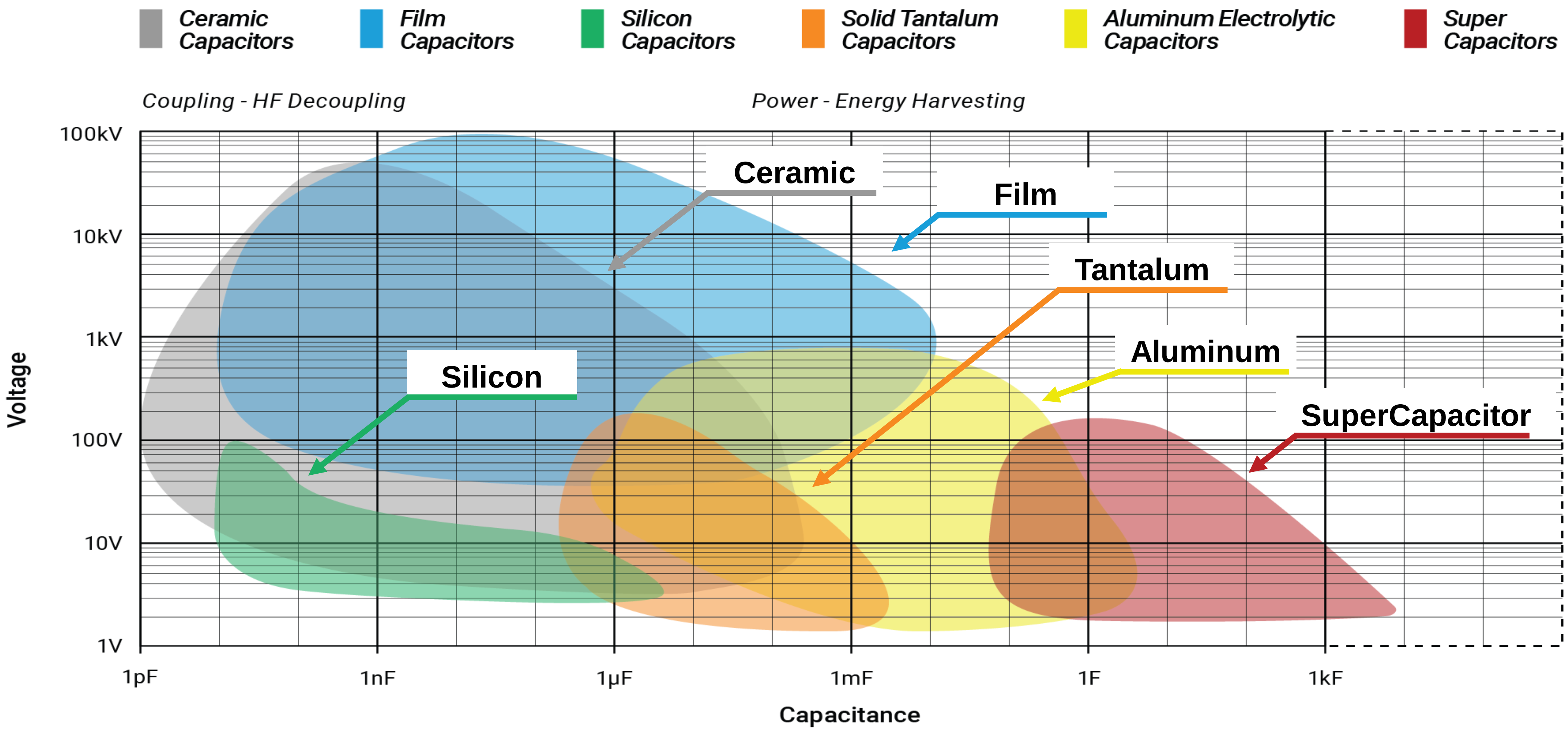
Novel Graphene Material for High Energy Storage Supercapacitors

CMSE April 28th 2022

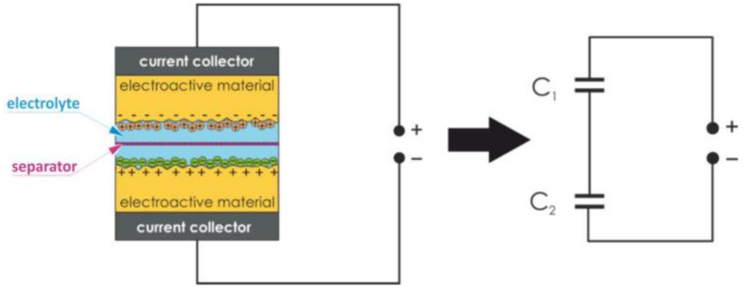
Presented by: T. Zednicek
EPCI European Passive Components Institute, Lanskroun, Czech Republic
www.passive-components.eu

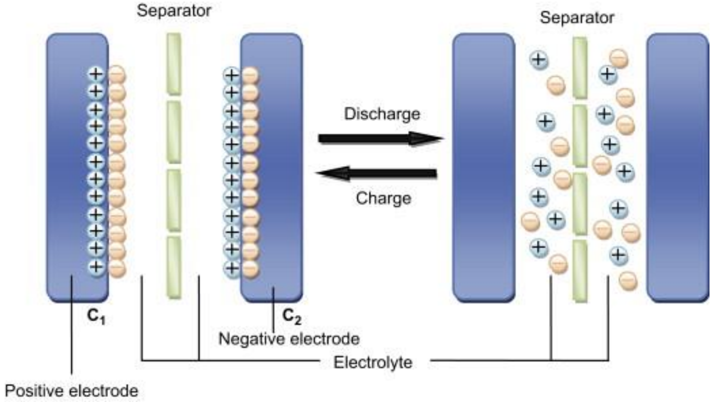
A.Bakandritsos, V. Sedajova, P. Jakubec, M. Otyepka
RCPTM Regional Centre for Advanced Technologies and Materials
Department of Physical Chemistry, Faculty of Science, Palacky University Olomouc, Czech Republic

