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Valorization of organic waste for energy storage applications

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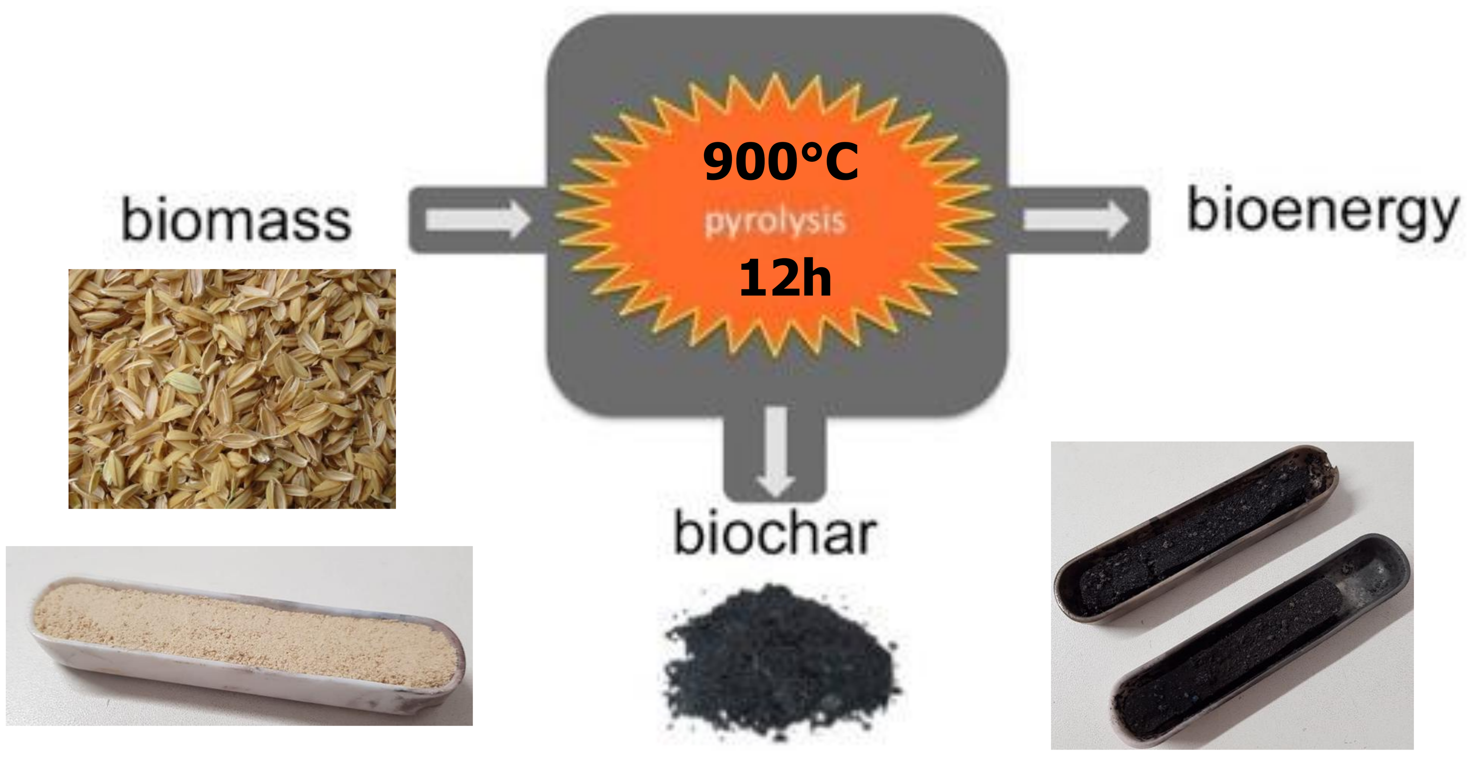
Abstract

In this work we use rice husk, an organic waste byproduct of rice refining processes, to produce innovative carbon based materials (activated biochars) as electrodes for supercapacitors (SCs).

The agricultural waste have been pyrolyzed under nitrogen flux at 900°C for 12h to obtain the carbonaceous product and we have performed a chemical activation with potassium hydroxide (KOH) in two different alkaline/C ratio (2:1 and 6:1) via controlled thermal treatment under Ar flux in order to obtain highly performing electrode materials. SCs have been produced assembling two highly-porous activated biochar electrodes supported on Ni-foams in a standard coin cell (CR-2032), separated by glass fiber soaked with the electrolyte. We have studied three different electrolytes, either aqueous such as KOH and Na_2SO_4 solutions, or organic such as TEA-BF_4 in CH_3CN in order to find those better matching the pore size of the carbon matrix. The electrochemical performances of the devices have been tested by means of cyclic voltammetry at different voltage rates, in order to determine the specific capacitance and the electrochemical stability window, and galvanostatic charge/discharge measurements up to 5000 cycles to test the behavior upon cycling.

