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EASY FABRICATION OF SUPERPOROUS ZEOLITE TEMPLATED CARBON ELECTRODES BY ELECTROSPRAY ON RIGID AND FLEXIBLE SUBSTRATES

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Characterization of ZTC

The structure of ZTC was studied by XRD using Cu-Kα radiation at 30 kV and 20 mA. Figure S1 shows the obtained XRD pattern. The small peak displayed at 2θ = 18.2º correspond to the PTFE used during the fabrication of the ZTC paste. ZTC shows a sharp peak at 2θ = 6.4º, corresponding to {1 1 1} planes of the ordered framework of the ZTC structure.

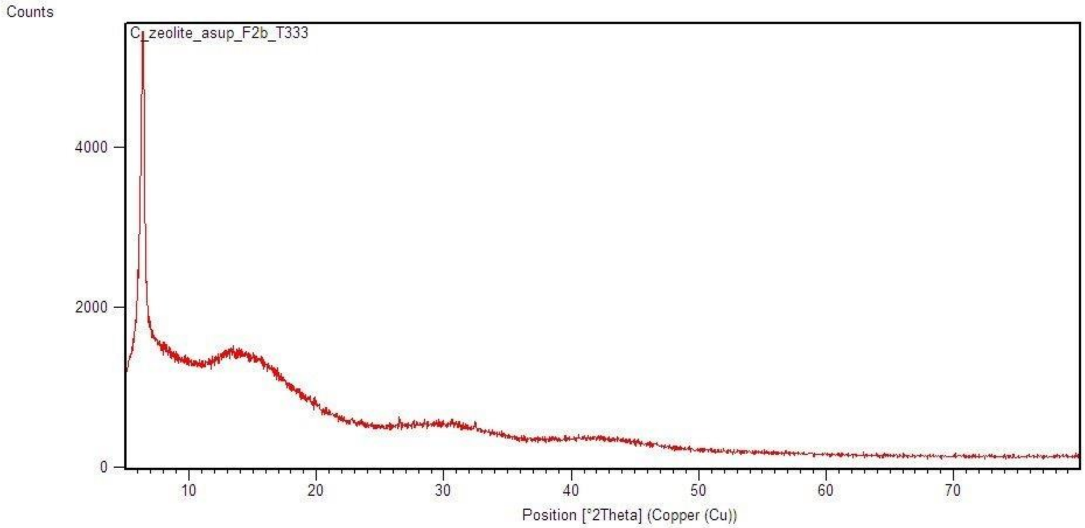

Figure S1. XRD pattern of as prepared ZTC.

N_2 physisorption of ZTC was carried out at −196 ºC by using a volumetric sorption analyzer (ASAP2020C, Micromeritics) and the resulting N_2 adsorption-desorption isotherm is depicted in Figure S2. Before the measurement the sample was outgassed at 150 ºC for 6 h. Specific surface areas was calculated using the Brunauer−Emmett−Teller (S_{BET}) method applied to their N_2 adsorption isotherms measured at −196 °C. Micropore volume ($V_{DR(N2)}$) were determined by the Dubinin−Radushkevich (DR) equation. Resulting values are summarized in Table S1.

Table S1. Porous texture characterization of the carbon samples in this study.

Sample	S_{BET} ($m^2\ g^{-1}$)	$V_{DR(N2)}$ ($cm^3\ g^{-1}$)
ZTC	3420	1.49

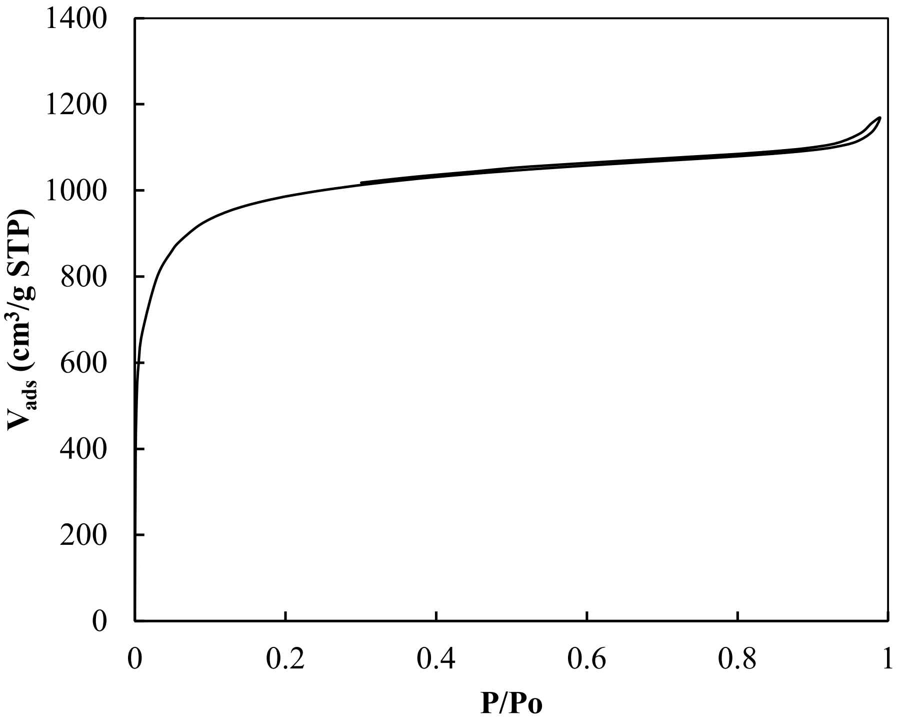

Figure S2. N_2 adsorption-desorption isotherm of ZTC at -196 ºC.