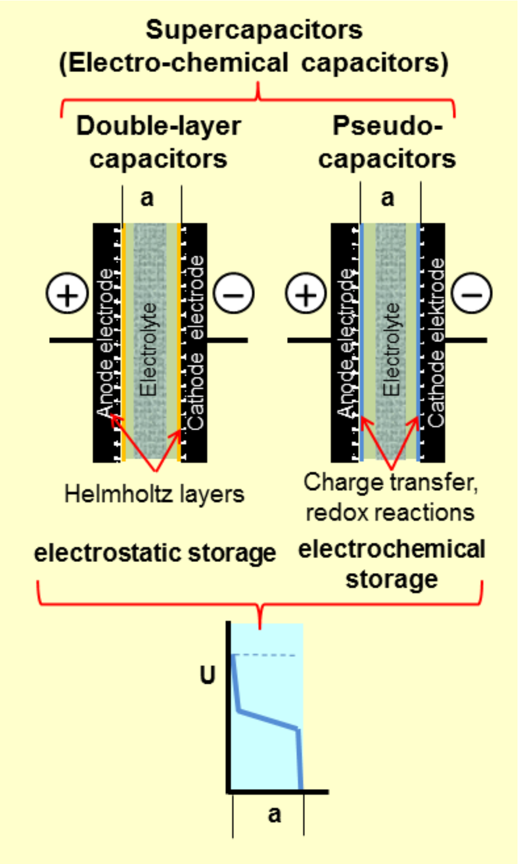
Capacitor Technologies



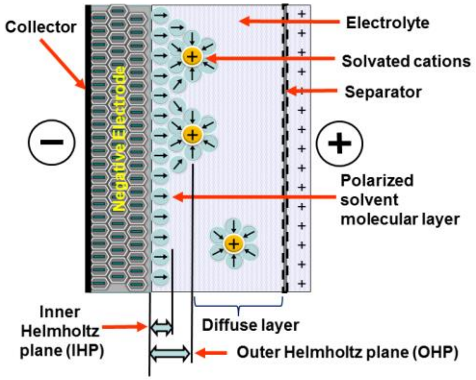
Supercapacitor Storage Mechanisms



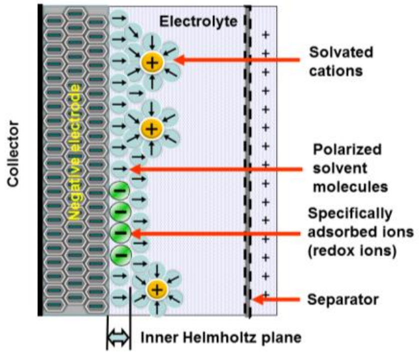




EDLC – Helmholtz Electrostatic Storage



Pseudocapacitance Electrochemical Storage



Supercapacitors Characteristics

Parameters of supercapacitors compared with electrolytic capacitors and lithium-ion batteries

Parameter	Aluminum electrolytic capacitors	Supercapacitors			Lithium-ion batteries
		Double-layer capacitors for memory backup	Super-capacitors for power applications	Pseudo and Hybrid capacitors (Li-Ion capacitors)	
Temperature range (°C)	−40 to 125	−20 to +70	−20 to +70	−20 to +70	−20 to +60
Cell voltage (V)	4 to 550	1.2 to 3.3	2.2 to 3.3	2.2 to 3.8	2.5 to 4.2
Charge/discharge cycles	unlimited	10^5 to 10^6	10^5 to 10^6	$2 \cdot 10^4$ to 10^5	500 to 10^4
Capacitance range (F)	≤ 1	0.1 to 470	100 to 12000	300 to 3300	—
Energy density (Wh/kg)	0.01 to 0.3	1.5 to 3.9	4 to 9	10 to 15	100 to 265
Power density (kW/kg)	> 100	2 to 10	3 to 10	3 to 14	0.3 to 1.5
Self discharge time at room temperature	short (days)	middle (weeks)	middle (weeks)	long (month)	long (month)
Efficiency (%)	99	95	95	90	90
Life time at room temperature (years)	> 20	5 to 10	5 to 10	5 to 10	3 to 5

Capacitor | Capacitor Like ← → Battery Like | Battery

source:Wikipedia

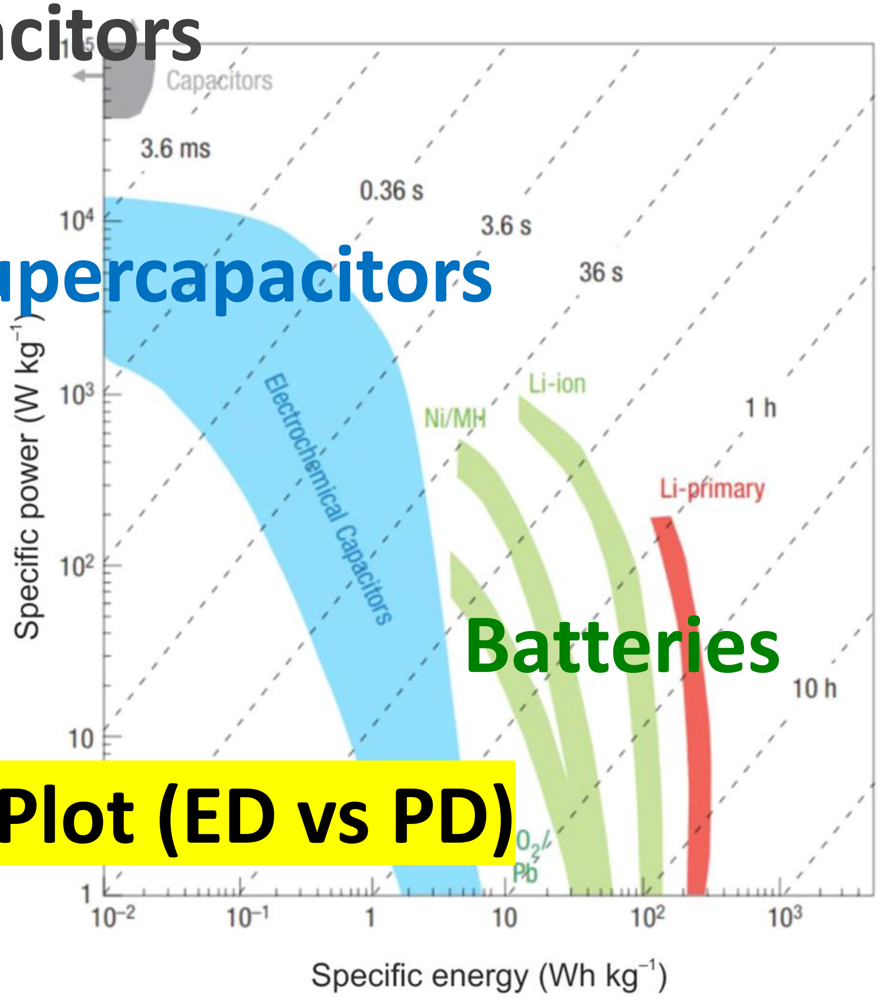
SC Energy & Power Density Benchmark

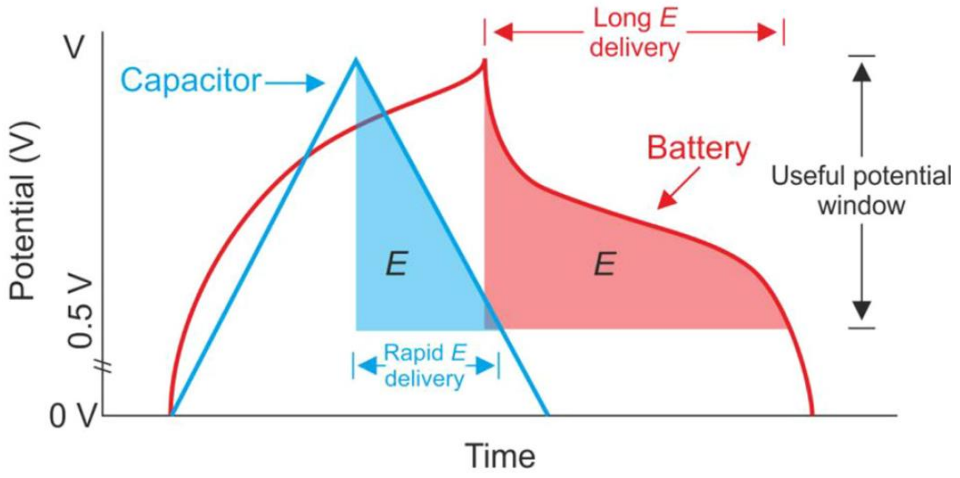
Capacitors

Supercapacitors

Batteries

Ragone Plot (ED vs PD)





source: https://www.sciencedirect.com/science/article/pii/S245226271830093X#b0360

