eMIM

Electrosprayed Metal-nanoparticles-Metal (eMIM) capacitor for energy storage

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Executive Summary Report

Metal-Insulator-Metal devices, called "MIM" have been mainly used as capacitors in integrated circuits due to its good specific capacitance (in the order of 1 µF/cm^2) and low parasitic capacitance. They are fabricated using conventional photolithography to deposit a dielectric layer as insulator between the two metal contacts. It was recently shown that it is possible to build an enhanced capacitor using nanoparticles of a dielectric material in between the electrodes, instead of the continuous dielectric layer.

The objective of eMIM project is to study the benefits that nanoparticles can bring to energy storage devices with the potential of industrial production. The main innovation is twofold: (a) demonstrate how an electrospray technology to deposit ordered nanoparticle layers from a colloidal solution can be used to create capacitors and (b) how these novel nanoparticle capacitors can show enhanced specific capacitance. A proof the concept is realised, building a MIM capacitor with dielectric nanoparticles – deposited by electrospray (eMIM) - instead of a continuous layer of dielectric material. Then, the objective is to bring both, the electrospray technology and the nanoparticles, to the broader field of supercapacitors or EDLC's (Electrochemical Double Layer Capacitors), which are energy storage devices with higher energy than capacitor and more power than batteries.

The first step was to increase the nanoparticles deposition area of the electrospray technique on carbon electrodes to prove the feasibility of the method for an industrial fabrication process. Electrospray technique is used to deposit the different kind of nanoparticles. The electrospray system was upgraded modifying the microfluidic and electrical components to increase the useful area. This is accomplished by increasing the number of needles from one to two needles to enable several jets, instead of a single Taylor cone (Figure 1). The objective of increasing the nanoparticles deposit area is achieved through the design and implementation of an electrospray set-up of two needles instead of just one needle. The upgraded electrospray set-up consisted in distributing the flow of the nanoparticles' suspension using splitter towards the needles, which were placed in a PLA support fabricated with a 3D printer. The PLA support and needles had to be metalized to get in electrical contact. Experiments were carried out using the electrospray approach of two needles with a modified nanoparticles suspension (mixed with isopropanol used solvent) in multiple jets mode for each needled, achieving an area of 62.4 cm^2 and requiring a time deposition of 120 minutes and a flow rate of 1 mL/h. The nanoparticles were well scattered with low amount of water reaching the carbon surface. There was no destruction and detachment of the nanoparticles layer. The average thickness of the nanoparticles structure in the central deposit area it was 26 µm.
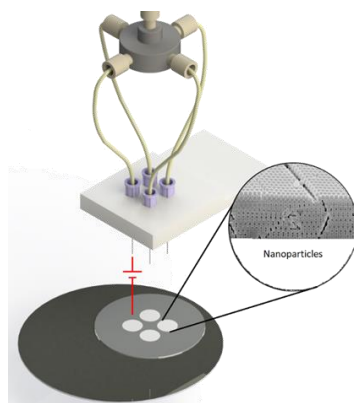
Figure 1. Electrospray setup modification to enlarge deposit area

In the following steps, three types of devices have been designed and fabricated:

> ➢ Vertical device with no electrolyte and no encapsulation:

Vertical eMIM devices have been fabricated using SiO_2, polystyrene, TiO_2 and Al_2O_3 nanoparticles as dielectric layers (Figure 2). These nanostructured layers have been fabricated using electrospray and microelectronic deposition techniques. The capacitive features have been evaluated using impedance spectroscopy.
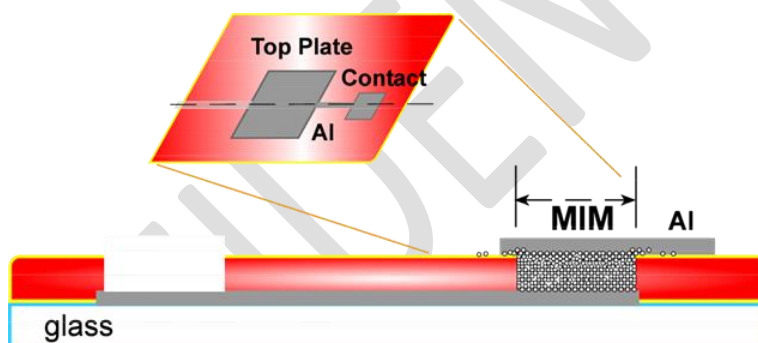

Figure 2 Cross section of the eMIM (red: resin, grey; Aluminium layer)

The Al_2O_3 eMIM had excellent performance, with highest capacitance around 5.7 µF/cm^2 and capacitive behaviour at the frequency range from 0.1 Hz to 90 kHz.

