Colloidal Processing & Additive Manufacturing
From Material to application

Fabrication of complex 3D energy storage devices by additive manufacturing technologies

Oxel Urra[1], A.J Sanchez-Herencia[1], B.Ferrari[1]

1. Instituto de Cerámica y Vidrio (ICV), CSIC, Madrid, Spain

oxel@icv.csic.es

Universidad de Castilla-La Mancha

43GERSEQ

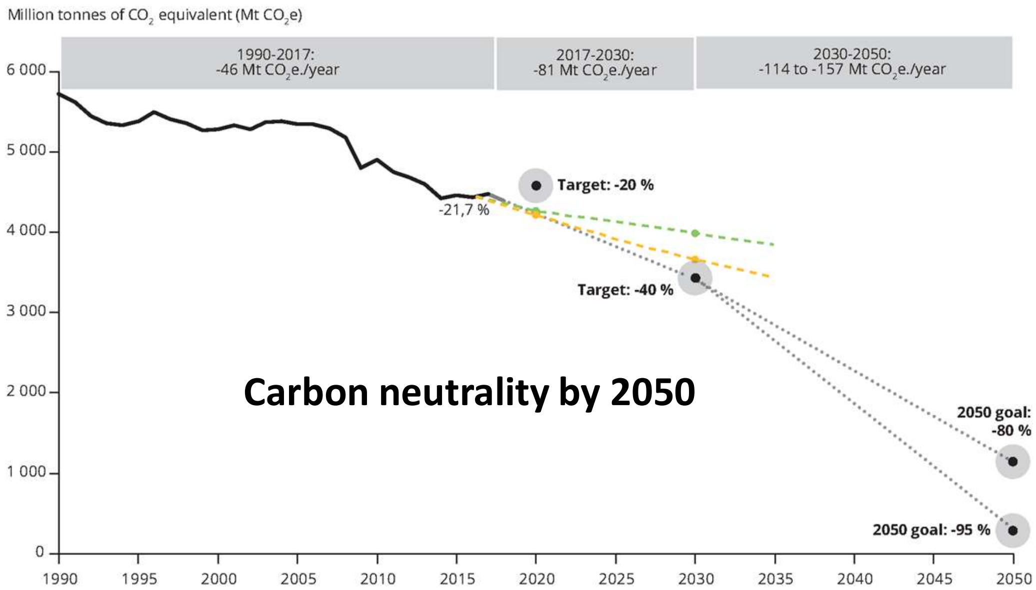
colloidal processing

ICV Instituto de Cerámica y Vidrio

CSIC

STATE OF THE ART - European Green Deal

Main objective



3 Key principles:

1. Ensuring a **secure** and **affordable EU energy supply**

2. Developing a **fully integrated, interconnected** and **digitalised EU energy market**

3. Prioritising **energy efficiency**, improving the **energy performance of our buildings** and developing a power sector based largely on **renewable sources**

Fashion's bright new future

Flash in the pan? The rise of the smart toilet

The Guardian

Gas firms may face windfall tax as energy crisis hits more households

Starmer lays down roadmap to the centre

'Donnez-moi un break' Johnson deepens rift with Paris over defence deal

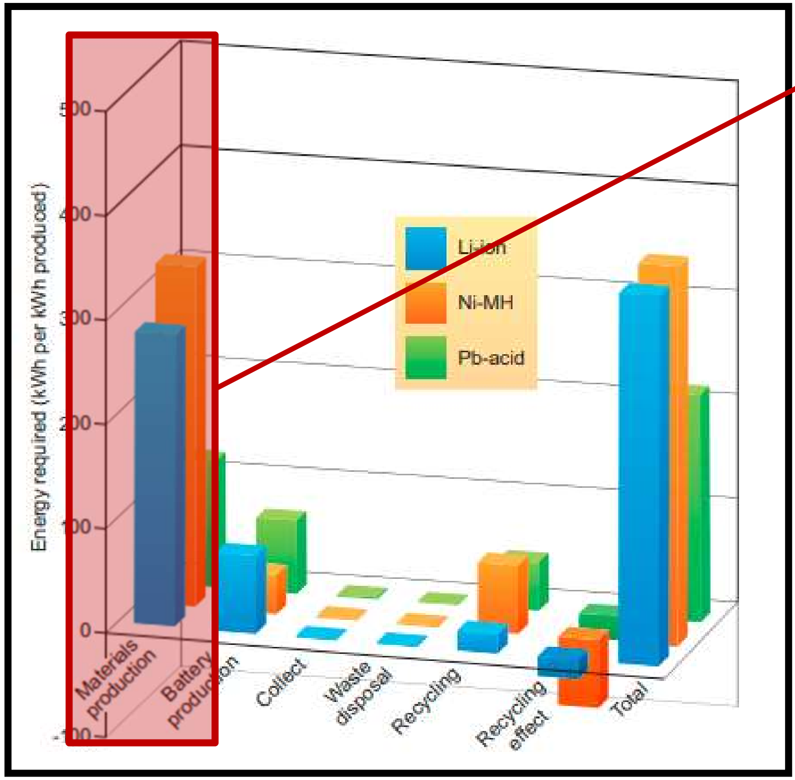
AI devises new way to treat brain cancer

NEWS | 11 May 2020 | Brussels | Energy

Energy storage is key for incorporating renewables into EU grid, new study suggests

STATE OF THE ART – New era: Material Science and Manufacturing

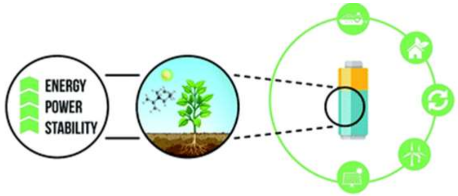
Electrochemical storage system → Energy required for the production of a 1 kWh

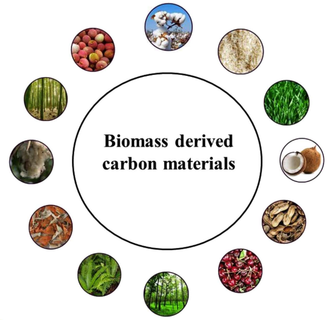


Larcher, D., & Tarascon, J. M. (2015). Towards greener and more sustainable batteries for electrical energy storage. *Nature Chemistry*, *7*(1), 19–29. https://doi.org/10.1038/nchem.2085