Electrospray of ZTC over different conductive substrates

Electrospraying of ZTC suspensions was carried out in a homemade device presented in Fig. 1. It consists of two syringe pumps (KD Scientific) equipped with 5 mL syringes (BD), a spinneret with two stainless steel coaxial needles and two high voltage DC power supplies (Glassman High Voltage, Series EL) that were connected to the metallic needle and the collector and oppositely polarized in order to generate the electric field required in the process. The solutions and experimental parameters of the electrospraying set-up were varied to obtain the optimal conditions. The concentration of ZTC in the suspension was ranged from 0.5 to 3 mg/mL; the suspension flow from 0.1 to 5 mL/h; the distance between the tip and the collector from 5 to 30 cm; the applied voltage from 1 to 20 kV and also different configurations of the set-up were tested, such as (i) connecting to the power supply of the surface targeted to be coated in order to use it as collector, (ii) the use of single or coaxial spinneret configurations and, with this last configuration, (iii) feeding the ZTC suspension through the inner or the outer needle. Ethanol was selected as the solvent because it was found to evaporate easily during the process of electrospray while also avoiding in a great extent the agglomeration of ZTC on the collector. However, it is difficult to achieve a stable dispersion due to the hydrophobicity of ZTC. In this sense, a ZTC suspension of 0.5 mg/mL was dispersed with ultrasonic bath for 2 h before placing into the syringe for the electrospray step. In the coaxial setup, the ZTC suspension was placed in the outer needle, while ethanol flowed through the inner needle in a proper rate for providing enough solvent to avoid fast evaporation in the tip of the cone. The optimal conditions were obtained by using ethanol as solvent in the suspension, a coaxial configuration of the spinneret, which allows to get a more stable Taylor cone when using feed rates of 0.5 mL/h for the ethanol solution and 1.0 mL/h for the ZTC suspension. An applied voltage of 10 kV, a tip of the needle to the collector distance of 10 cm and connecting the targeted surface to the power supply for using it directly as the collector were also set as the most adequate conditions for achieving electrospray conditions.

Electrospray was carried out targeting four different surfaces that have been used as the current collector by directly connecting them to the positively polarized high voltage power supply: a stainless steel (SS) mesh, a conductive carbon paper (TGP-H-030, Toray) referred to as TGP, which is a support used in the preparation of the gas diffusion layer in fuel cells, and two macroporous graphite sheets (DFP-1, POCO graphite) with different thicknesses (0.25 and 2.5 mm, labelled as PGT and PGW, respectively, along the text).

The scanning electron micrographs presented in Fig. S3 show the deposition of different amounts of ZTC on a SS mesh that was placed over the metallic collector of the electrospray setup (the mesh was not directly used as the current collector). The amount of electrosprayed ZTC was controlled by regulating the time of the electrospray treatment. The formation of ZTC films by electrospray deposition without using any binder or conductive promoter was aimed in these initial tests. As can be seen, the micrographs shows that the stainless steel wires were coated at different times with a homogenous ZTC coating, obtaining deposits of different surface loadings with an amount that was gradually increased with the time of electrospray. However, and considering the total amount of electrosprayed ZTC, the yield of the process (ie amount of ZTC collected on the top of the stainless steel substrate) at long times was quite low, approximately 10%, which is clearly related to the low stability of the ZTC suspension and to part of the ZTC particles being deposited outside the surface of the SS mesh. Moreover, the Taylor cone was unsteady, and dripping mode or clogging of the spinneret was achieved when the environmental conditions, i.e. temperature or humidity of the chamber, fluctuated during the course of the experiment.

On the other hand, the adherence of ZTC to the metallic mesh was found to be low, and important loss of the carbon material occurs when using ZTC loadings higher than 0.25 mg/cm^2. At loadings under that value, ZTC was deposited over the entire body of the stainless steel wires that compose the mesh (Fig. S3c-d), but beyond that surface loading value, ZTC was found to be deposited forming several layers of carbon particles that are loosely connected between them (Fig. s1e-f). Similar results were found over the carbon-based collectors, as can be seen in the SEM images of TGP substrate loaded with different amounts of electrodeposited ZTC, Fig. S4, with the maximum allowable loading of ZTC being related to the roughness of the substrate more than to the surface composition. Similar results were achieved when using PGT and PGW electrodes. For avoiding these limitations, the use of Nafion as binder and as suspension stabilizer was proposed. The results obtained using such approach are shown in the main text.

