

CUBAN GRAPHENE OXIDE (C-NANO) FOR ELECTROCHEMICAL CAPACITORS

ÓXIDO DE GRAFENO CUBANO (C-NANO) PARA CAPACITORES ELECTROQUÍMICOS

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In current years, Electrochemical Capacitors (EC) have attracted a major attention, essentially due to their long life-cycle, high power density, and linking role between traditional dielectric capacitors and batteries/fuel cells in vehicle application [1]. EC is a charge-storage device that contains two electrodes and an electrolyte as the most important components. Among the more suitable electrode material for EC are the carbon-based nanomaterials [1–3] because of its high electrical conductivity, electrochemical stability, rectangular shape of cyclic voltammetry curves and symmetrical galvanostatic charge-discharge profile. The Ionic Conducting Group of IMRE-UH recently reported [2, 3] a first graphene oxide (C-Nano) synthesized from national precursors. It was demonstrated that this disordered carbon combines a large specific surface area ($467 \text{ m}^2\text{g}^{-1}$) and high electronic conductivity (aprox 0.1-1 S/cm from 173 to 293 K, respectively) [2]. In addition, the surface of C-Nano contains 14.2% wt of doping heteroatoms like O, N, S, H [2, 3] which is much desired for carbon-based materials used as EC. However, this carbon synthesized from Cuban precursors (C-Nano) has not yet been studied as an EC electrode. Herein, we report the electrical and electrochemical properties of C-Nano-based electrodes prepared to work in an EC.

The electrodes were prepared dispersing C-Nano powders in a polyvinyl alcohol (PVA) polymeric alcoholic suspension (Merck), stirring until a rubber-like paste is formed, and after rolling up to a film is obtained. The electrical characterization of this C-Nano film was carried out in a automatized homemade probe, coupled to a Keithley 2636B source-measure unit, by using the Hall [3] and Seebeck effects [3] (for determination of sign, concentration and mobility of charge carriers) and the Van Der Paw technique [3] (for determination of the electronic conductivity). The experiment were carry out in a wide temperature range from 175 to 300 K, controlled by a Lakeshore 336 that guarantees ± 0.001 K, under vacuum condition (10^4 Pa). In order to put the contacts on the sample silver paint was used. The transport

charge activation energy was determined from an Arrhenius plotting (\ln conductivity vs $1/T$). For the electrochemical measurements the as-prepared C-Nano film was cut in disc-shaped films, weighted and then pressed in stainless steel 304 wire meshes (current collector) at 10 MPa for 1 min. The tests were carried out by Cyclic Voltammetry (CV) and Galvanostatic charge-discharge, in a Biologic VMP3 electrochemical workstation, in the fully voltage window – 0.45 V and 1.25 V vs Ag/AgCl, using H_2SO_4 aqueous dissolutions (0.5 M) as electrolyte.

In Fig. 1 are shown the dependencies of the logarithm of the conductivity ($\ln\sigma$), concentration (n) and mobility (μ) of the positive charge carriers with temperature in the range 175 to 300 K. The transport charge activation energy ($E_a = 22 \text{ meV}$), charge sign (positive) and charge carriers concentration (10^{19} - 10^{20} cm^{-3}) registered for C-Nano film (C-Nano with binder) in whole studied temperature range are similar to those reported [2] for pristine C-Nano powder (without binder), which indicates the preservation of the pristine C-Nano electric nature (p-type semiconductor) during electrode preparation.

However, the charge mobility and the electronic conductivity diminished one and three orders of magnitude, respectively [2]. This fact can be explained considering the presence of binder (insulating nature) in a proportion with respect to the conductive carbon that hinders the percolation of carriers in the prepared C-Nano electrode. This low value of electronic conductivity is still enough for Electrochemical Capacitors applications [4–9], but could be improved preparing the electrode with a lower binder composition than that used in this work.

The electrochemistry tests between -0.34 and 1 V (not shown) did not show any redox irreversible peaks indicating that the C-Nano-based electrode is stable in a wide voltage window (1.34 V). The CV curves at different scan rates between 0 and 0.85 V (Fig. 2) have a semi-rectangular shape with very little

deformation for all scan rates, typical for faradic redox process in disordered carbon [4–9]. The voltammograms seem to be sloped 45 grades for scan rates values higher than 70 mV/s indicating an appreciable increment of the material resistance [4–9].

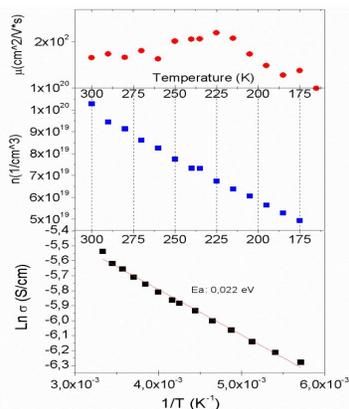


Figure 1. Electric properties vs temperature of C-Nano electrode.

