Screen Printable Electrochemical Capacitors on Flexible Substrates

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UNIVERSIDAD DE GRANADA

IARIA

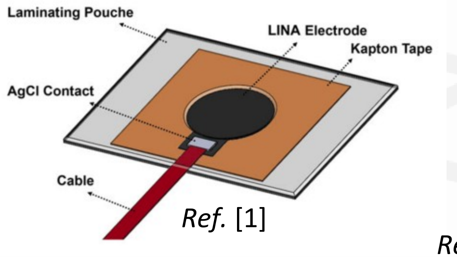
PEARL
Pervasive Electronics Advanced Research Laboratory

About us

- **Presenter:**
  - Francisco J. Romero, PhD. Student
  - Thesis:

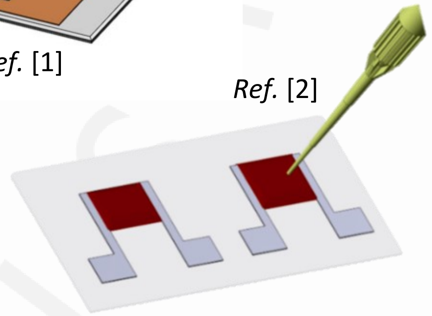
    Design, Modelling and Fabrication of Sensors for Internet-of-Everything Applications based on Emerging Flexible Materials and Technologies

- **Research Group:**
  - Pervasive Electronics Advanced Research Laboratory, University of Granada, Spain
  - Research Lines:
    - Graphene-based Materials:
      - Laser-reduced Graphene Oxide (GO), Graphene Oxide (rGO), Laser Induced Graphene (LIG)
    - Printable Materials:
      - Silver Nanoparticles (AgNPs), Silver Nanowires (Ag NWs), Silver Chloride (AgCl), carbon-based inks, etc.
    - Flexible Electronics Fabrication Techniques:
      - Laser-Assisted Fabrication, Screen-Printing, Inkjet-Printing
    - Applications:
      - Temperature Sensors, Humidity Sensors, Heaters, Electrodes for Biosignals Acquisition, Supercapacitors, Memristors, etc.



Ref. [1]

Ref. [2]



OUTLINE

- Introduction
- Fabrication
- Results and Discussion
- Conclusions

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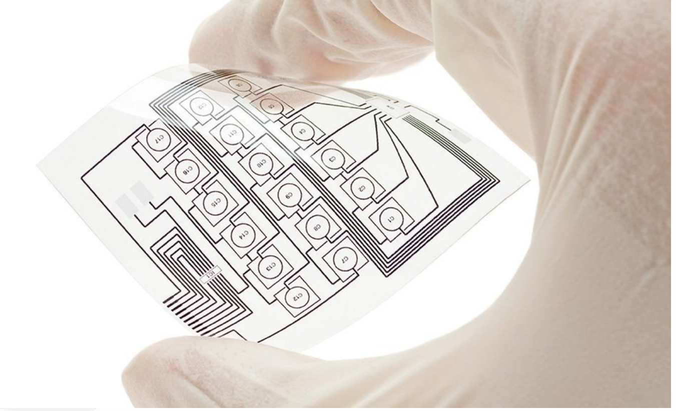
INTRODUCTION

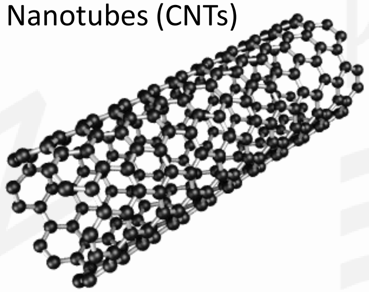
- **Flexible Electronics** is expected to cause a disruption in the field of electronics devices for diverse applications:
  - Wearables
  - Electronics skin (e-skin)
  - Biomedical applications (e-health)
  - Robotics

Source: news.mit.edu

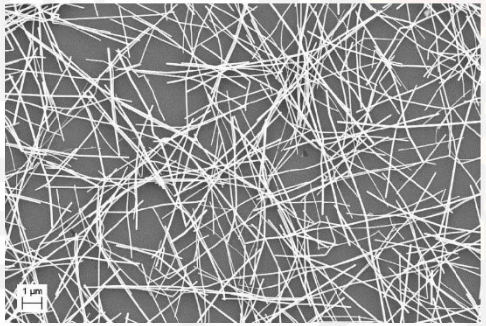


- **Consequence:** Emergence of new electrical conductive and flexible materials

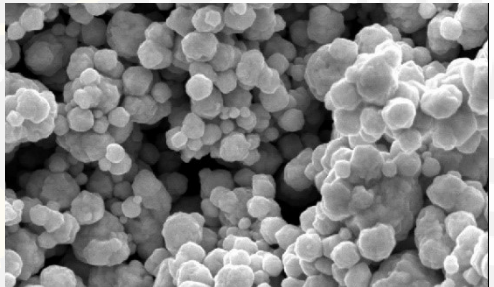
Carbon Nanotubes (CNTs)



AgNWs *Ref.* [3]

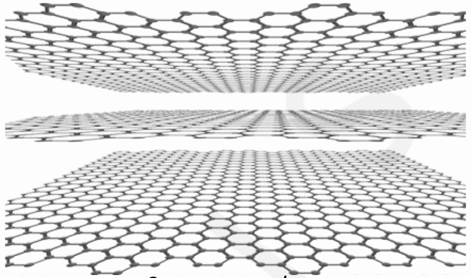


AgNPs



Source: getnanomaterials.com

Graphene-based Materials



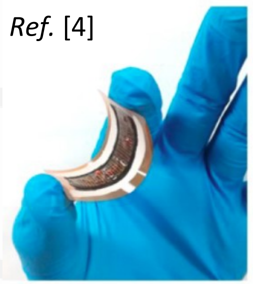
Source: graphenomenon.com

INTRODUCTION

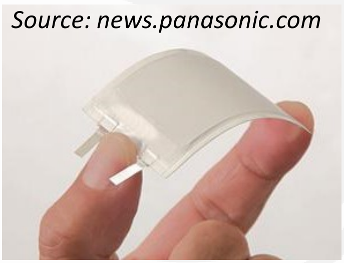
- **Flexible Electronics for a Generic IoT Device**

Power Supply

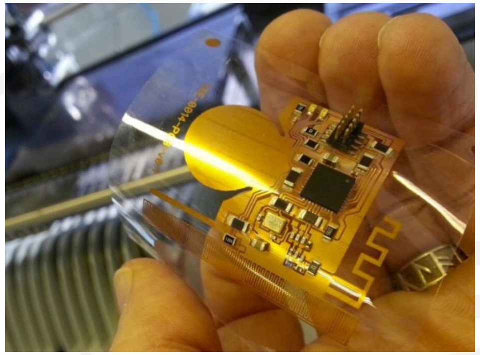
Ref. [4]



