Biowaste-derived hard carbons from hazelnut shells for sustainable hybrid energy storage

S. Volante[1], A. Hainthaler[2], D. Licursi[1], S. Fulignati[1], A.M. Raspolli Galletti[1], A. Balducci[2], C. Antonetti[1]

[1] Department of Chemistry and Industrial Chemistry, University of Pisa, Via G. Moruzzi 13, 56124 Pisa, Italy

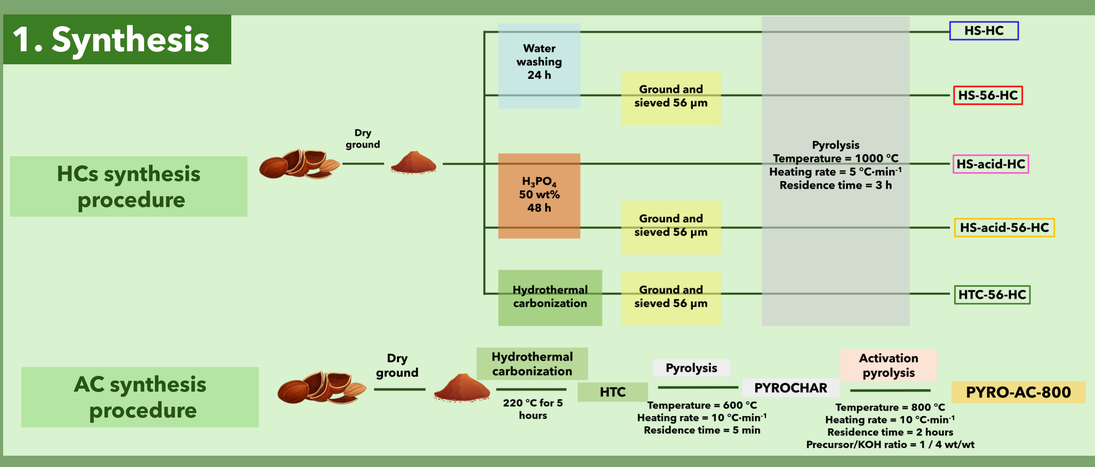
[2] Friedrich-Schiller-University Jena, Institute for Technical Chemistry and Environmental Chemistry Philosophenweg 7a, 07743 Jena, Germany

Introduction

Hard carbons (HCs) derived from **sustainable biomass sources** are attracting growing interest as **electrode materials** for next-generation **hybrid energy storage systems**, due to their favorable charge storage properties [1]. Among biomass precursors, lignin-rich materials are particularly promising because they promote disordered carbon structures with enlarged interlayer spacing, beneficial for ion storage [2]. In this work, **hazelnut shell** (HS) waste biomass was investigated as a low-cost and sustainable precursor for the synthesis of HC anodes for **lithium-ion capacitors**, since its use in HC synthesis remains scarcely explored [2-4]. Different mild pre-treatments, including water washing, particle-size selection, acid treatment, and hydrothermal carbonization (HTC), were applied before pyrolysis to evaluate their influence on the electrochemical performances of the resulting materials [2-3]. The synthesized HCs were first tested in half-cell configurations and then implemented in full-cell devices using HS-derived activated carbon (AC) as the cathode (PYRO-AC-800). The study aims to develop **sustainable hybrid energy storage systems** by valorizing waste-derived biomass in practical **full-cell applications**.

