Influence of electrode distance on porous silicon supercapacitor internal resistance

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1. Abstract

Supercapacitors are energy storage devices very attractive due to their inherent durability and high power density. Although it has energy density less than Pb-acid batteries, higher operating voltage and thus higher energy density can be achieved with different electrolytes like organic electrolytes or room temperature ionic liquids (RTIL). Unfortunately, they have higher resistivity too compared with aqueous electrolytes supercapacitors, which compromises the available power density of the device. This work focus on the study of porous silicon electrodes, passivated with graphene, for supercapacitors applications with a different approach on the separator topology made with SU-8 to achieve electrodes distance smaller than commercial separators so that the device internal resistance due to electrolyte resistance become as low as possible.

2. Introduction

Electricity is intimate related with technology and it is the most versatile form of energy but it lacks an efficient way to be stored with an energy density comparable to fossil fuels. Li-ion batteries are state-of-the-art commercial devices that reach energy densities as high as 200 Wh/kg, with cyclability (number of charge/discharge cycles before losing significant amount of capacity) that can reach 1000 cycles and power densities on the order of 300 W/kg.

Supercapacitors, also known as electrochemical capacitors, have a storage mechanism different from the redox reactions found in batteries. They have poorer energy density around 5 Wh/kg, cyclability on the order of 100000 cycles and power density that surpass 1000 W/kg. It has two parallel high surface area electrodes immersed in an electrolyte that, when charged, attracts co-ions that adsorb on their surfaces, creating tinny capacitors at the solid/liquid interfaces with separation distance between charges of few angstroms formed at each interface [1].

This can give around 20 µF/cm² [1] and using porous electrodes that have high surface areas, hundreds of Faradays per gram of electrode can be achieved. Power density and cyclability are the two characteristics that make this device so attractive to be used with high current peaks and/or maintenance free applications.

The first devices ever used had activated carbon electrodes and aqueous electrolytes like acidic or basic solutions. Aqueous electrolytes have an electrochemical window (which is the maximum voltage that the device can work without solvent breakdown) of approximately 1V. Organic electrolytes based in acetonitrile or polycarbonate have electrochemical windows of 2.5V and higher resistivity compared with aqueous electrolytes. RTILs can have electrochemical window of 5 V but with a higher resistivity than organic electrolytes.

3. Objective and methodology

The objective of this work is to study porous silicon supercapacitor internal resistance (which is directly related to the power density) as function of the electrode separation distance. To achieve this objective, 3” P^+ silicon wafers with 1-5 mΩ.cm were cleaved with the aid of a UV laser as squares of 25 mm x 25 mm. The samples are submitted to a RCA clean and then anodically corroded in an ethanoic HF solution [2] to produce a porous silicon film containing mesoporous (with porous sizes between 2 nm and 50 nm, according to IUPAC).

Porous silicon is very reactive and easily oxidizes in air. To passivate it, a graphene deposition must be performed by means of catalytic growth on porous silicon in an oven with a mixture of gases (acetylene, hydrogen and argon) and using an adequate thermal profile [3][4][5].

A control sample is fabricated using a commercial separator and 1 M TEABF4 in acetonitrile as the electrolyte. The supercapacitor will be a sandwich of (electrode – separator – electrode) with the porous film and separator soaked with the electrolyte. Another similar device is fabricated, now by depositing SU-8 on the porous silicon electrode and defining by photolithography a specific geometry, according to figure 1.

The final device will be mounted as exemplified in figure 1 forming a sandwich (electrode – SU-8 separator – electrode) making an electrolyte reservoir between electrodes.

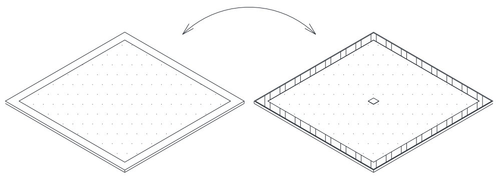

Fig. 1. *Joining two electrodes soaked in electrolyte to form a supercapacitor. The electrode from the right contains the SU-8 separator defined by photolithography.*

Using the proposed method devices will be produced with three different separator heights: 25 µm (the same of the commercial separator thickness), 15 µm and 5 µm. Those devices will be characterized by cyclic voltammetry, Galvanostatic charge/discharge curve and Electrochemical Impedance Spectroscopy, which will give specific capacitance, energy density, power density and internal resistance.

By analyzing the device ESR in function of inter-electrode distance, some characteristics can be extracted as the electrolyte resistance between electrodes, intrinsic resistance (Ri, which accounts to the resistance of electrode and electrolyte inside pores) and commercial separator resistance (R_{sep}) will be deduced like shown in an example in figure 2. It is expected that the internal resistance, also known as Equivalent Series Resistance (ESR), will fall linearly with the electrode separation distance (d) according Ohm's second Law. Deviations may be observed due to the Wien´s effect [6]. This will tell us the contribution percentage of the inter-electrode resistance to the internal resistance of such devices.

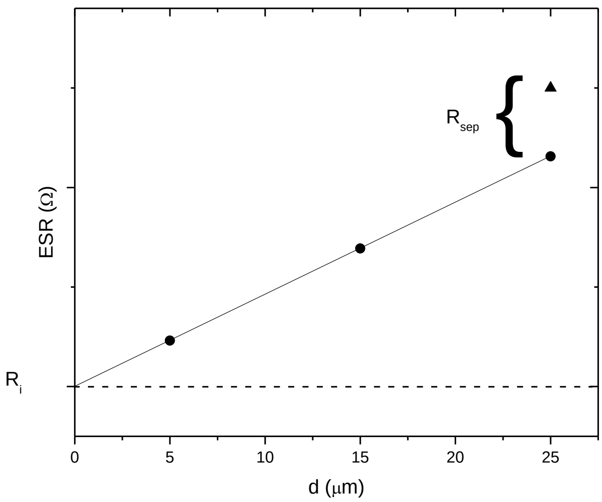

Fig. 2. *Example of the expected results on ESR in function of distance between electrodes. Intrinsic resistance, Ri, will be deduced by the point where the fit line cross the Y axis. Commercial separator resistance, Rsep, is the difference between control device ESR (filled triangle) and 25 µm separator device ESR (filled circle). The inter-electrode electrolyte resistance at any data point is ESR minus Ri.*

4. Conclusions

This work intends to fabricate a different kind of separator and at such thin thickness, never seen before in literature, for porous silicon supercapacitor and study the electrolyte influence on the internal resistance by using different separators thicknesses. Results could lead to a major improvement in power density of such devices.

Porous silicon electrodes passivated with graphene are not the best electrodes nowadays, but they are rigid, which is essential to SU-8 uniform deposition in this work. They may have other advantages like to integrate a solar cell with porous silicon electrode in their back that can be seen elsewhere [7]. And putting an integrated circuit in the back of a porous silicon electrode is something never seen in the literature but has a tremendous potential in the energy harvesting scene and, consequently, applications in internet of things are possible.

Acknowledgments

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