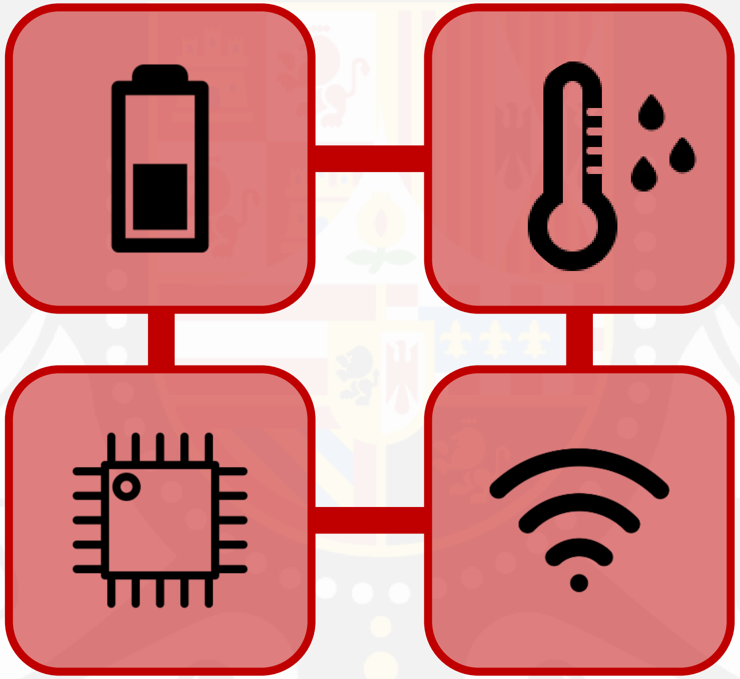
Source: news.panasonic.com



Microcontroller Unit

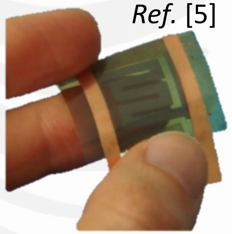


Source: edn.com



Sensors

Ref. [5]



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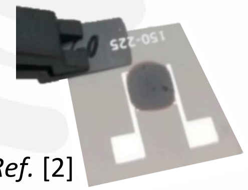

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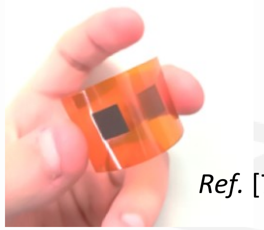
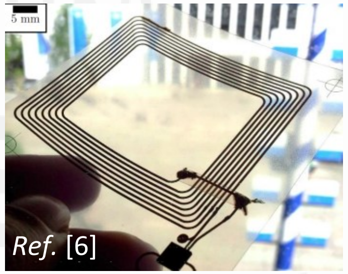


Ref. [7]

Antennas



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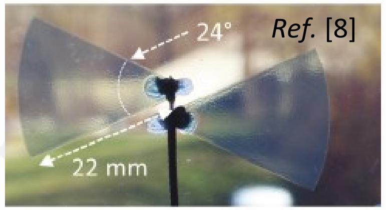

Ref. [8]

INTRODUCTION

- **Flexible Electronics for a Generic IoT Device**

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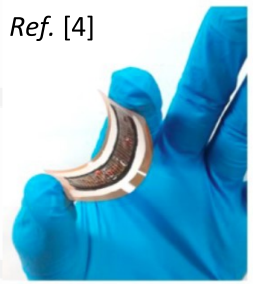
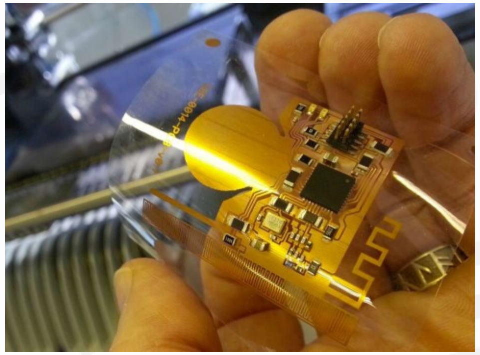


Source: news.panasonic.com

Topic of this work

Microcontroller Unit



Source: edn.com

Current greatest barrier

Intermediate solution: Ridig-Flex implementations

INTRODUCTION

- **Supercapacitors (SCs):**
  - ✓ High-capacity capacitors with higher power when compared to conventional batteries
  - ✓ Faster and higher charging/discharging cycles than rechargeable batteries
  - ✓ Up to 100 times more energy per unit of volume or mass than electrolytic capacitors
  - X Lower operation voltage

- **Basic Structure:**
  - Collector → Electrode → Electrolyte | Separator | Electrolyte ← Electrode ← Collector

- **SCs Types:**
  - Electrochemical double-layer capacitors (EDLCs):
    - The electrode material is not electrochemically active, therefore the capacitance is associated with the pure physical charge accumulation at the electrode/electrolyte interface
  - Pseudocapacitors:
    - The energy storage relies on fast and reversible faradaic redox reactions occurring on the electrode surface

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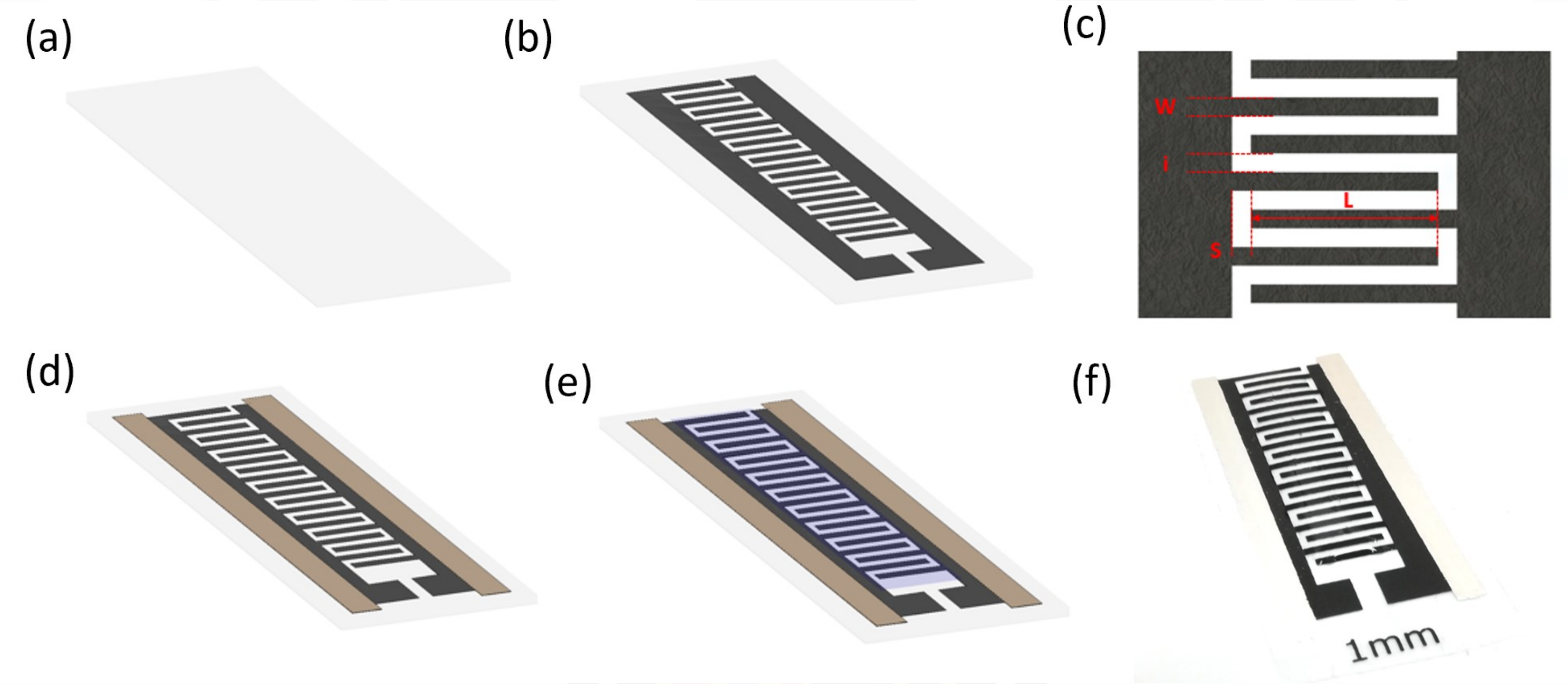
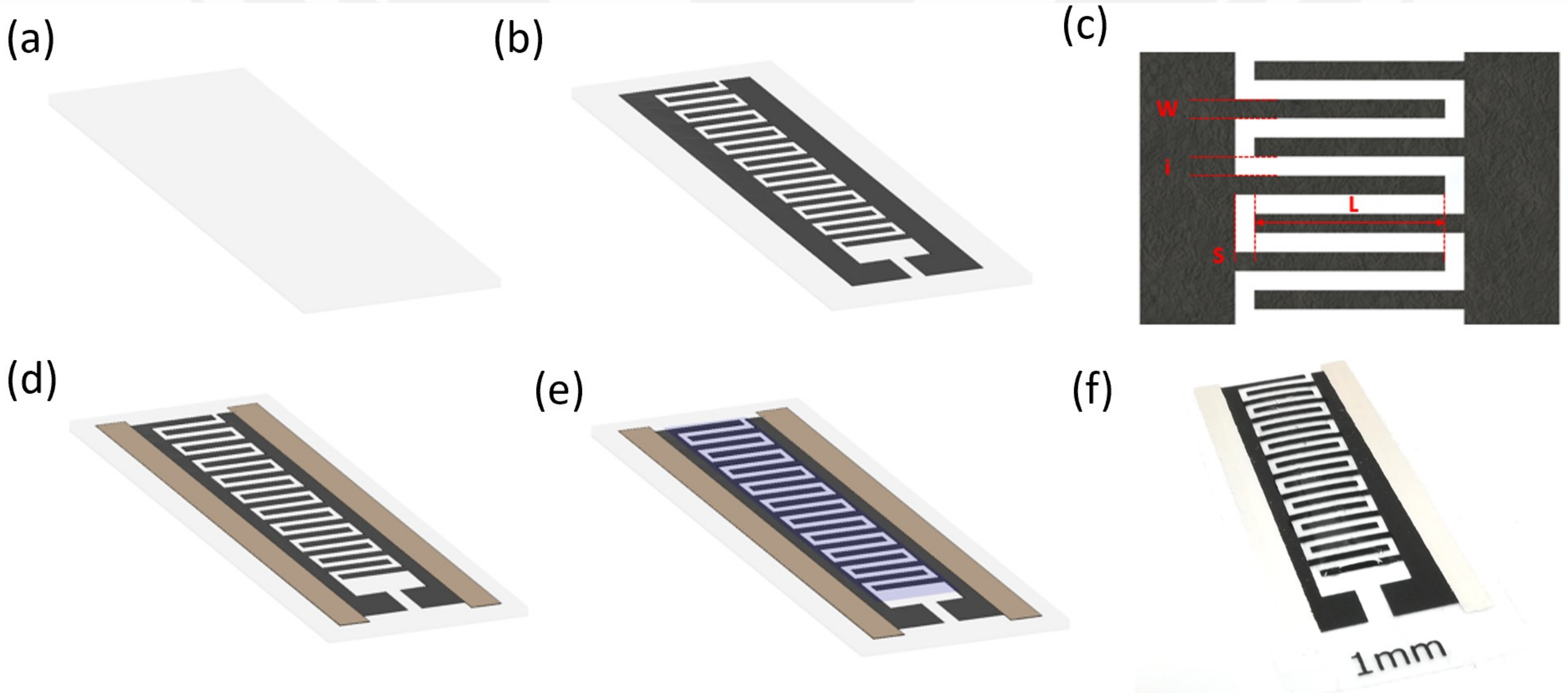
Fabrication