HCs synthesis and electrochemical characterization

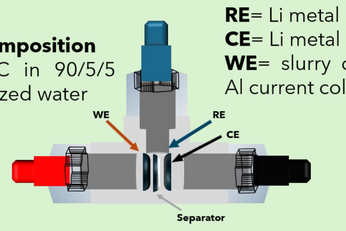
1. Synthesis



2. Half-cell measurements

Activated carbon as positive electrode

Slurry composition
AC/CB/CMC in 90/5/5 wt in deionized water

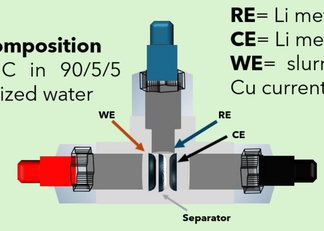


RE= Li metal
CE= Li metal
WE= slurry deposited on Al current collector

AC = Activated Carbon; CB = Carbon Black; CMC = Carboxymethyl cellulose

Hard carbon as negative electrode

Slurry composition
HC/CB/CMC in 90/5/5 wt in deionized water

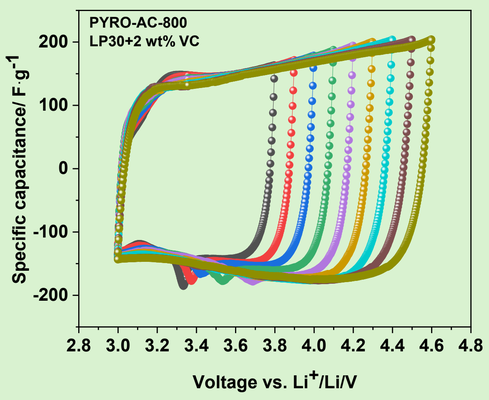


RE= Li metal
CE= Li metal
WE= slurry deposited on Cu current collector

HC = Hard Carbon; CB = Carbon Black; CMC = Carboxymethyl cellulose

3. Half-cell measurements results

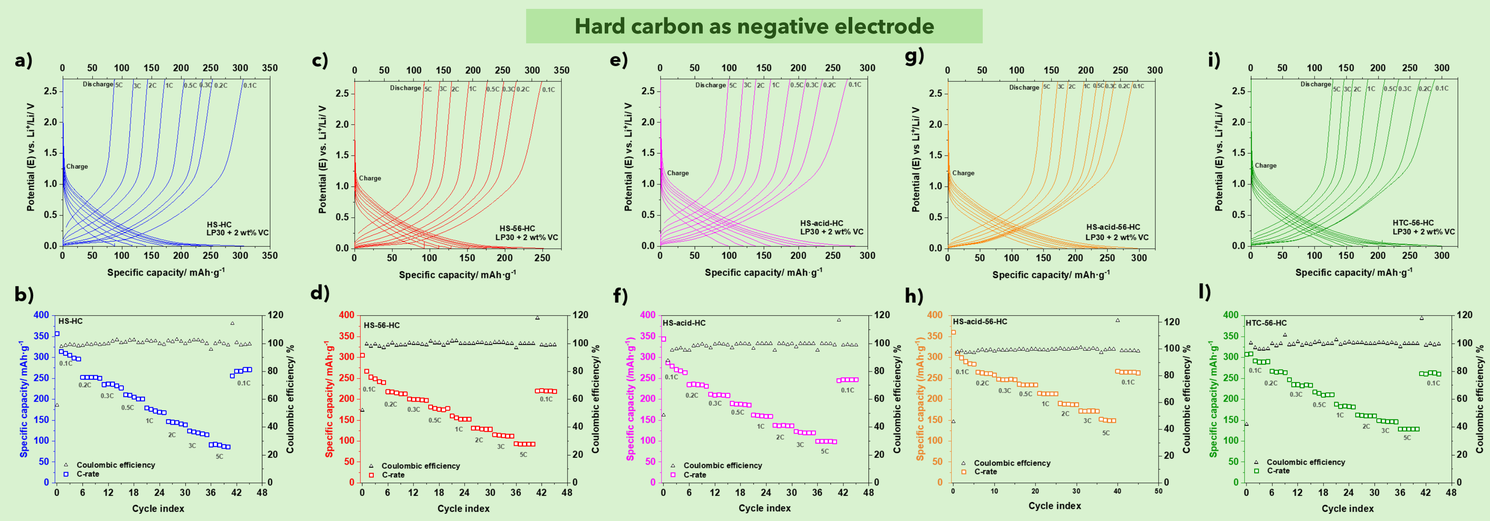
Activated carbon as positive electrode



Cyclic voltammetry curves of PYRO-AC-800 electrode scanned at 5 mV·s^{-1} in the potential range between 3-4.6 V vs. lithium metal, in 1 M $LiFP_6$ in ethylene carbonate: dimethyl carbonate (1:1 wt:wt) + 2 wt% vinylene carbonate (LP30 + 2 wt% VC) electrolyte.

- The **good overlap** of the **CV profiles** over successive cycles demonstrates stable and reversible electrochemical behavior in the selected potential window;
- The predominantly **capacitive response** confirms the suitability of the **AC** electrode within the selected voltage range for device applications.

Hard carbon as negative electrode



Galvanostatic charge/discharge (GCD) curve and C-rate performance of HS-derived HCs: a-b) HS-HC, c-d) HS-56-HC, e-f) HS-acid-HC, g-h) HS-acid-56-HC, i-l) HTC-56-HC in half-cell measurement at different current densities in LP30 + 2 wt% VC electrolyte.

