ITALIAN NATIONAL AGENCY FOR NEW TECHNOLOGIES, ENERGY AND SUSTAINABLE ECONOMIC DEVELOPMENT

EnerHarv 2024

Supercapacitors Based on Sustainable Materials from Renewable Resources

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Landi Giovanni, PhD – DUEE-SPS-SIE

26-28 June 2024 Perugia, Italy

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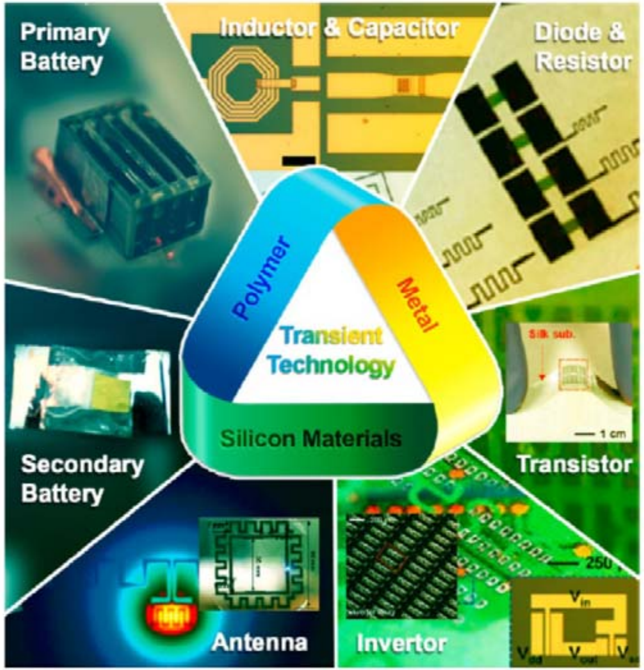
Transient and eco-friendly/sustainable energy systems and electronics

Transient and <u>environmentally friendly energy systems and electronics</u> are emerging technologies characterized by the **ability to physically disappear**, either partially or entirely, in a controlled manner **after a period of stable operation, leaving harmless end products.**

Potential applications *include for example* ***<u>zero-waste environmental sensors</u>****, hardware-secure memory modules, and* ***eco-friendly energy storage devices (e.g. supercapacitor and battery).***



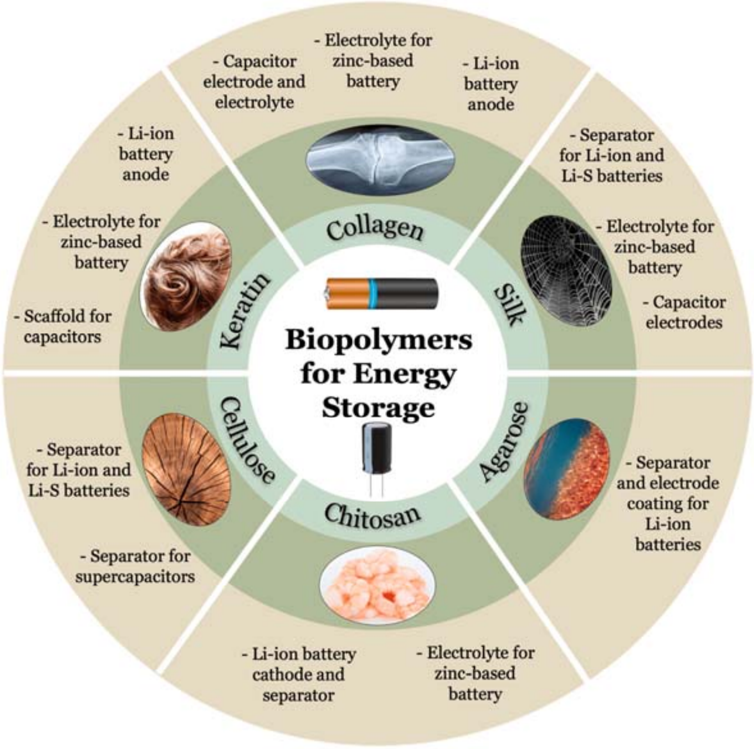
K.K. Fu, Z. Wang, J. Dai, M. Carter, and L. Hu, **Chem. Mater**. 28, 3527 (2016).

Transient and environmentally friendly/sustainable energy systems

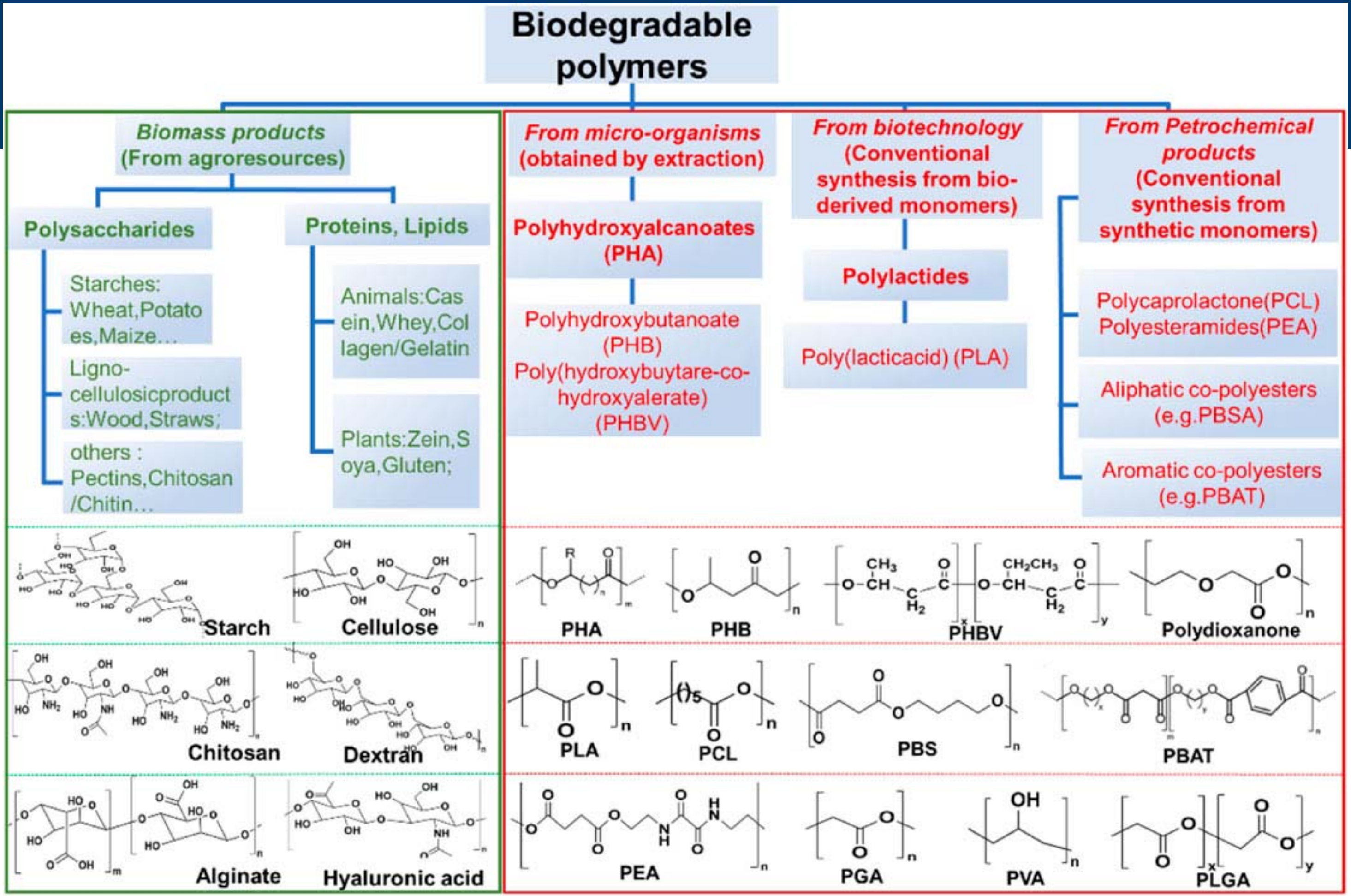
Transient and environmentally friendly energy systems and electronics are emerging technologies characterized by the **ability to physically disappear**, either partially or entirely, in a controlled manner **after a period of stable operation, leaving harmless end products.**

Potential applications *include for example* ***zero-waste environmental sensors****, hardware-secure memory modules, and* ***eco-friendly energy storage devices (e.g. supercapacitor and battery).***

Biopolymer composites obtained from renewable resources (such as **gelatin**, wool, silk, casein, and zein) have a dominant **hydrophilic character, fast degradation, and the ability to fast dissolve under wet conditions.**

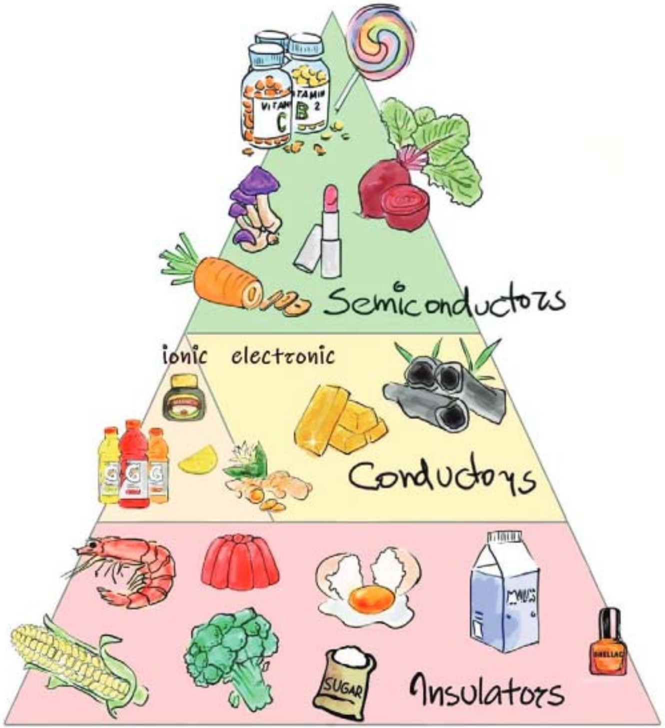


S. Dalwadi, A. Goel, C. Kapetanakis, D. Salas-de la Cruz, X. Hu, **Int. J. Mol. Sci.** 2023, 24



Z. Zhai, X. Du, Y. Long, H. Zheng, ***Front. Electron***. 2022, *3*, 1.

Edible materials classified for their basic electrical property: electronic/ionic conductors, insulators, and semiconductors (1/2)

