WATER-IN-SALT ELECTROLYTES FOR SUPERCAPACITORS

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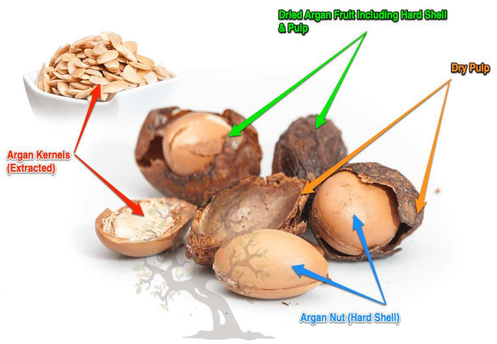
Supercapacitors (SC) are playing a central role in the transition to a green economy based on renewable energy sources and electric vehicles. The exponentially growing market of supercapacitor requires that flammable, volatile and toxic chemicals such as acetonitrile are replaced by cheap and environmentally friendly components. Valuable strategies are the use of aqueous electrolytes and biochar-based carbon that enable the valorisation of wastes in a circular economy approach. Here we report about a physicochemical study and preliminary electrochemical characterization of a supercapacitor based on Argan fruit shell derived carbon electrode and a non-toxic super-concentrated aqueous electrolyte, i.e. a Water In Salt (WIS) solution of ammonium acetate. This preliminary work aims at paving the way towards the design of novel, green SCs.

Electrode material

- Raw material: Argan hard shells collected from the southern region of Morocco.



Argan fruit (www.arganfarm.com)

❖ Carbonization:
- 700 °C for 1 h under N_2 flow 100 cm^3/min, 10 °C/min heating rate

The resulting carbonized product is denoted as ARG-C.

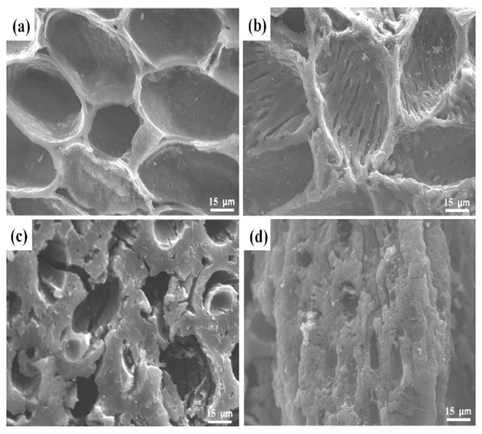
❖ Chemical activation :
- Activating agents: sodium hydroxide (NaOH) or potassium hydroxide (KOH)
- two different methods: impregnation (Im) or physical mixing (PM)

The resulting samples are denoted ARG-K-Im, ARG-K-Pm, ARG-N-Im and ARG-N-PM.

Honeycomb-like structure with large spherical cavities.

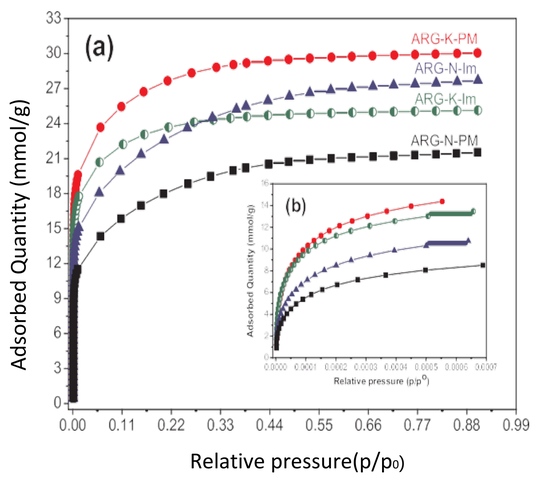
SEM

(a) ARG-K-PM,
(b) ARG-K-Im,
(c) ARG-N-PM
(d) ARG-N-Im.