- **Typical Li⁺ intercalation material** behavior:
  - sloping region → Li adsorption;
  - low-voltage plateau → Li insertion + nano-pores filling.
- The samples **HS-acid-56-HC** and **HTC-56-HC** deliver the best performances:
  - **230** and **180** mAh·g^{-1} at 1C (1C = 372 mA·g^{-1});
  - good rate capability.

$$Initial\ Coulombic\ Efficiency\ (iCE) = \frac{\text{Discharge } capacity}{\text{Charge } capacity} \times 100$$

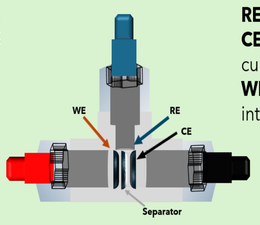
HC samples	iCE (%)
HS-HC	56
HS-56-HC	52
HS-acid-HC	49
HS-acid-56-HC	46
HTC-56-HC	42

Despite lower **iCE** values (46% and 42%), both samples, **HS-acid-56-HC** and **HTC-56-HC**, show improved cycling stability and reversible Li⁺ storage. Moreover, they retain higher capacities even at high current densities.

4. Full cell measurements results

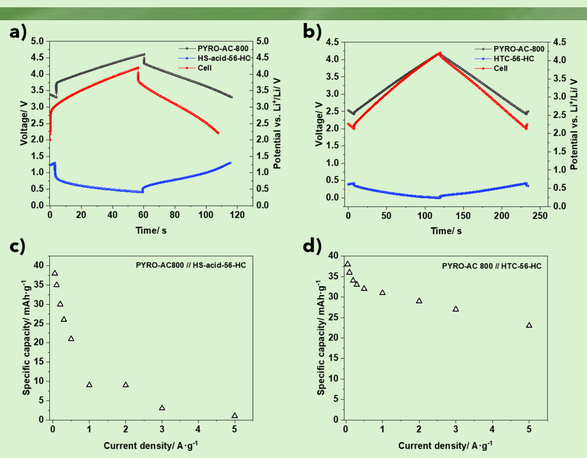
WE slurry composition
HC/CB/CMC in 90/5/5 wt in deionized water

CE slurry composition
AC/CB/CMC in 90/5/5 wt in deionized water



RE= Li metal
CE (positive electrode)= PYRO-AC-800 into aluminum current collector
WE (negative electrode)= HS-acid-56-HC or HTC-56-HC into copper current collector

HC = Hard Carbon; AC = Activated Carbon CB = Carbon Black; CMC = Carboxymethyl cellulose



Galvanostatic charge/discharge (GCD) curves of the two assembled LICs: a) PYRO-AC-800//HS-acid-56-HC and b) PYRO-AC-800//HTC-56-HC, and specific capacity vs. current density for the two full devices: c) PYRO-AC-800//HS-acid-56-HC and d) PYRO-AC-800//HTC-56-HC in the potential window between 2-4.3 V employing LP30 + 2 wt% VC as electrolyte.

- Both devices (based on **HS-acid-56-HC** and **HTC-56-HC**) exhibit **quasi-linear** and **symmetric charge-discharge curves** (graphs a) and b)), confirming stable operation and predominantly capacitive behavior in the selected voltage window;
- The **HTC-56-HC** device (graph b)) shows **more linear GCD profiles**, delivering **higher specific** capacity and **better capacity retention** at increasing current densities (graph d)) compared to **HS-acid-56-HC** based device.

Conclusions

- ✓ **Hazelnut shell** waste biomass was successfully **valorized** into **high-value carbon materials**, demonstrating its potential for energy storage applications.
- ✓ The **PYRO-AC-800** showed **high specific capacitance**, while the **HS-acid-56-HC** and **HTC-56-HC** samples exhibited **promising reversible capacities** in **half-cell configurations** and **good performances** in full **lithium-ion capacitor** devices.
- ✓ The **HTC-56-HC-based device** achieved the best electrochemical performances, with **high specific capacitance**, **improved rate capability,** and **good capacity retention**, highlighting its potential for advanced lithium-ion capacitor applications.

References

[1] C.M. Ghimbeu, A. Beda, B. Réty, H.E. Marouazi, A. Vizintin, B. Tratnik, L. Simonin, J. Michel, J. Abou-Rjeily, R. Dominko, *Advanced Energy Materials*, 14, 2303833, 2024.
[2] C.J. Chng, X. Ma, Y. Abe, S. Kumagai, *Journal of Energy Storage*, 92, 112193, 2024.
[3] H. Moon, A. Innocenti, H. Liu, H. Zhang, M. Weil, M. Zarrabeitia, S. Passerini, *ChemSusChem*, 16, e202201713, 2023.

Acknowledgments

This study was carried out within the MOST– Sustainable Mobility Center and received funding from the European Union Next-Generation EU (PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR)-MISSIONE 4, COMPONENTE 2, INVESTIMENTO 1.4-D.D.1033 17/06/2022, CN00000023).