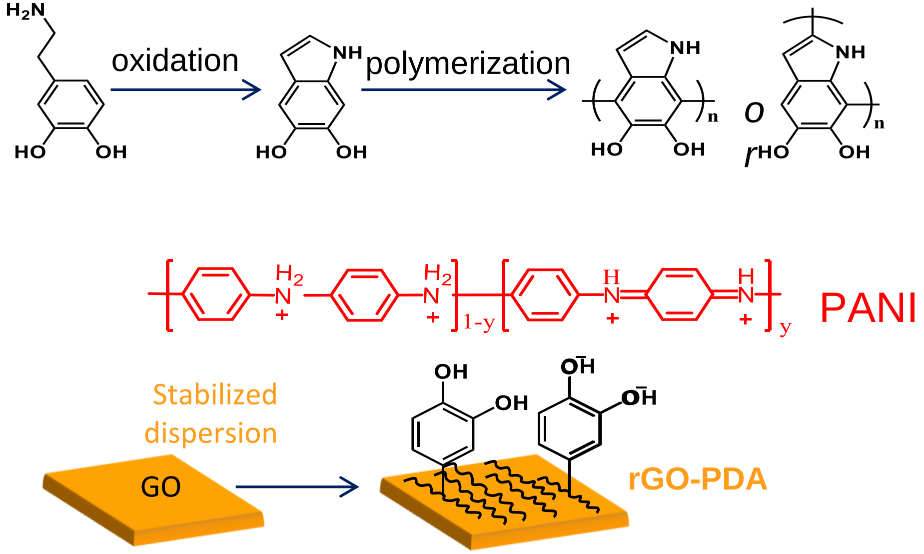
Graphitic PANI-composites as electrode material

“Green” strategies for development of PANI/rGO and PANI/GNP composites

- Use of dopamine (**DA**) [1], tannic acid (**TA**) [2] or other natural products for **GO reduction** and **morphology stabilizer**
- Graphite nanoplates – **GNP** or reduced graphite oxide – **rGO** acting as **electrochemical double layer** capacitor (EDLC) and PANI providing **pseudocapacitance**

Stabilized dispersion



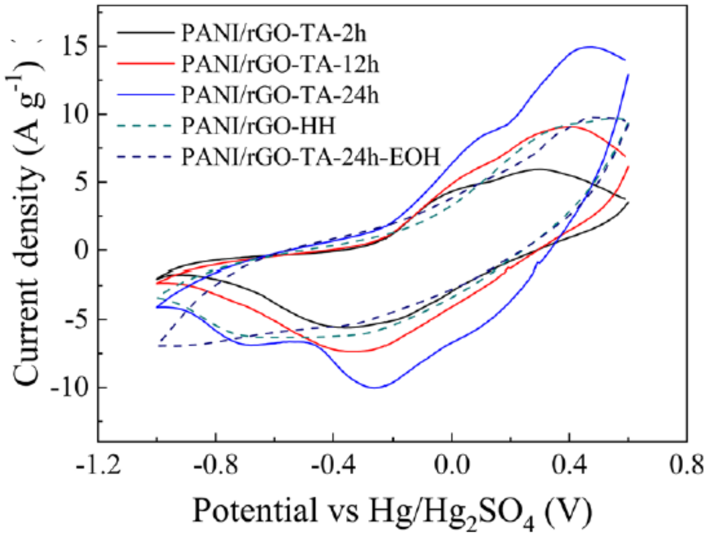


[1] - Zhao X, Pionteck J, et al., J. Mater. Sci. (2019) 15, 10809
[2] -Zhao X, Pionteck J, J. Appl. Polym. Sci. 2021; 138:e50663

Graphitic PANI-composites as electrode material

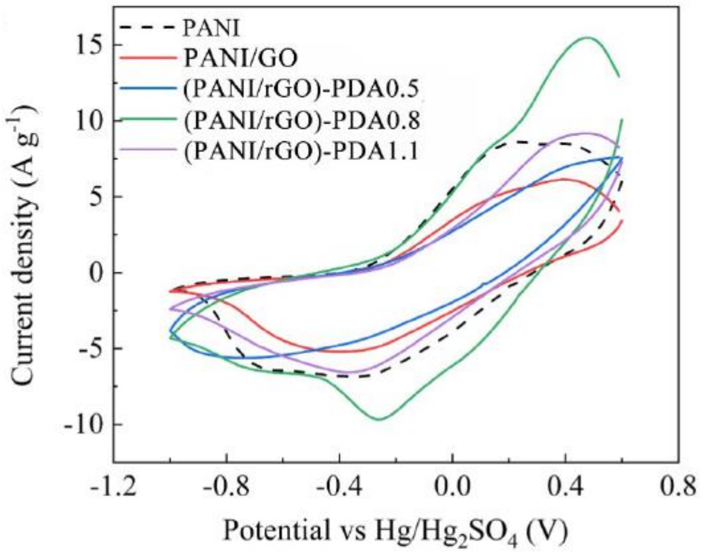
- Cyclic voltammograms of PANI/rGO composites at a scan rate of 20 mV s^{-1}