Active materials production and devices realization

Biochar production from rice husk



Precursor made of rice husk

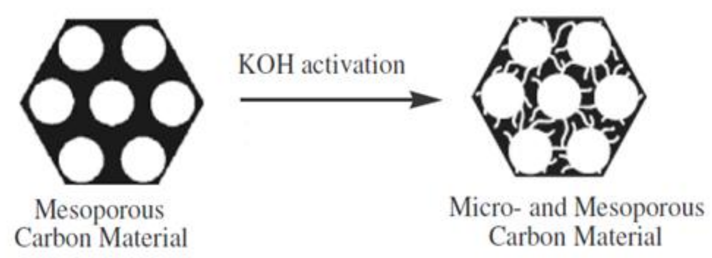
Charcoal from the pyrolysis of biomass
Low cost and recycled material

Activation process to increase specific surface area

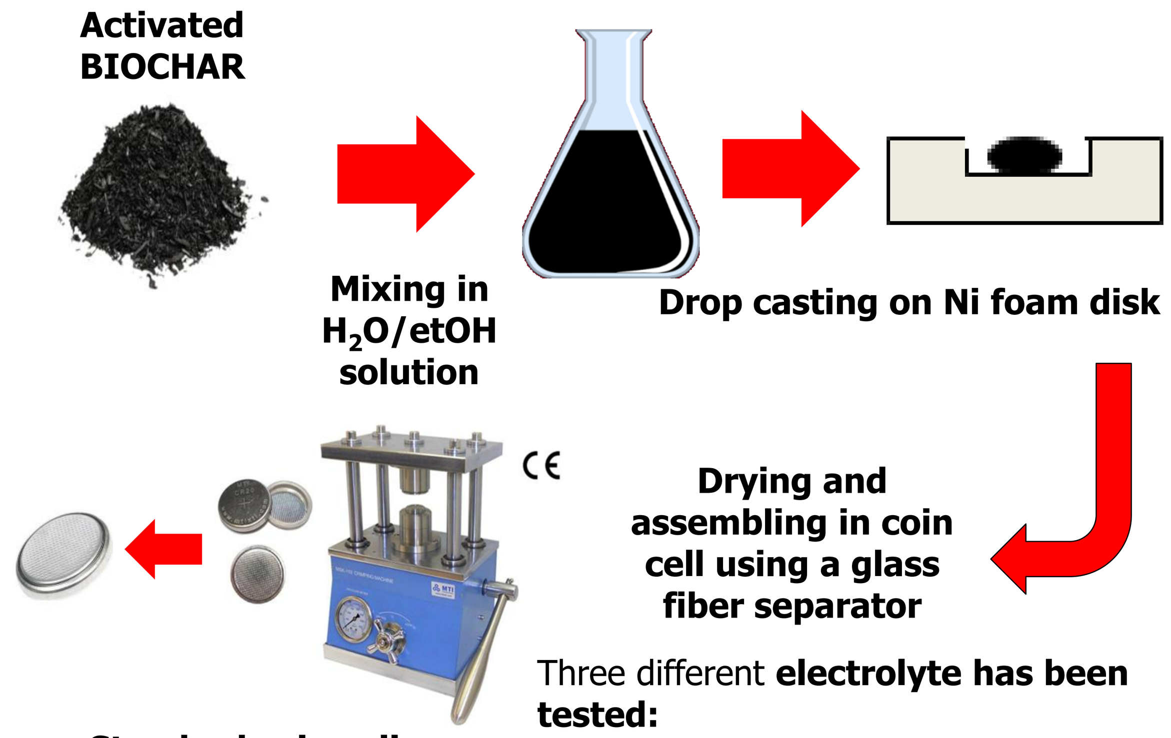
Biochar + KOH pellets (solid state) or impregnation with aq. **7M KOH** solution

Heating treatment in **Ar flux at 800°C**

Washing in water + HCl and **drying**



SCs devices realization



Three different **electrolyte has been tested:**

- **Aqueous electrolytes 7M KOH or 1M Na_2SO_4**
- **Organic electrolyte 1M TEA-BF4/ACN**