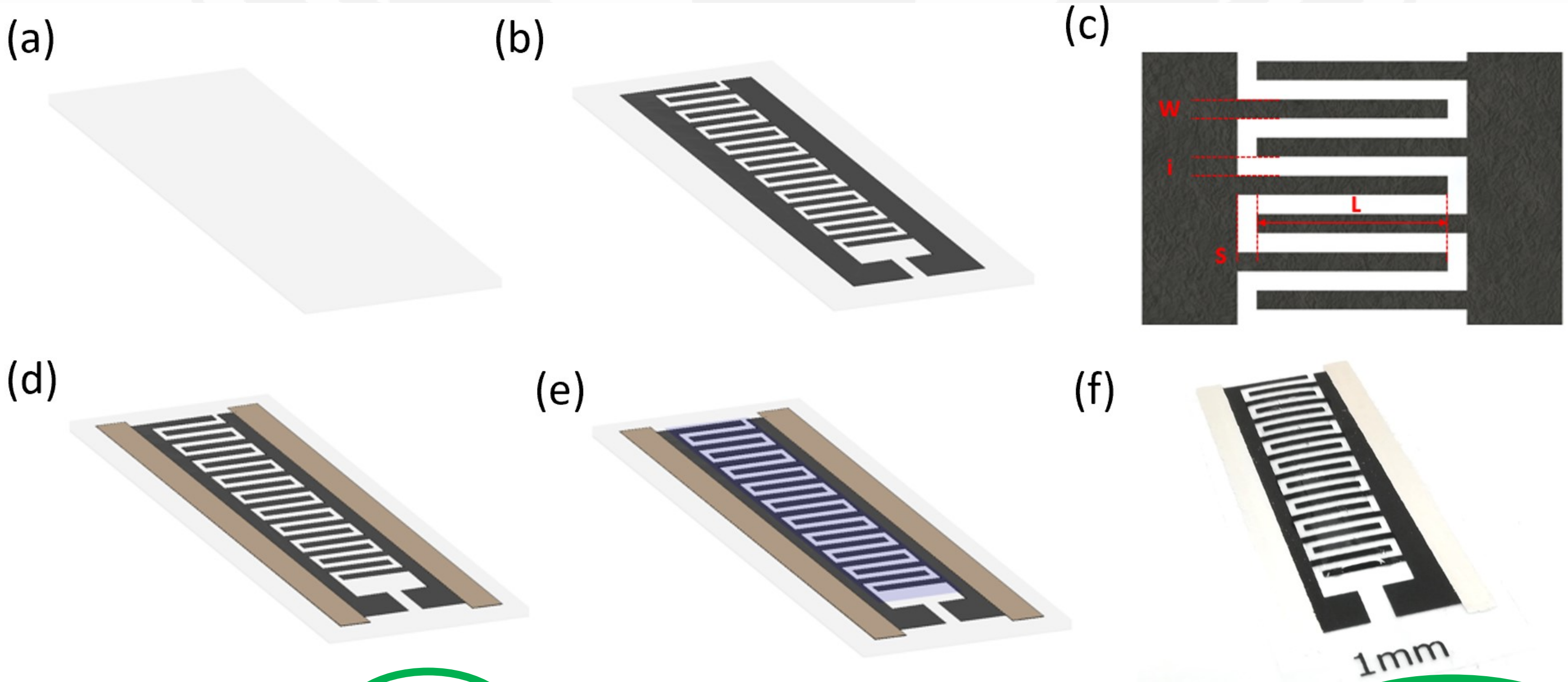
a) Flexible and transparent polyester films for water-based inks with a thickness of 160 µm

Fabrication



b) InterDigital Electrodes (IDEs) **screen-printed** on the substrate using a carbon-based commercial ink, model C-220 (Applied Ink Solutions).