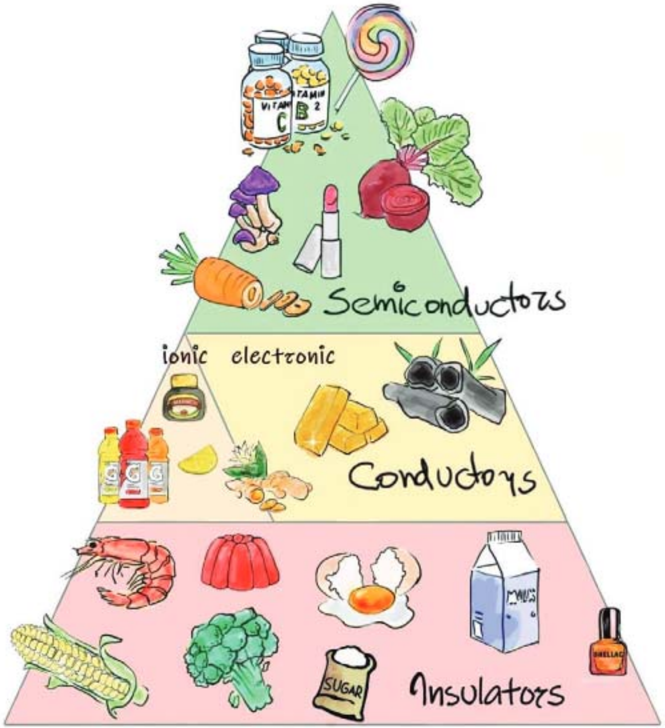


Electronic conductors	Conductivity [S cm^{-1}]	Daily intake
Gold [E175]	4.10×10^5	0.1–1.32 μg kg^{-1}
Silver [E174]	6.30×10^5	5–8.5 μg kg^{-1}
Activated carbon [E153]	0.001–1.940	0.5–1 g kg^{-1}
Magnesium	2.3×10^5	5.6 mg kg^{-1}
Zinc	1.69×10^5	40 mg
Copper	5.96×10^5	1.6 mg
Iron	1.00×10^5	8–45 mg
Calcium	2.98×10^5	2500 mg

Ionic conductors	Conductivity [S cm^{-1}] (frequency range [Hz])	Daily intake
Gatorade drink	$>2 \times 10^{-3}$ ($0.01–10^5$)	Not specified
Vegemite/Marmite	$20 \pm 3/13 \pm 1$ (frequency not specified)	Not specified
Hydrogel (gelatin powder + sodium alginate powder (E 401) + tap water) + NaCl	$(200 \pm 20) \times 10^{-3}$ ($1–10^5$)	Gelatin, not specified Na: 1.5–2.3 g Cl: 3.1 g
Chitosan + $NH_4CH_3CO_2$ (E264)	$(1.47 \pm 1.17) \times 10^{-4}$ ($1–10^6$)	Chitosan >0.05 g kg^{-1}[74] $NH_4CH_3CO_2$, not specified

A. S. Sharova, F. Melloni, G. Lanzani, C. J. Bettinger, and M. Caironi, **Adv. Mater. Technol**. 2000757 (2020).

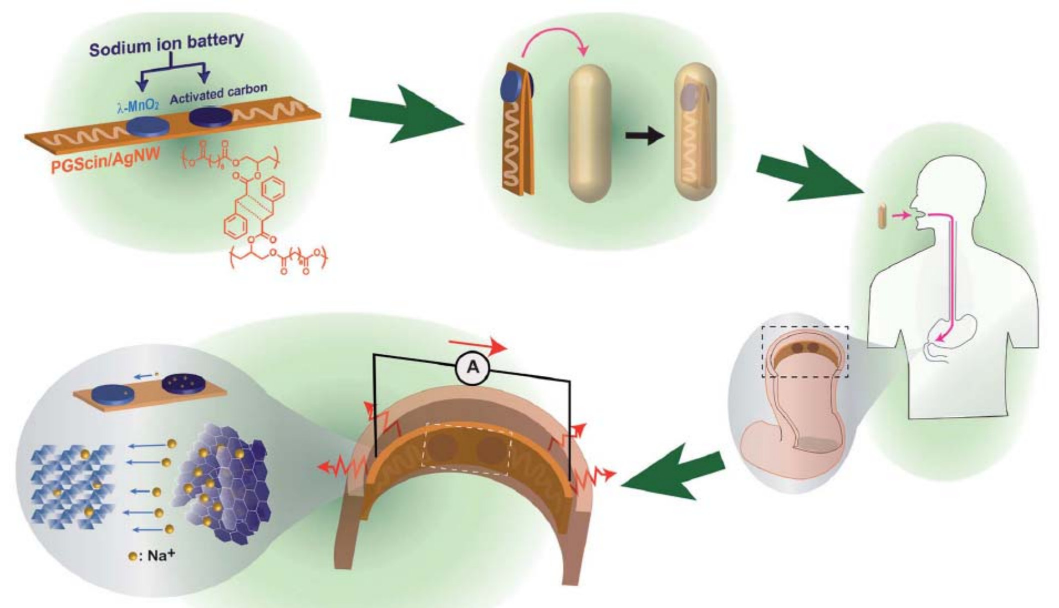
Edible materials classified for their basic electrical property: electronic/ionic conductors, insulators, and semiconductors (2/2)

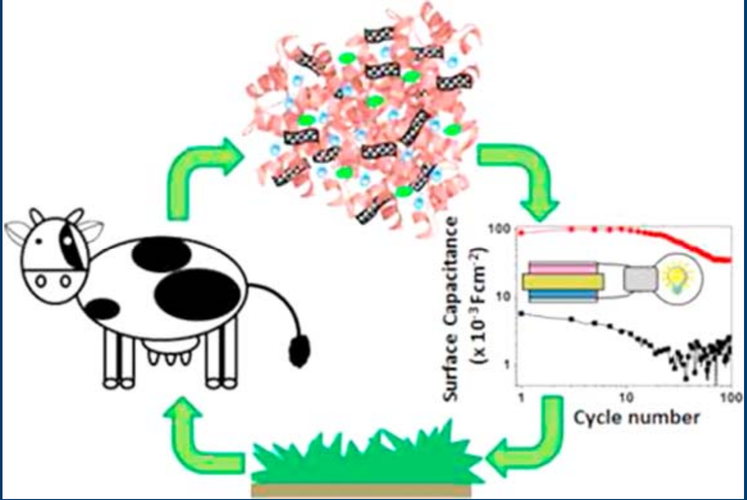


Insulators	Relative dielectric constant (frequency range [Hz])	Daily intake
Cellulose (E 460 (i); E 460 (ii); E 461–466; E 468; E 469)	1.3–6 (100–1 × 10^6)	Not specified Suggested total daily exposure 660–900 mg kg^{-1}
Shellac (E904)	3–4 (50–500 × 10^3)	Not specified
Albumen	5–7 (100–1 × 10^6)	Not specified
Polyethylene oxide + I_2 (90/10 wt%) (E1521)	3–12 (1–50 × 10^3)	PEG: 5–10 mg kg^{-1} I_2: 600 µg per day
Powdered infant milk	1.6–3 (10 × 10^6–3 × 10^9)	Not specified
Glucose	6.35 (1 × 10^3)	Not specified
Aloe vera	3.39	Not specified
Starch	2.2–3.20 (2.2 × 10^9)	Not specified
Natural rubber	3.5–3.8 (≈5)	Not specified
Natural rubber + Sisal oil palm fibers	4–5 (≈5)	Not specified

Semiconductors	Carrier mobility [$cm^2 V^{-1} s^{-1}$]	Daily intake
β-Carotene	$\mu_h = 4 \times 10^{-4}$	5 mg kg^{-1}
Indigo	$\mu_{e,h} = 1 \times 10^{-2}$	5 mg kg^{-1} for indigo carmine
Perylene diimide	$\mu_e \leq 2 \times 10^{-2}$	8000 mg kg^{-1} in mice

A. S. Sharova, F. Melloni, G. Lanzani, C. J. Bettinger, and M. Caironi, **Adv. Mater. Technol**. 2000757 (2020).



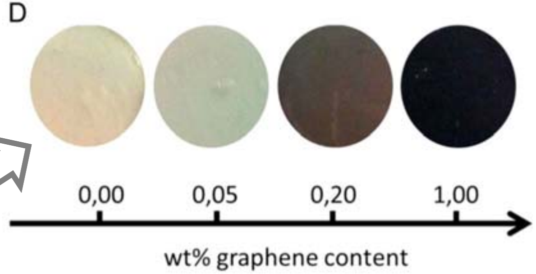


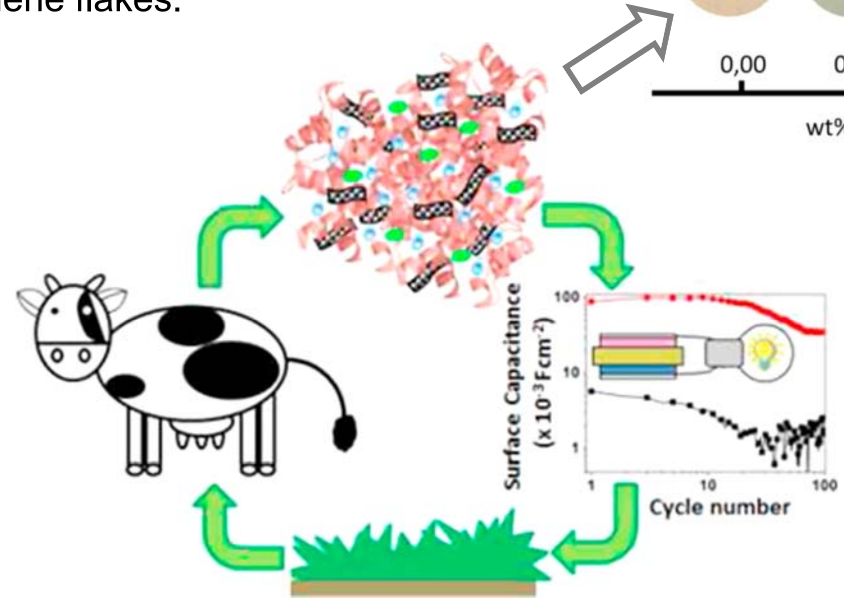
Transient and environmentally friendly/sustainable energy systems