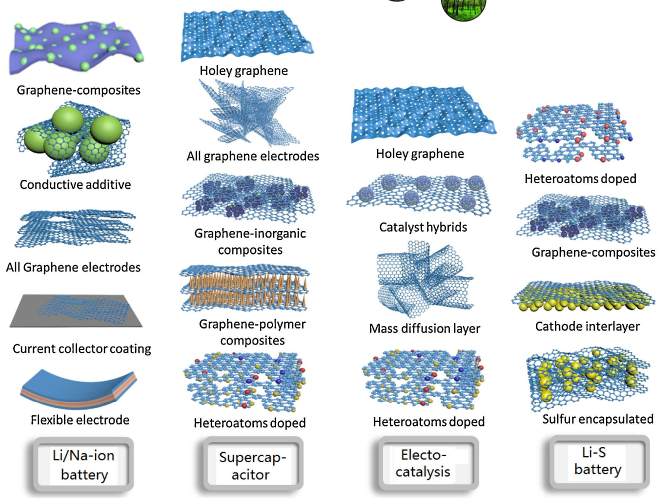
Materials production

- Sustainable source materials





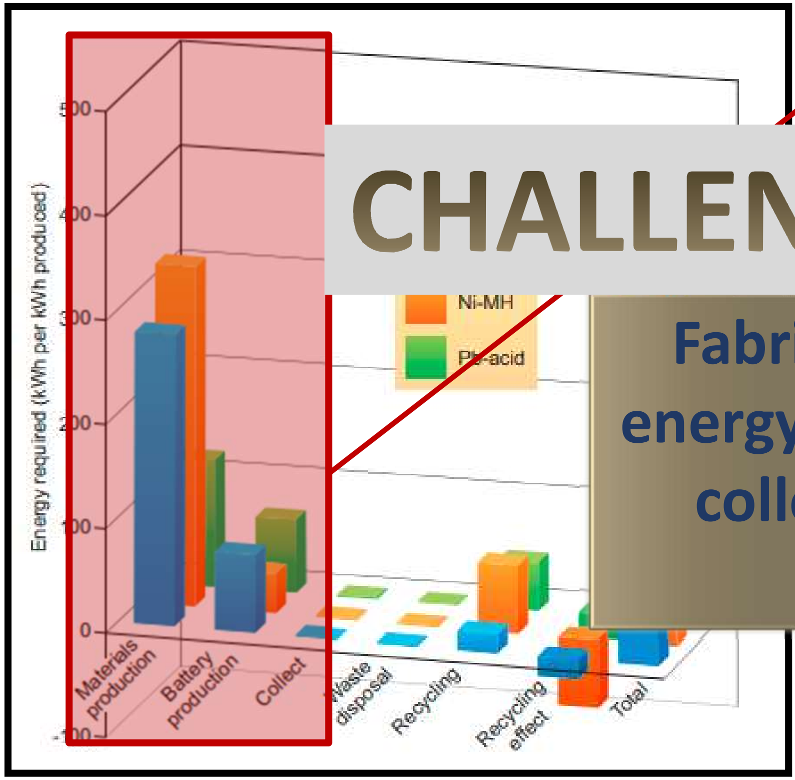
- Within 2D materials, graphene-based composites **exhibited a wide application range in energy storage systems.**



Xu, B., Qi, S., Jin, M., Cai, X., Lai, L., Sun, Z., Han, X., Lin, Z., Shao, H., Peng, P. (2019). 2020 Roadmap on Two-Dimensional Materials for Energy Storage and Conversion. *Chinese Chemical Letters*, *30*(12), 2053–2064. https://doi.org/10.1016/j.cclet.2019.10.028

STATE OF THE ART – New era: Material Science and Manufacturing

Energy required for the production of a 1 kWh electrochemical storage system



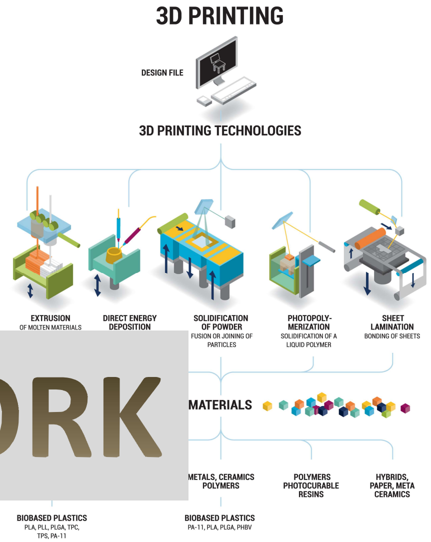
Larcher, D., & Tarascon, J. M. (2015). Towards greener and more sustainable batteries for electrical energy storage. *Nature Chemistry*, *7*(1), 19–29. https://doi.org/10.1038/nchem.2085

Battery production

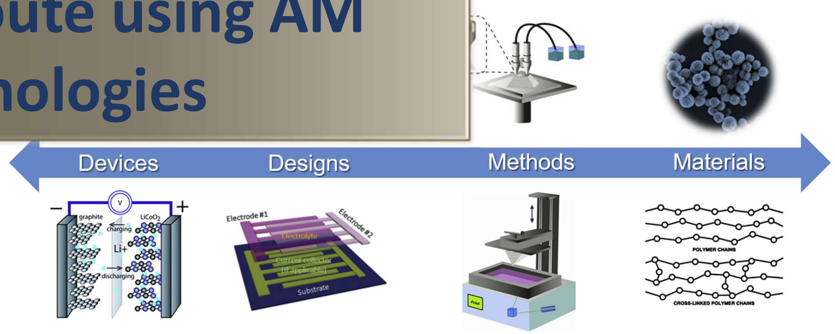
- Additive manufacturing **can lead a 25% decreasing of the global energy**

CHALLENGE OF THIS WORK

Fabrication of complex 3D energy storage devices from a colloidal route using AM technologies



L.A. Verhoef, B.W. Budde, C. Chockalingam, B. García Nodar, A.J.M. van Wijk, The effect of additive manufacturing on global energy demand: An assessment using a bottom-up approach, Energy Policy. 112 (2018) 349–360. https://doi.org/10.1016/j.enpol.2017.10.034.



U. Gulzar, C. Glynn, C. O'Dwyer, Additive manufacturing for energy storage: Methods, designs and material selection for customizable 3D printed batteries and supercapacitors, Curr. Opin. Electrochem. 20 (2020) 46–53. https://doi.org/10.1016/j.coelec.2020.02.009.

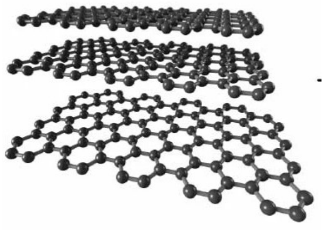
RAW MATERIALS

Commercial sustainable powders

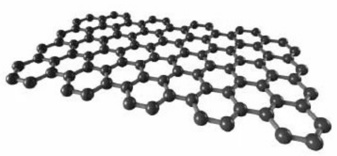
Electroactive synthesis materials

Inorganic precursors

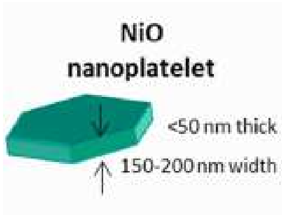
Graphite (CMO3)



Graphene (GPA)



$Ni(OH)_2$ & NiO



SiO_2 & ZrO_2

1. **Morphological characterization**
2. **Surface characterization**
3. **Colloidal stabilization**

1. Morphological characterization

- Particle size
- BET area
- SEM analysis

Commercial sustainable powders

Electroactive synthesis materials

Inorganic precursors

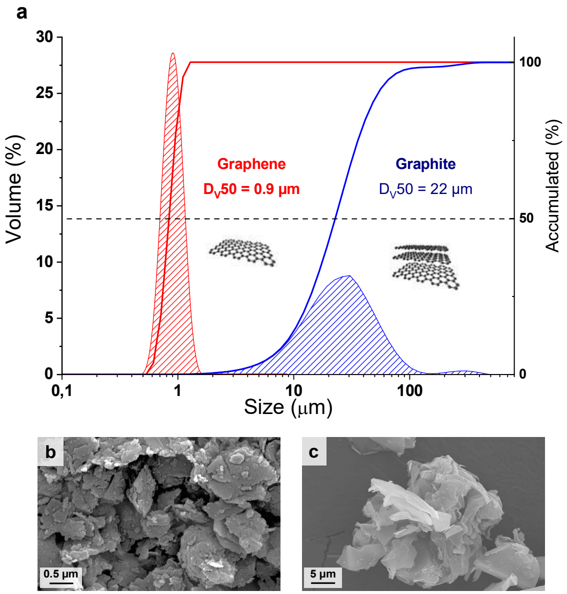
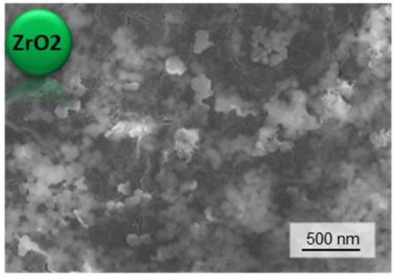
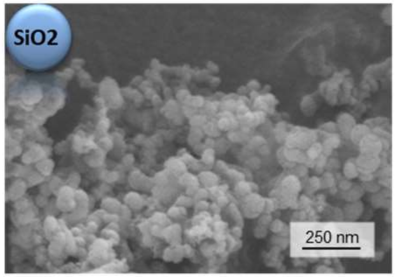
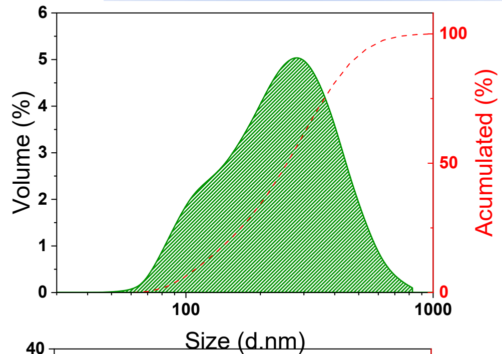