The SiO_2 eMIM (which has a nanoparticles layer thickness of 1.5 µm) showed capacitances up to 2.6 µF/cm^2, being this value 1000 times larger than the theoretical capacitance of an equivalent capacitor with a continuous dielectric layer. It had capacitive behaviour at frequency ranges from 0.1 Hz to 2.6 Hz and from 2.1 kHz to 100 kHz. The gravimetric capacitance was 22.2 mF/g.

The TiO_2 eMIM (nanoparticle layer thickness not yet been measured) showed a good capacitive behaviour from 0.1 Hz to 5 kHz, and a capacitance of up to 3.8 µF/cm^2 at low frequency.

The Polystyrene eMIM (which has a nanoparticle layer thickness of 1.75 µm) showed a capacitance per unit area of up to 15 nF/cm^2, being only 12 times larger than the theoretical capacitance of an equivalent capacitor with a continuous dielectric layer. It had capacitive behaviour in the whole frequency range measured, from 0.1 Hz to 100 kHz. The gravimetric capacitance was 5.91 mF/g. As a first approach, we can say that the silicon oxide nanoparticles contain more electricity charges than the polymer nanoparticles.

All vertical devices showed both high magnitude impedance and high capacitance, that decreases when frequency increases. The novelty of these devices is that the measured capacitance was higher than the

theoretical capacitance, even a thousand times greater in the SiO_2 eMIM. Knowing the area and the measured dielectric layer thickness (SEM/FIB characterization), the theoretical capacitance was calculated for an equivalent capacitor with a continuous dielectric layer. The high capacitance values can be due to humidity, bringing water molecules which attracts charges to the nanoparticle interfaces. This charge is produced by ions localized at the nanoparticle surface and depends on the chemical nature of these nanoparticles. The humidity not only improves the capacitance but also the contacts. The Al_2O_3 MIM turned out to have the highest capacitance and the best top contact. In contrast, polystyrene eMIM had the worst performance due to its low values of capacitance and high values of resistance. Therefore, the ability to adsorb or retain moisture of the nanoparticle type influences both the capacitance and the contact resistances of the eMIM.

➢ Vertical devices with electrolyte and encapsulation:

Carbon-carbon supercapacitor devices have been assembled using carbon electrodes containing SiO_2 particles and 1M Et_4NBF_4 in acetonitrile as electrolyte in CR2032 coin cell (Figure 3). This configuration is classic for commercial supercapacitor, except the presence of the SiO_2 particles. The best capacitance was obtained with 351 nm SiO_2 particles, reaching 500 mF/cm^2. Other supercapacitor devices were assembled using SiC "core/shell" particles instead of SiO_2. These nanoparticles are formed by a Si core in a shell of C and are then electrically conductive. The result obtain is a decrease of the capacity as its porosity may not be adapted to the ion size of the electrolyte. Indeed, if the ion size does not fit with the size of the electrode pore, the capacity will not correspond to the maximum number of ions that it can adsorb. Further study on compatibility between the nanoparticles deposited and the electrolyte used would be needed to take advantage of them.
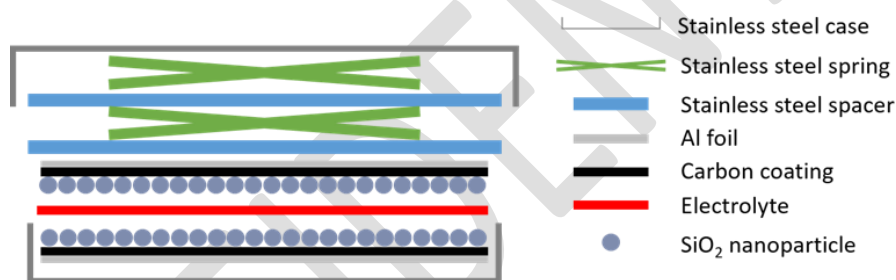

Figure 3 Schematic of cell encapsulation with electrolyte

➢ Lateral device with electrolyte and no encapsulation.