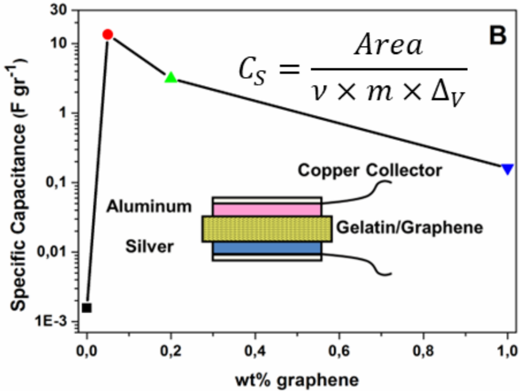
State of art

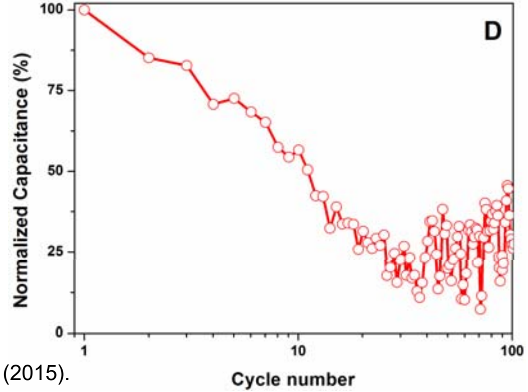
Dielectric capacitance based on gelatin nanocomposite for low-cost energy storage device

A biodegradable low-cost energy storage material has been obtained by using a self-assembly nanocomposite gelatin and graphene flakes.







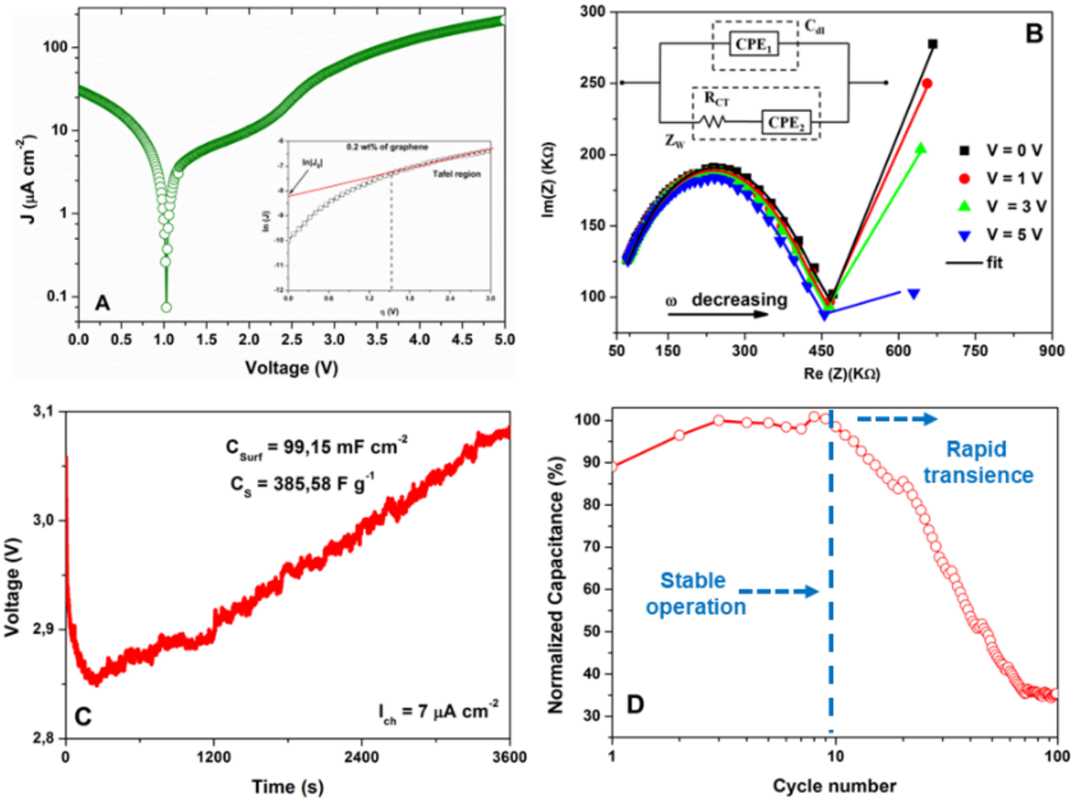


G. Landi et al. **Nano Energy** 17, 348 (2015).

Enhancement of the dielectric properties induced by voltage stress

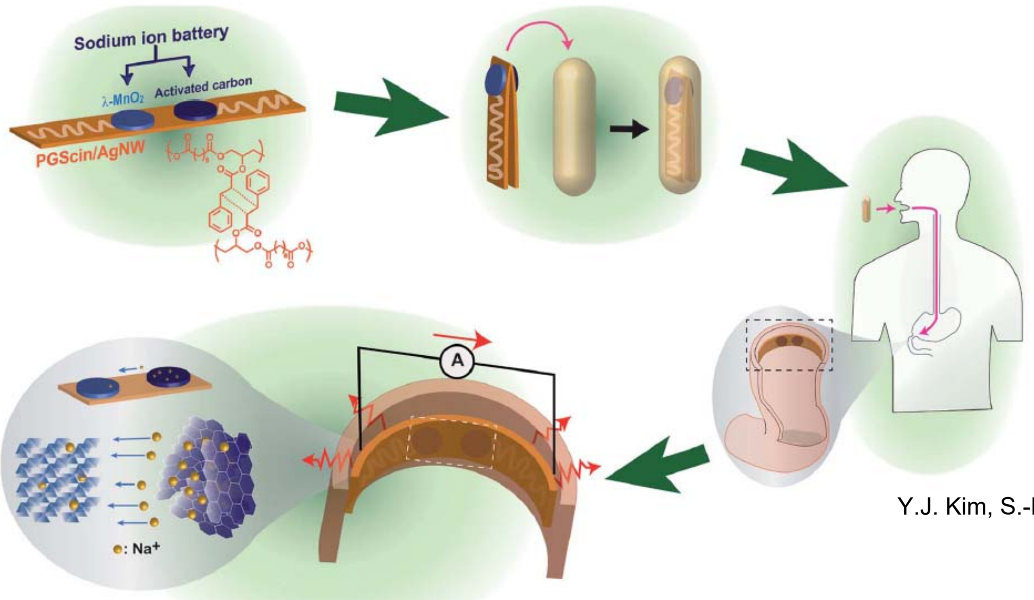
The ability of the biopolymer to bind the water–glycerol molecules and the graphene flakes leads to an **improvement in the dielectric properties**.

An electrical oxidation at the anode contact has been observed **by applying** to the device **a higher bias voltage.** The modified active material exhibits an **enhancement of the cycle stability with a further increase of the specific capacitance** up to a value of **380 F/g**.



G. Landi et al. **Nano Energy** 17, 348 (2015).

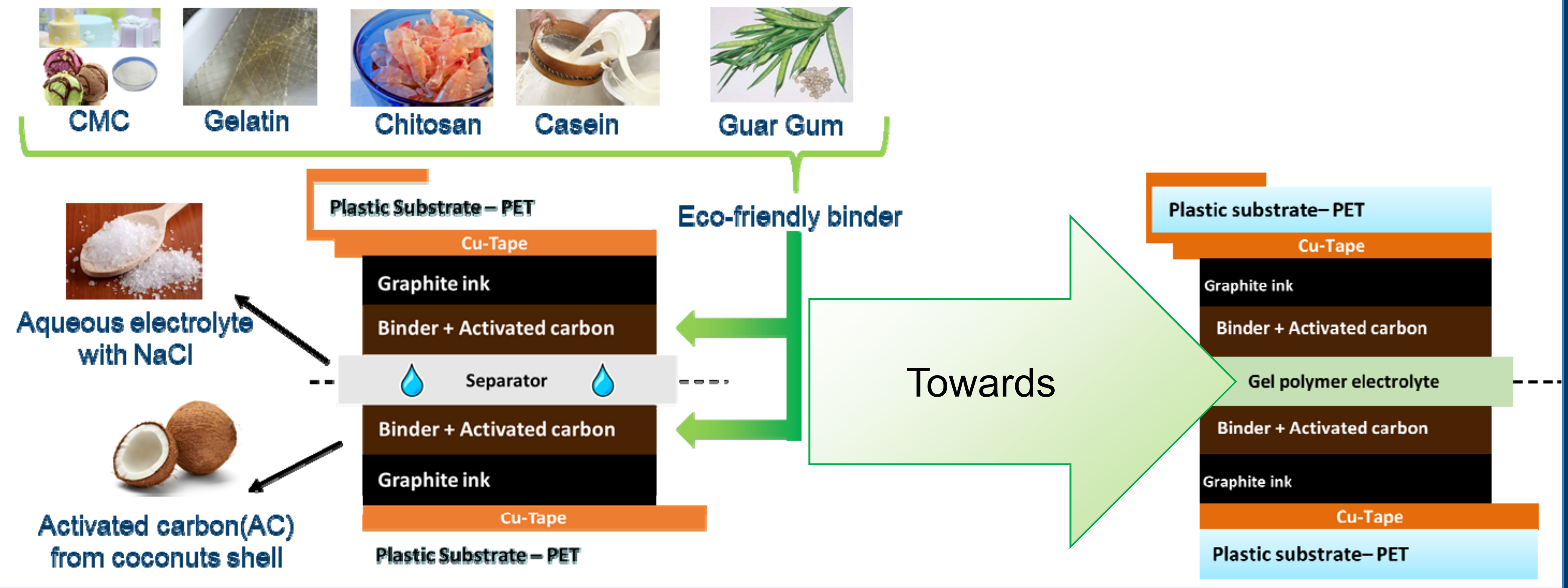
Self-deployable current sources fabricated from edible materials



They introduce electrochemical electronic power sources compatible with non-invasive deployment strategies and are composed entirely of edible materials and naturally occurring precursors consumed in common diets.

Y.J. Kim, S.-E. Chun, J. Whitacre, and C.J. Bettinger, **J. Mater. Chem**. B **1**, 3781 (2013).