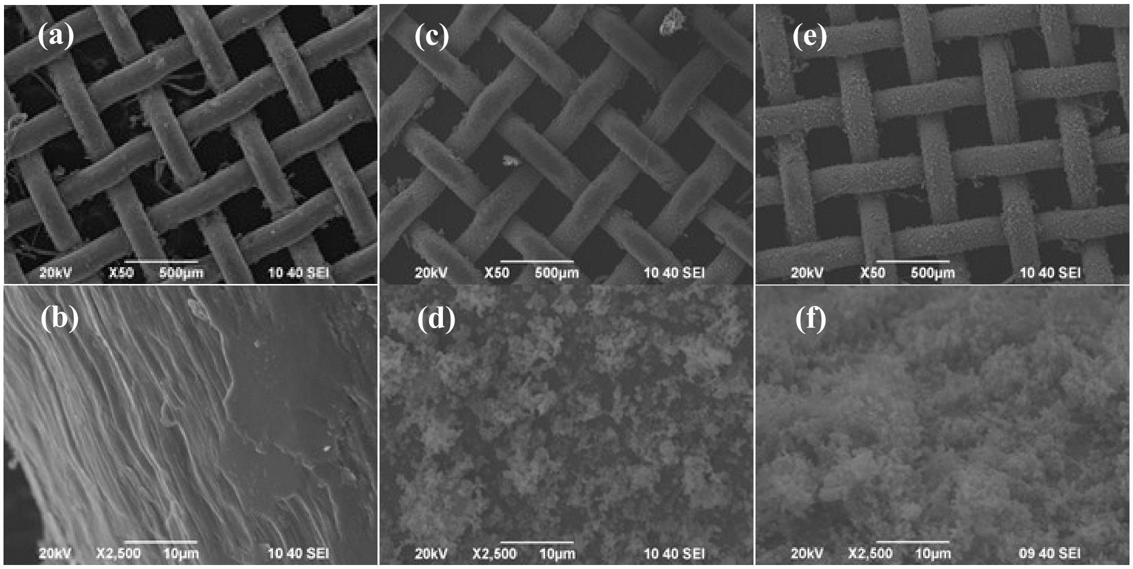

Figure S3. SEM micrographs of the SS mesh covered with different amounts of ZTC: (a,b) 0 mg; (c,d) 0.21 mg/cm^2; (e,f) 0.48 mg/cm^2 (geometrical surface of the electrode has been employed for the estimation of the surface area). Bar length: 500 (a,c,e) & 10 (b,d,f) microns.

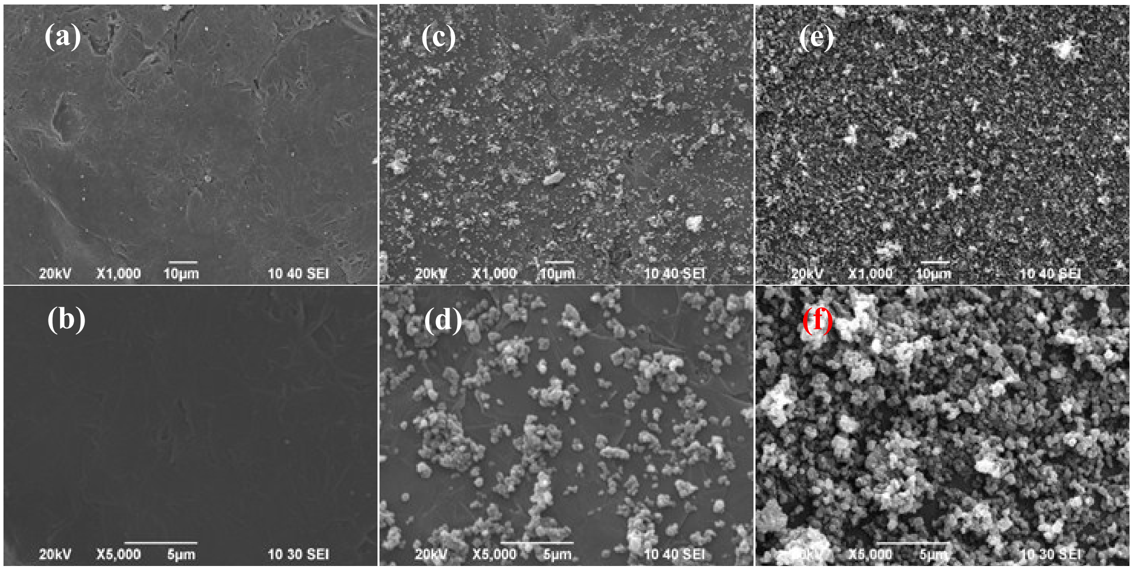

Figure S4. SEM micrographs of the PGT substrate covered with different amounts of ZTC: (a,b) 0 mg; (c,d) 0.12 mg/cm^2; (e,f) 0.30 mg/cm^2 (geometrical surface of the electrode has been employed for the estimation of the surface area). Bar length: 500 (a,c,e) & 10 (b,d,f) microns.