Organic-Inorganic Hybrid Materials for Supercapacitors

Vanessa Ruiz*, Julieth Suárez-Guevara*, Pedro Gomez-Romero**
* Centro de Investigación en Nanociencia y Nanotecnología, CIN2 (CSIC). Phone: +34 935868531
** MATGAS Research Center. Phone: +34 935929950.
UAB Campus, 08193 Bellaterra, Spain
vanessa.ruiz@cin2.es, julieth.suarez@cin2.es, pedro.gomez@cin2.es

We present the design and development of hybrid organic – inorganic materials with improved electrochemical performance to be used in energy storage applications (e.g. supercapacitors). The systematic study carried out shows various carbon–based materials (e.g. activated carbons, graphene based materials) working as active substrates where the anchoring of inorganic species takes place (i.e. polyoxometalates POM, such as H₃PMO₁₂₃₀₆₀, PMO₁₂₃) in search of synergic properties.

Polyoxometalates represent the greatest degree of dispersing oxides at the nanometer scale. Indeed, they are molecular clusters of V, Mo or W oxides (with possible substitutions) with well–defined solid structures, a rich redox chemistry and capacity to accept electrons and protons, making them reproducible models for oxide quantum dots [1-3]. They have a well – known electrochemical activity and thus, they are an attractive alternative to induce pseudocapacitance in electrochemical devices. One gram of dried activated carbon, AC (Super-DLC-30 kindly supplied by Norit Chemicals®) was added into a 50 ml 10mM H₃PMO₁₂₃₀ aqueous solution. The mixture was kept under stirring for 24 hours at room temperature, then filtered, washed and dried at 80 °C for 24h in a vacuum oven as described in ref [4]. By weight difference the amount of PMO₁₂₃ impregnated was obtained. A 54 wt.% increase in weight was calculated.

The surface area, SA, of the starting activated carbon material was 1436 m²/g. After impregnation the AC- PMO₁₂₃ sample showed a SA = 682 m²/g. Since the POM has no porosity, its weight contribution should not be accounted for the SA calculations, leaving a SA value of 1470 m²/g, which demonstrates that the PMO₁₂₃ does not block the porosity of the activated carbon.

The electrochemical characterization of the materials was tested by cyclic voltammetry and galvanostatic charge – discharge tests in two–, three– and combined two and three– electrode configurations, where platinum wire and Ag/AgCl were used as counter and reference electrode, respectively. 1 M H₂SO₄ was the electrolyte.

Figure 1 shows CVs for AC and the hybrid material. The former shows a typical rectangular shaped capacitive behavior. The hybrid (AC/ PMO₁₂₃) material shows well – defined redox peaks on top of a rectangular–shaped envelop, indicating the coexistence of double layer and pseudocapacitance in that material. The specific capacitance values of carbon electrodes were improved by following this hybrid approach, not only in terms of Farads per gram, Fig. (see Fig 1), but more importantly in terms of Farads per square centimeter, which can be considered more relevant for practical applications. The specific capacitance values of the activated carbon used in this study was increased from 10 μF/cm² to 28 μF/cm²

when H₃PMO₁₂₃₀ was anchored to its structure.

Symmetrical supercapacitors with ACPMO₁₂₃ electrodes were characterized in synchronous experiments (two- and three- electrode configuration). In such set – up, the cell works as a two electrode cell and the variations of potential of each electrode are monitored. Figure 2 shows a galvanostatic cycle (left Y-axis) and the positive and negative electrode potentials (top blue and bottom green line, respectively). Efficiencies ranged 95 – 100% for the range on current densities tested. The overall cell voltage is split between positive and negative electrodes (~0.5 V for each electrode).

The stability of the materials was evaluated by means of long-term cycling where a two electrode assembly was cycled over more than 10,000 galvanostatic cycles (1,300 mAh/g of current density) showing no reduction in capacitance values demonstrating the strong interaction between the carbon substrate and the POM thus, validating the suitability of such material to be used in supercapacitors.