Fabrication

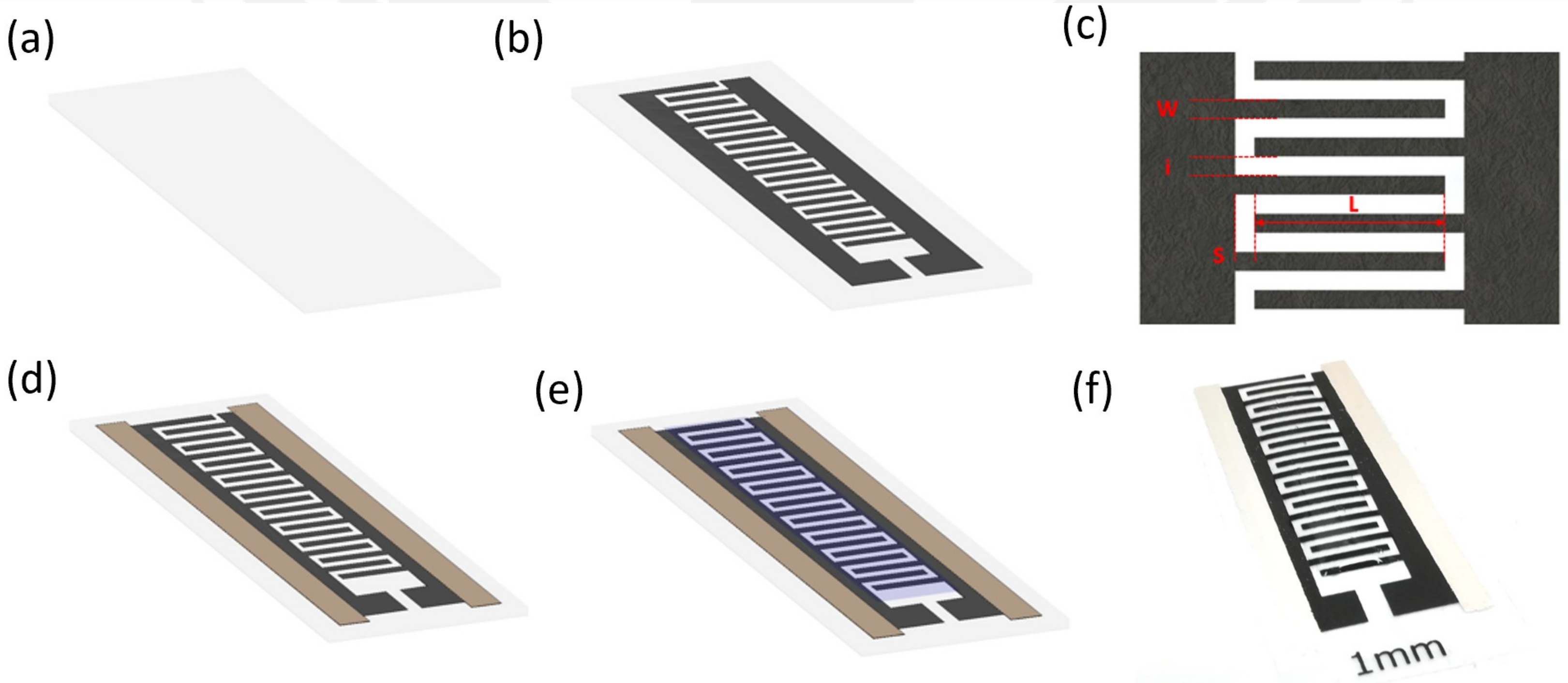


b) InterDigital Electrodes (IDEs) **screen-printed** on the substrate using a carbon-based commercial ink, model C-220 (Applied Ink Solutions).

Lower thicknesses and smaller distances between electrodes than stacked structures

- ***i) exceptionally high surface area***
- *ii) relatively high electrical conductivity*
- *iii) acceptable cost*

Fabrication

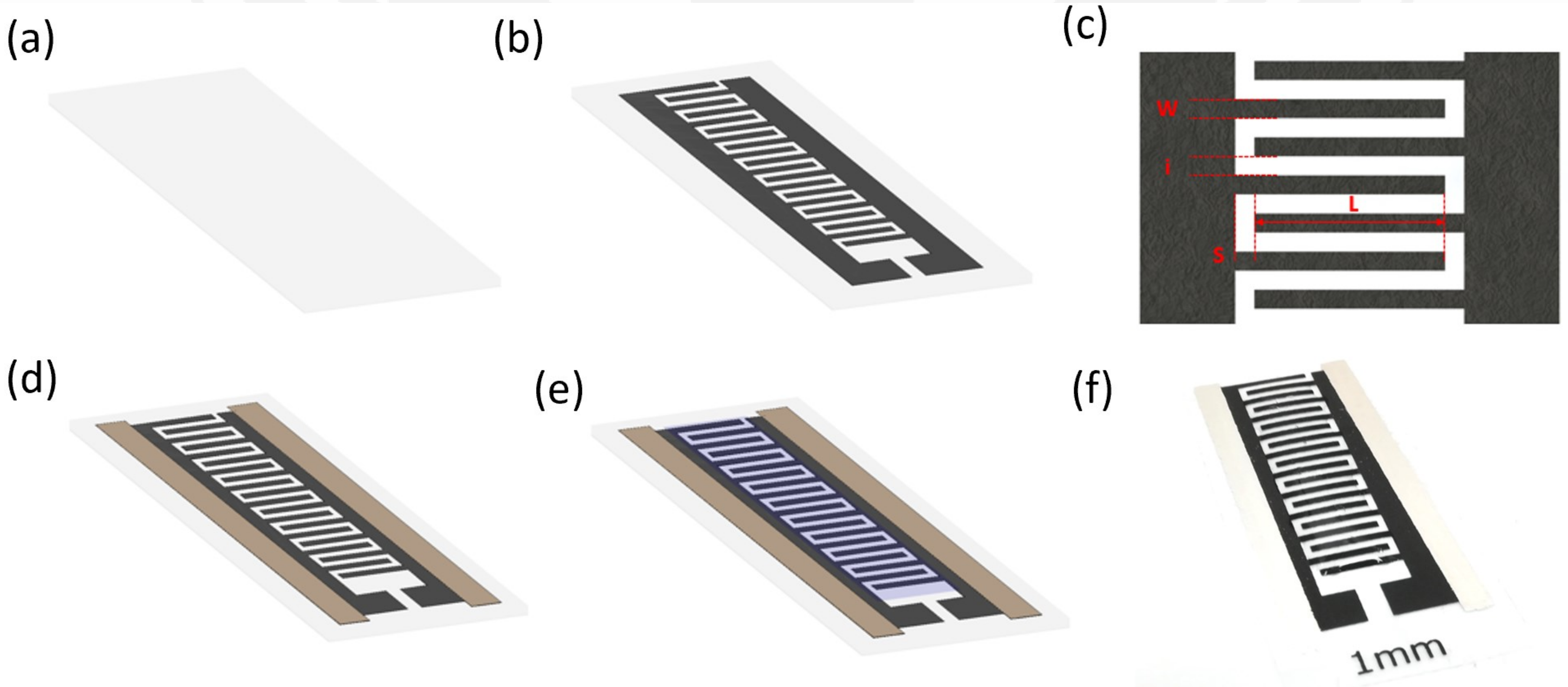


c) IDE Dimensions:

- Width (W) = 1 mm
- Separation (S) = 1 mm
- Interspacing (i) = 1 mm
- Length (L) = 1 cm
- Number of Fingers (N) = 20
- Effective Area (A) = 4 cm^2

