

New Electrode Material Based on Mn₃O₄ Nanoparticles Embedded in Organometallic-Derived Carbon (ODC)

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The electrochemical double layer capacitors (EDLC) exhibit greater power density than batteries and fuel cells, however, the amount of energy they are able to store is much lower [1]. Electric double-layer capacitors EDLCs, the most common devices at present, use carbon-based active materials with high surface area, where the charge is stored on the surface of the electrode and therefore the higher the surface area, the higher the capacitance. On the other hand, pseudo-capacitors such as transition metal oxides or conductive polymers are able to store energy by fast and reversible surface processes originated from the redox reaction of the electrode material with the electrolyte on a Faradaic process where the electrons produced by the redox reaction are transferred across the electrolyte-electrode interface. Here, we propose a new electrode material able to exhibit both mechanisms. In order to achieve pseudo-capacitance compounds with high number of electrons involved on their redox reactions and low molar mass are needed, such as metal oxides of the first transition series. We chose manganese oxides due to their well-known redox behavior and their promising pseudo-capacitance properties.

Carbide-derived carbons, known as CDC, are porous carbons obtained by extraction of metals from carbides (TiC, SiC...) by reaction with chlorine at elevated temperatures. In this reaction, the metal is leached out from the starting carbide, and carbon atoms self-organize into an amorphous or disordered, mainly sp²-bonded, structure with a pore size that can be fine-tuned by controlling the chlorination temperature and other process parameters [2]. This synthetic concept has also been applied to organometallic precursors in order to produce disordered carbon materials for their application in EDLCs [3]. At low chlorination temperatures, the metal extraction is always not complete, remaining as metal halide nanoparticles embedded in the carbon matrix. It has been demonstrated that these halides can be hydrothermally transformed into the corresponding metal oxide [4].

A new carbon-based material ODC@Mn₃O₄ has been prepared by chlorination at 700°C of Mn(II) acetylacetonate (Mn(acac)₂) as precursor. The presence of MnCl₂ in the carbon material is not evident on the HRTEM images, but in HAADF mode brighter areas corresponding to a higher Z are observed and the EELS analysis of those areas confirms the presence of manganese (Fig. 1). Subsequently, the sample was introduced into a steel autoclave under basic conditions (KOH) which was placed in an oven at 200°C for 2 days. The obtained material is composed by a disordered carbon matrix containing metal oxide nanoparticles (Fig 2a), identified as Mn₃O₄ from the HRTEM micrograph oriented along the zone axis [100] (Fig 2b). In addition, the EELS analysis performed in the nanoparticle (Fig. 2c), clearly shows the O-K and Mn-L_{2,3} absorption edges. In order to extract the textural parameters of this new material isothermal N₂ adsorption measurements have been performed. Using the BET method a surface area of 753 ± 1 m²/g is determined. The presence of both the carbon and the manganese oxide nanoparticles, suggests that both Faradaic and non-Faradaic processes to store charges could coexist in the same electrode [5].

References:

