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Eco-friendly carbon-based supercapacitors: Electrochemical properties and charge storage mechanisms

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Summary. — The components of electronic devices represent a problem for the production of hazardous waste, as many materials used are toxic. Sustainable electronic components made from eco-friendly materials have attracted attention for their promising electrical performance. The work presented in this study is based on the fabrication and characterization of supercapacitors using eco-friendly materials. The results demonstrate that these devices represent a valid alternative to conventional supercapacitors, offering high gravimetric capacity, excellent energy properties and robust resistance properties.

1. – Introduction

Every year millions of electrical and electronic devices are discarded as products break or become obsolete and are thrown away. These discarded devices are considered electronic trash and can become a threat to the environment and to human health if they are not treated, disposed of and recycled appropriately. Furthermore, it is well known that the climate of our earth is changing, and one of the causes must be attributed to global warming due to the use of fossil fuels. Therefore, the scientific community and politics of many countries are focusing on renewable energy to curb fossil fuels. Since this type of energy comes from intermittent energy sources, energy storage devices are needed to maintain a constant supply. As a result, there has been great interest in the development of efficient electrochemical energy storage devices [1, 2]. Among such technologies, rechargeable batteries and supercapacitors (SCs) are the two most desired candidates for powering a range of electrical and electronic devices [3, 4]. In light of these considerations, new electrochemical storage components must be make of environmentally friendly materials and require an environmentally friendly manufacturing process [5]. In this scenario, a large scientific literature [6-8] is present where it is demonstrated that

SCs can be fabricate using natural materials, making them completely sustainable from the environmental point of view. SCs are composed of a medium sandwiched between two high-surface-area electrodes [9]. In an SCs, the storage of the charge occurs at the interface between the electrodes and a liquid medium, the electrolyte. The latter can be either organic or ionic. These types of electrolytes have excellent properties but are toxic and harmful to the environment. Therefore, a water-based electrolyte remains the most environmentally friendly and economical alternative [10], but because it is liquid, it can easily leak and volatilize during the manufacturing process [11, 12]. In this regard, gel electrolytes based on natural biopolymers obtained from renewable resources have attracted considerable attention as they are not very volatile, cost little, and have a very low environmental impact [8, 13].

In this paper, SCs based on elecyrode of activate carbon (AC) were made and studied with the aim of being candidates as components for environmentally sustainable electronics. In this case, however, it is necessary to add a binder to agglomerate the powder particles in order to obtain strong bodies. While a water-based hydrogel was chosen as the electrolyte. The fabricated devices were characterized electrochemically, studying charge storage mechanisms, and dielectric properties at the electrode/hydrogel interface.

2. – Materials and methods

The devices were fabricated on a polyethylene terephthalate (PET) substrate covered with 40 μm thick copper (Cu) tape. The copper layer is intended to maintain a low ohmic contribution. Using a blade coater, a graphite ink, 50 μm thick, Henkel Electrodag PF407C was deposited on the PET+Cu substrates. This layer is necessary to protect the copper from oxidation, it also guarantees excellent adhesion of the subsequent layer, and has high electrical conductivity. The active layer of the electrodes was made by a nanostructured powder (Kuraray YP 80F) of AC, obtained from coconut shells, mixed with a binder in a ratio of 95:5 wt.%. Activated carbon powder is composed of micrometer-sized particles (see fig. 1), which have a nanopore structure on their surface, of the order of 2 nm in diameter [14]. In this way, the electrode has a complex structure with a very large surface area. The key point of the study presented in this work is precisely the use of a nanocomposite material to make the electrodes, as the increase in the surface area of the electrodes leads to an increase in the performance of the SCs, in particular it increases its capacity. The devices were made with three types of binders, chitosan, casein and sodium carboxymethylcellulose (CMC). The AC/binder mixture was deposited onto the

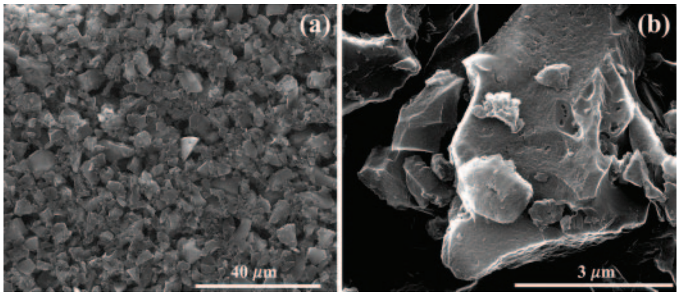

Fig. 1. – Scanning Electronic Microscope (SEM) images of the surface morphology of the electrode made by activated carbon powder at (a) 40 μm, and (b) 3 μm, respectively.

PET/Cu/graphite structure by blade coating and dried at room temperature. As for the electrolyte, it was obtained by mixing 2 g of porcine skin gelatin with 15 ml of 2 M NaCl aqueous solution. NaCl was added to increase the conductivity of the electrolyte. Furthermore, to improve the elasticity of the film and the mobility of the polymer chains, 1.5 ml of glycerol was added to the solution. Finally, the devices were obtained by coupling two electrodes (area 2.5×4 cm^2) with a layer of electrolyte, obtaining a symmetric sandwich structure (symmetric SCs).