A lateral device based on interdigitated electrodes has been designed, fabricated and preliminary electrical measurements have been made (Figure 4). The electrical measurements show that SiO_2 nanoparticle do not seem to work properly when mixed with an electrolyte, whereas the use of SiC exhibit very promising results.
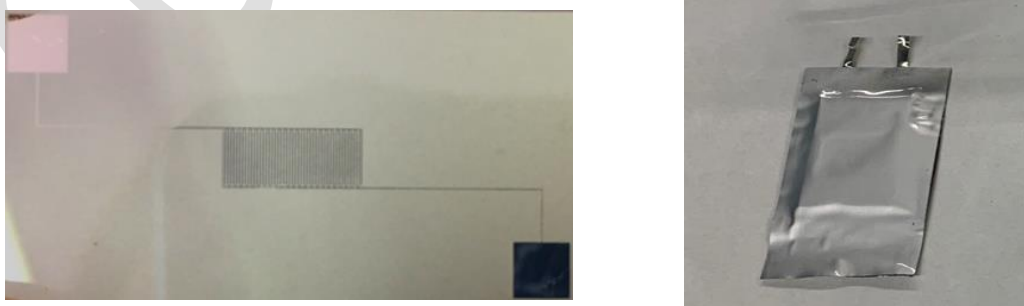

Figure 4. a) Top view of a lateral device where only the electrodes are present. b) Encapsulated lateral capacitor devices with electrolyte

The electrical measurements performed with the lateral-interdigitated devices, fabricated with different electrolyte composition, show that the electrolyte enables to increase the capacitance. In particular, it has been found that the capacitance of the device with electrolyte is 6 orders of magnitude higher than that obtained with a lateral device without electrolyte or nanoparticles. Nevertheless, the devices fabricated with a mixture of the electrolyte and SiO_2 nanoparticles show smaller capacitance values than that of devices with only the electrolyte. This could be due to the fact that the capability of the SiO_2 to attach the charge diminishes when it is mixed with the electrolyte and act only as a resistive path. Further research is needed to analyse these results.

On the other hand, depositing SiC nanoparticles with the electrolyte allows to increase the effective capacitance. In particular, the lateral device with electrolyte mixed with SiC has a factor 2.7 larger of specific capacitance than the lateral device with electrolyte. This effect may be due to the conducting surface of SiC nanoparticles, which helps enhancing the ion exchange mechanisms between the electrolyte and the conducting electrodes.

Furthermore, the presence of SiO_2 and SiC nanoparticles provokes an increase of the series resistances since there is worse contact between nanoparticles and electrodes. But, the resistance also increases because the conductivity of the electrolyte decreases when it is mixed with the SiO_2 or SiC nanoparticles suspension due to the water.

As a summary, the use of SiC nanoparticles seems to show a slightly better electrical performance than SiO_2 nanoparticles, this may be because the conducting surface of SiC nanoparticles helps to make the ion exchange of the electrolyte to the conducting electrodes.

Modelling is also performed using a spectral equivalent circuit formed by four sub-circuits in series (Figure 5), where the sub-circuit 2 (Q2 and R2) represents the bottom nanoparticles-metal interface, sub-circuit 3 (Q3 and R3) and sub-circuit 4 (Q4 and R4) represent the top nanoparticles-metal interface and the sub-circuit 1 (Q1 and Z_W) presents the intermediate nanoparticles.
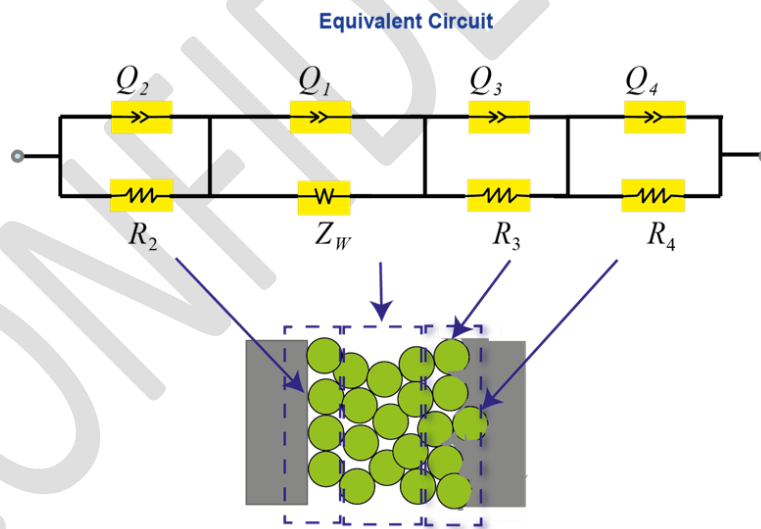

Figure 5. Equivalent circuit for eMIM device.