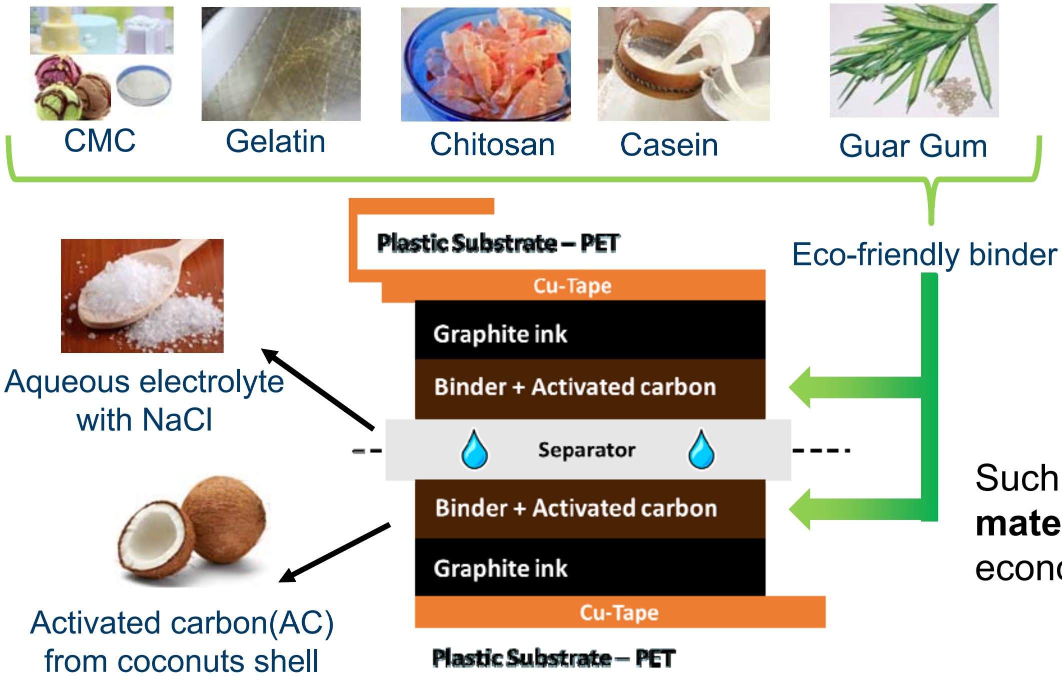
The current sources developed herein were powered by onboard sodium ion electrochemical cells. **Potentials up to 0.6 V and currents in the range of 5-20 μA could routinely be generated**. These devices were envisioned as an enabling platform technology for edible electronics employed in non-invasive sensing and stimulation of tissues within the human body.



Development of a high-performance eco-friendly supercapacitor using waste material obtained from renewable, low-cost, and water-processable resources

Sustainable binders for environmentally friendly carbon-based supercapacitors with aqueous electrolyte (1/2)

Environmentally friendly energy storage devices have been fabricated by using **functional materials obtained from completely renewable resources.**

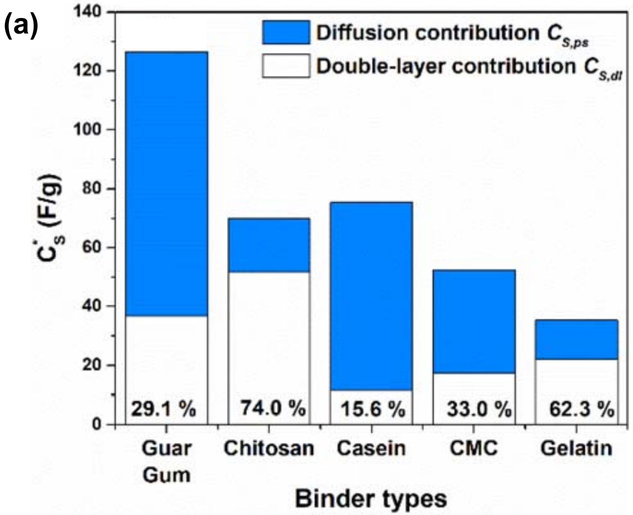


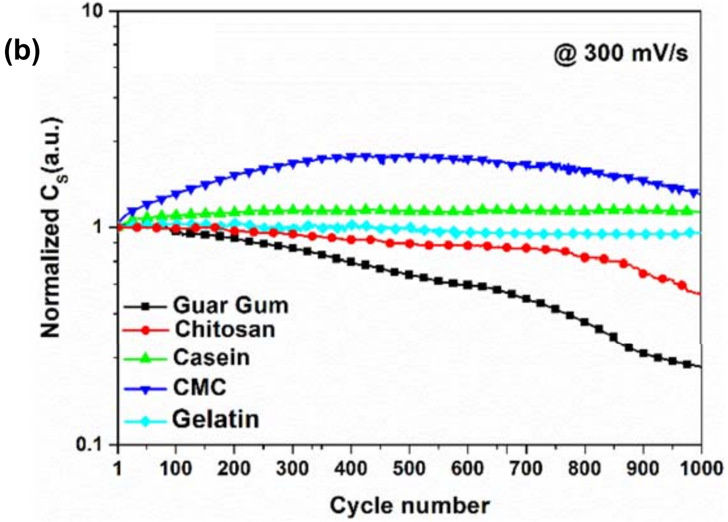
Sustainable and low-cost binders within the electrode active material of **water-processable** symmetric carbon-based supercapacitors.

Such **binders** are selected from **natural-derived materials and industrial by-products** to obtain economic and environmental benefits.

G. Landi, et al., *Nanomaterials* **2021**, *12*, 46.

Sustainable binders for environmentally friendly carbon-based supercapacitors with aqueous electrolyte (2/2)



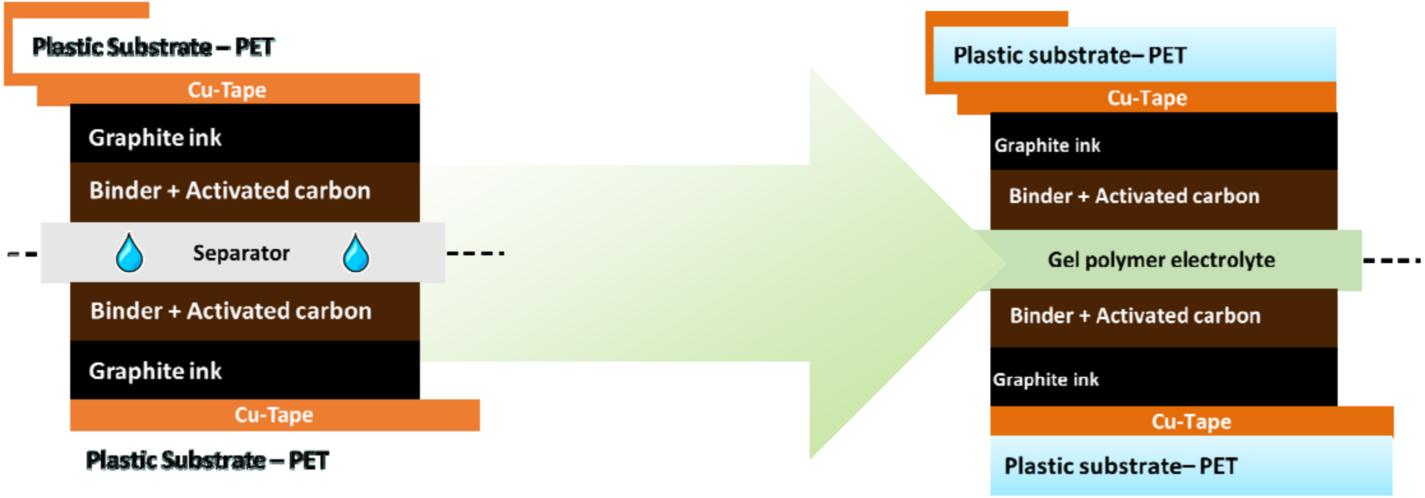


A detailed **analysis of charge storage mechanisms** (e.g., involving faradaic and non-faradaic processes) at the **electrode/electrolyte interface reveals pseudocapacitance behavior** in the supercapacitors.

Good cycle stability is observed with casein, CMC, and gelatin as electrode binders for **up to 1000 cycles**.

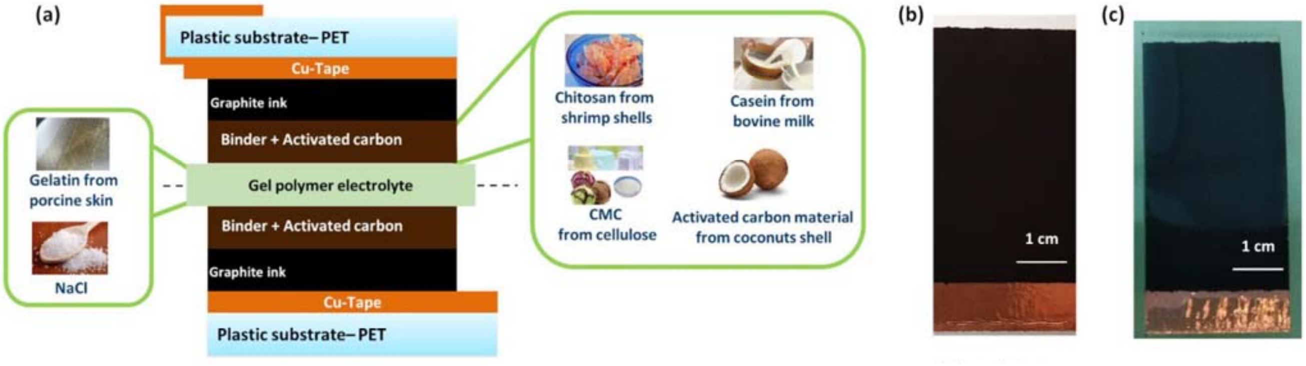
The highest-performing device delivers 3.6 Wh/kg of energy with a power density of 3925 W/kg.

Actions to enhance the performance of sustainable supercapacitors

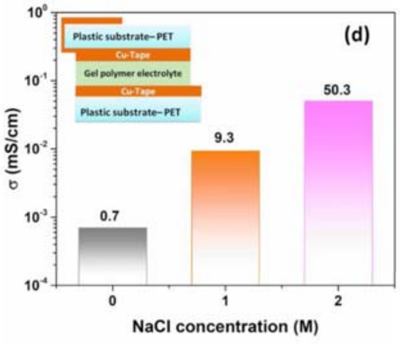


- **Increase the cycle stability:** e.g., by replacing the aqueous electrolyte with a gel-polymer electrolyte (GPE).
- **Improve/maintain sustainability**: e.g., by using a substrate with metallized biodegradable plastic (PLA /gelatin + Cu film) and exploring other GPEs with different salts.
- **Enhance energy performance**: e.g., by using more effective electrode binders and GPEs to improve ion accumulation and pore filling at the electrodes, increase the voltage window, etc..