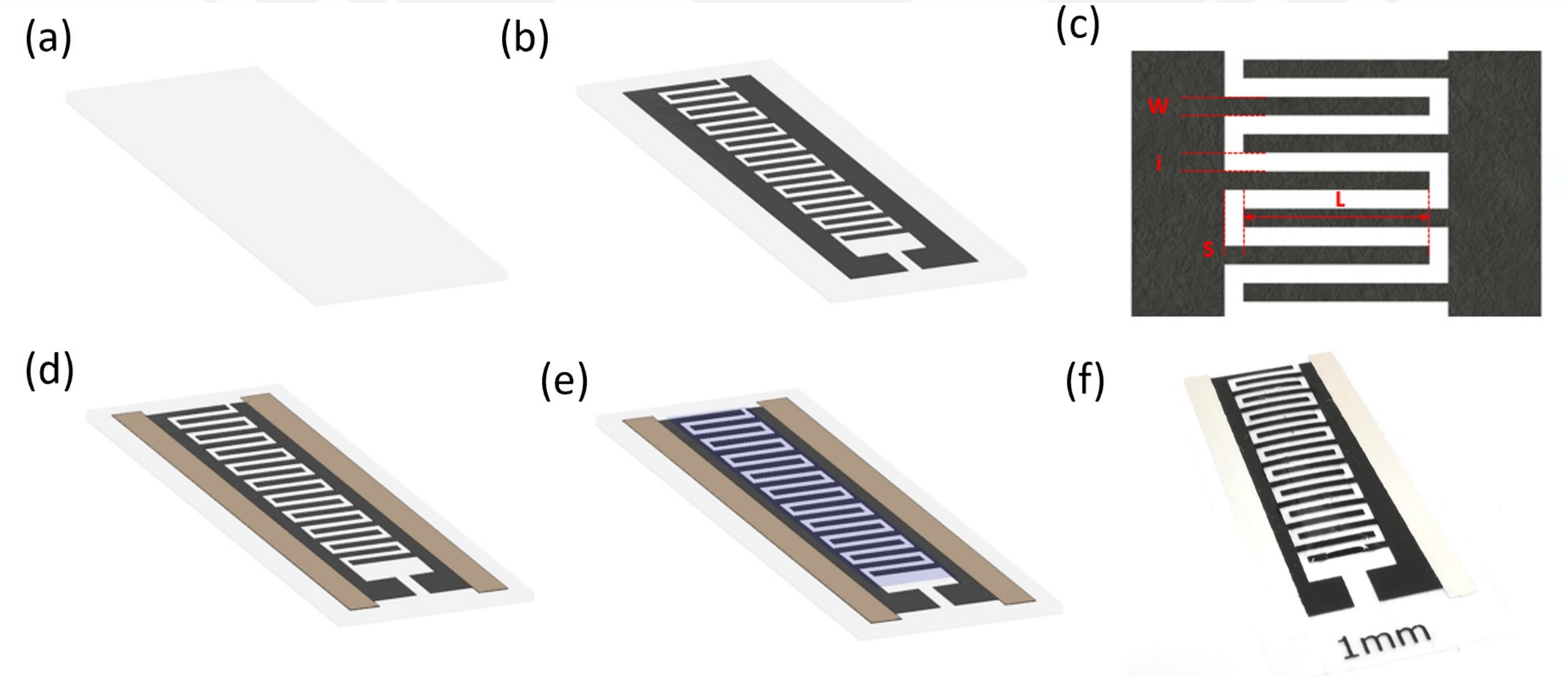
d) After drying the IDE structure at 130 ^{o}C for 3 min, electrical contacts were printed as current collectors using a AgNPs-based ink (LOCTITE® ECI 1010 E&C from Henkel AG)

Fabrication



e) Electrolyte Preparation and Deposition:
   1. 1 g of PVA was dissolved in 10 mL of de-ionized water (10 wt%) with stirring at 80 ^{o}C for 2h
   2. Once the PVA was dissolved, 1.2 g of H_3PO_4 was added to the solution, and it was stirred again (1 h)
   3. 1.5 mL of the final homogeneous gel solution was drop-casted on the capacitive IDE structure
   4. The samples were left standing overnight to remove the excess of water

Fabrication



e) Real view of the final EDLC

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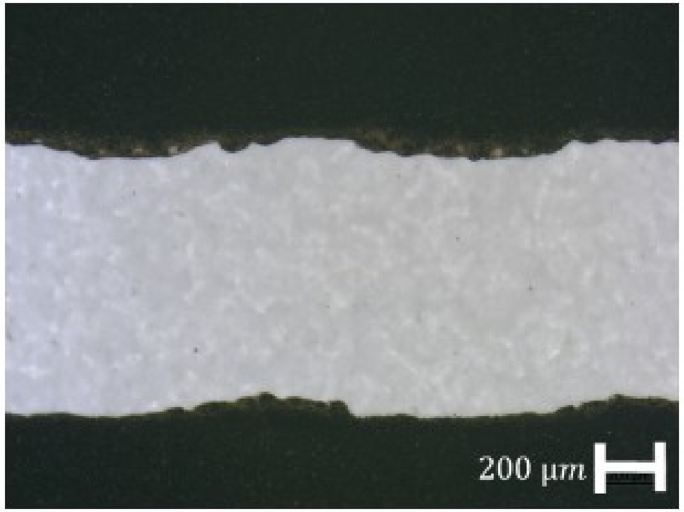
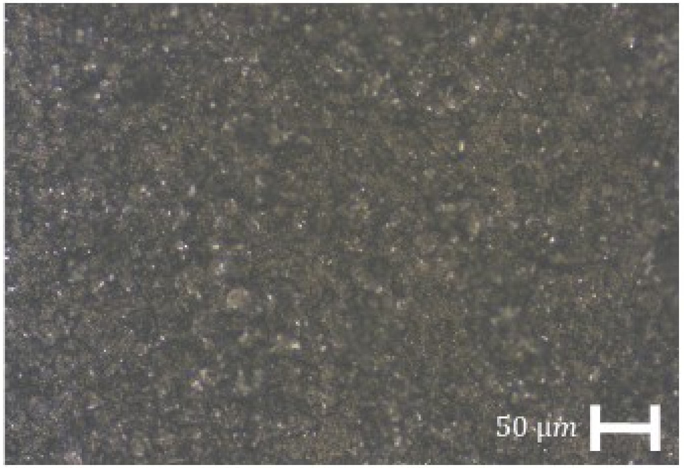
RESULTS AND DISCUSSION

- **Microscope Images**
  - Real dimensions as a consequence of the paste spreading once it is deposited on the substrate:
    - W = 1.168 mm
    - S = 0.902 mm
    - *i* = 0.892 mm
  - Porous morphology which is highly supportive for the electrostatic double-layer capacitance of the IDE structure.
- **Sheet Resistance:** 500 ± 70 Ω/sq.

(a)

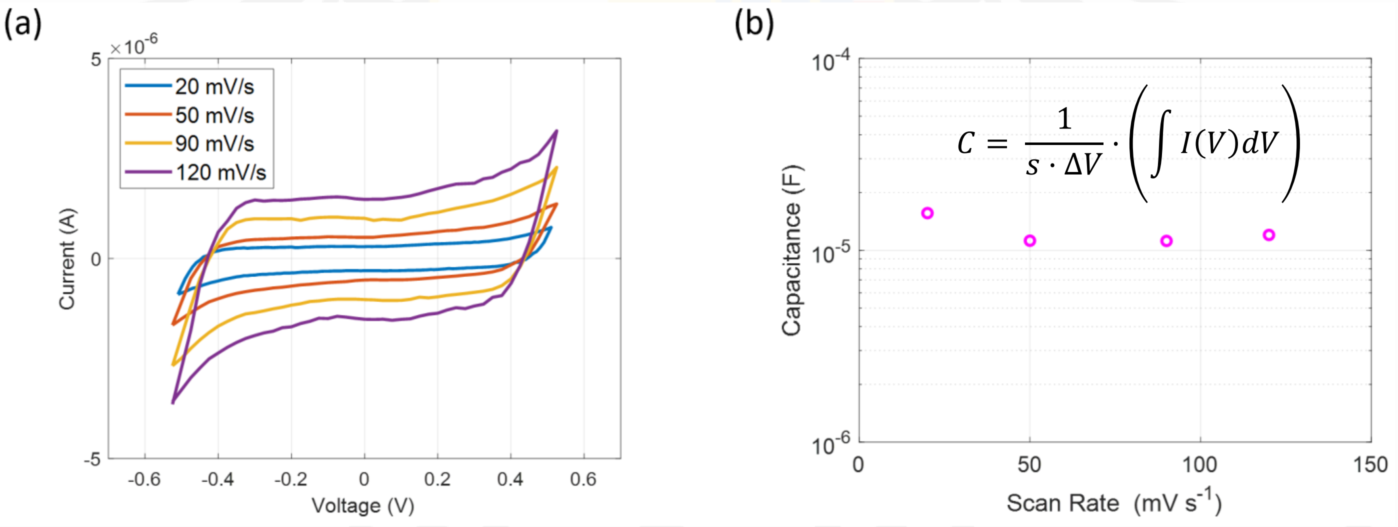


(b)



