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Laser scribing of 2D materials for supercapacitive applications

Master thesis

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Abstract

This thesis is focused on the study of the laser scribing of 2D materials onto a substrate (kapton, usually) for supercapacitive applications. The modern era has led to a growing interests in energy storage devices. Recently, supercapacitors are much appreciated and studied since they can provide and store high energy in short times and for their promising stability in time. The laser scribing has come in for a lot of attention because it allowed the activation of porous materials onto flexible substrates, adding a further degree of freedom (the flexibility, precisely) for the possible applications of the device. In this thesis, electrodes and devices had been fabricated with laser induced graphene (LIG) and MXene materials. For both the types of device several approaches had been followed in order to improve the capacitive effects. These approaches were based on the use of different electrolytes, mainly aqueous and organic, the variation of the laser parameters in order to vary the power transferred to the substrate, the use of different compounds that characterized the MXene-based material, and the design of different shapes for the electrodes in the LIG case.

Introduction

0.1 Microsupercapacitors

With the advent of the modern era humans developed a tightening bound with electronic devices: this include not only smartphones but also computer, domotic products, smart cars, biomedical devices and so on and so forth. It followed that the request for energy has globally increased more and more. According to the IRENA roadmap to 2050, however, the energy will mainly rely on renewable energies, abandoning gradually the oil, natural gases and coal based[**1**].
So, in this kind of landscape, it is strongly important to find ways to safely and effectively store energy, producing devices that can be compatible with renewable sources. Here is where supercapacitors came out for: these devices, considered complementary with respect to the batteries, can store less energy than these last, but they can store or provide big amount of energy in short times(very high electronic power).
These features make the supercapacitors suitable for several application. Maxwell technologies ultracapacitors, e.g., are currently employed in the Vossloh-Van Hool electric buses in Milan. Their aim is to collect the power generated by the braking and give it back for a bust when the bus has to restart again. Aggiungi le applicazioni murata o Scheleton

0.2 Thesis content

This work is basically an analysis of microsupercapacitor laser scribing onto flexible substrate. It has been carried out through a collaboration between the Department of Applied Science and Technology(DISAT) in Turin and the Centre Inter-universitaire de Recherche et d'Ingénierie des Matériaux in Toulouse. In the first department the experiments were based on the graphenization of polyimide sheets by laser scribing, characterization and improvement of the capacitance with techniques to boost the EDL effect. In the CIRIMAT, instead, a UV laser has been exploited to sinter a mixture of $HAuCl_4.3H_20$, cellulose acetate and MXene derived from molten salt or by HF-etching. In this latter experience only squared electrodes had been studied, while in the first the whole device had been characterized.

Supercapacitors are defined by some keys parameters such as density of capacitance, potential window, power and energy density, time constant and equivalent series resistance. To derive these parameters in the most accurate way several techniques had been proposed: in this work cyclic voltammetries, galvanostatic analysis and eletrochemical impedance spectroscopy have been exploited.

Cyclic voltammetry The voltammetry consists in a cycle of measurements of the current generated by the capacitor when different values of voltage are applied. The voltage will be linearly increased until an upper bound, and then linearly decreased to the chosen lower limit: after this cycle an hysteresis IV curve will be generated. From these kind of measures it can be primarily defined the potential window, the density of capacitance and the resistive or capacitive behaviour of the device.

Galvanostatic measurement In the galvanostatic measurement a step of current is set and the variation of voltage at the working electrode is measured. After a defined amount of time, or after the voltage reaches the desired value, the step current changes sign. With this method is possible to calculate the capacitance, as well as the IR drop of the device.

Electrochemical impedance spectroscopy The EIS is a frequency dependent analysis: here we can apply a voltage and measure the resulting current, or vice versa. The applied voltage will be a superposition of a bias and a sinusoidal signal. Usually, lower levels of amplitude for the sines are more appreciated since the device does not move too far from the wanted bias condition, but for very low amplitudes there is the risk that the sine is comparable to background noise, obtaining a corrupted measure. In this measure the frequency of the sine will be varied within a defined range and the device impedance will be measure. It will be possible to generate a Nyquist plot as well as magnitude and phase bode plots.

0.3 Laser induced graphene microsupercapacitors

Bibliography

[1] IRENA (2019), *Global energy transformation: A roadmap to 2050 (2019 edition)*, International Renewable Energy Agency,Abu Dhabi.