Electrochemical performance of biopolymer-based hydrogel electrolyte for supercapacitors with eco-friendly binders (1/2)



An environmentally friendly hydrogel based on gelatin has been investigated as a gel polymer electrolyte in a symmetric carbon-based supercapacitor.

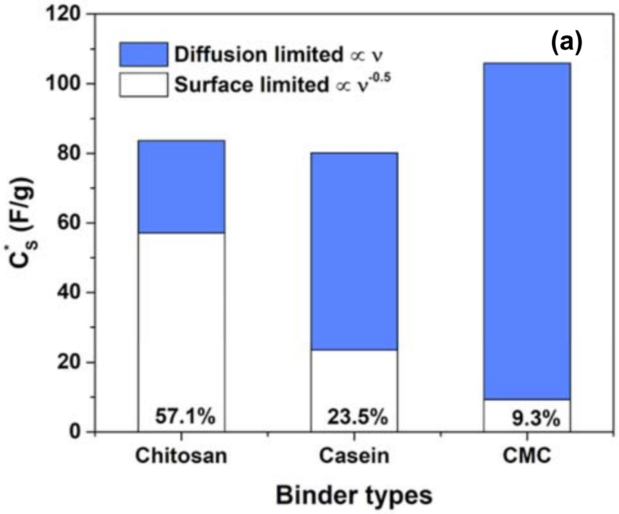


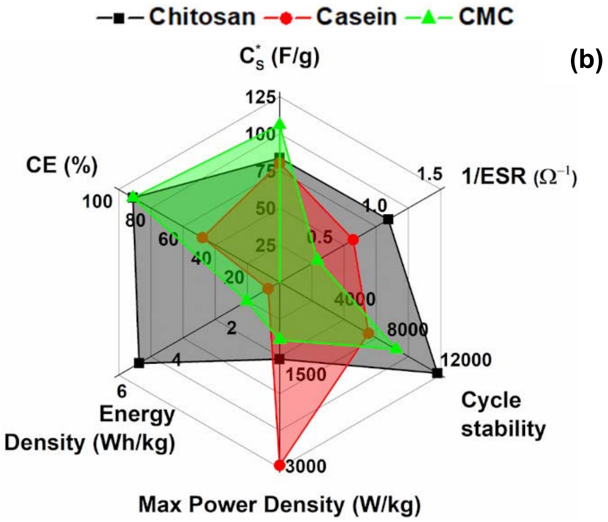
Increasing the salt concentration in the hydrogel (e.g., 3 M NaCl) slightly raises the ionic conductivity (σ) value, but high levels of hydrated ions reduce capacitance retention and cycle stability during charge/discharge tests.

G. Landi et al. **Polymers** 2022, *14*, 4445.

Electrochemical performance of biopolymer-based hydrogel electrolyte for supercapacitors with eco-friendly binders (2/2)

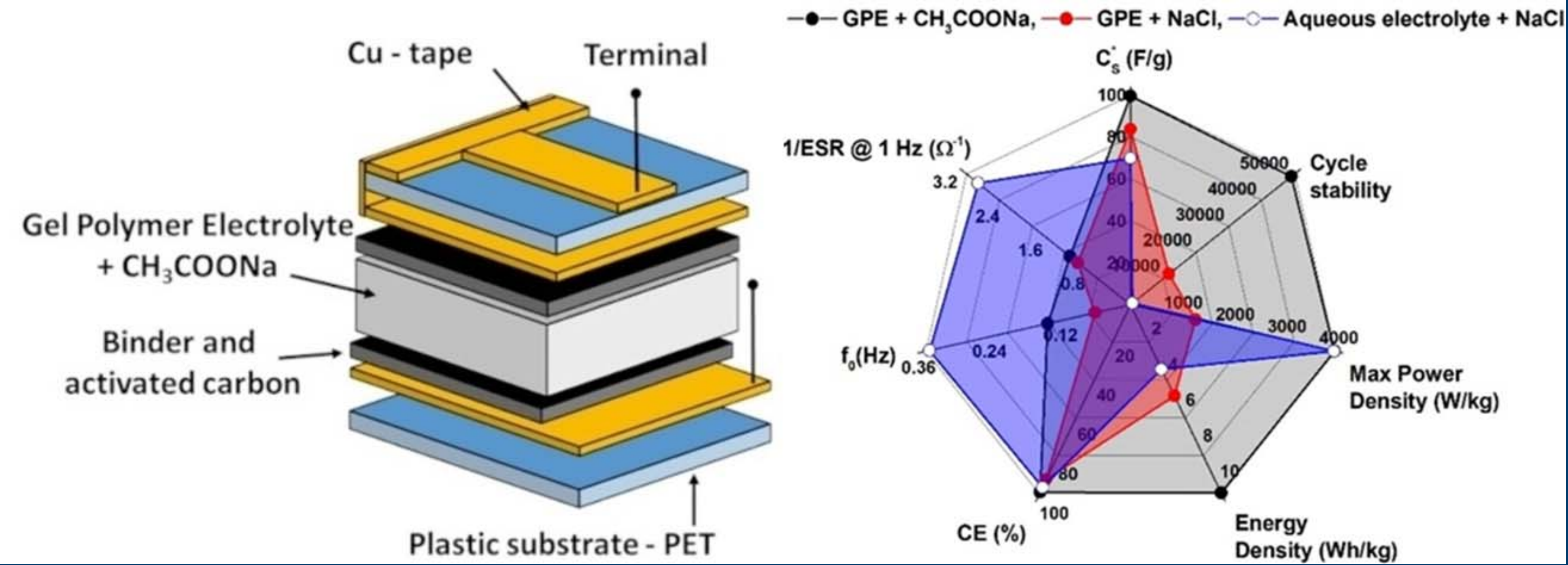
The use of the **hydrogel electrolyte with 2M NaCl** modifies the contribution of the double-layer capacitance compared to the SCs fabricated with the aqueous electrolyte showing a **dominant pseudocapacitive behavior**.





Compared to the aqueous electrolyte, **the gel-polymer supercapacitor has improved cycle stability** of up to **12000 cycles** (e.g. with chitosan as a binder) and low ESR values (≈ 3.6 Ω).

G. Landi et al. **Polymers** 2022, *14*, 4445.

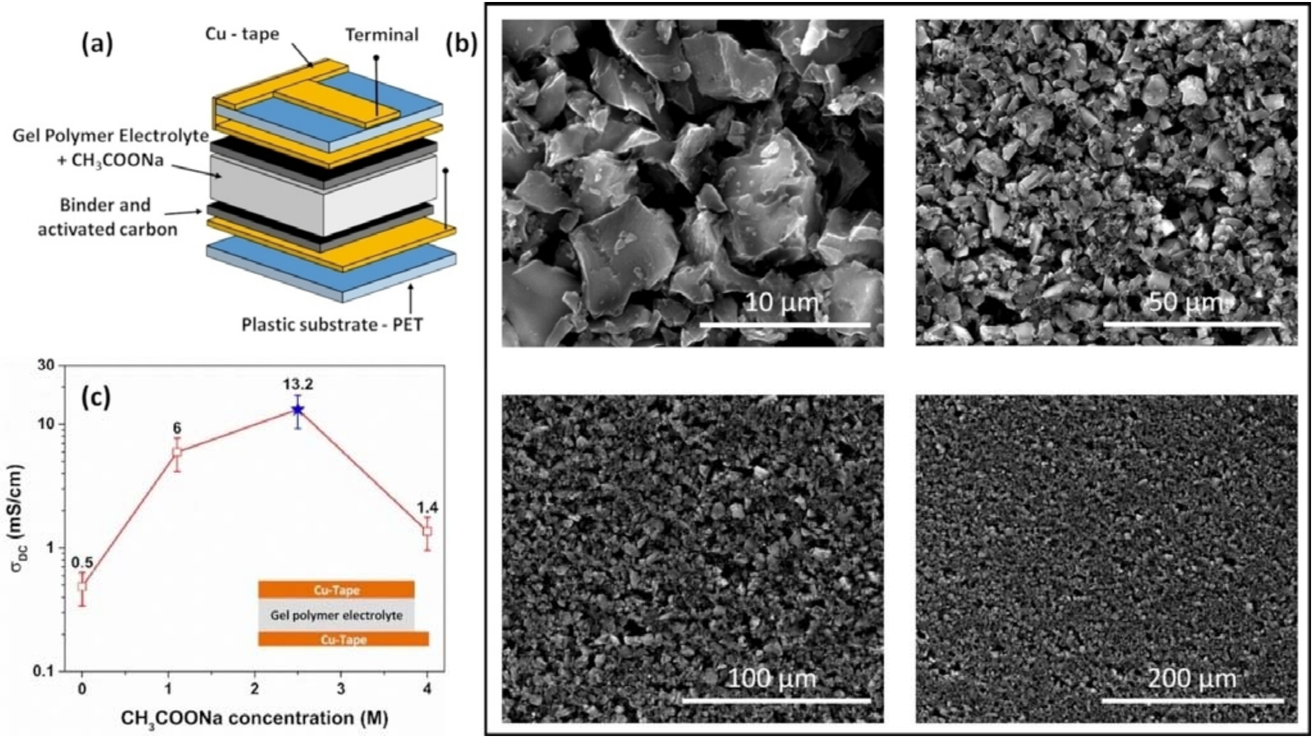


Eco-friendly supercapacitors with high energy performance

Acetate-based hydrogel electrolyte for high performance eco-friendly supercapacitors

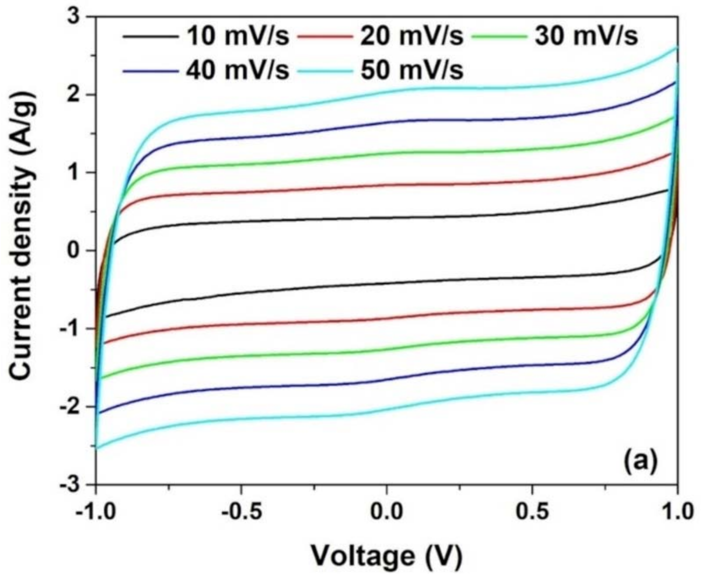
The incorporation of the **CH_3COONa salt** into the pristine gelatin blend changes the value of the ionic conductivity σ_{DC}. Here, the binder used within the electrode is **chitosan**.