Reference [1]



CV plot of PANI/rGO-TA-24 h
owns the highest magnitude and most
pronounced redox peaks

Reference [2]



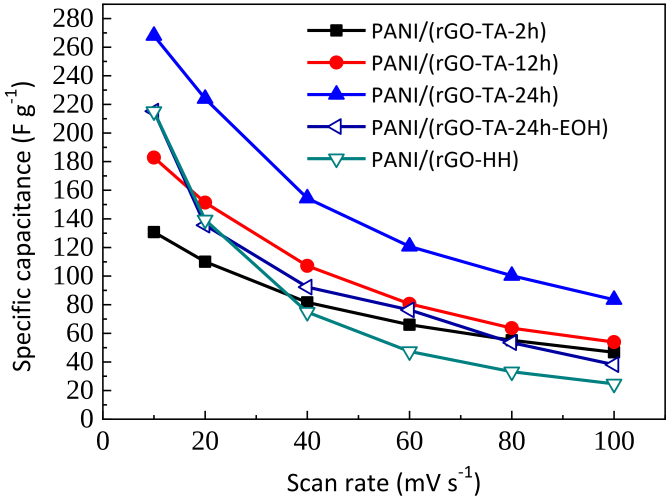
(PANI/ rGO)-PDA0.8 exhibits
highest specific capacitance

[1] - Zhao X, Pionteck J, et al., J. Mater. Sci. (2019) 15, 10809
[2]- Zhao X, Pionteck J, J. Appl. Polym. Sci. 2021; 138:e50663

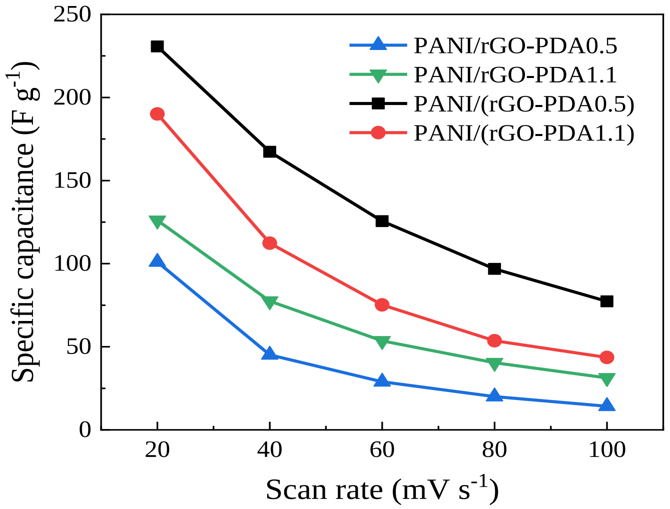
Graphitic PANI-composites as electrode material

- Cyclic voltammetry results of PANI/rGO composites at different scan rates

Reference [1]



Reference [2]



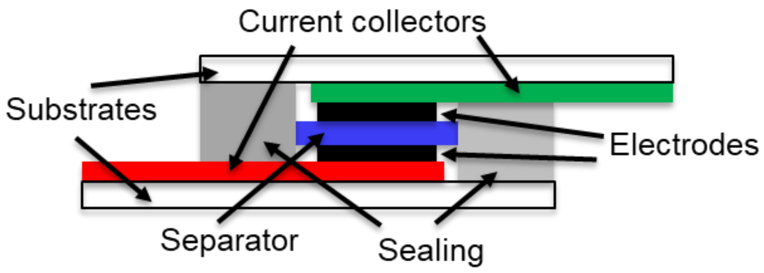
Capacity dependence on scan rate (3-electrode system)

[1] - Zhao X, Pionteck J, et al., J. Mater. Sci. (2019) 15, 10809
[2] -Zhao X, Pionteck J, J. Appl. Polym. Sci. 2021; 138:e50663

PART-2

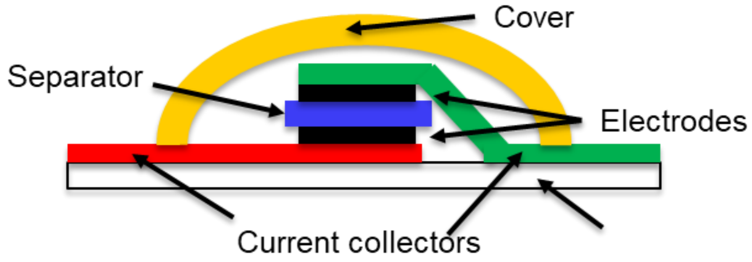
Monolithic supercapacitor fabrication process