RESULTS AND DISCUSSION

- **Cyclic Voltammetry (CV)**
  - The CV curves mantain a quasi-rectangular shape over increasing scan rates (*s*), which indicates a good reversible EDLC behaviour.
  - The slight inclination of the CV curves arises from the Equivalent Series Resistance (ESR) of the capacitor as a consequence of, mainly, the high sheet resistance of the carbon patterns.
  - The devices mantain almost entirely their capacitance (*C*) even at high scan rates indicating that, for the scan rates considered, this does not have a large impact on the penetration depth of the electrolyte ions into the electrodes.



RESULTS AND DISCUSSION

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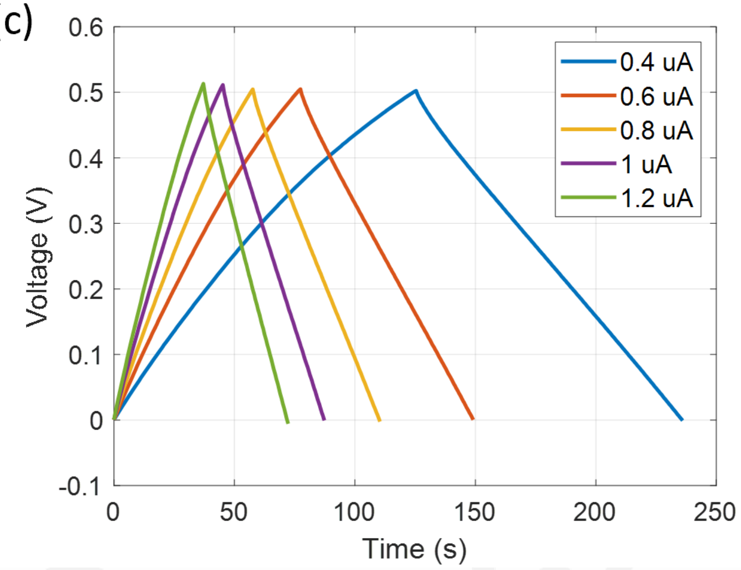
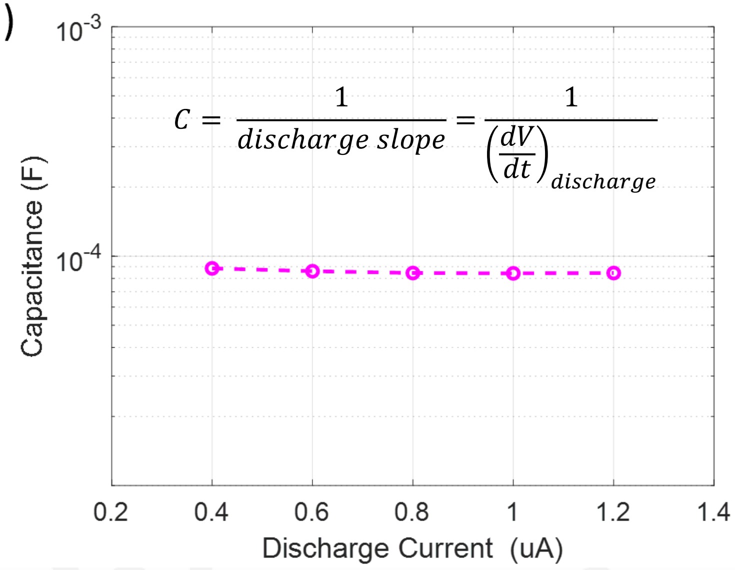
- **Galvanostatic Charge/Discharge**
  - The quasi-triangular shape of the galvanostatic charge/discharge curves at constant current demonstrates the good charge propagation across the carbon electrodes, i.e., the good interaction electrode-electrolyte.
  - The capacitance presents a slight decrease as the dischargue current increases ($\Delta C/C_0$ = 4.7 %), indicating that the rate of discharge is not greatly affected by the load.
  - The capacitance obtained is about 86 µF (22 µF/cm^2).

(c)

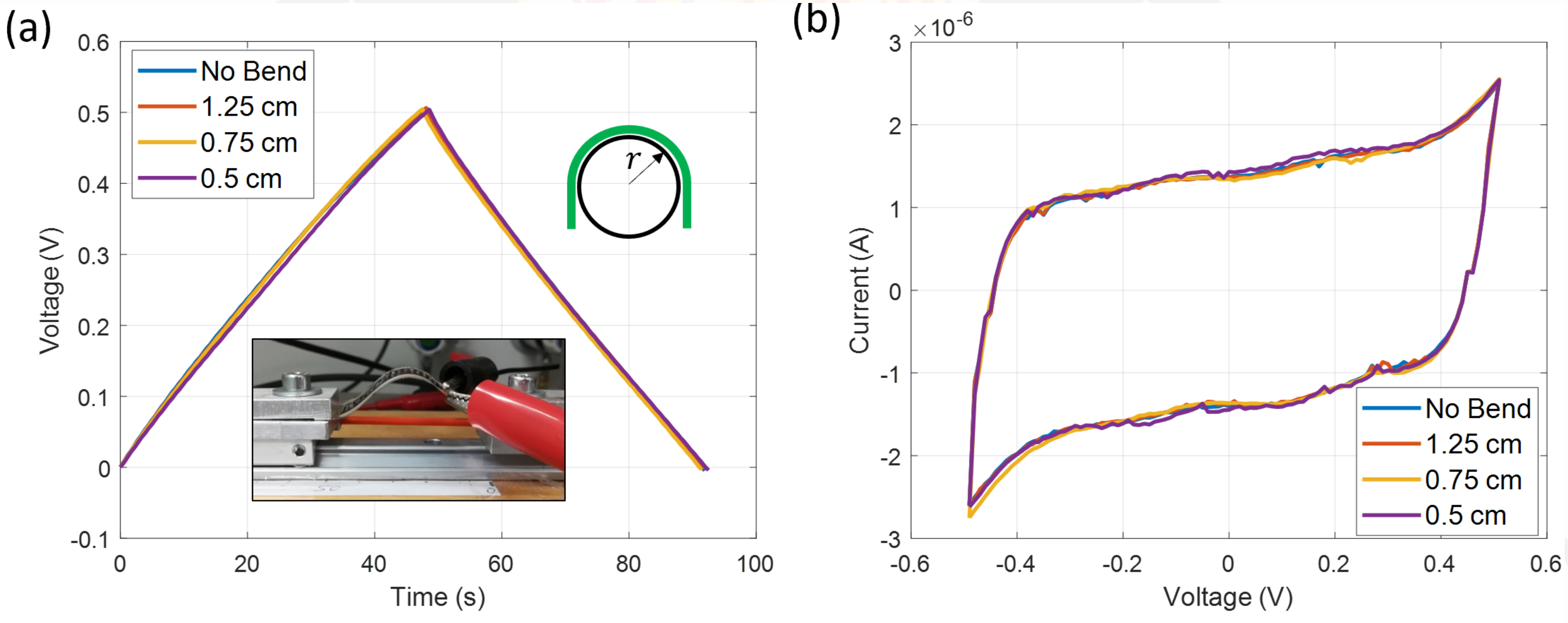


(d)