Results

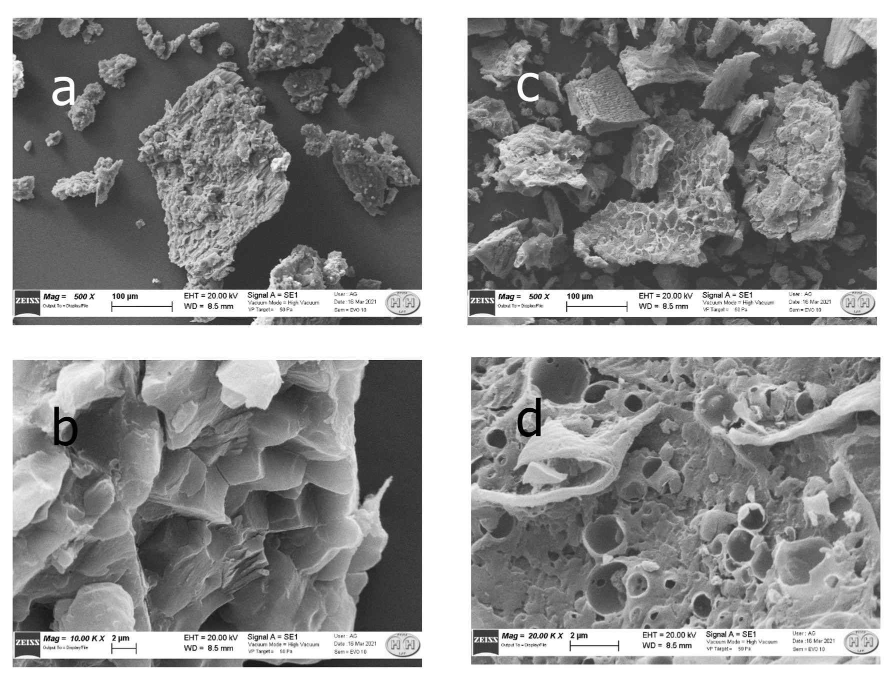


Figure 1: on the left (a and b): SEM images of waste rice husk. The sample appears largely inhomogeneous, with the presence of porous carbon agglomerates and more regularly-shaped chips. Right (c and d): SEM image of activated char. The sample appears more homogeneous, with **large porosity at the micrometer scale**.