High Energy Supercapacitors

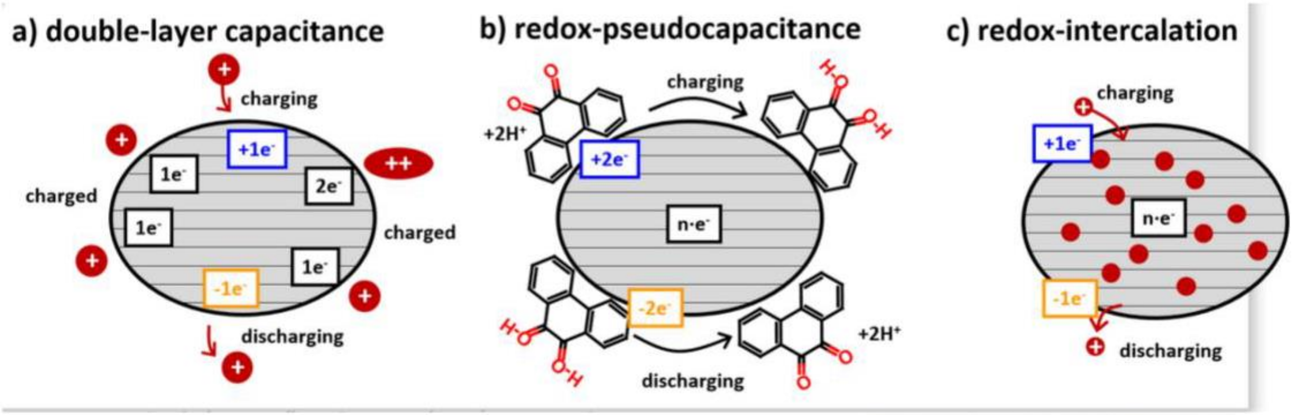
High Energy SC Key Design Consideration:

Electrode System Design
Electrolyte Matching

- High Surface Area
- High Ability to Acumulate Electrostatic or Electrochemic Charge
- High Density (nano-pores) in Thin Layer
- High Electrical (nano-channels) Conductivity for Power Density

Energy Storage Mechanisms

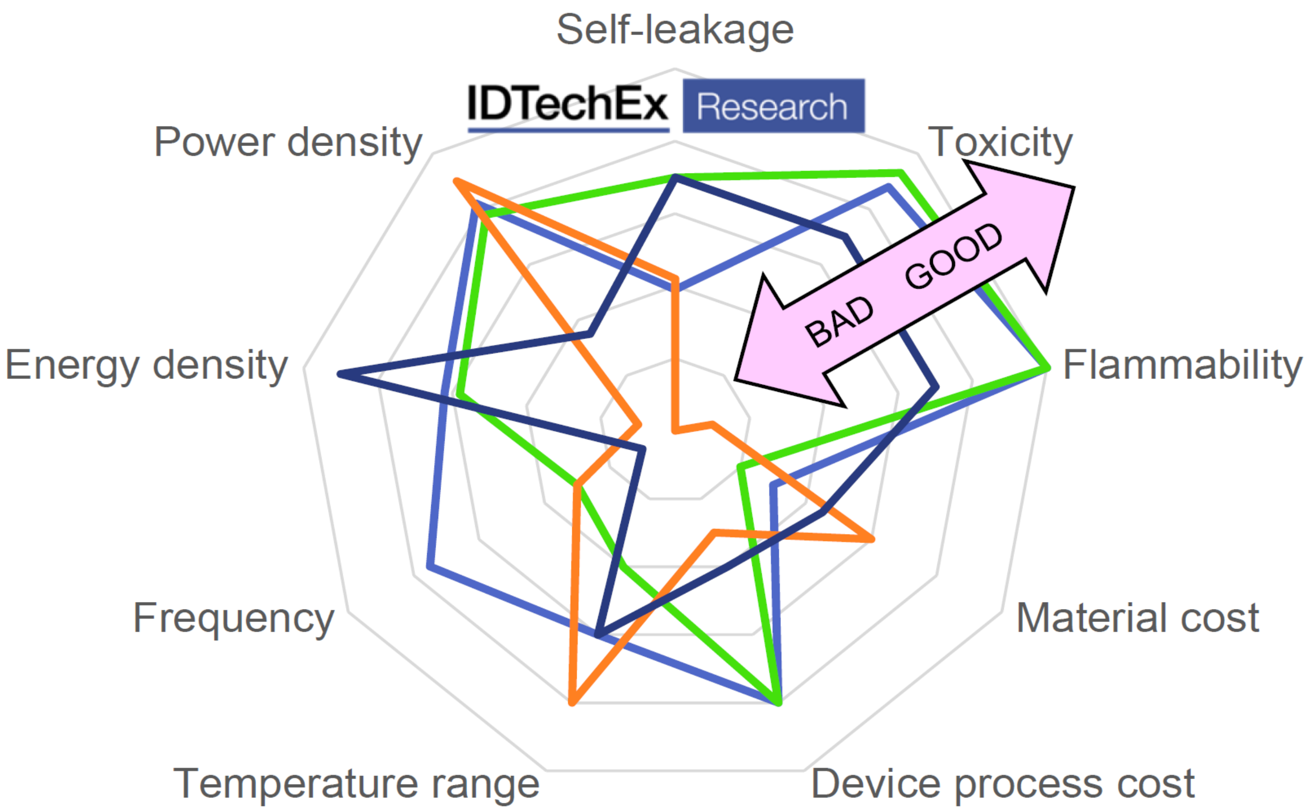
Electrostatic Pseudocapacitance



Source: Leibniz Institute of New Materials

High Energy Supercapacitors

Electrolyte



- **Aqueous Electrolyte**
- **Ionic Liquid**
- **Organic Electrolyte**
- **BSH** = Battery Supercapacitor Hybrid

Source: IDTechEx „Supercapacitor Materials and Formats 2020-2040“ report; published under IDTechEx permission

High Energy Supercapacitors

OUR RESEARCH

RCPTM Regional Centre of Advanced Technologies and Materials

Olomouc, Czech Republic

Regional Centre of Advanced Technologies and Materials (RCPTM)

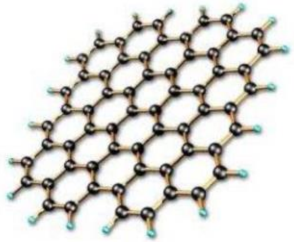
Institute of Molecular and Translational Medicine (IMTM)

Centre of the Region Haná for Biotechnological and Agricultural Research (CR Haná)

Novel Graphene Material for High Energy Storage Supercapacitors

Doubling of Supercapacitors' Energy and Power Density

Electroactive Electrode Design



Graphene Miracles

- 2D one-atom thick
- 200x stronger than steel
- 3x better electron mobility than silicon
- Lightweight
- Flexible
- Thin
- Large surface area
- High electrical conductivity
- High thermal conductivity
- Low Cost
- Transparent
- Bio-degradable

Graphene vs Carbon Benefits:

- cheaper, enormous surface area (2630m^2/g) and higher power density
- 10x more conductive
- theoretical max capacitance of 2D graphene is 550 F/g (~ 200F/g achieved in practice)
- easy team up with various other nanomaterials, prominently carbon nanotubes (CNTs), to create low cost, lightweight and high-performance supercapacitors.