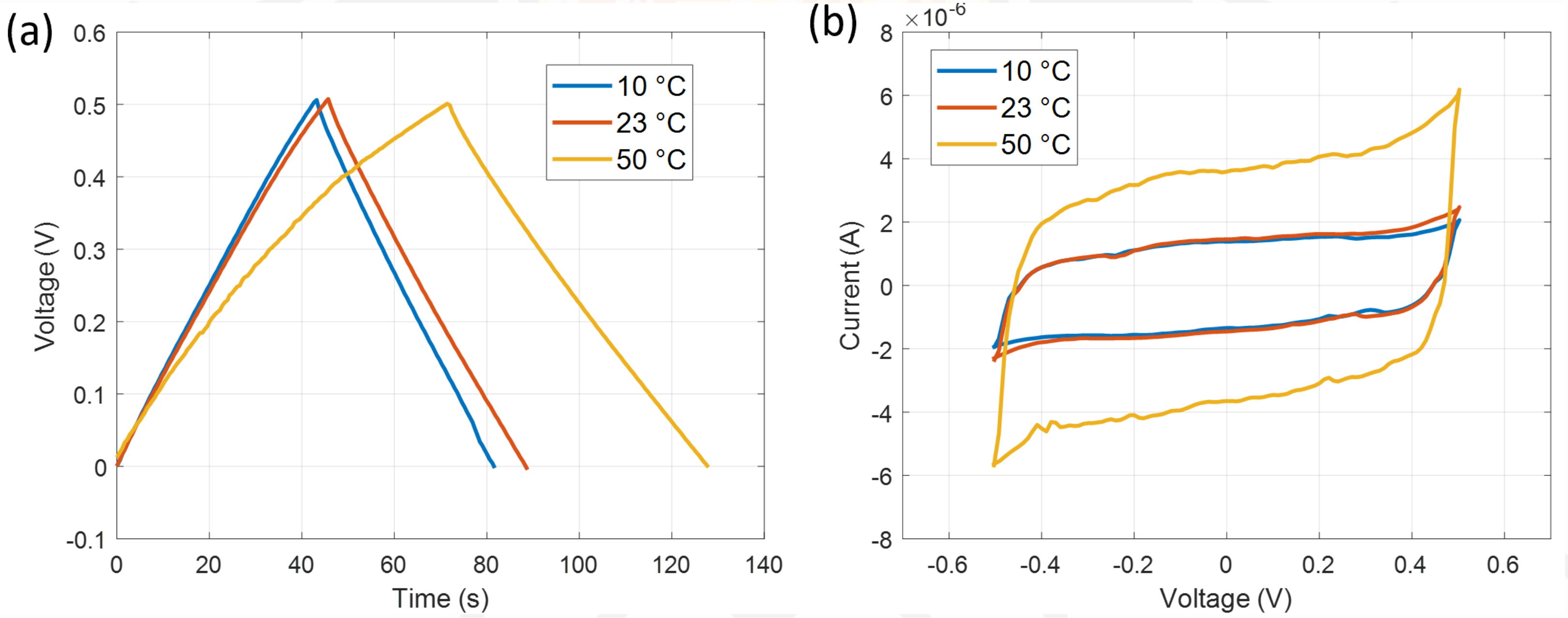
RESULTS AND DISCUSSION

- **Tests Under Mechanical Stress**
  - The performance of the ECs was studied under different bending conditions (r = 1.25 cm, 0.75 cm and 0.5 cm).
  - These EDLCs present almost unchanged CC and CV curves for the different bending states, demonstrating that they could be used in conformal applications with no significant effect on their electrochemical performance.



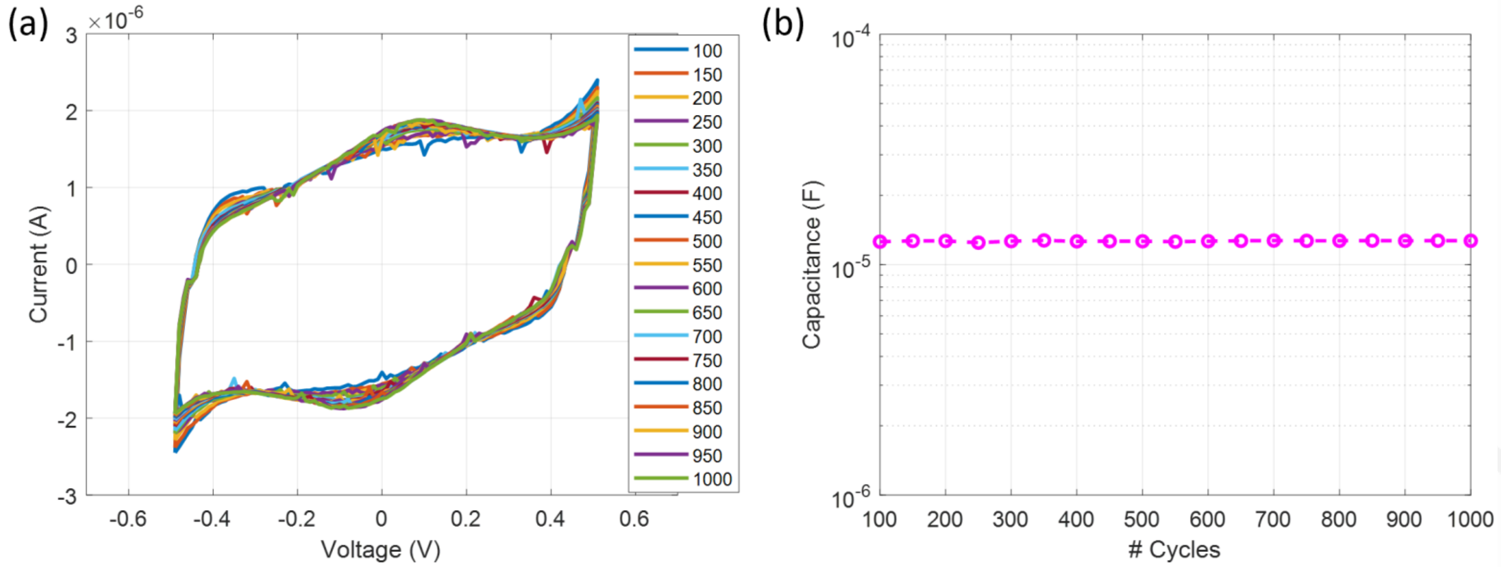
RESULTS AND DISCUSSION

- **Tests Under Thermal Stress**
  - The performance of the ECs was also tested at different temperatures. The results showed that the specific capacitance increases as the temperature increases.
  - This effect has been attributed to changes in the electrolyte, since an increase of the temperature possibly leads to the physisorption of the electrolyte ions [9,10].



RESULTS AND DISCUSSION

- **Cyclability**
  - The electrochemical cycling durability tests showed that the capacitors are able to retain their capacitance even after 1000 charge/discharge cycles ($\Delta C/C_0 < 1\%$).
  - It can also be noticed how the rectangular shape of the CV curves was progressively deformed, which might be attributed to the appearance of reversible pseudocapacitive effects, indicating that an increasing number of continuous cycles boosts the electrosorption, redox and intercalation processes on the surface of the porous electrodes [11-13].