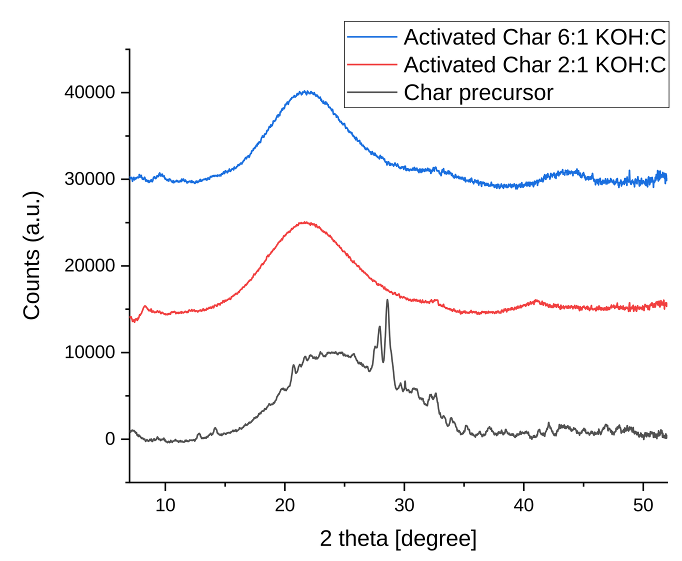
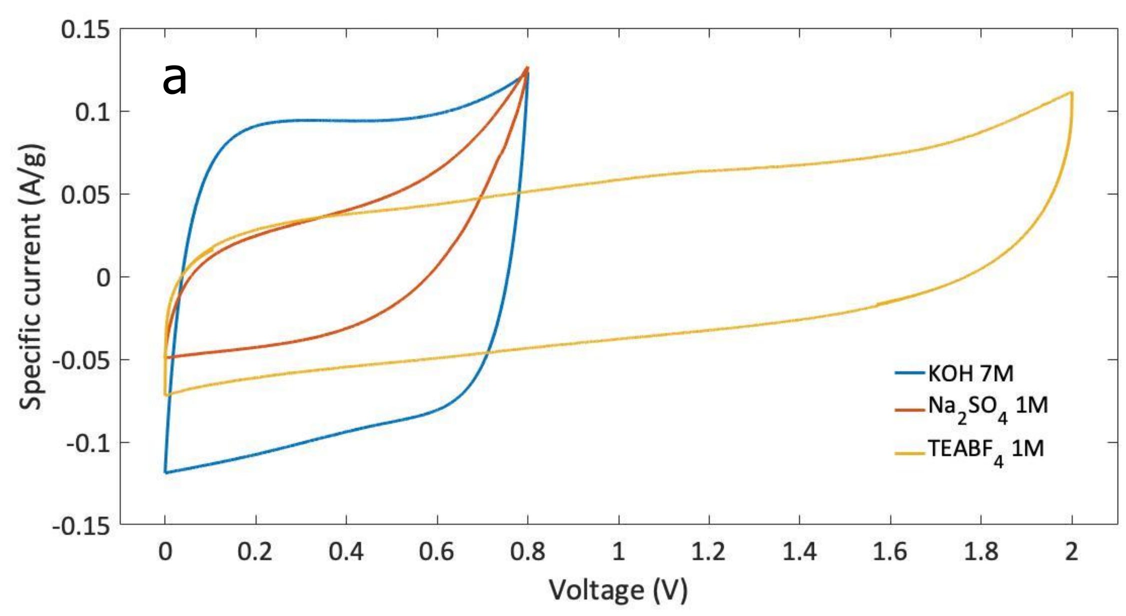
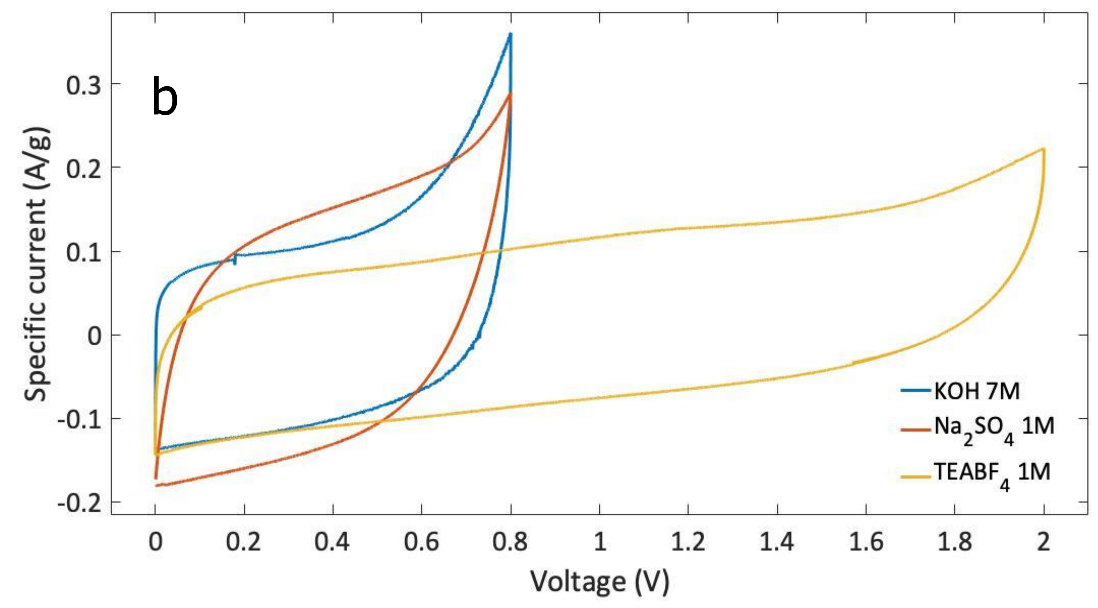


Fig. 3. PXRD pattern: comparison between pyrolyzed rice husk (black line) and activated chars (red and blue lines)

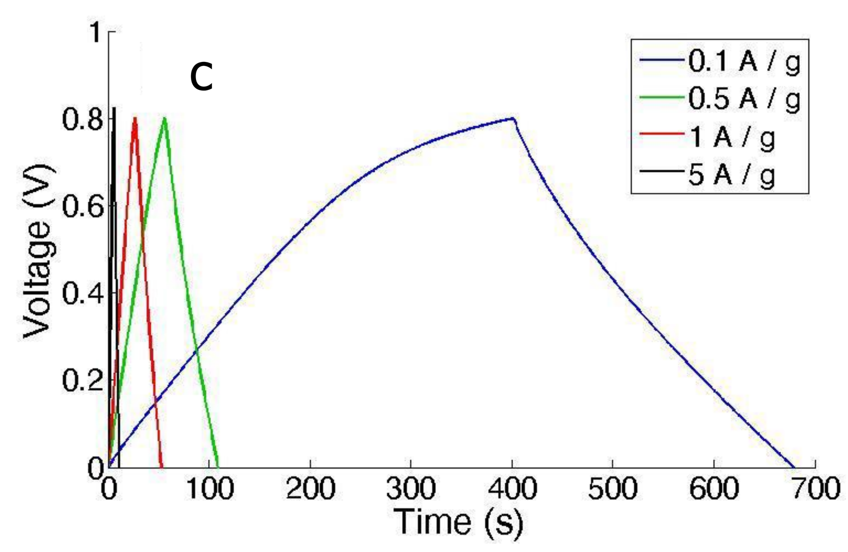
Working voltage window stability at 5 mV/s for activated char 2:1 KOH:C