3. – Results and discussion

In order to study the conduction properties of the devices, electrochemical measurements were performed. In particular, current density as a function of voltage curves (cyclovoltammetry curves) were acquired at different scan rates for the devices with different binders used (chitosan, casein and CMC) and using the hydrogel as electrolyte. In fig. 2(a) only the curves acquired at 20 mV/s for the three devices are shown, in the voltage range ±1 V. For further details on the cyclovoltammetry curves at different scanning speeds refer to [8]. The curves show a fairly rectangular shape, thus demonstrating the accumulation of charge at the interface between electrode and electrolyte. The slightly inclined trend of the curves indicates the presence of a non-negligible ohmic contribution generated by conduction through the electrolyte. From the cyclovoltammetry curves it is possible to calculate the gravimetric capacity C_s, defined as the area under the curves, according to the equation reported in [15]. The gravimetric capacitance C_s thus calculated as a function of the voltage scan rate for the three devices is shown in fig. 2(b). For all scan rate values, the device with chitosan shows the largest values of the gravi-

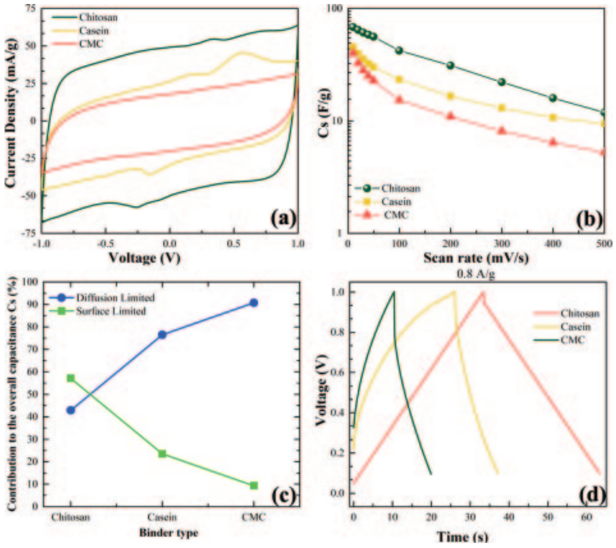

Fig. 2. – (a) Current density as a function of voltage at a scan rate of 20 mV/s for supercapacitors with chitosan, casein, and CMC binders. (b) Gravimetric capacitance as function of scan rate for chitosan, casein and CMC binders. (c) Contributions to gravimetric capacity: diffusive (blue curve) and superficial (green curve) contributions. (d) Charge-discharge curves with a current density of 0.8 A/g for the device with chitosan, casein and CMC binders.

metric capacitance C_s. It is also possible to observe that the capacitance values decrease with the increase in v for all three devices. This can be attributed to the fact that at low scan rate, the ions have sufficient time to diffuse into the pores of the activated carbon at the electrode-electrolyte interface, and their accumulation occurs as a result. This leads to the formation of a double-layer charge on the electrodes which generates capacitive effects. The capacitance C_s is the sum of two contributions, the pseudocapacitance (diffusion-limited) and the double-layer capacitance (surface-limited). These contributions were calculated for the different values of v and for the various types of binders used and they are reported in fig. 2(c). It is important to underline that the sum of the two contributions in all three cases is 100%. However, chitosan shows a significantly higher double-layer contribution to the total capacitance than the other binders, indicating significantly pure capacitive behavior. Conversely, electrodes using casein and CMC predominantly show pseudocapacitive behavior. This pseudocapacity also influences the charge and discharge curves acquired on the three types of devices, shown in fig. 2(d). For the device in which chitosan was used as a blinder, the curves show a linear trend. Instead, those of devices with casein and CMC show a non-linear discharge curve. This tendency may be related to the cited faradaic currents that influence the charge accumulation on the electrode surface [8].

4. – Conclusions

It is possible to conclude that the device with the chitosan binder shows the highest value of capacitance and the lowest dependence on the scan rate and this device also shows more stable charging and discharging curves when compared to the casein and CMC based devices. The same performances of this device are confirmed by the measurements of energy efficiency and stability even after a large number of cycles.

REFERENCES

[1] Detka K. and Górecki K., *Energies*, **16** (2023) 5034.

[2] Zhao Wen *et al.*, *ACS ES&T Eng.*, **2** (2022) 20.

[3] Jung H. Y., Lee J. S., Han H. T., Jung J., Eom K. and Lee J. T., *Polymers*, **14** (2022) 673.

[4] Gilshtein E., Flox C., Ali F. S., Mehrabimatin B., Fedorov F. S., Lin S., Zhao X., Nasibulin A. G. and Kallio T., *J. Energy Storage*, **30** (2020) 101505.

[5] Pacchioni G., *Nat. Rev. Mater.*, **7** (2022) 844.

[6] Cossutta M., Vretenar V., Centeno T. A., Kotrusz P., McKechnie J. and Pickering S. J., *J. Clean. Prod.*, **242** (2020) 118468.

[7] Jiang Z., Zou Y., Li Y., Kong F. and Yang D., *Biochar*, **3** (2021) 701.

[8] Landi G., La Notte L., Palma A. L. and Puglisi G., *Polymers*, **14** (2022).

[9] Amiri A., Bruno A. and Polycarpou A. A., *Carbon Energy*, **5** (2023) e320.

[10] Menzel J., Frackowiak E. and Fic K., *J. Power Sources*, **414** (2019) 183.

[11] Guo J., Ma Y., Zhao K., Wang Y., Yang B., Cui J. and Yan X., *ChemElectroChem*, **6** (2019) 5433.

[12] Landi G., La Notte L., Palma A. L., Sorrentino A., Maglione M. G. and Puglisi G., *Nanomaterials*, **12** (2022) 46.

[13] Xu T., Liu K., Sheng N., Zhang M., Liu W., Liu H., Dai L., Zhang X., Si C., Du H. *et al.*, *Energy Storage Mat.*, **48** (2021) 244.

[14] Piwek J., Platek A., Fic K. and Frackowiak E., *Electrochim. Acta*, **215** (2016) 179.

[15] Esawy T., Khairy M., Hany A. and Mousa M., *Appl. Phys. A*, **124** (2018) 1.