BET

N_2 adsorption isotherms at 77 K



Sample	ARG-K-Im	ARG-K-Pm	ARG-N-Im	ARG-N-PM.
Surface area (m^2/g)	1890	2250	1830	1460

Electrolyte

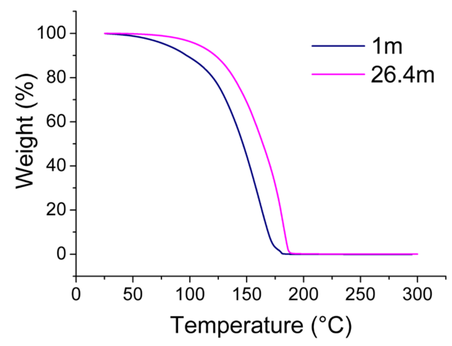
Electrolyte: Ammonium Acetate / **NH_4OAc** / 1m , 26.4m
LSV=Linear Sweep Voltammetry at Glassy Carbon electrode
TGA= Termogravimetric Analysis; Argon flow 60 mL/min , scan rate 10 °C/min
ESW=Electrochemical Stability Window with LSV data
IR= Infrared Spectroscopy

Chemical physical properties at room temperature

Concentration / molality	Density / kg/L	Viscosity / cP	Conductivity / mS/cm	pH	ESW / V
1.0 m	1.02	0.992	62.5	6.97	2.6
26.4 m	1.10	10.75	48.8	7.97	2.9