Working voltage window stability at 5 mV/s for activated char 6:1 KOH:C



Charge / discharge cycles at different currents for activated char 6:1 KOH:C



Capacity retention, specific capacity and specific energy for activated char 6:1 KOH:C

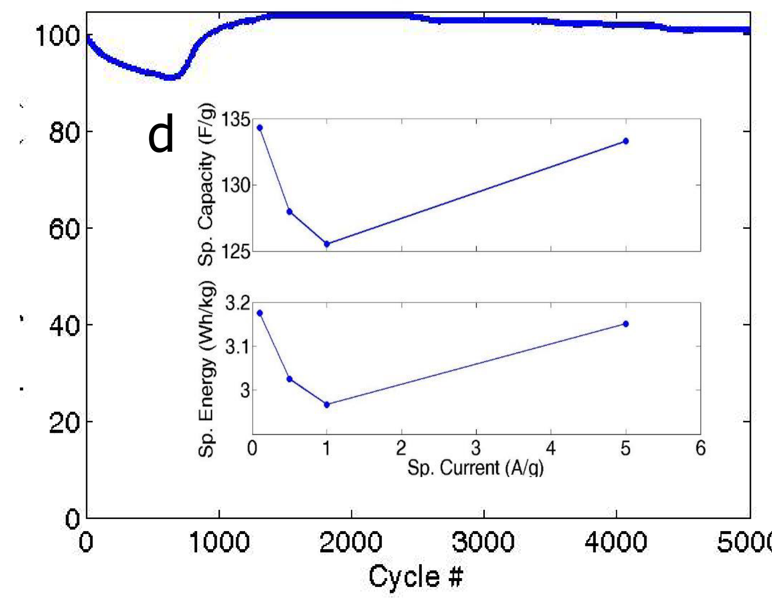


Fig. 2. a,b) **Cyclic voltammetry** of **symmetrical SCs** obtained from activated chars at different scan rates for devices with **KOH-based electrolyte, Na_2SO_4-based electrolyte** and with **$TEABF_4$-based electrolyte**

c) **Galvanostatic charge and discharge** at different currents for a selected device with **KOH**-based electrolyte

d) **Capacity retention** of a SC with KOH-based electrolyte (at 1 A/g). Inset: **Discharge specific current dependence of average specific capacity and energy** for a selected SC (6:1 KOH:C) with KOH-based electrolyte. Specific capacity and energy are the average of 10 cycles at each different specific current.

Conclusions

• The chemical activation process with KOH of biochar derived by rice husk allowed to obtain a **carbon material** displaying a specific surface area **exceeding 1600 m²/g**, with **hierarchical porous structure**.

• Scanning electron microscopy analysis have shown the huge porosity of the materials and the positive action of KOH in further increasing the surface area and roughness, fundamental requirements for optimal SCs performance. The activation process also revealed to be effective in purifying the material from elements other than carbon, also confirmed by powder X-Ray diffraction measurements.

• The obtained porous compound demonstrated to behave as an excellent electrode material for high-performance symmetric supercapacitors, reaching **good specific capacitance up to over 130 (13) F/g**.

• Biochar-based supercapacitors show an almost ideal electrical double layer capacitance and electrochemical performances of specific capacitance, energy density and power density that are perfectly in accordance with the values of state-of-the-art materials. In addition, we have the possibility to obtain environmentally friendly and biocompatible devices, giving a "second life" to byproducts bringing benefits from a point of view of waste minimization and valorization.

References

❖ E. Frackowiak, F. Béguin, *Carbon*, **39** (2001) 937-950.

❖ X. Zhang, X. Cui and W. Chen, *RSC Adv.*, **5** (2015) 77629

❖ D. Pontiroli et al., *J. Phys. Chem. C*, **118** (2014) 7110–7116

❖ D. Pontiroli, G. Magnani, L. Fornasini et al., *Microporous and Mesoporous Materials*, **285** (2019) 161–169