Monolithic Supercapacitor



Laminated face-to-face

Targeted structure in the InComEss



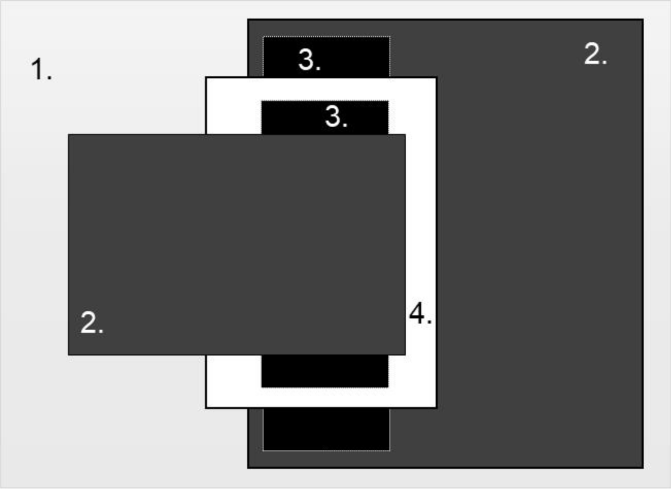
Monolithic

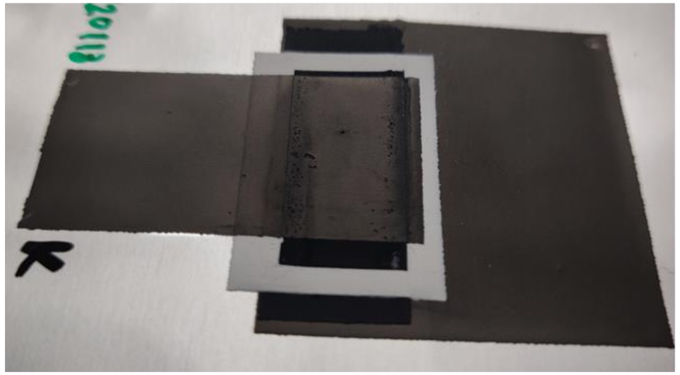
Manufacturing process only by additive manufacturing – no need for lamination

- SC fabricated by depositing layers on top of each other with printing techniques and raw material inks
- Eliminates the assembling step required to seal and separate electrodes during fabrication
- **Critical component:** separator layer acts as the substrate for the upper layers and must not let the inks penetrate to lower layers – risk of short-circuit. Simultaneously the separator needs to be porous to allow ionic conductivity between the electrodes
- **Separator materials:** chitosan, chitosan with cellulose, chitosan with filler materials – targeting to dimensionally stable material with long life-time when impregnated with electrolyte
- Electrically comparable with face-to-face laminated supercapacitors

Supercapacitor structure

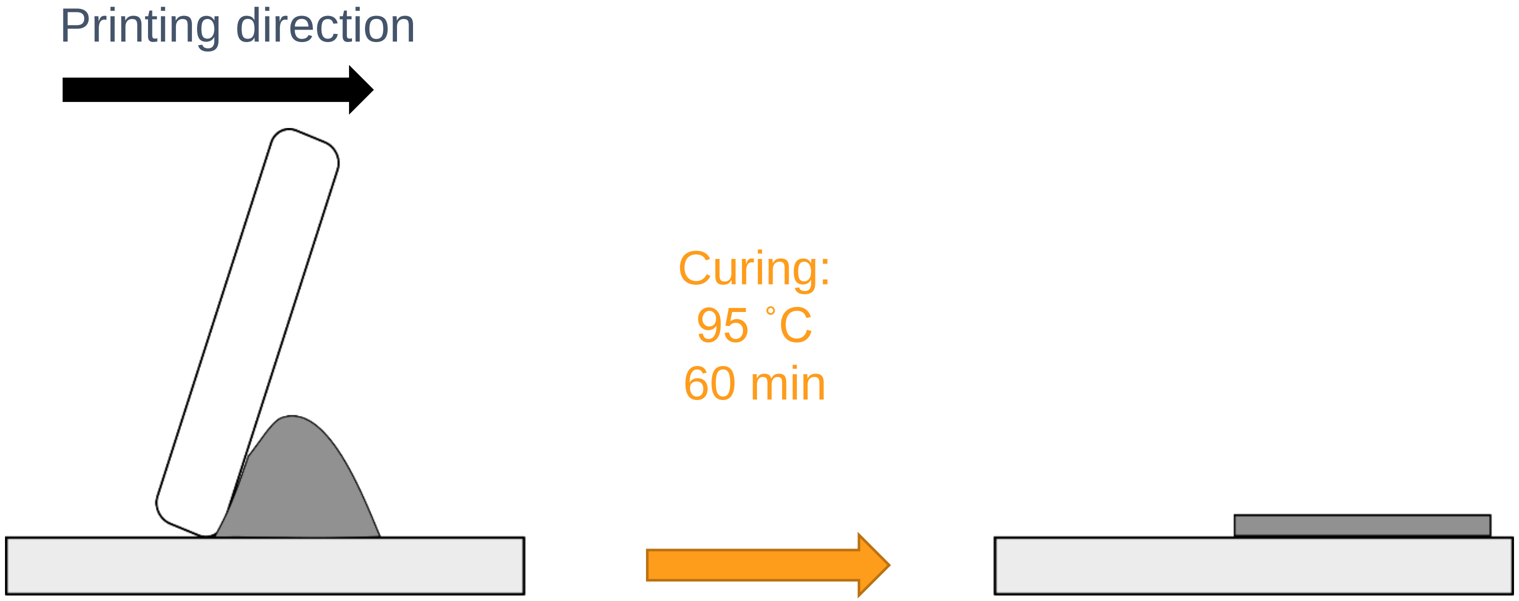
1. Substrate
2. Current collector
3. Electrode
4. Separator