High Energy Supercapacitors

Electrodes: Charge Boosting Options

Structural Design Strategies to Boost Electrode Material Charge Storage Potential

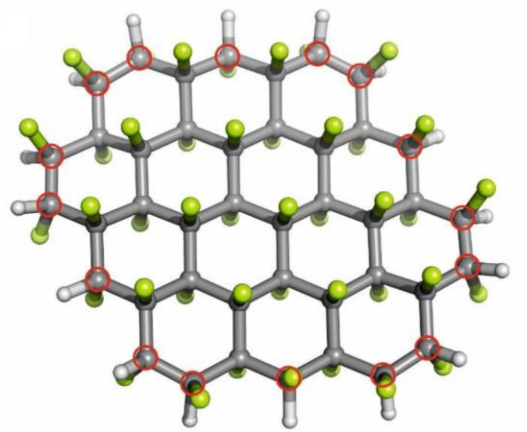
- increase the surface area – microporous 3D structure
- reduce restacking
- increase the packing density and conductivity
- accomplish defect control
- functionalization and hybridization of materials

Capacitance of graphene-based electrode materials can be significantly boosted by:

- assembling them with redox-active reversible materials, e.g., transition metal oxides, such as MnO2, iron oxides or 2D Mxenes
- doping with heteroatoms such as N-doping that increase the electronic conductivity and improves the solid-electrolyte interface, allowing solvated ions to better infiltrate the pores of the electrode – increasing both electrostatic and pseudocapacitance mechanisms
- mounting of longer functional groups perpendicular to the graphene surface may enhance the capacitance further.

Structural Electrode Design – Combining the Boost Options

- **Covalent functionalization of graphene** - allow fine control over the hierarchy of SC electrode materials and bring the 3D micro/nano-porous structure
- **N-Doping**
- **Fluorographene** proposed as the precursor for functionalization – as low cost, ideal high-density matching material with graphene monolayer



carbon atoms are grey
fluorine green
hydrogen white

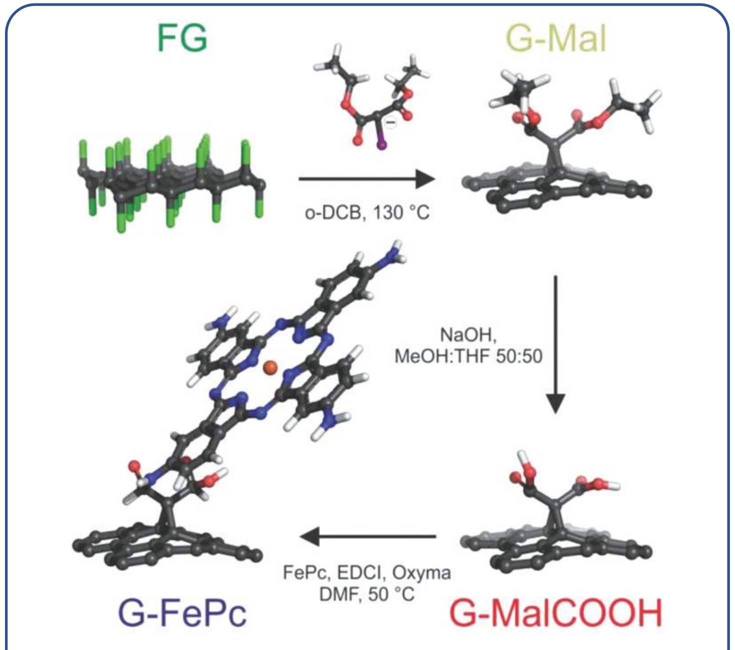
Fluorographene Structure

1st Approach

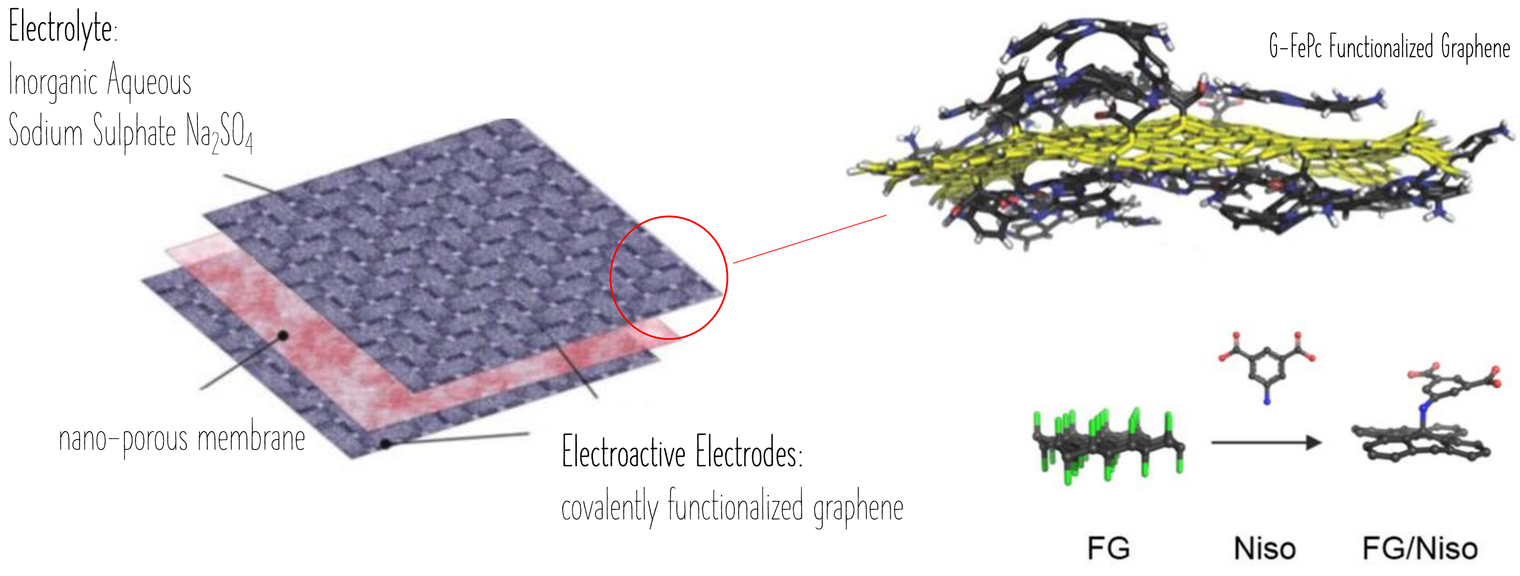
Supercapacitors based on Fluorographene Chemistry