The specific capacitance (C , F/g), energy density (E , Ah/Kg), and the maximum instantaneous density Power (P_{max} , kAh/Kg) that C-Nano electrode is able to deliver at low and high speed conditions are shown in the Table 1. These values are among the best reports for carbon-based symmetrical electrochemical capacitor [1,3–6].

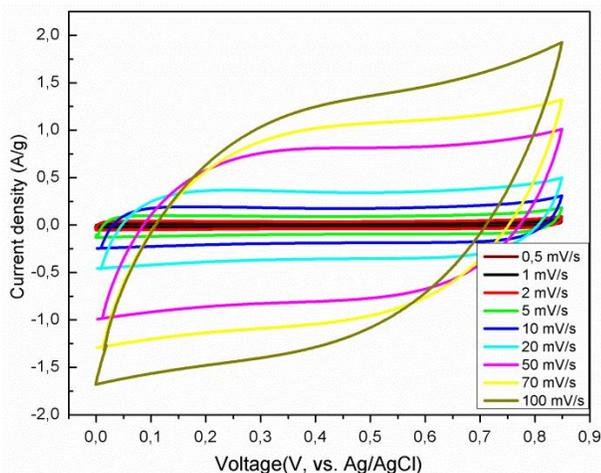


Figure 2. Electric properties vs temperature of C-Nano electrode.

In addition, the charge/discharge process, showed from P_{max} vs time delivered by the C-Nano EC (Fig.3), at very low (10 mA/g) and high (1500 mA/g) current density display a triangular shape confirming the capacitive behavior of the C-Nano-based electrode [1,4–9]. The not constant slope and deformation observed at low current density is associated to the diffusion of electrolytes ions into small pores of electrode and redox reactions that typically have much slower kinetics than double layer charging predominating at very higher current.

This behavior is explicated from the compositional and textural properties of the Cuban C-Nano graphene oxide [2,3] since this material has heteroatoms on its surface [2,3] that selectively react with the electrolytes ions as in FEC at low scan rates [2,3] providing a good capacitance, while also presents

an adequate morphology and porosity [2,3], which allows an acceptable power density at high scan rates as in EDLC [2,3].

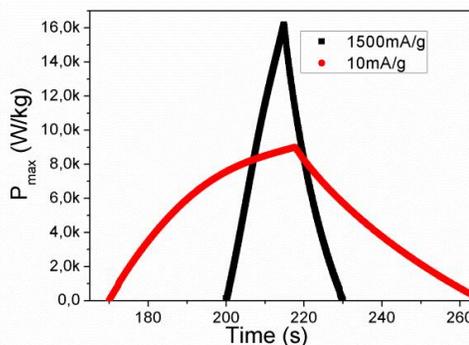


Figure 3. Galvanostatic charge-discharge curves of C-Nano-based electrode in positive window.

In summary, C-Nano can be prepared as an electrode material for hybrid electrochemical capacitors. The electrode preserves the electronic transport behaviour observed in the pure C-Nano, except that the conductivity and mobility of the positive charges carriers decreases as a consequence of the binder influence. The prepared electrode presents a wide electrochemical window and displays acceptable specific capacitance, energy and power densities values, in the positive voltage window, when works in acid electrolyte. This behaviour could be improved by working in the percolation threshold of the C-Nano/binder composite during the electrode preparation.

Table 1. The specify capacitance (C), energy density (E), and Power (kAh/Kg) that C-Nano electrode is able to deliver in low and high rate speed conditions in the 0-0.85 V window.

Scan rates (mV/s)	C (F/g)	E (Ah/kg)	P (kAh/kg)	Current density (mA/g)
0.5	332	119	9	10
70	184	66	16	1500

BIBLIOGRAPHY

- [1] Poonama, K. Sharmab, A. Arora, S.K. Tripathi, Journal of Energy Storage **21**, 801 (2019).
- [2] E.Danguillecourt, Y.Mosqueda, L.Montoro, N.Mohallem, H.Cabrera and E.Pérez, J. Solid State Electrochem. **246**, 404 (2017).
- [3] E.Danquillecourt, “Nuevos materiales carbonosos para baterías de iones litio y condensadores electroquímicos”. Tesis de doctorado, Universidad de La Habana, 2019.
- [4] A.Muzaffar, M.B.Ahamed, K.Deshmukh, J.Thirumalai, Renewable Sustainable Energy Rev. **101**, 123 (2019).
- [5] A. González, E. Goikolea, J. A. Barren, R. Mysyk, Renewable Sustainable Energy Rev. **58**, 1189 (2016).
- [6] A. Borenstein, O. Hanna, R. Attias, S. Luski, T. Brousseau and D. Aurbach, J. Mater. Chem. A. **5**, 12653 (2017).
- [7] F. Beguin, V.Presser, A. Balducci, E. Frackowiak, Adv. Mater. **26**, 2219 (2014).
- [8] A. Kurniawan, L. Ong, F Kurniawan, C. Lin, F. Soetaredjo, S. Zhao and S. Ismadji, RSC Adv. **4**, 34739 (2014).
- [9] J. Wang, H. Xian, T. Peng, H. Sun and F. Zheng, RSC Adv. **5**, 13607 (2015).

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