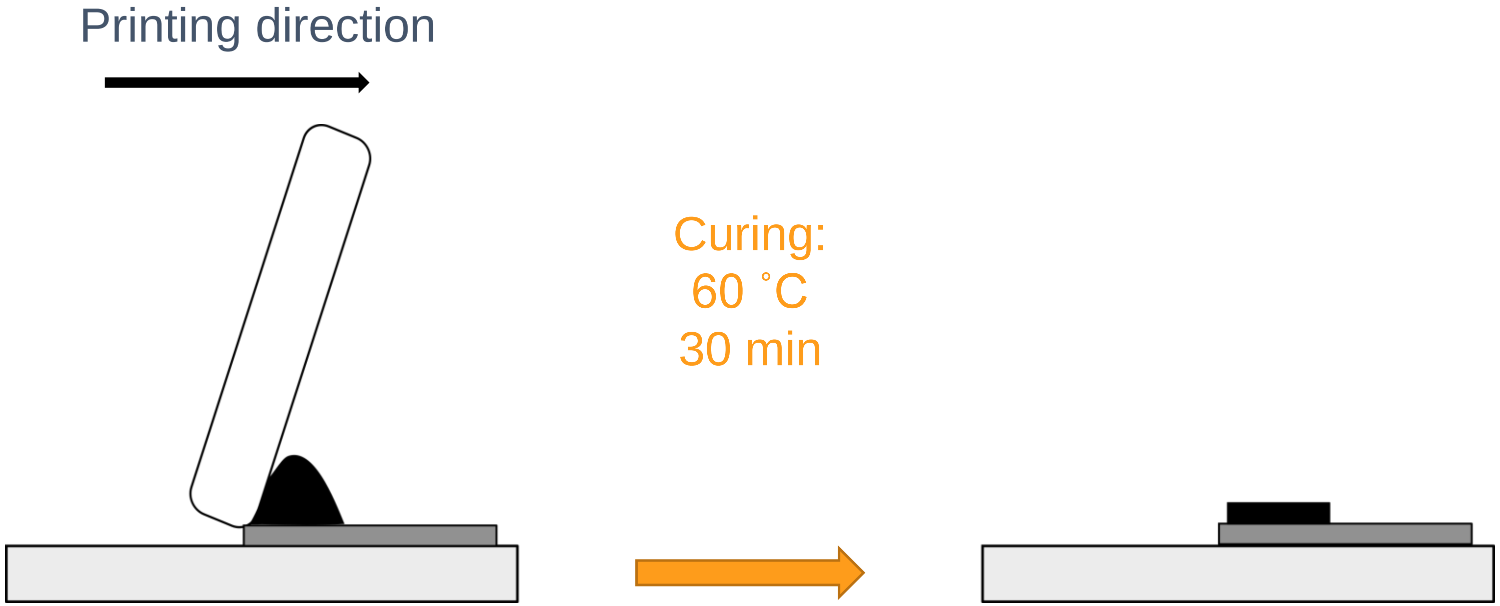
Supercapacitor structure

Step 1: Lower current collector



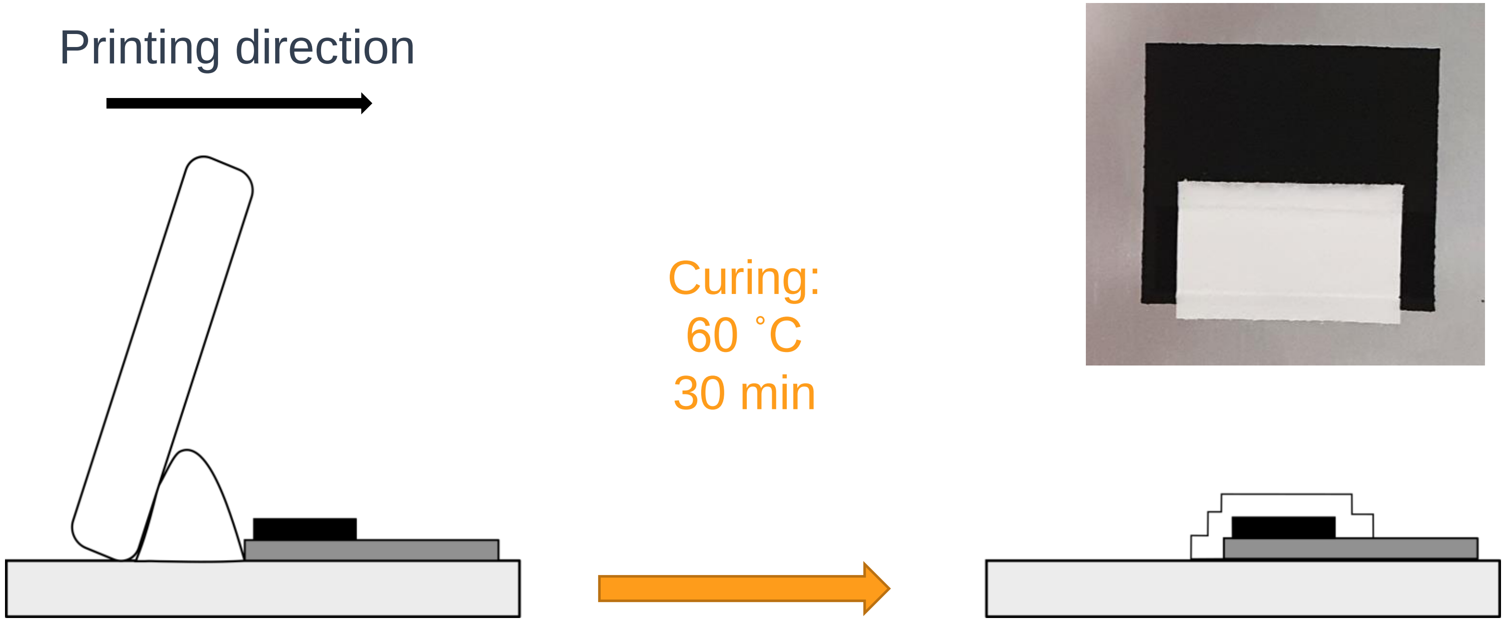
Supercapacitor structure

Step 2: Lower electrode



Supercapacitor structure

Step 3: Separator

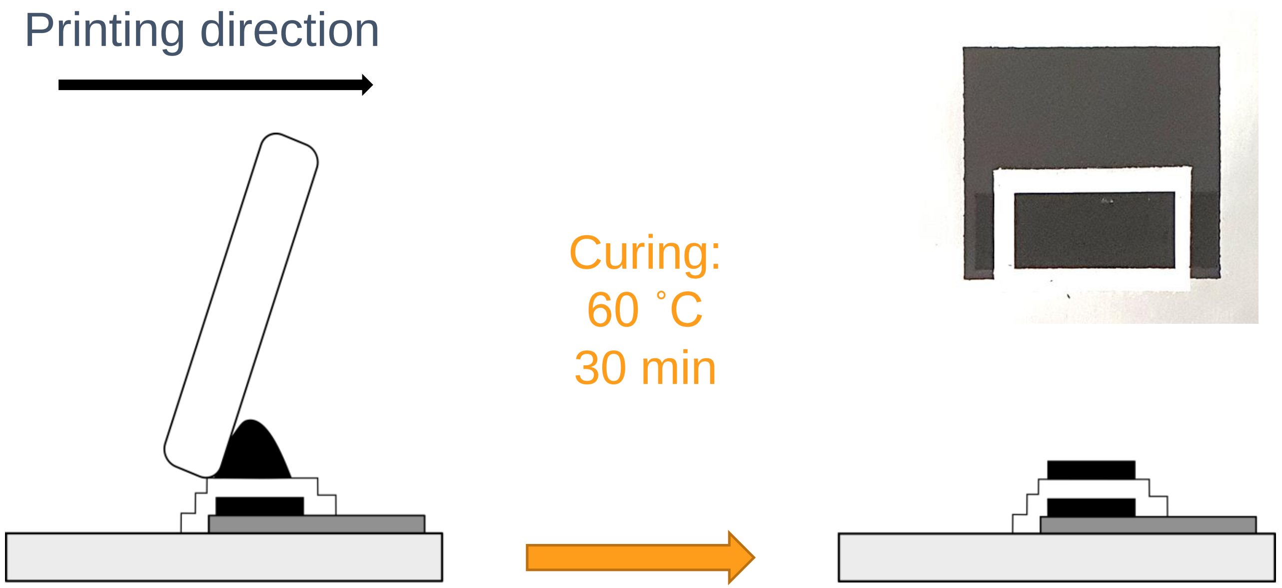


Printing direction

Curing:
60 ˚C
30 min

Supercapacitor structure

Step 4: Upper electrode

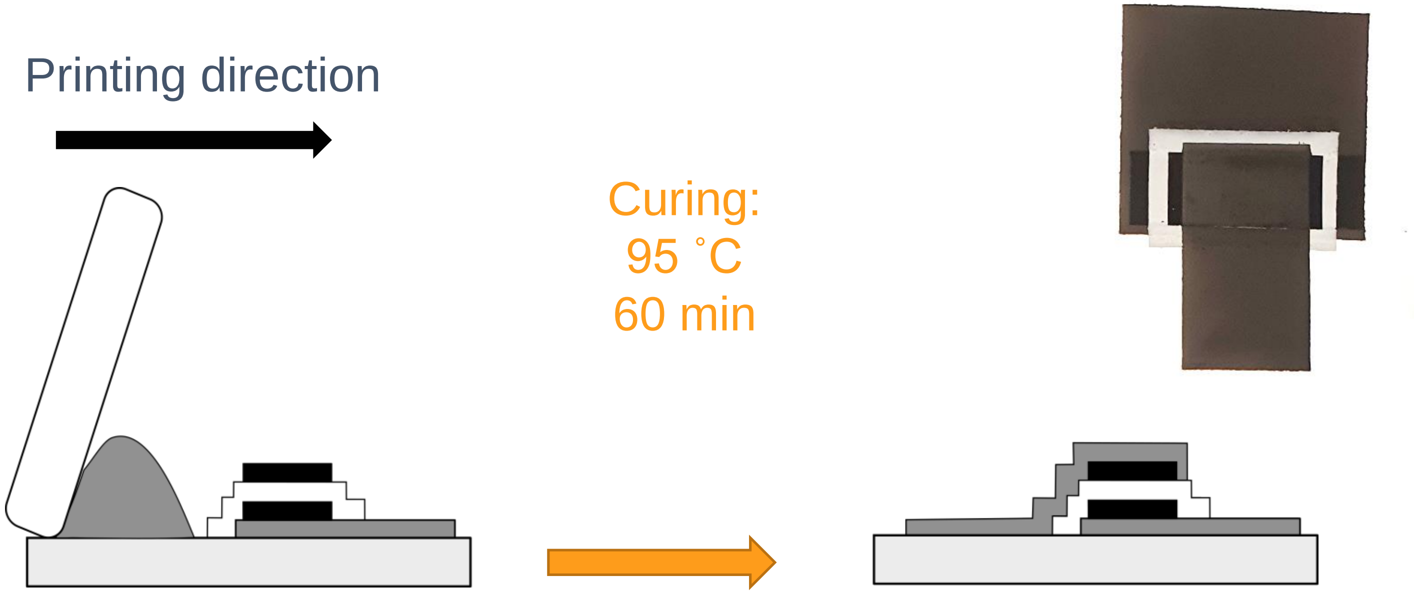


Printing direction

Curing:
60 ˚C
30 min

Supercapacitor structure