Research Areas

- Synthesis, characterization and applications of low-dimensional carbon-based materials.
- Functionalization and chemical modification of graphene and its derivatives – aim to maximize pseudocapacitance.
- **Iron tetraaminophthalocyanine G-FePc** selected as the functionalization element based on previous experience



A. Bakandritsos et al. *Adv. Funct. Mater.* **2018,** *28 (29),* 1801111

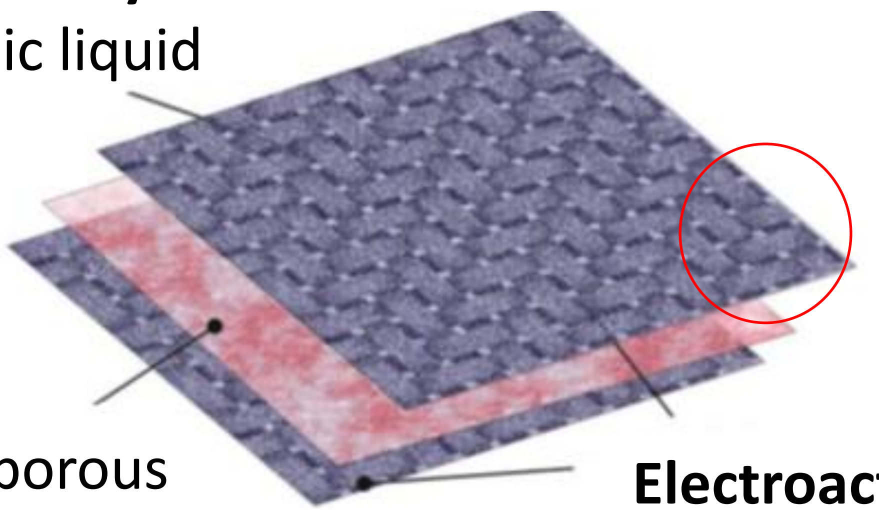


E. C. Vermisoglou et al. *Chem. Mater.* **2019,** *31 (13)*, 4698-4709

2nd Approach

2D N-Doped Graphene SC Structure

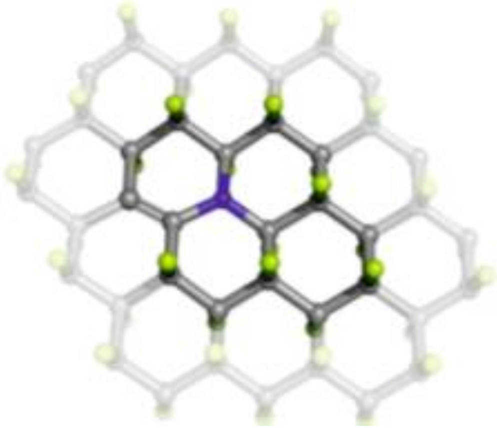
Electrolyte: Ionic liquid



nano-porous membrane

Electroactive Electrodes:
2D N-doped graphene

Synthesized Nitrogen Doped 2D Graphene Layer (extra N-doped & tunable)



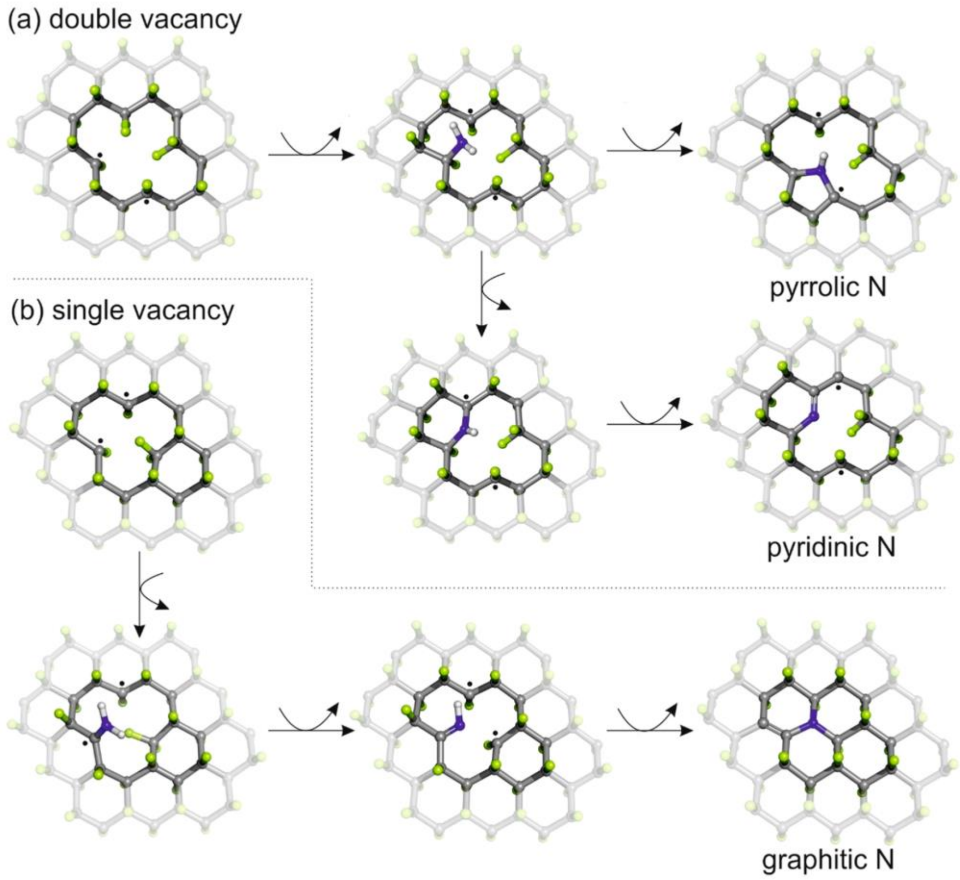
carbon atoms are grey
fluorine green
hydrogen white
nitrogen blue