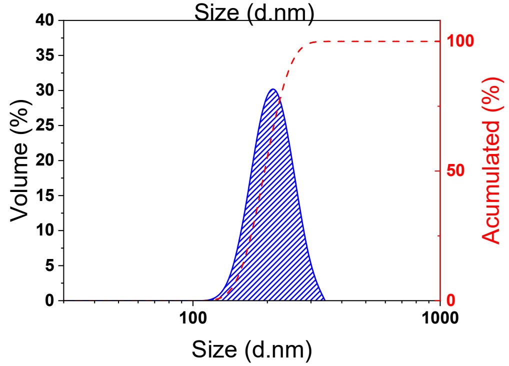
Table 1. Properties of synthetized nickel hydroxide ($Ni(OH)_2$) and nickel oxide (NiO)

	$Ni(OH)_2$	NiO
Diameter (nm)	100-200	100-200
Thickness (nm)	10-15	10-15
BET SSA ($m^2.g^{-1}$)	39,9	189,5
Open SSA by t-plot ($m^2.g^{-1}$)	37,1	175,6
% SSA contributed by micropores	7%	7,30%
Total N2 pore volume ($cm^3.g^{-1}$)	0,205	0,42
Micropore volume by t-plot ($cm^3.g^{-1}$)	0,001	0,0034
% Micropore on N_2 pore volume	0,50%	0,81%
Interplanar distance c (Å ± 0.2)	7,1	2,43
Crystal size Lklm (nm ± 0.3)	2,4	9,54





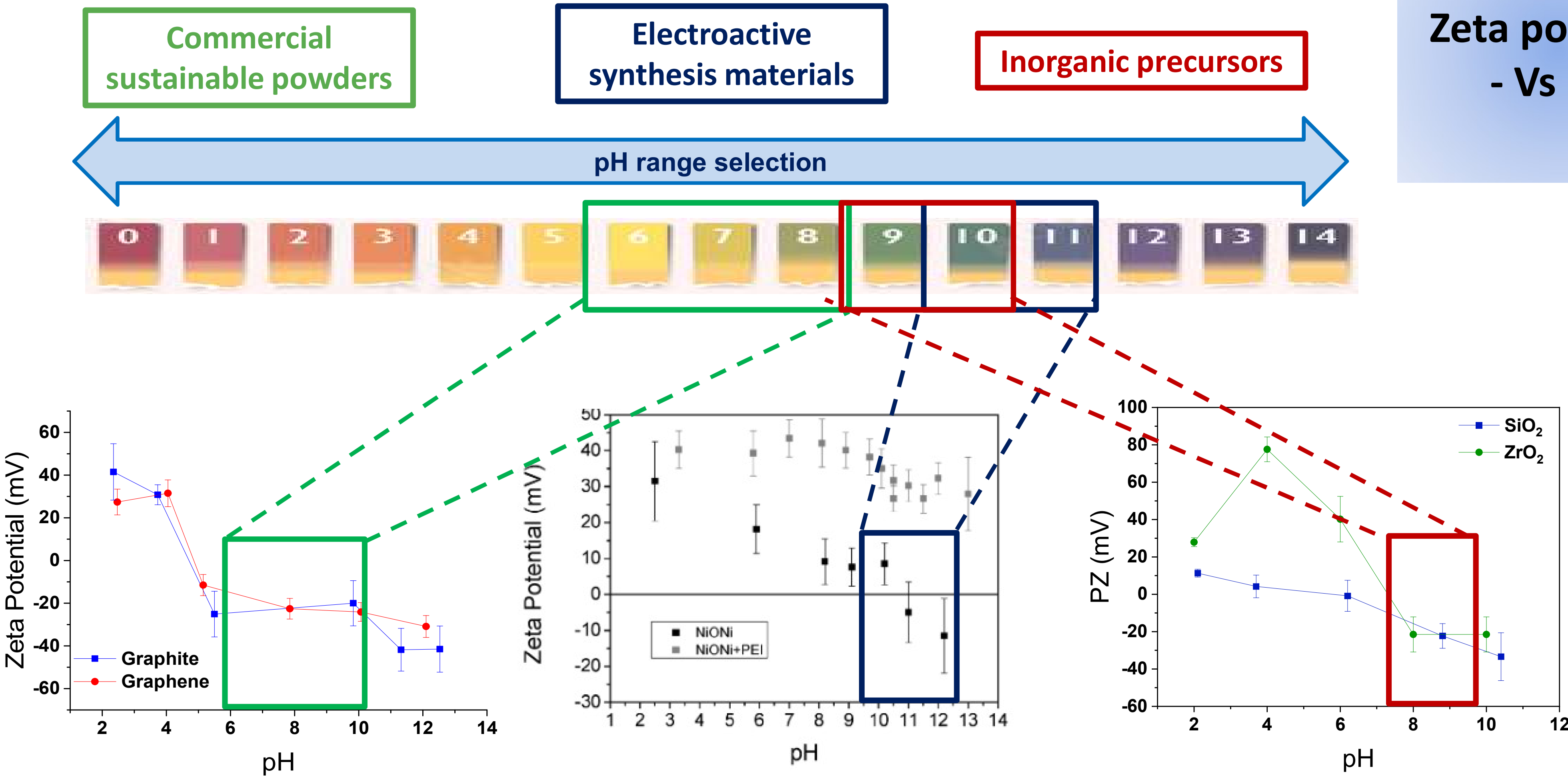




- **Provide us with information for the colloidal stabilization of the inorganic particles**
- **Even so, the surface modification will be finally defined by Zeta potential measurements**

2. Surface characterization

Zeta potential - Vs pH

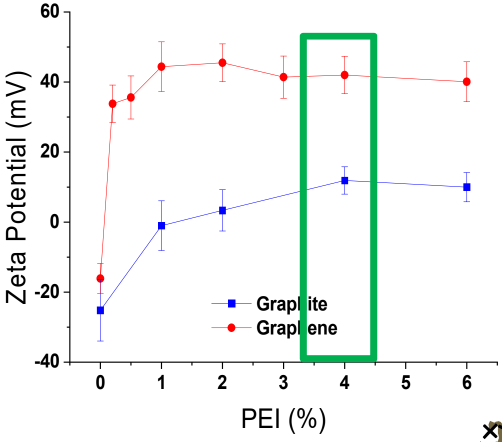


- **The working pH range in the aqueous medium will be selected depending on the surface modifier charge**