Step 5: Upper current collector

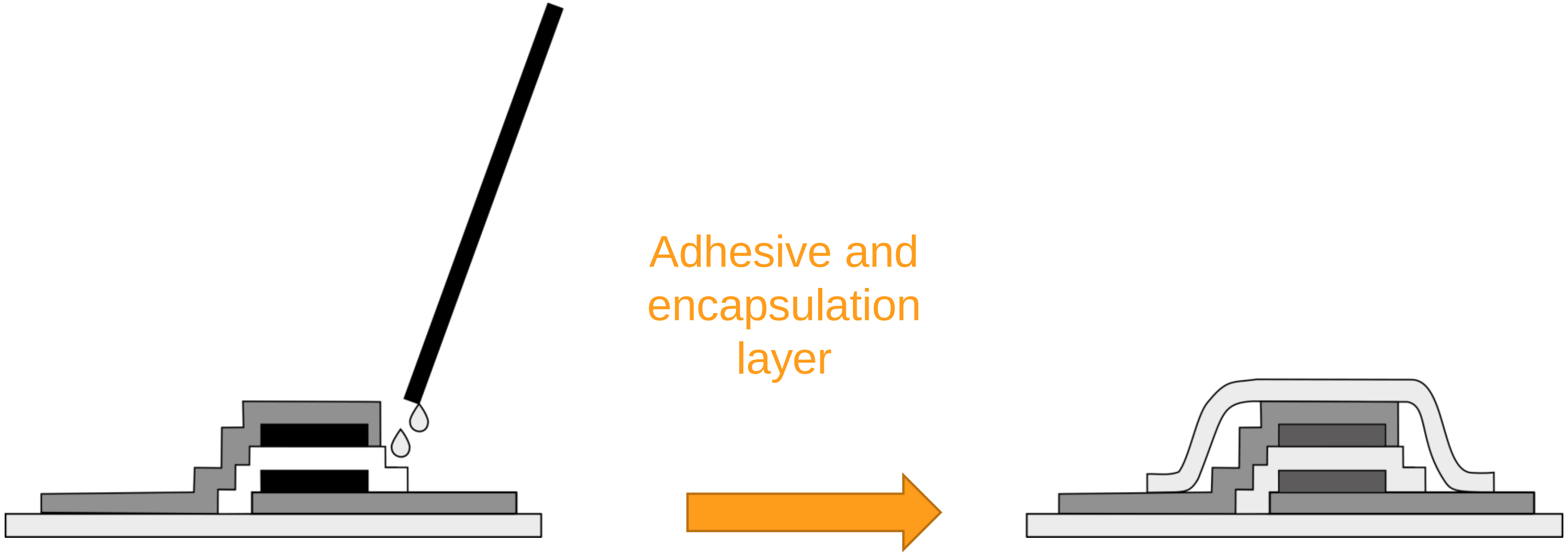


Printing direction

Curing:
95 ˚C
60 min

Supercapacitor structure

Step 6: Electrolyte and encapsulation

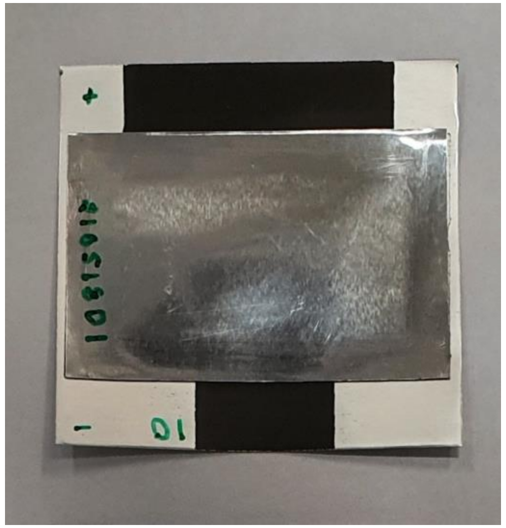


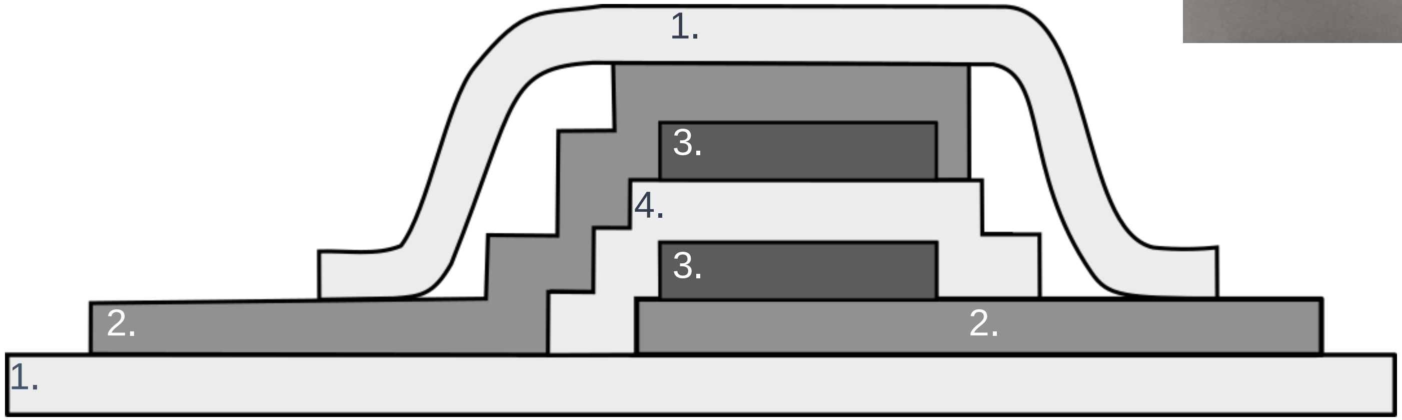
Adhesive and encapsulation layer

Supercapacitor structure

The final structure

1. Al PET (substrate + encapsulation)
2. Current collector
3. Electrode
4. Separator





Summary and Outlook

- Supercapacitors generally possess higher power density than batteries and higher energy density than conventional capacitors
- Various PANI/carbon composites were produced by in-situ chemical oxidation polymerization by using APS as an oxidant
- PANI/rGO and PANI/GNP have capacitance values between 200 and 300 F/g at lower scan rate (20 mV/s) [1,2]
- The monolithic supercapacitor configuration has been fabricated using a doctor blade coating technique

In the frame of InComEss:

- Different carbon sources combined with PANI are used and compared with other available materials
- Environmentally friendly chitosan binders are used for electrode preparation
- Neutral aqueous and gel electrolytes are applied
- Monolithic fabricated supercapacitors are developed by utilizing printing technologies

In addition, two other training presentations prepared by TAU are available:

- Cyclic Bending Test Method for Flexible Supercapacitors
- (X-Ray) Micro (µ)-CT for Non-destructive Inspection of Structural Failure of Flexible Supercapacitors