2D N-Doped Graphene SC Manufacturing

- Doping graphene with heteroatoms can significantly alter its electronic structure
- Nitrogen doping can imprint **active centers** on graphene supporting charge nano-traps and introduce N-type semiconductivity to graphene

carbon atoms are grey
fluorine green
hydrogen white
nitrogen blue

Tunable Synthesis of GN3 Nitrogen Doped Graphene from Fluorographene

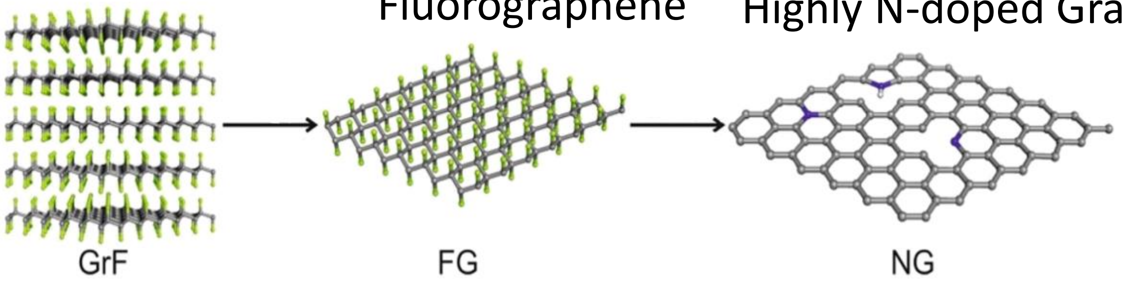


The Process Can Be Tuned To Modify 2D Structure

Graphite Fluoride

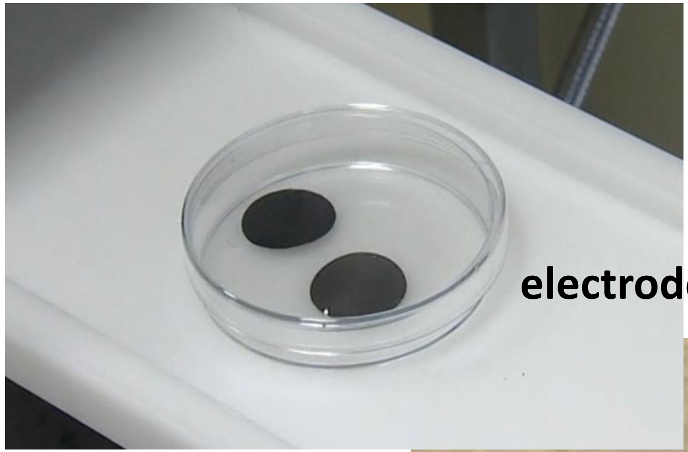
Fluorographene

Highly N-doped Graphene

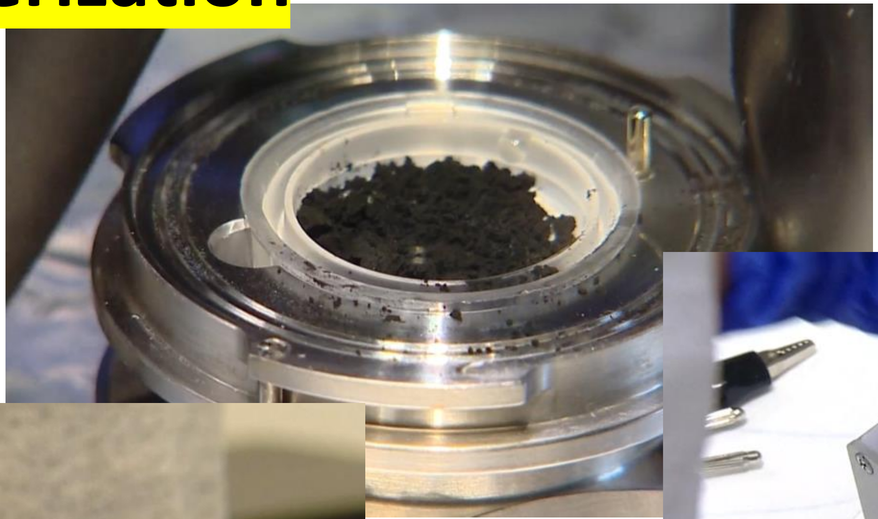


High Energy Supercapacitors

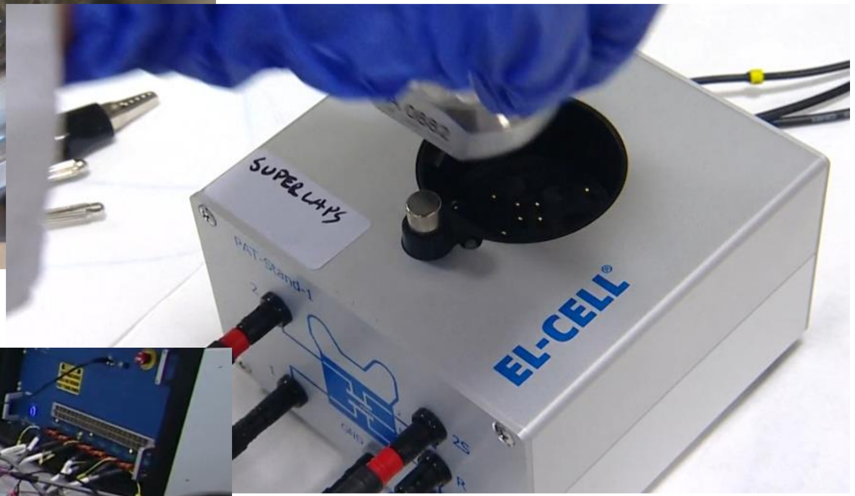
Material Testing & Characterization



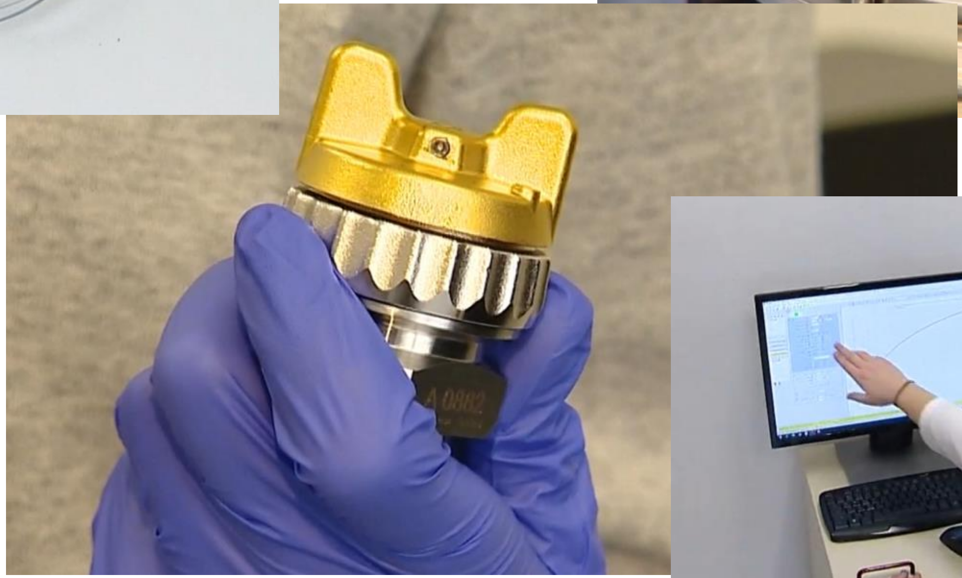
electrodes



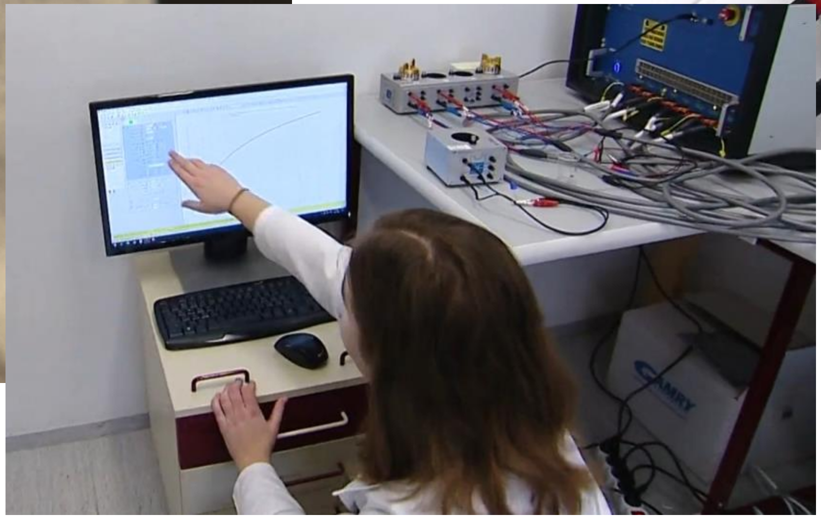
active electrode powder