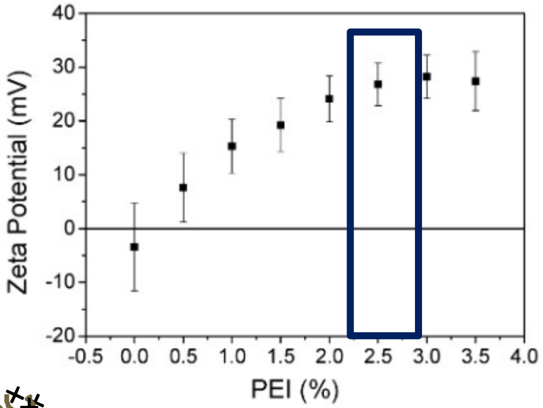
3. Surface modification

Zeta potential - Vs PEI wt.%

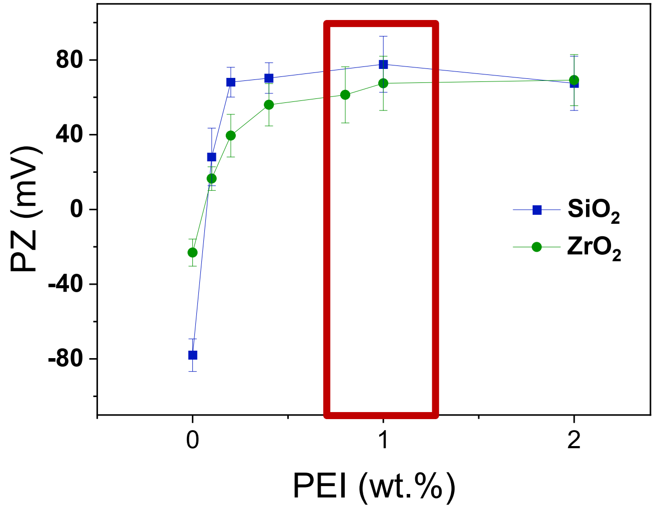
Commercial sustainable powders

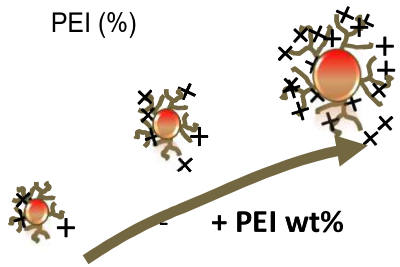


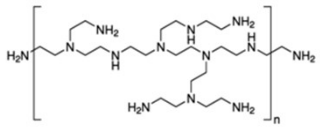
Electroactive synthesis materials

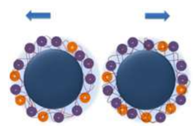


Inorganic precursors





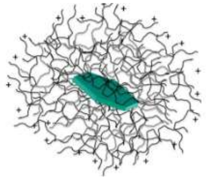




- **Electrosteric repulsion forces Electrostatic + Physical**

- **Polyethylenimine (PEI), amine functional groups generate electrostatic interaction forces with negatively charged inorganic particles**
- **Once adsorbed on the surface through hydrogen bonds, electrosteric repulsion forces are generated between particles, obtaining completely stabilized**

From inorganic particles to a colloidal feedstock for different AM technologies

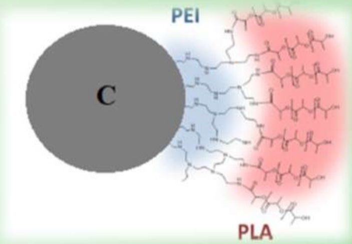


Composite feedstock

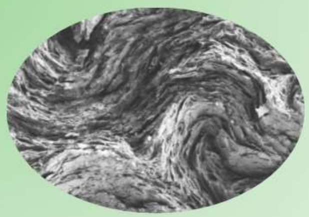
COLFEED4Print

CO2 NEUTRAL

Thermoplastic polymer (PLA)



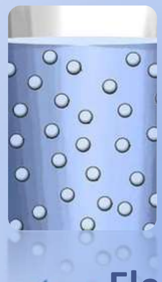
Conductive thermoplastic-based filament with highly loaded-oriented graphite and graphene platelets (25 vol.%)



Material thermal extrusion MTE

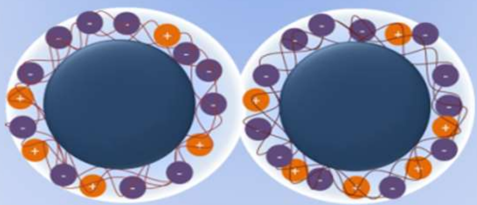
ADDITIVE MANUFACTURIN TECHNOLOGIES

Liquid feedstock



Stabilized suspension with the desired surface charge on the particles

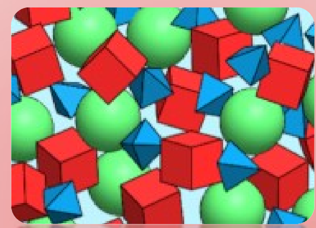
Electrosteric



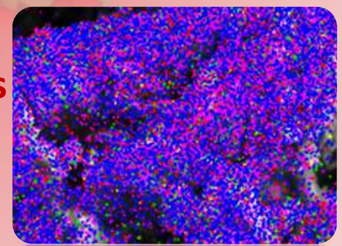
Electrophoretic deposition

Functionalization Technology

Yield feedstock



Homogeneously distributed precursors for optimized solid-state reactions

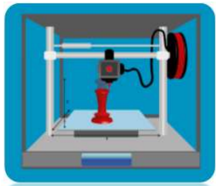


Direct ink writing

ADDITIVE MANUFACTURIN TECHNOLOGIES

From inorganic particles to a colloidal feedstock for different AM technologies

Material thermal extrusion
MTE

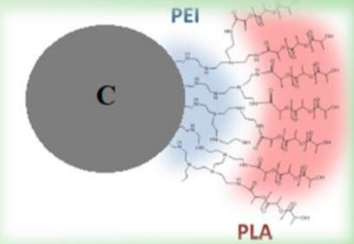


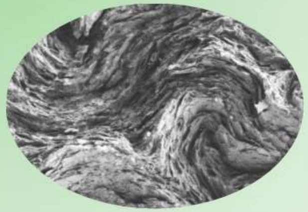
Complex conductive frameworks: Variable mesh and different architectures

Composite feedstock

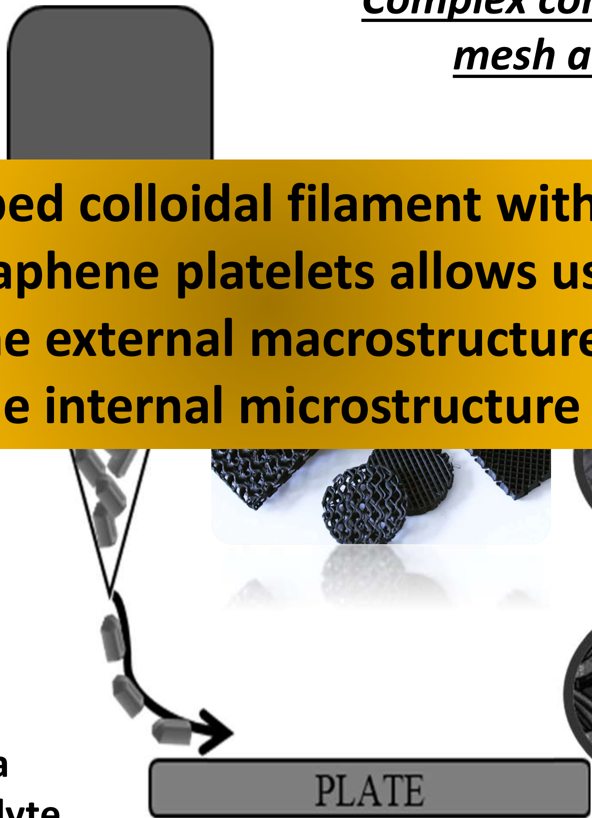
COLFEED4Print

Thermo
Condu
based
loaded-
graphen





The developed colloidal filament with oriented graphite/graphene platelets allows us not only to design the external macrostructure but also the internal microstructure