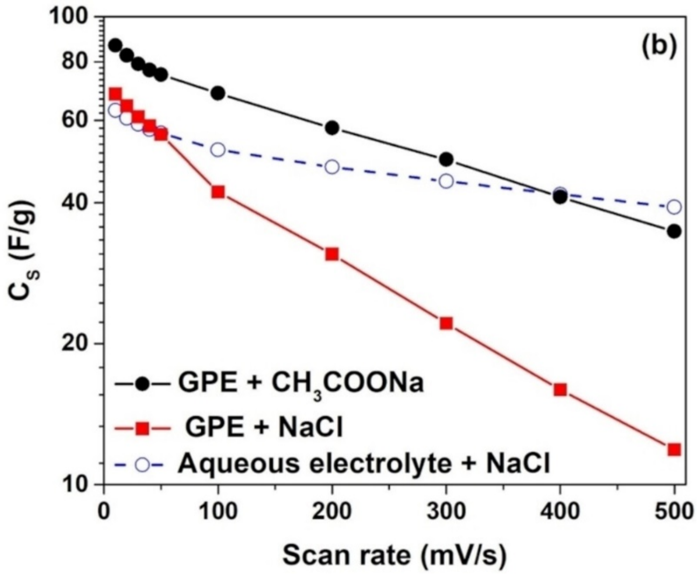
It progressively increases, reaching a value of 13.2 mS/cm at 2.5 M, and then gradually decreases to 1.4 mS/cm at 4 M.



G. Landi et al. **ChemElectroChem** 10, (2023).

Impact of acetate-based hydrogel electrolyte on electrical performance of eco-friendly supercapacitors (1/4)

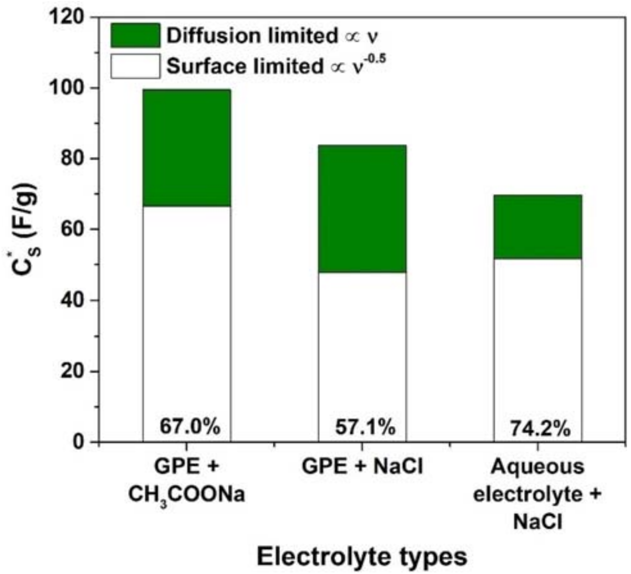




Acetate enhances ion accumulation and pore filling at the electrodes/hydrogel interface due to the smaller radius of the acetate anion, compared to the SC with GPE+NaCl. This leads to a **diminishment of the loss of capacitance as a function of the scan rate**.

G. Landi et al. **ChemElectroChem** 10, (2023).

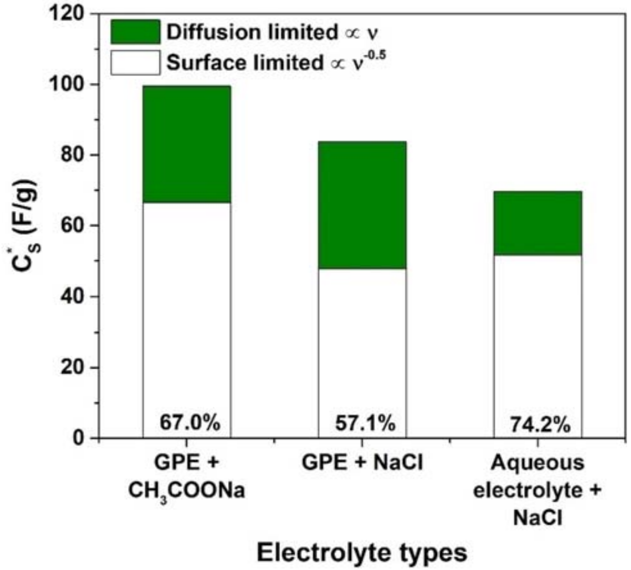
Impact of acetate-based hydrogel electrolyte on electrical performance of eco-friendly supercapacitors (2/4)

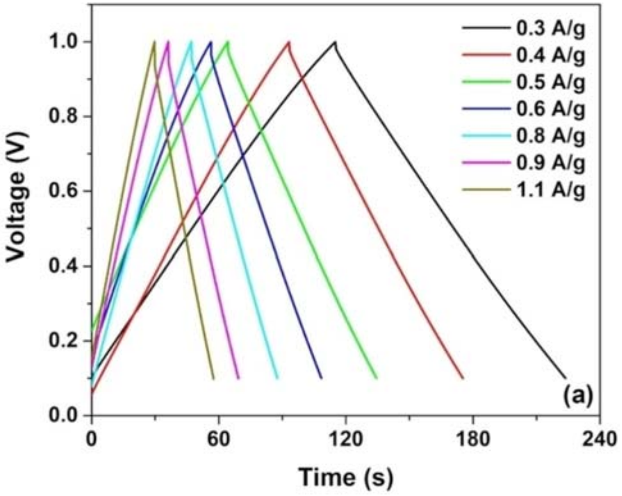


The addition of **acetate to the hydrogel enhances the double-layer contribution**, approaching a value (67%), similar to that observed for the aqueous electrolyte (74.2%).

G. Landi et al. **ChemElectroChem** 10, (2023).

Impact of acetate-based hydrogel electrolyte on electrical performance of eco-friendly supercapacitors (3/4)



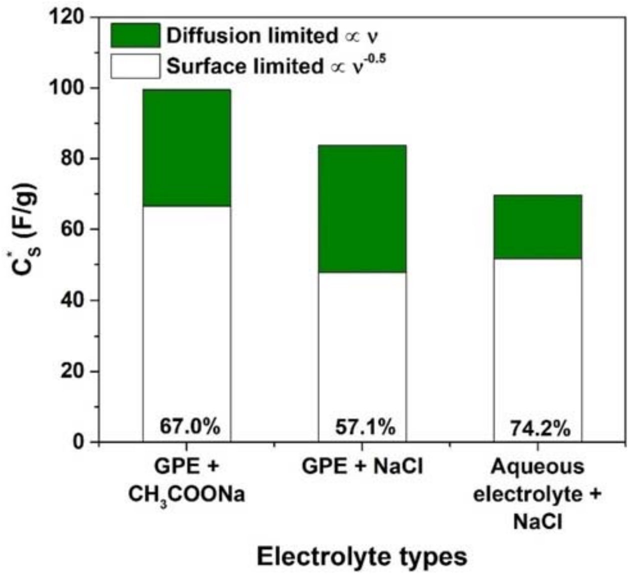


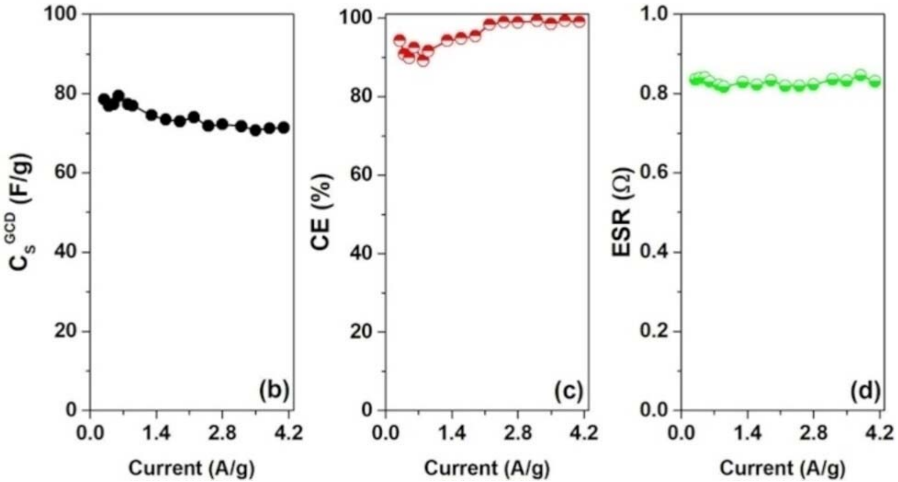
As expected, the dominant capacitive contribution of the double layer results in linear charging and discharging curves.

The addition of **acetate to the hydrogel enhances the double-layer contribution**, approaching a value (67%), similar to that observed for the aqueous electrolyte (74.2%).

