Modified Carbon Nano-onions in Supercapacitor Electrodes

Marta E. Plonska-Brzezinska, a,b Olena Mykhailiy, a Agustin Molina-Ontoria, a Luis Echegoyen a

a Institute of Chemistry, University of Bialystok, Hurtowa 1, 15-399 Bialystok, Poland, mplonska@uwu.edu.pl. b Department of Chemistry, University of Texas at El Paso, 500 W. University Ave., El Paso, TX 79968, USA, echegoyen@utep.edu.

In the recent years, the ability of carbon to exist in different allotropic forms has provided, besides C60 and the other fullerences, many new varieties of nanoscale sized shapes with fascinating properties, such as the “higher” fullerences 1,2 endohedral fullerenes, 3 carbon nano-onions (CNOs), 4,5 and single and multi-walled carbon nanotube, 6 among many.

CNOs were first produced by irradiation of nanoparticles under an electron beam by Ugarte in 1992. 8 The first time onion-like structures were observed in 1980 by lijima, in amorphous carbon films prepared by a vacuum evaporation method.9 These carbon nanoparticles show perfectly spherical multilayered fullerene structures and consist of a hollow spherical fullerene core surrounded by concentric graphene layers with increasing diameter, so they resemble Russian doll-style - “Matrioshka”.

Because of the high surface area of carbon nano-onions, these structures have been frequently used to prepare Electrical Double Layer Capacitors (EDLCs). 8 Due to the small particle size of CNOs (<10 nm) and zero-dimensional structures compared to other carbon-based materials and can possess better mesoporous characteristics than many carbon-based materials and can be potentially better for double layer capacitors. 8 Non-modified CNOs have somewhat limited charge accumulation properties, thus research has focused on their chemical derivatives, which possess different physico-chemical characteristics. So far, many reactions have been published concerning chemical modification of CNO surfaces, but only a few of them have yielded materials which could potentially be applied in ECs.

The structural and electrochemical properties of CNOs were investigated in the solid phase, for both plain as well as post-modified CNOs in the absence/presence of carbohydrates in an air atmosphere or post-modified in different atmosphere (N2, CO2 air or air). The structural properties of the CNOs were changed as a consequence of the post-modification during temperature annealing. This process changes the carbon structures into predominantly higher ordered graphitic layers (Fig. 1). TEM, SEM and TGA studies showed graphitization of the CNOs and their transformation upon annealing as a function of the ratio of the carbohydrate mass in the samples. Post-modification of CNOs by low-temperature annealing lead to an increase of the BET specific surface area, with a maximum of 511 m² g⁻¹ observed for modified-CNOs with starch. 10 According to the pore size distribution curves of the BJH adsorption, the pore diameters were in the 2–50 nm range. Moreover, there is a small fraction of micropores (<2 nm) available in all of the CNO materials.

The electrochemical properties of the CNO films depend on the porous structures of the carbon surface. In aqueous solutions, all CNO films show the typical behaviour of an ideal double layer capacitor. Further studies of CNO structural changes as a function of temperature and atmosphere are required to fully understand the correlation between the physico-chemical properties of CNO particles with their electrochemical properties.

Figure 1. HRTEM images of (a) CNO; post-modified at 450°C; (b) m-CNO (post-modified 1 h); (c) m-CNO/glucose (post-modified 1 h; mCNO:mGl=2:1). (d) m-CNO/starch (post-modified 2 h; mCNO:mSt=1:1) and (e) m-CNO/starch (post-modified 1 h; mCNO:mSt=2:1).