Grid
Mesh opening > 1mm

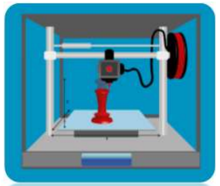
Grid
Mesh opening < 0.5 mm

Gyroid
Filament distance < 1 mm

- Increase the exposed specific surface area
- Modulate the permeability of the electrolyte

From inorganic particles to a colloidal feedstock for different AM technologies

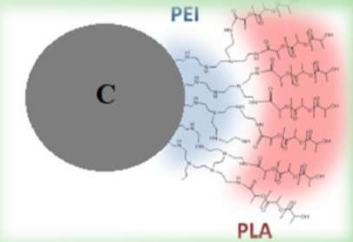
Material thermal extrusion
MTE



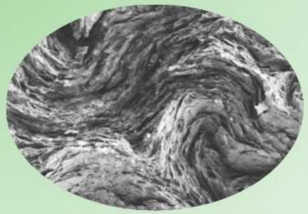
Composite feedstock

COLFEED4Print

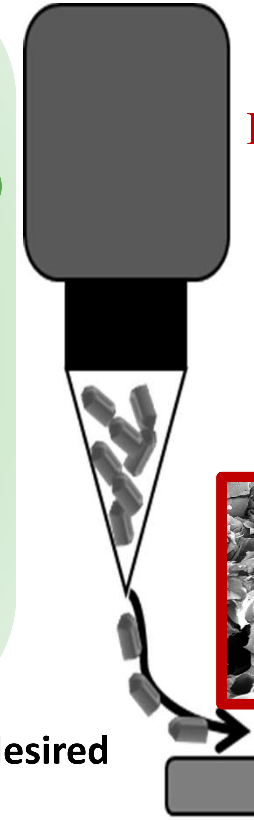
Thermoplastic polymer (PLA)



Conductive thermoplastic-based filament with highly loaded-oriented graphite and graphene platelets (25 vol.%)

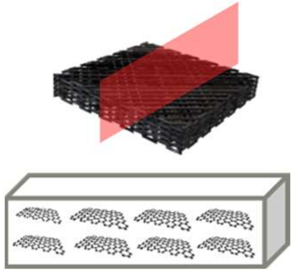


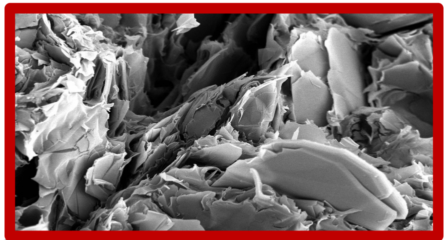
- **Define the microstructure to obtain the desired electrical or electrochemical properties**



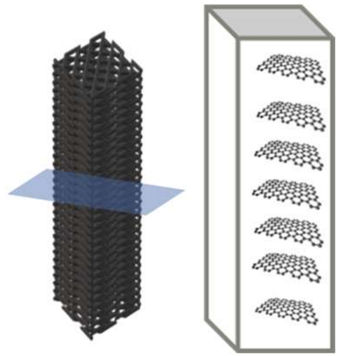
Modulating the orientation of the inorganic filler on the 3D-printed electrodes

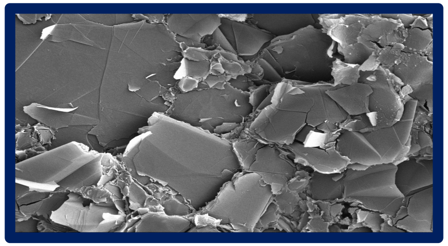
Horizontal configuration





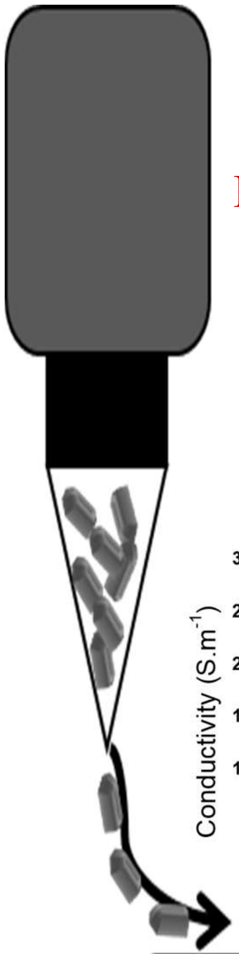
Vertical configuration





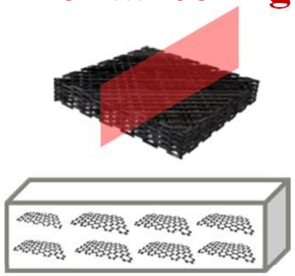
Cross-section micrographs

From inorganic particles to a colloidal feedstock for different AM technologies

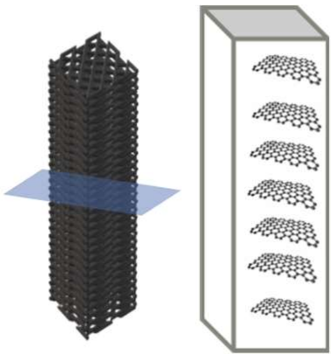


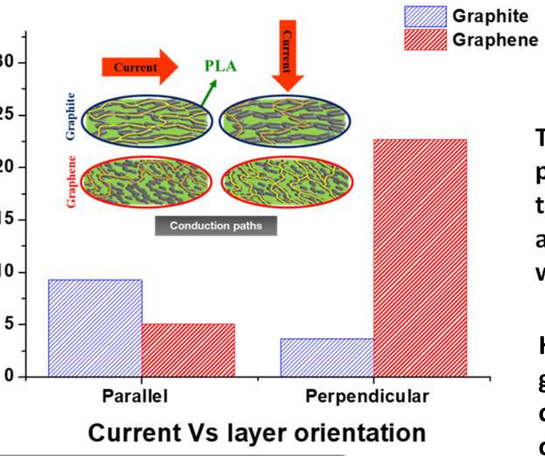
Modulating the orientation of the inorganic filler on the 3D-printed electrodes

Horizontal configuration



Vertical configuration





The graphite electrodes with a more pronounced orientation of flakes, due to their stronger structural strength, achieves higher conductivities (9 S/m) when the current is applied parallelly

However, the graphene electrodes generate more conduction paths when the current is applied perpendicular to the orientation of the graphene nanoflakes


Additive Manufacturing
Volume 72, 25 June 2023, 103643

Material thermal extrusion of conductive 3D electrodes using highly loaded graphene and graphite colloidal feedstock

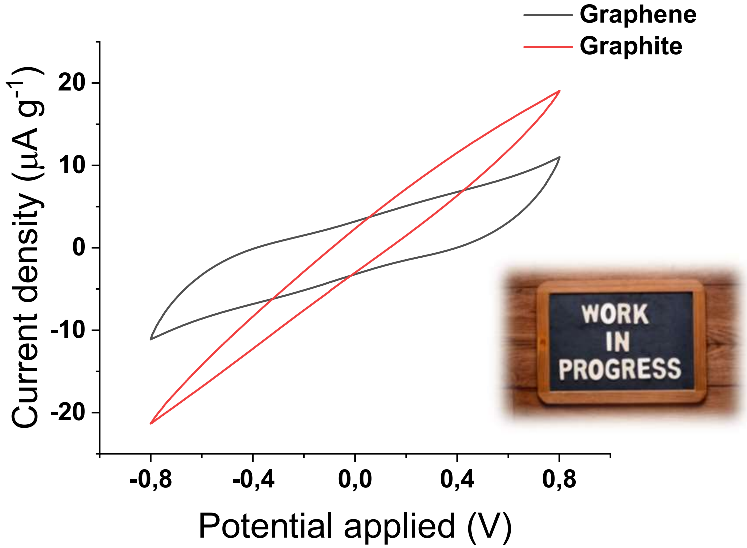
Oxel Urra Sanchez [a], Hossein Besharatloo [a b], Joaquin Yus [a c], Antonio Javier Sanchez-Herencia [a], Begoña Ferrari [a]

https://doi.org/10.1016/j.addma.2023.103643

Electrochemical performance of 3D-printed electrodes in symmetric solid-state capacitors