G. Landi et al. **ChemElectroChem** 10, (2023).

Impact of acetate-based hydrogel electrolyte on electrical performance of eco-friendly supercapacitors (3/4)



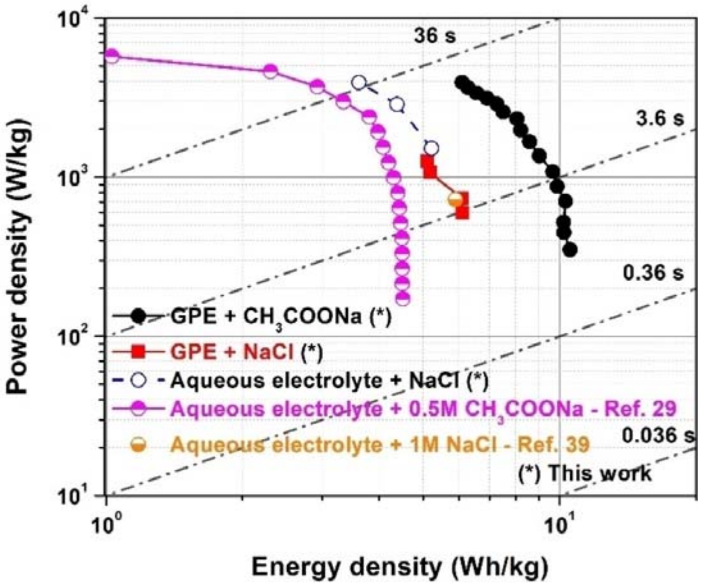


The addition of **acetate to the hydrogel enhances the double-layer contribution**, approaching a value (67%), similar to that observed for the aqueous electrolyte (74.2%).

The fabricated supercapacitors exhibit a gravimetric capacitance value of approximately **100 F/g, a series resistance of 0.8 Ω, and higher coulombic efficiency.**

G. Landi et al. **ChemElectroChem** 10, (2023).

Impact of acetate-based hydrogel electrolyte on electrical performance of eco-friendly supercapacitors (4/4)

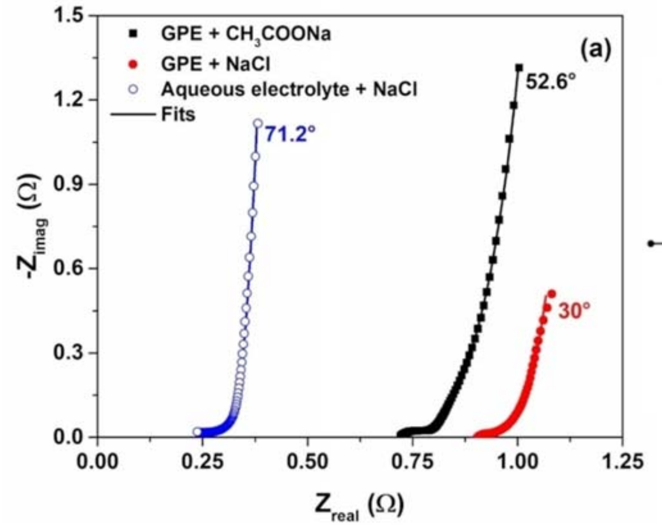


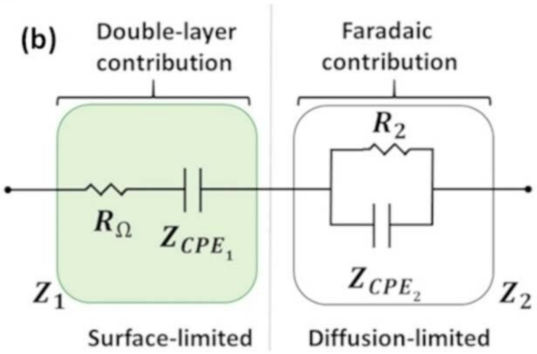
The most efficient device has been delivered approximately **10.6 Wh/kg of energy at a high-power density of about 3940 W/kg**.

G. Landi et al. **ChemElectroChem** 10, (2023).

Correlation between dielectric properties and charge storage mechanisms (1/3)

The **spectra** obtained for the **supercapacitors** exhibit a **characteristic extended tail at lower frequencies**, typical of charge storage mechanisms of dielectric materials and their related interfacial phenomena.

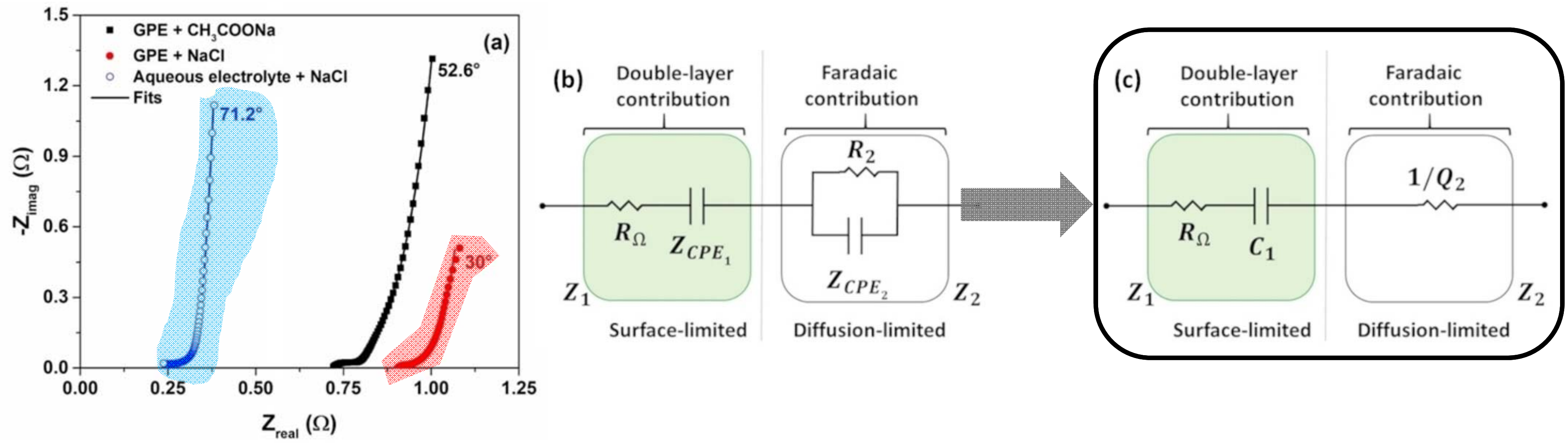




G. Landi et al. **ChemElectroChem** 10, (2023).

Correlation between dielectric properties and charge storage mechanisms (2/3)

In the case of **electrolytes containing NaCl** as the salt the corresponding CPE_2 impedance transforms into an ohmic contribution and Z_2 can be considered negligible.

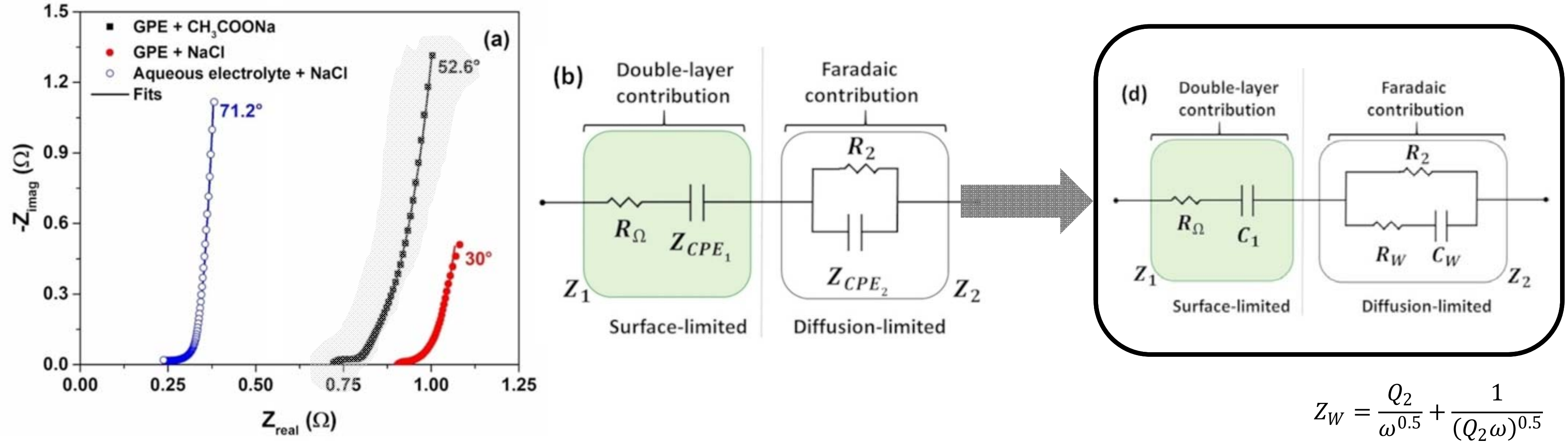


Consequently, the overall impedance is predominantly influenced by the impedance Z_1, where n_1 approaches 1 indicating a **purely capacitive behaviour**.

G. Landi et al. **ChemElectroChem** 10, (2023).

Correlation between dielectric properties and charge storage mechanisms (3/3)

The presence of **sodium acetate** in the hydrogel leads to a **further contribution related to the faradaic diffusion process** at the porous electrode, characterized by an n_2 value of approximately 0.5.



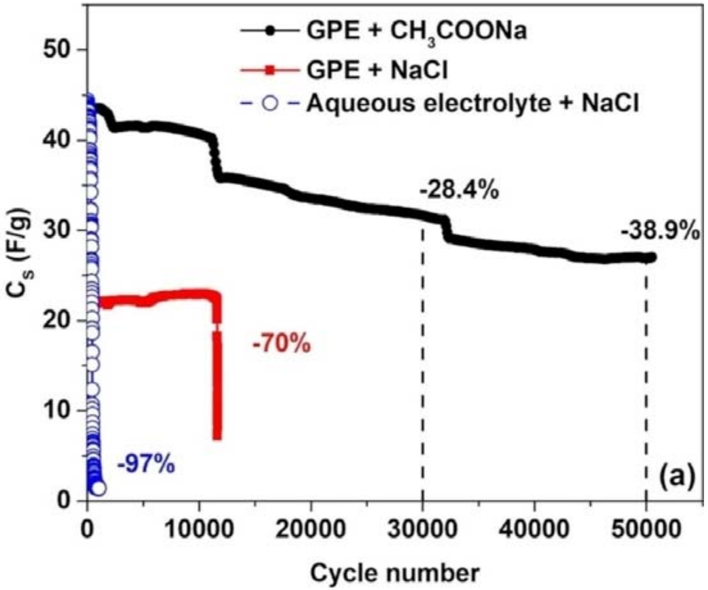
$$Z_W = \frac{Q_2}{\omega^{0.5}} + \frac{1}{(Q_2\omega)^{0.5}}$$

Z_W models the presence of **pseudocapacitance** resulting in a **significant increase in overall capacitance**

G. Landi et al. **ChemElectroChem** 10, (2023).

Correlation between dielectric properties, charge storage mechanisms and cycling stability

The devices with **GPE** exhibit **more stable dielectric properties** compared to the device with aqueous electrolyte (stability below 1000 cycles).