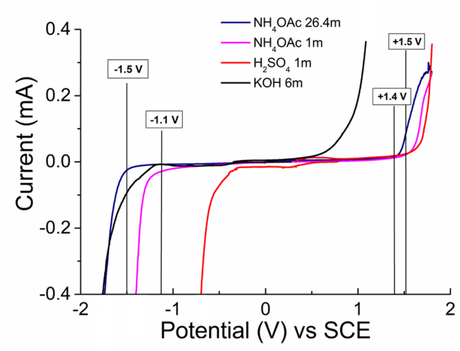
TGA

Argon flow 60 ml/min
Scan rate 10 °C/min



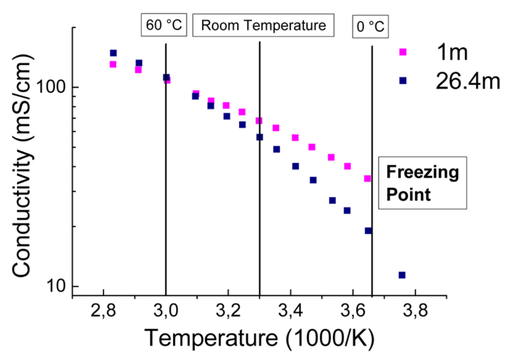
GC - LSV

Reference electrode: SCE

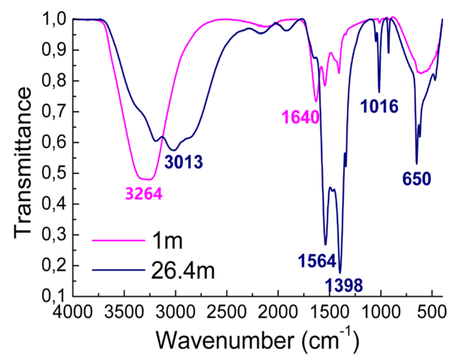


Ion Conductivity

Arrhenius plot



IR

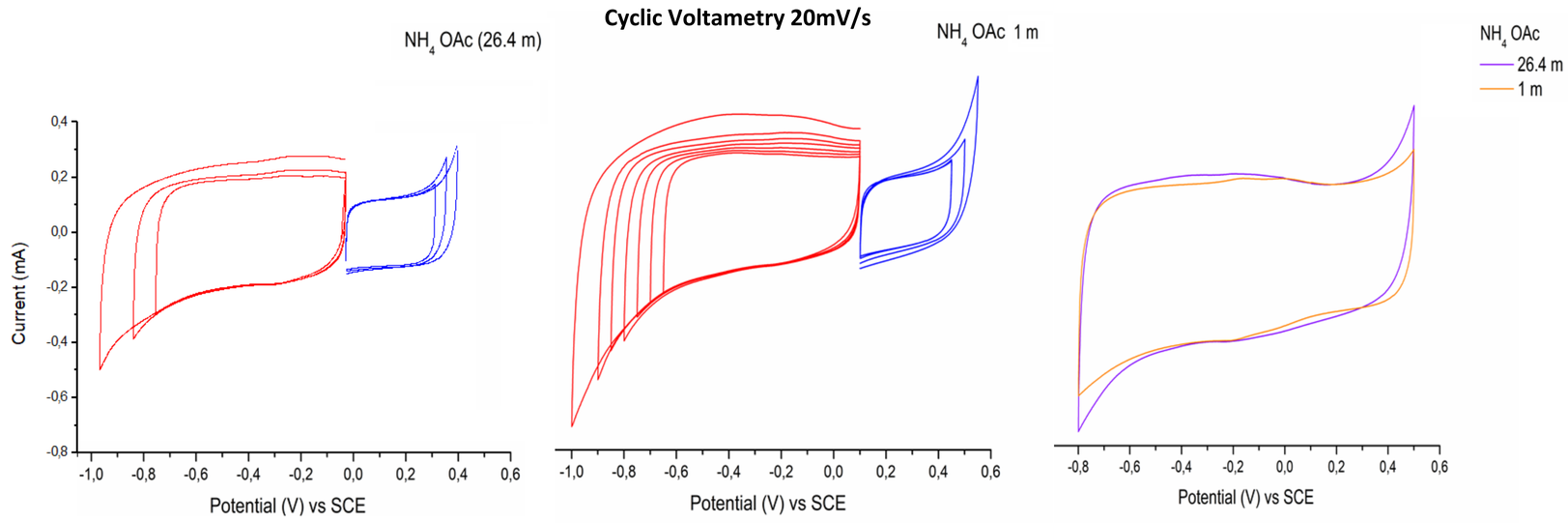


26.4m WIS electrolyte enables higher ESW at good conductivity even at temperatures below 0°C

Electrochemical measurement

- Electrode preparation : 8 mg of powder (80% ARG-K-PM - 10% acetylene black carbon) in 1 ml solution of water, ethanol (200 µl) and Nafion (20 µL, 5%). After 1h sonication, 4 µL of the ink was drop cast on the GC (3 mm diameter) .
- 3 electrode glass cell: ARG-K-PM Working electrode, SCE Reference electrode, Pt Counter electrode.

- ARG-K-PM specific capacitance ca. **300 F/g**.
- ESW at ARG-K-PM **ca 1.3V** and narrower than that at GC.
- **10 Wh/kg** expected Specific Energy of an **asymmetric SC** with $m_{negative}$=1/4 $m_{positive}$



$C_{sc} = (1/C_+m_+ + 1/C_-m_-)^{-1}/m_{sc} = 50$ F/g $E = {}^1/_2 C_{sc} V^2/3600 = 10$ Wh/kg

Conclusions

- High surface area Argan derived carbon was successfully prepared and featured extremely high specific capacitance in 26.4 m NH_4OAc, i.e. ca. 300 F/g, thanks to its honeycombe-like structure.
- The WIS 26.4 m NH_4OAc solution is a good aqueous electrolyte alternative to KOH and H_2SO_4 for its wider ESW, lower corrosion activity and cinductivity below 0°C. However, ESW is still narrower than that of organic electrolytes.
- The asymmetry of the ESW requires that the SC electrodes are properly balaced in terms of mass. By this approach we expect to achieve 10 Wh/kg at 1.3 V.

Acknowledgments

This research has been carried out under the support of the:
- Italy-South Africa joint Research Programme 2018-2020 (https://site.unibo.it/isarp/en), Italian Ministers of Foreign Affairs and of the Environment.
- National Center for Scientific and Technical Research (CNRST), Morocco.

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