[1] - Zhao X, Pionteck J, et al., J. Mater. Sci. (2019) 15, 10809
[2] -Zhao X, Pionteck J, J. Appl. Polym. Sci. 2021; 138:e50663

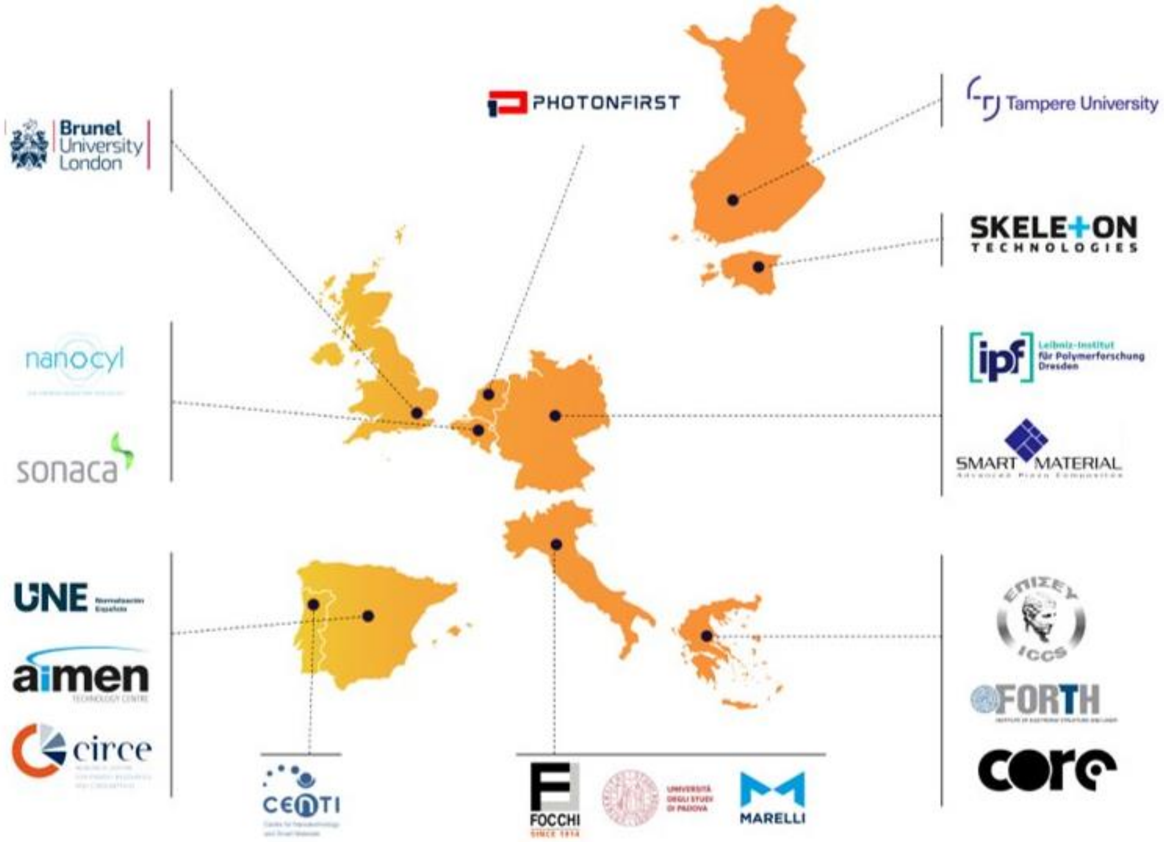
References

- https://www.incomess-project.com/
- Liu, Ying, et al. "Vanadium nitride for aqueous supercapacitors: a topic review" Journal of materials chemistry A (2020) 8 (17), 8218-8233
- Jiang, Yuqi, and Jinping Liu. "Definitions of pseudocapacitive materials: a brief review" Energy & Environmental Materials (2019) 2(1), 30-37
- Wang, Huanhuan, Jianyi Lin, and Ze Xiang Shen. "Polyaniline (PANi) based electrode materials for energy storage and conversion" Journal of Science: Advanced materials and devices (2016) 1(3), 225-255.
- https://www.maxwell.com/products/ultracapacitors/
- Simon, Gogotsi, Nature Materials (2008) 7(11), 845-854
- Zhao X, Pionteck J, et al., J. Mater. Sci. (2019) 15, 10809
- Zhao X, Pionteck J, J. Appl. Polym. Sci. (2021); 138:e50663

Tampere University

ipf

InComEss



Tampere University

ipf

InComEss

Innovative polymer-based composite systems
for high-efficient energy scavenging and storage

Thank you

IPF- Department Functional Nanocomposites and Blends

TAU -Faculty of Information Technology and Communication Sciences

Tampere University

Date of creation: March 2023

This project receives funding in the European Commission's Horizon 2020 Research Programme under Grant Agreement Number 862597

ipf