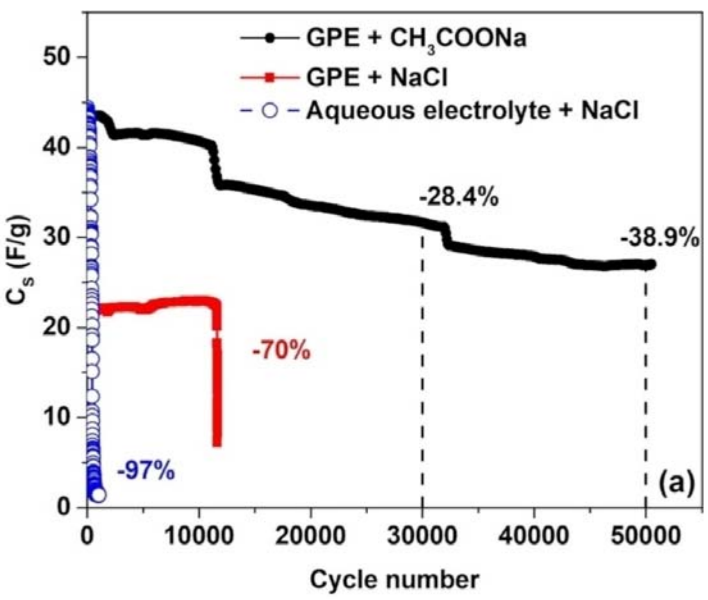


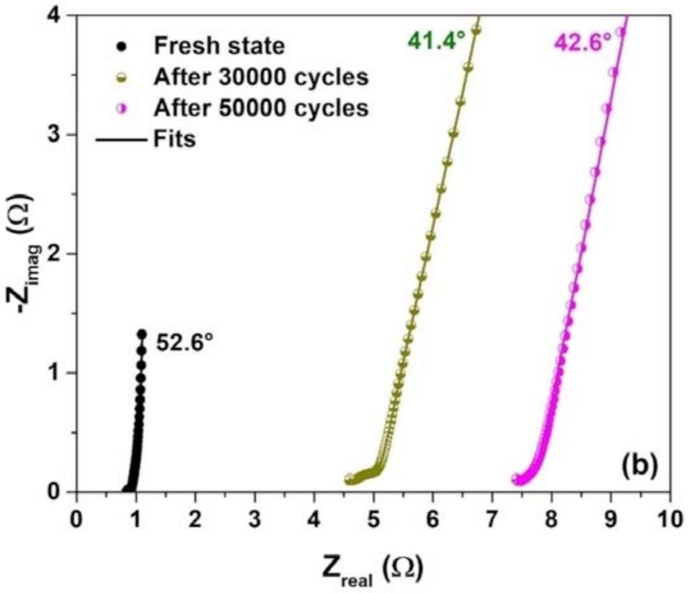
The GPE with NaCl is stable up to 12000 working cycles, whereas the **device containing sodium acetate shows extended stability up to 50000 cycles with only a 39% reduction in its initial capacitance value.**

G. Landi et al. **ChemElectroChem** 10, (2023).

Correlation between dielectric properties, charge storage mechanisms, cycling stability and ageing phenomena (1/2)

To understand the **ageing mechanisms during the cycling procedure** the impedance spectra have been measured after **30000 and 50000** cycles, respectively.

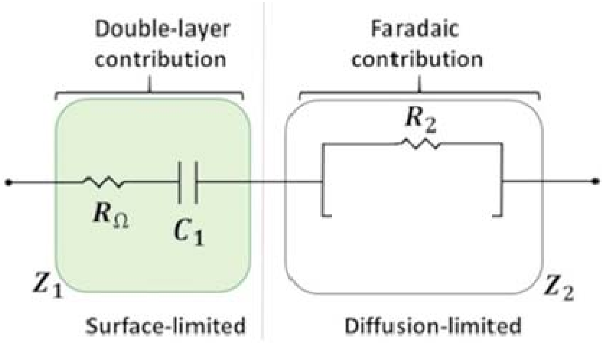




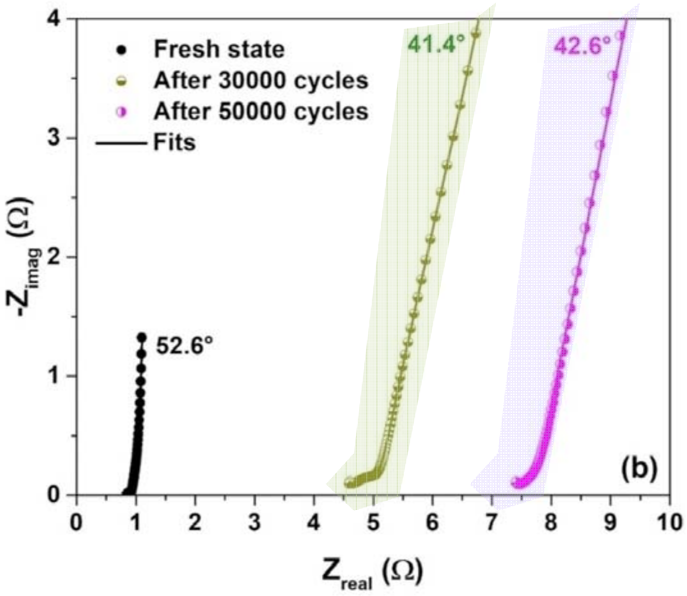
G. Landi et al. **ChemElectroChem** 10, (2023).

Correlation between dielectric properties, charge storage mechanisms, cycling stability and ageing phenomena (2/2)

To understand the **ageing mechanisms during the cycling procedure** the impedance spectra have been measured after **30000 and 50000** cycles, respectively.

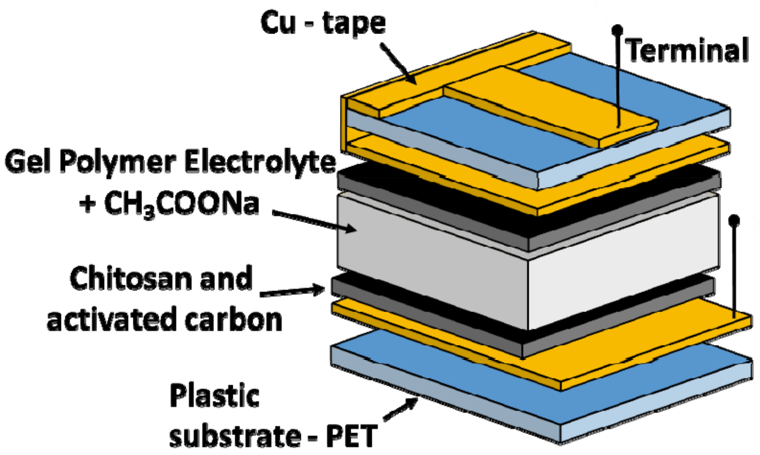


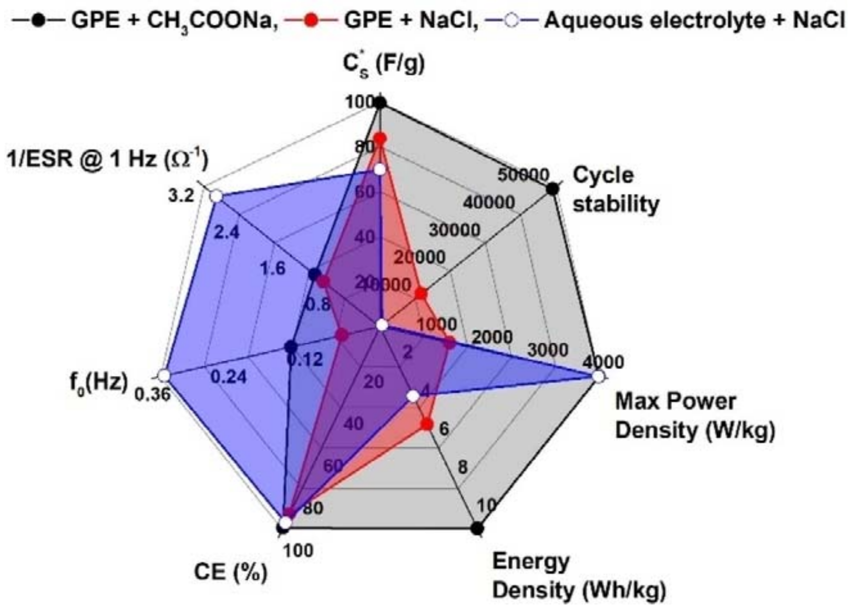
During cycling procedure, **the device becomes more resistive and the contribution of the pseudocapacitance is strongly reduced**, as evidenced by the significant drop in the Q_2 parameter.



G. Landi et al. **ChemElectroChem** 10, (2023).

Impact of acetate-based hydrogel electrolyte on electrical performance and stability of eco-friendly supercapacitors





Compared to reference electrolytes containing NaCl, the utilization of **sodium acetate exhibited enhancements in energy performance, and stability up to 50000 cycles with a value of internal resistance lower than 1 Ω.**

G. Landi et al. **ChemElectroChem** 10, (2023).

Conclusions

- **Development of symmetric carbon-based environmentally friendly supercapacitor**, employing natural polymers in both electrode slurry and aqueous and gel polymer electrolyte systems based on NaCl, gelatin, and sodium acetate, respectively.

- **The most efficient supercapacitors, utilizing sodium acetate and hydrogel,** demonstrate a gravimetric capacitance value of approximately **100 F/g**, **a series resistance of 0.8 Ω, and higher coulombic efficiency.**

- **The addition of acetate increases cycle life** enabling the supercapacitors to endure **up to 50000 cycles, surpassing the performance of hydrogel with NaCl (12000 cycles).**

- The best-performing device delivers **about 10.6 Wh/kg of energy at a high-power density of 3940 W/kg.**

Thanks for your attention

This research was funded in the Program Agreement between the Italian National Agency for New Technologies, Energy and Sustainable Economic Development (ENEA) and the Ministry of Environment and Energy Safety for Electric System Research, in the framework of its Implementation Plan for 2022-2024. In particular, the activity is included in Project 1.5 "High-efficiency buildings for the energy transition", Work Package 3 "Innovative technologies and components for increasing the energy performance of buildings.

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