RESULTS AND DISCUSSION

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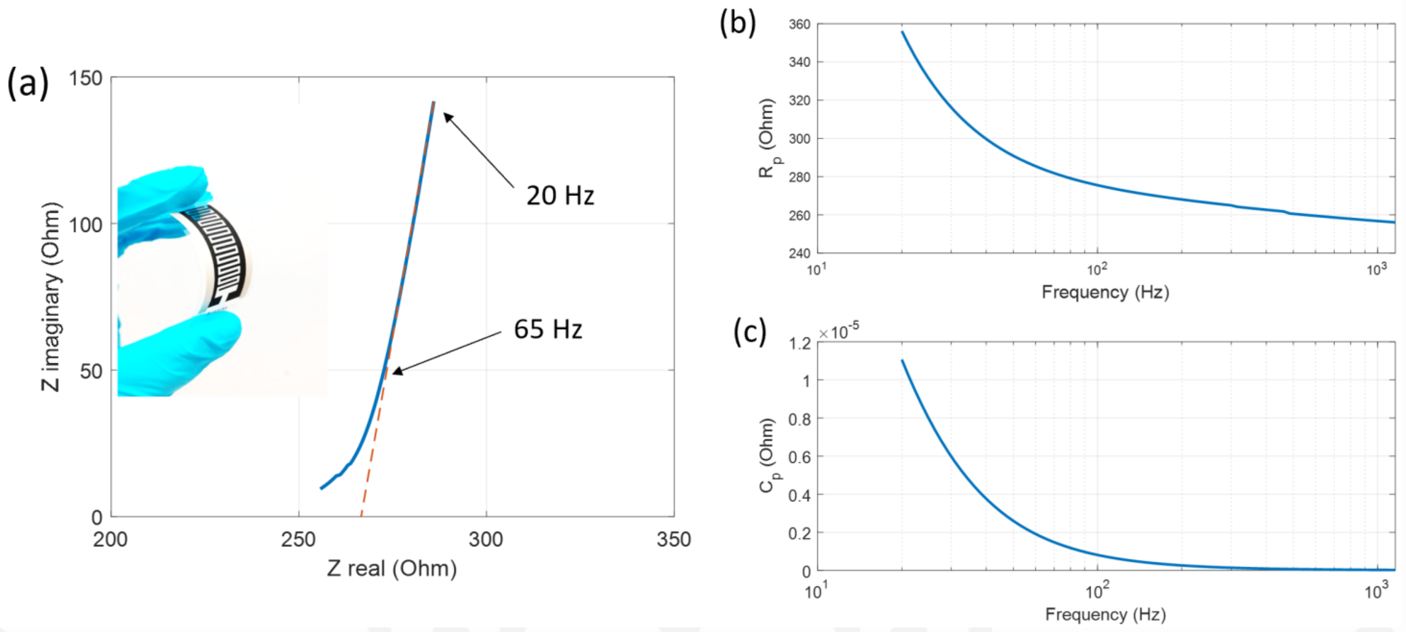
- **Electrochemical Impedance Spectroscopy (EIS)**
  - At low frequencies, the imaginary part of the impedances against the real one is almost linear (up to ~65 Hz), then a semicircle appears in the high frequency region indicating the transition between both capacitance and resistance behaviors.
  - The interception with the real axis (high frequencies) is associated with the Equivalent Series Resistance (ESR), which is estimated to be ~250 Ω.



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CONCLUSIONS

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- We reported the fabrication of thin-film flexible electrochemical capacitors by means of the screen-printing of a commercial carbon-based conductive ink on a flexible substrate using PVA/H_3PO_4 as electrolyte.

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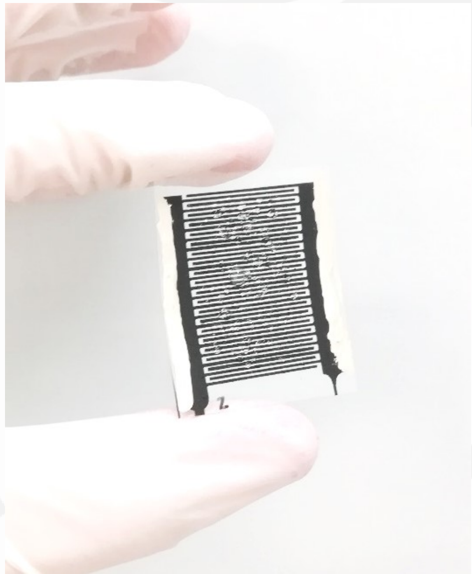
- The devices present good performance as ECDL capacitors with outstanding flexibility and cyclability, which has been demonstrated through cyclic voltammetry, charge-discharge experiments and electrochemical impedance spectroscopy.

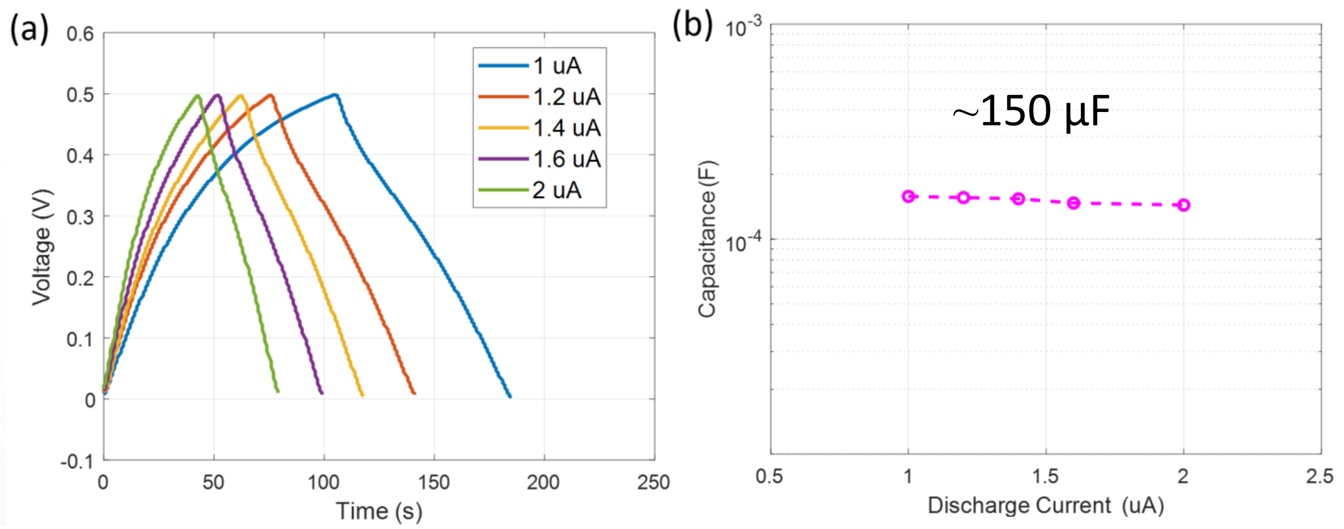
CONCLUSIONS

- We reported the fabrication of thin-film flexible electrochemical capacitors by means of the screen-printing of a commercial carbon-based conductive ink on a flexible substrate using PVA/H_3PO_4 as electrolyte.
- The devices present good performance as EDLC with outstanding flexibility and cyclability, which has been demonstrated through cyclic voltammetry, charge-discharge experiments and electrochemical impedance spectroscopy.
- Although the specific capacitances obtained for this electrode material do not achieve those obtained with other carbon-based materials, further studies aim to treat the conductive ink in order to optimize its properties and increase its specific capacitance.

CONCLUSIONS

- Alternatively, as it has been demonstrated in other works [4], by means of reducing the width of the fingers and the distance between them, hence increasing the density of fingers, it is possible to enhance the capacitance of the this kind of EDLCs.





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