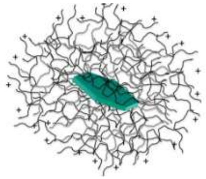
15 wt.% PVA – 200 wt.% H_3PO_4

Drop casting



CSIC
ICV Instituto de Cerámica y Vidrio
colloidal processing
O. Urra, 2023

From inorganic particles to a colloidal feedstock for different AM technologies

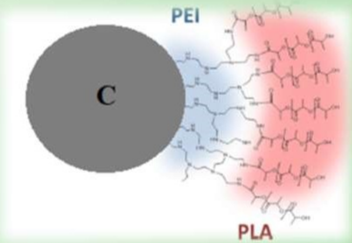


Composite feedstock

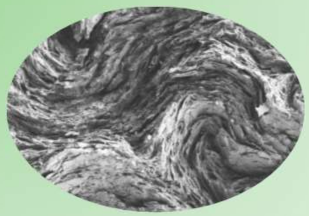
COLFEED4Print

CO2 NEUTRAL

Thermoplastic polymer (PLA)



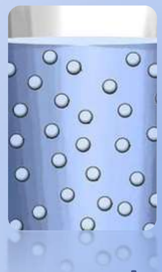
Conductive thermoplastic-based filament with highly loaded-oriented graphite and graphene platelets (25 vol.%)



Material thermal extrusion MTE

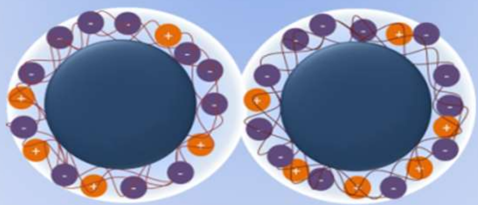
ADDITIVE MANUFACTURING TECHNOLOGIES

Liquid feedstock



Stabilized suspension with the desired surface charge on the particles

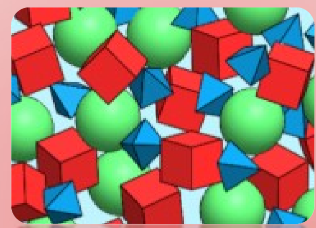
Electrosteric



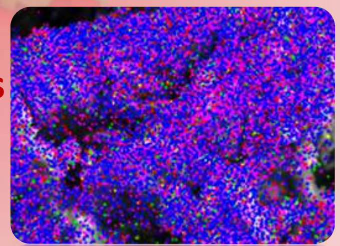
Electrophoretic deposition

Functionalization Technology

Yield feedstock



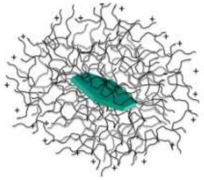
Homogeneously distributed precursors for optimized solid-state reactions



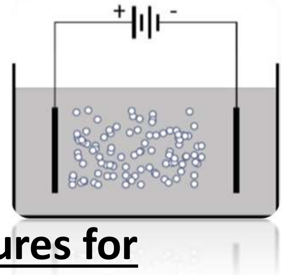
Direct ink writing

ADDITIVE MANUFACTURING TECHNOLOGIES

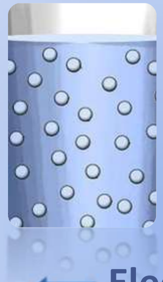
From inorganic particles to a colloidal feedstock for different AM technologies



Electrophoretic deposition

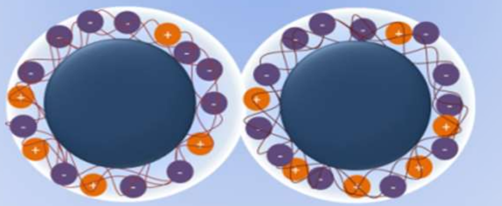


Liquid feedstock



Stabilized suspension with the desired surface charge on the particles

Electrosteric



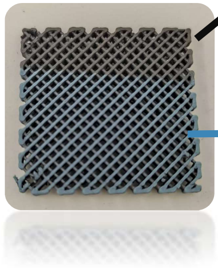
Functionalization of conductive 3D structures for binder-free hybrid electrodes

3D-printed conductive frameworks

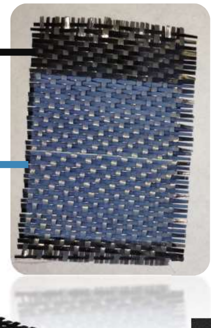
Commercial conductive frameworks

Printed graphene electrode

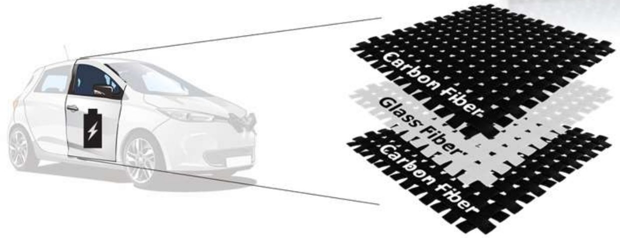
Commercial carbon fibers

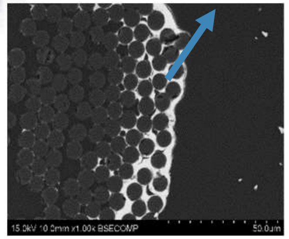


Ni(OH)2



Ni(OH)2 coating



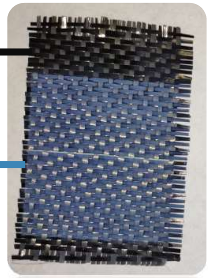


- Functionalization of commercially used carbon fibers (Automotive and aerospatial) to fabricate thin energy storage devices with major mechanical properties

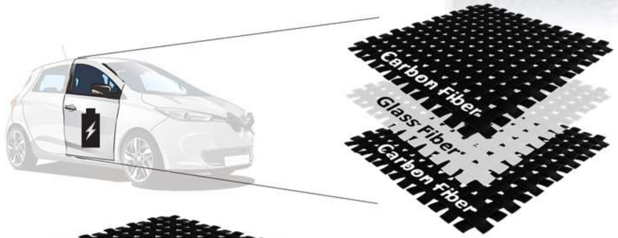
From inorganic particles to a colloidal feedstock for different AM technologies