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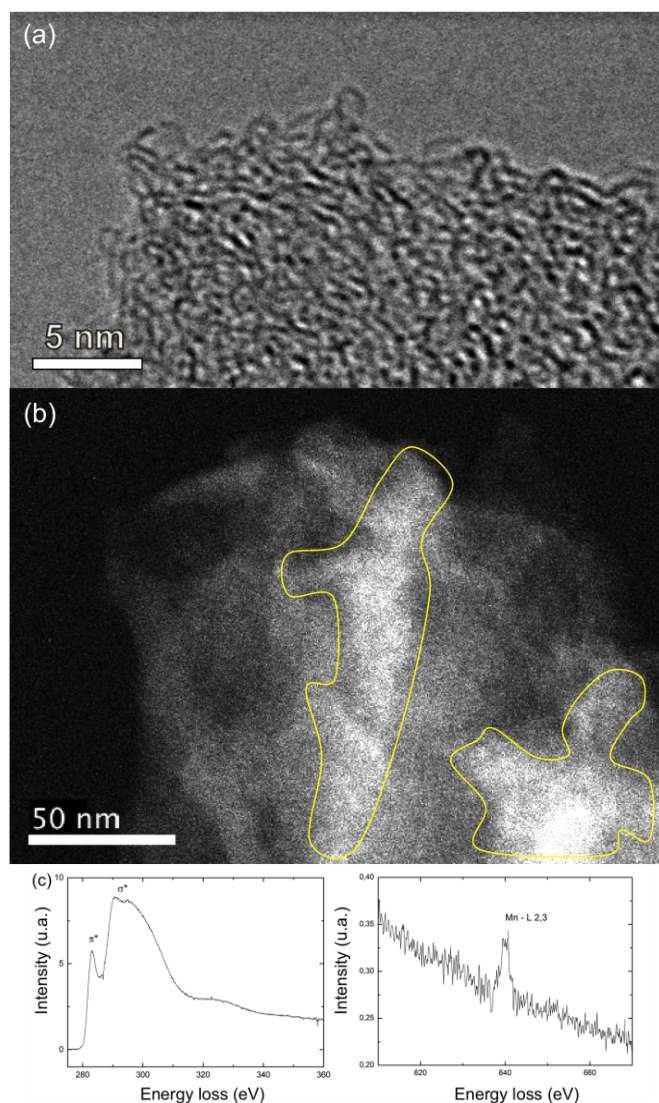


Figure 1. HRTEM (a) and HAADF (b) images of ODC from $\text{Mn}(\text{acac})_2$ where brighter areas of higher Z are shown in yellow. EELS spectra (c) showing the carbon K and manganese L_{2,3} edges.

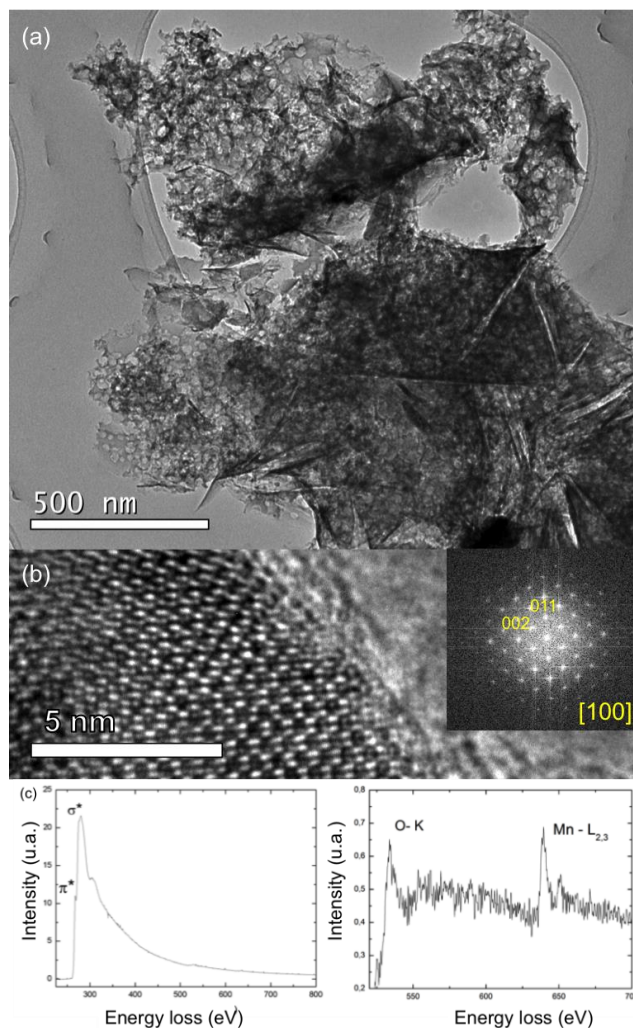


Figure 2. (a) TEM micrographs of the ODC@Mn₃O₄ Nps material at low magnification (b) HRTEM of a single nanoparticle identified as the spinel Mn₃O₄ along the [100] zone axis (c) EELS spectra showing the carbon K, oxygen K and manganese L_{2,3} edges.