measurement jig



capacitor contact holder



characterization

1st Approach Results

Covalently Functionalized Graphene SC- Achievements

Record high gravimetric ED

SC Cell Voltage: 1.0V

Driven by Aquous Electrolyte that had to be used

Up to 1000 F/g at 59Wh/kg and 0.3kW/kg

Relatively low power density

main issue: **G-FePc**

High Cost

2nd Approach Results

GN3 2D N-Doped Graphene SC- Achievements

Lower gravimetric ED Compare to Covalently Functioned Graphene

SC Cell Voltage: 3.7V

High Cell Voltage Compare to Conventional SCs

Up to 100 F/g at 55 Wh/kg and 2 kW/kg
corresponds to 320 F/cm^3 at 150 Wh/l and 5 kW/l

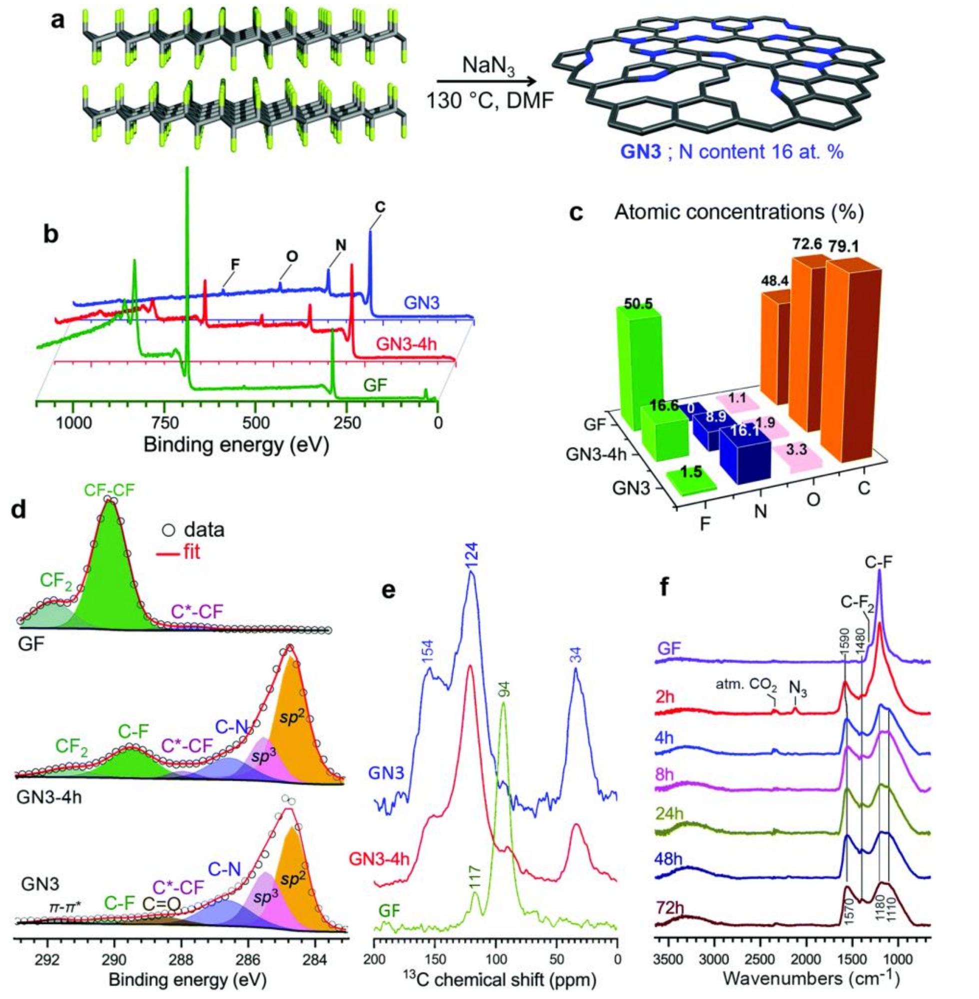
Record Volumetric Energy Density. BEST IN CLASS ever reported on SC Comparable to Batteries !!!

At higher power density (required for SCs)
up to 300 F/cm^3 at 130 Wh/l and 50 kW/l