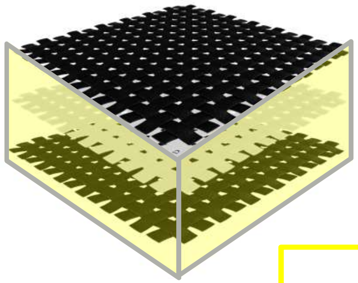
Commercial carbon fibers

Ni(OH)2



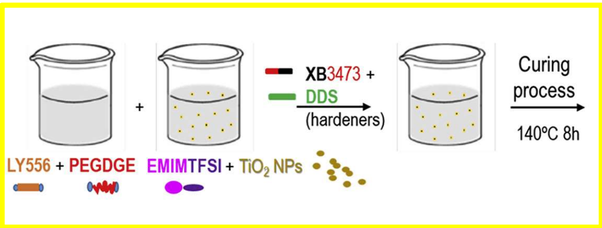
Commercial conductive frameworks

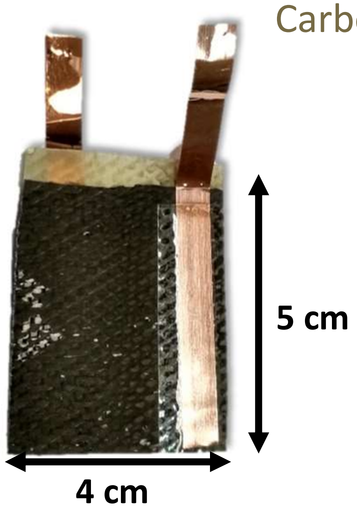




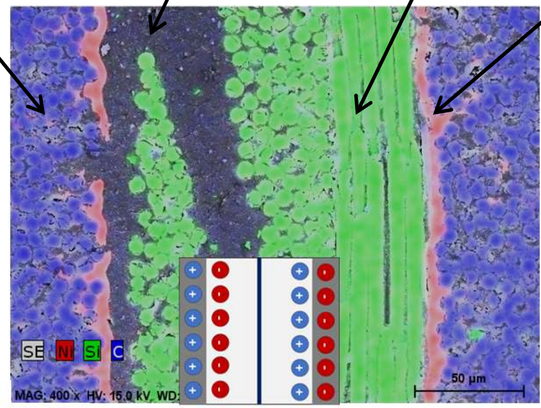
Solid Electrolyte

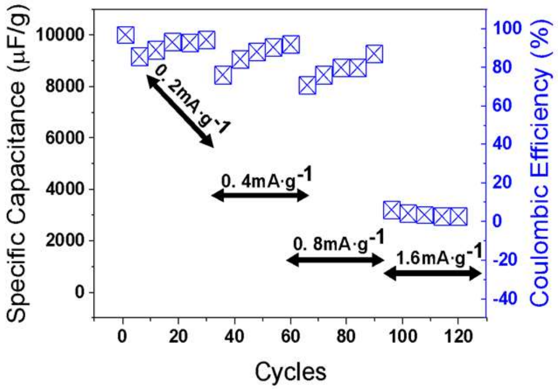
Symmetric cell: Coated Carbon fiber/Solid electrolyte/ Coated carbon fiber

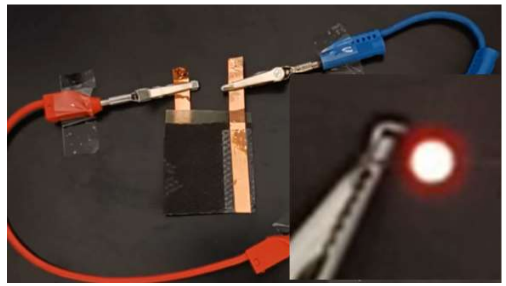




Carbon Fiber Electrolyte Glass Fiber NiO

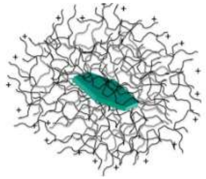






- Fabrication of thin solid-state pseudocapacitor with major mechanical and thermal properties
- Good electrochemical stability

From inorganic particles to a colloidal feedstock for different AM technologies

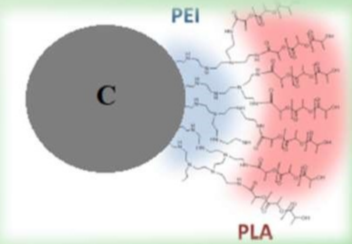




Composite feedstock

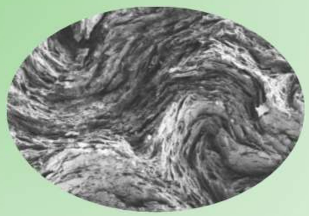
COLFEED4Print

CO2 NEUTRAL

Thermoplastic polymer (PLA)



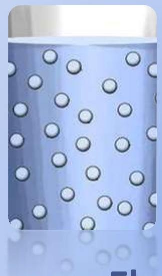
Conductive thermoplastic-based filament with highly loaded-oriented graphite and graphene platelets (25 vol.%)

ADDITIVE MANUFACTURING TECHNOLOGIES

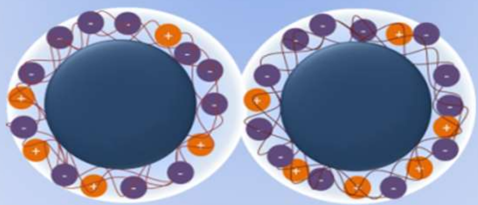
Material thermal extrusion MTE

Liquid feedstock



Stabilized suspension with the desired surface charge on the particles

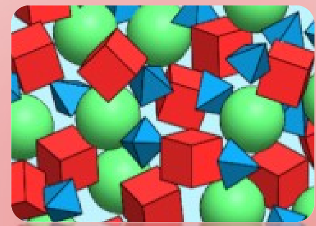
Electrosteric



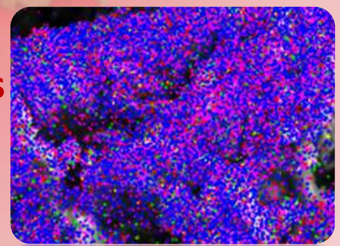
Electrophoretic deposition

Functionalization Technology

Yield feedstock



Homogeneously distributed precursors for optimized solid-state reactions

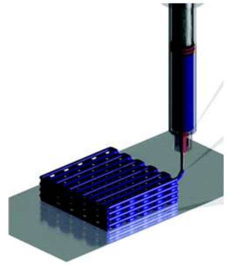


Direct ink writing

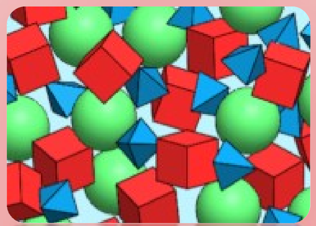
ADDITIVE MANUFACTURING TECHNOLOGIES

From inorganic particles to a colloidal feedstock for different AM technologies

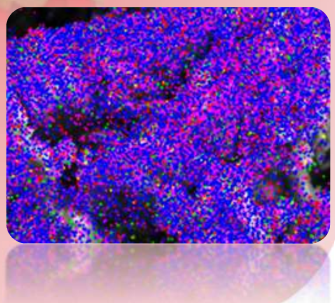
Direct ink writing



Yield feedstock

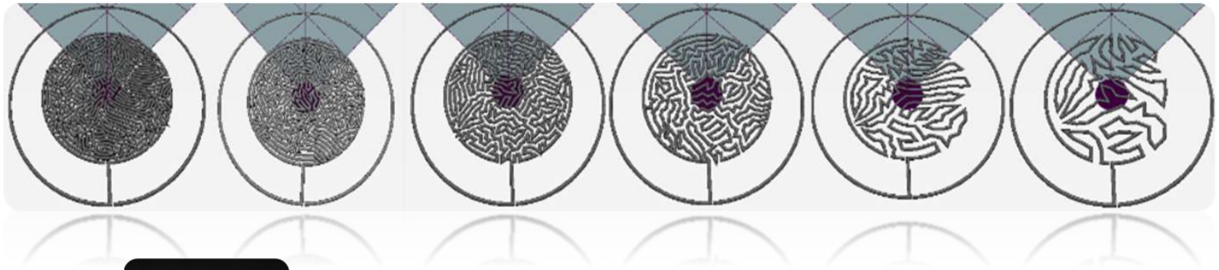


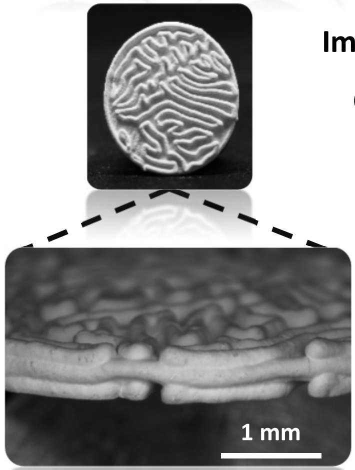
Homogeneously distributed precursors for optimized solid-state reactions



SSR of NASICON precursors colloidal mixture to obtain a thin (40µm) NASICON phase powder for DIW