Record Power Density Significantly Higher Compare to Conventional SCs

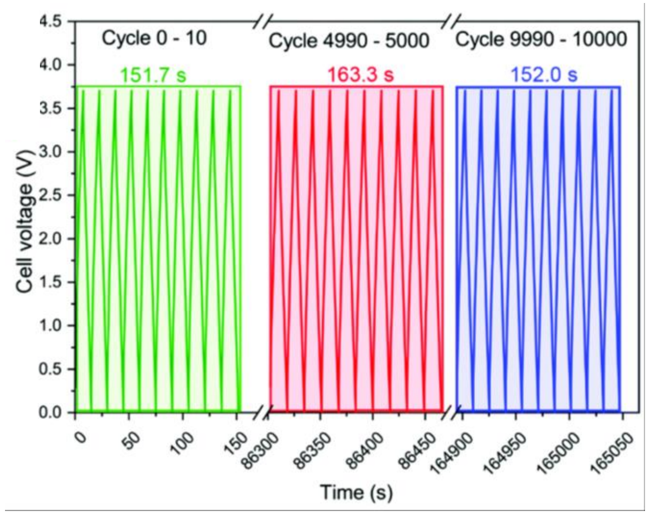
Performance Evaluation

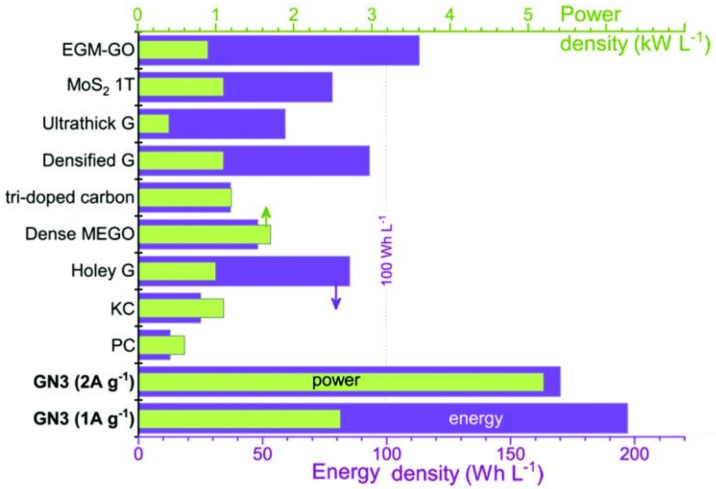
Synthesis and Characterization



Performance evaluation

10 000 Charge/Discharge Cycles



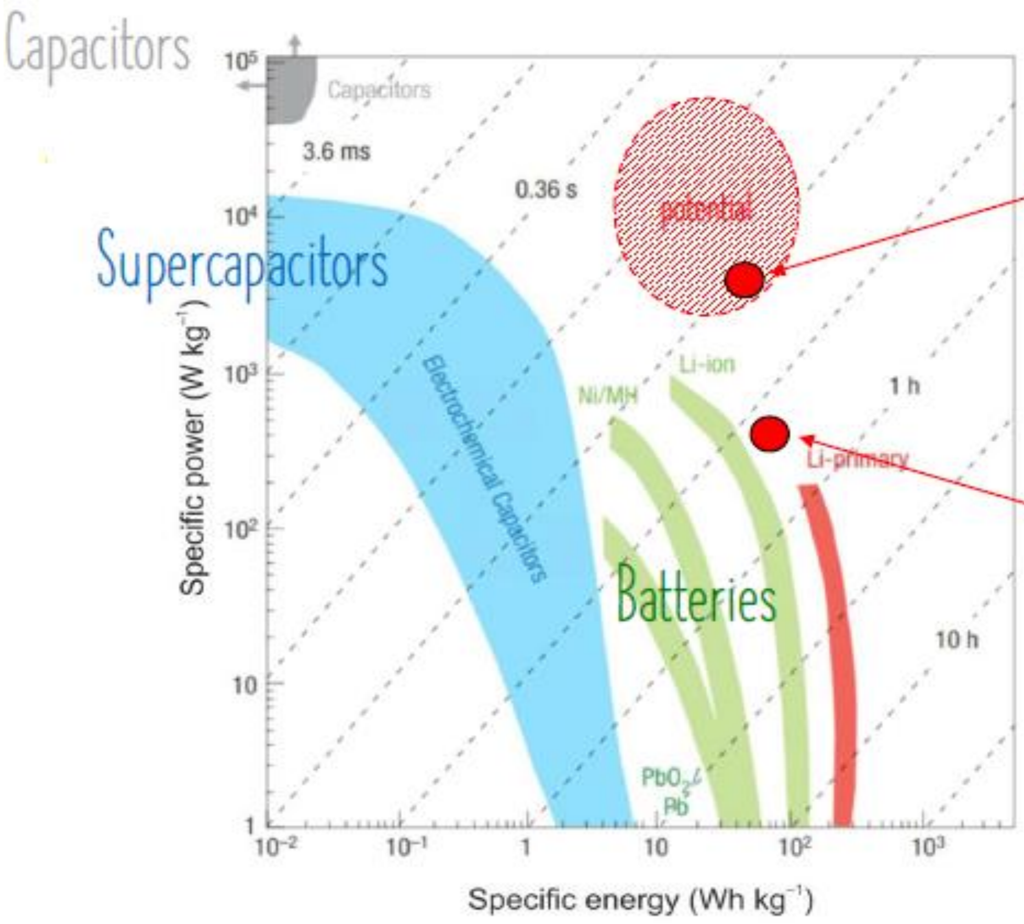


Literature

Our Results

Ref.: Nitrogen doped graphene with diamond-like bonds achieves unprecedented energy density at high power in a symmetric sustainable supercapacitor
Energy Environ. Sci. 2022, *15 (2),* 740-748

Research Achievements



N-Doped 2D Graphene

ED up to 55 Wh/kg at PD 2 kW/kg

Potential:

ED 50-60 Wh/kg at PD 2-50 kW/kg

Covalently Functionalized 3D Graphene

ED up to 59 Wh/kg at PD 0.3 kW/kg

High Energy Supercapacitors

Summary Record, Highest Energy and Power Density Ever Supercapacitor Structures Have Been Demonstrated

- ED of GN3 2D N-doped synthetized graphene up to **150Wh/l, 60 Wh/kg** at PD 2 kW/kg with **2–50 kW/kg** possible
- Novel Process: Tunable synthesis of N-doped 2D graphene using fluorographene
- Safe, environmental friendly construction, no heavy metals or hazardous substances
- High Capacitance retention and „no“ charging/discharging cycle wearout (10K cycles tested)

matching top Ni-MH / std Li-ion Battery

! THIS IS A MAJOR BREAKTHROUGH IN SC CLOSING THE GAP with ED to Batteries and PD to Capacitors !

the fluorographene based processes to prepare high energy graphene electrode material has been filed for patent

Next Step

1. Mass Production Ready High Energy Graphene-Based Supercapacitors

- optimizing the properties of GN3 material
- pilot pre-production of the graphene-based electrode supercapacitors in pouch and wound types (ERC project)
- aim is to increase the energy density of supercapacitors beyond 50 Wh L^{-1}
- Industry partners: Itelcond (Milano,Italy); Bar-Ilan university (Ramat Gan, Israel)

2. Use of Fluorographene Process to Enhance LiS Batteries

Li-S batteries advantage:

- 3-5x higher energy density ~ 2,500 Wh/kg
- Nickel and cobalt free solution (conflict/resource issues free)
- No heavy metals / 3x lighter compared to Li-Ion
- No / suppressed thermal runaway failure
- Cheaper: ~200 tons of sulfur equals to ~1 ton of cobalt
- Lower carbon footprint, RoHS friendly
- 3x Faster charging
- No extra pressure needed (unlike solid states)
- Vigorous 100% charge/discharge depth rate

Issues:

shuttling-effect of the formed lithium polysulfides, as well as their low conductivity limit charge/discharge cycle life to low hundreds of cycles

Our First Experiments:
Fluorographene LiS batteries cycle life capable up to 250-500hours

Thank You !

RCPTM Regional Centre of Advanced Technologies and Materials

European Passive Components Institute

Contact:
Tomas Zednicek Ph.D.
tom@passive-components.eu

www.passive-components.eu
| Passive Components Educational & Information Blog

Acknowledgement

Ministry of Education, Youth and Sports of the Czech Republic
- LO1305, CZ.1.05/2.1.00/19.0377
- Research Infrastructure NanoEnviCz: project No. LM2015073

European Regional Development Fund
- Operational Programme Research, Development and Education CZ.02.1.01/0.0/0.0/16_019/0000754

European Union's Horizon 2020
- ERC project No. 683024

European Union’s ERC Grant
- ERC PoC 899245

The student authors acknowledge the support from the Internal Student Grant Agency of the Palacký University in Olomouc, Czech Republic, IGA_PrF_2019_031 and IGA_PrF_2020_022