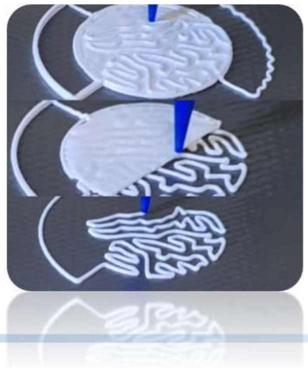
Development of complex NASICON patterns with defined interlinear spacing



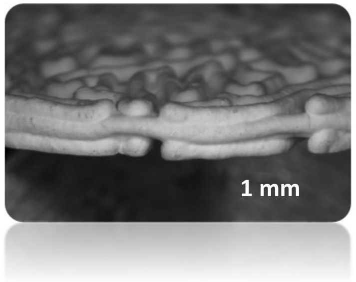


Improvement of rheological properties of NASICON CMC-based ink to print 1 dense layer impacted between 2 complex patterns

Increased electrode/electrolyte interface for high-performance energy storage devices

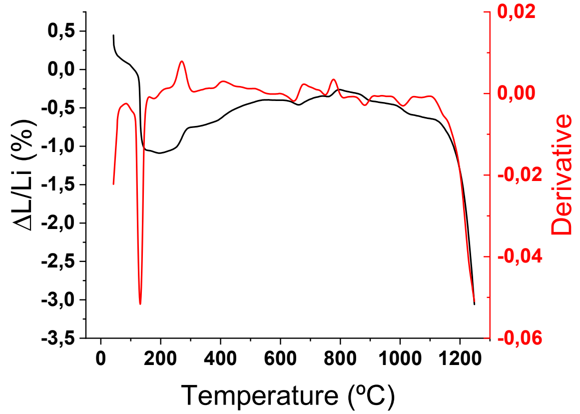


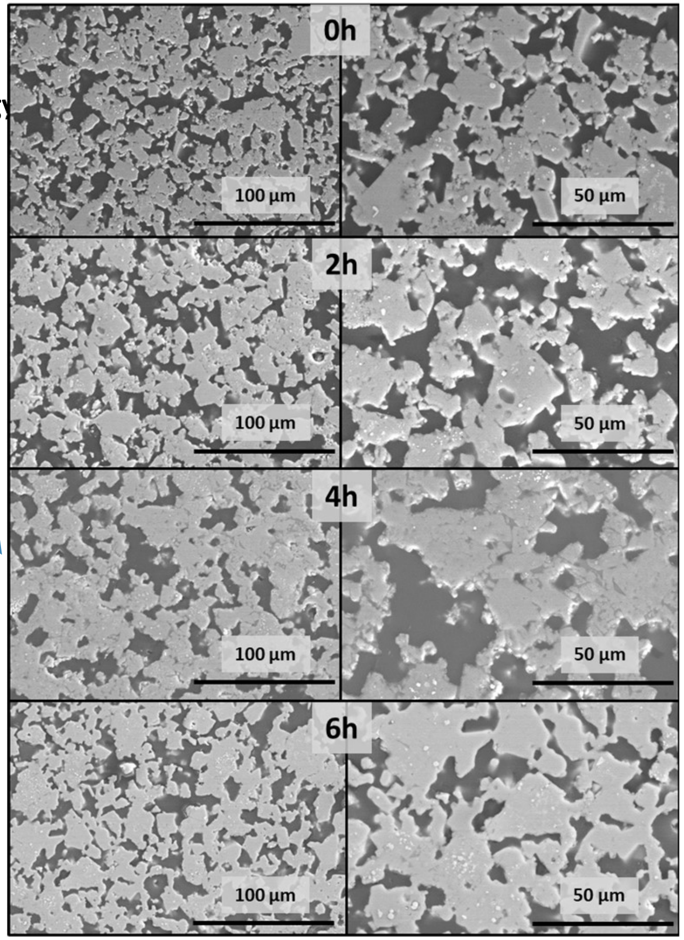
From inorganic particles to a colloidal feedstock for different AM technologies

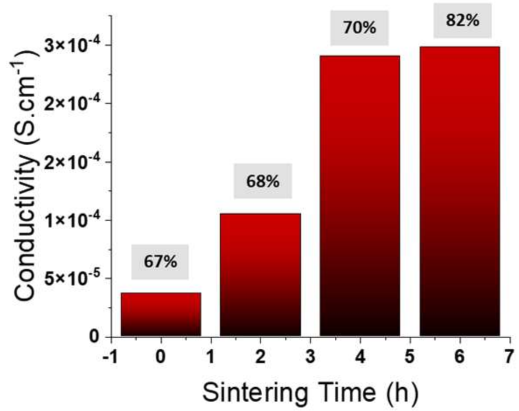


Increased electrode/electrolyte interface for high-performance energy storage devices

Densification of 3D-printed electrolytes to increase its electrochemical performance





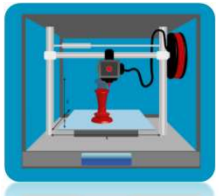


6h densification process 82% of density and a major ionic conductivity of 3E-4 S/cm were achieved for 3D-printed NASICON solid electrolytes

CONCLUSIONS

○ Colloidal approach allows us to:

Composite feedstock → **Material thermal extrusion MTE**

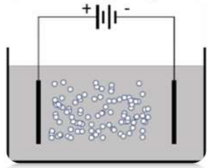


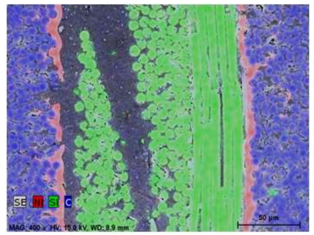
ADDITIVE MANUFACTURING TECHNOLOGIES

Conductive logo printed with 25% Graphene filament

- Introduce high content of 2D nanoflakes into a biodegradable thermoplastic matrix (PLA).
- The oriented filaments allow the configuration of the microstructure of the electrode during the material extrusion 3D printing increasing the electrical properties up to 22 S/m in printed graphene-based electrodes.

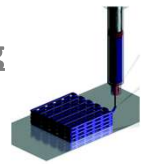
Liquid feedstock → **Electrophoretic deposition EPD**



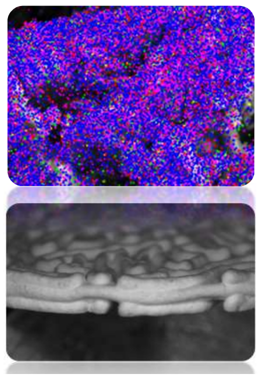


- Fabricate binder-free coatings (100% active material) over conductive frameworks.
- Homogeneous coatings are formed over complex conductive architectures without damaging the original properties of the deposition substrates.
- Electrochemically stable thin (<500 µm) solid-state pseudocapacitors were fabricated with major mechanical and thermal properties.

Yield feedstock → *SSR previous* → **Direct ink writing DIW**



ADDITIVE MANUFACTURING TECHNOLOGIES



- Green homogeneous mixture of NASICON precursors for solid-state reaction (SSR) was developed by colloidal stabilization.
- Obtained thin NASICON pure powder was printed using CMC-based ink by DIW. Complex patterns separated by a dense layer (Acting as a separator in the battery) were developed.
- Novel ionic conductivity of 3E-4 S/cm was achieved at room temperature.

ACKNOWLEDGMENT

Thank you for your attention.

ADiT! MAT

Comunidad de Madrid

www.madrid.org

colloidal processing

Think Different

FAB3D

Plataforma CSIC para el Desarrollo de la Fabricación Aditiva

PID2019–106631GB-C42

CSIC ICV

CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

INSTITUTO DE CERÁMICA Y VIDRIO (ICV)

GOBIERNO DE ESPAÑA

MINISTERIO DE CIENCIA E INNOVACIÓN

COLFEED4Print