Enhanced Charge Capacity in Iridium Oxide-Graphene Oxide Hybrids

N.M. Carretero [a], M.P. Lichtenstein [b], E. Pérez [a], S. Sandoval [a], G. Tobias [a], C. Suñol [b,c], N. Casan-Pastor [a,*]

[a] Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus de la UAB, E-08193, Bellaterra, Barcelona, Spain
[b] Institut d'Investigacions Biomèdiques de Barcelona (IIBB-CSIC); Institut d'Investigacions Biomèdiques August Pi i Sunyer (IDIBAPS). c/Rosselló 161, 08036 Barcelona, Spain
[c] CIBER Epidemiología y Salud Pública (CIBERESP), Spain

ABSTRACT

Hybrid materials based on iridium oxide and graphene oxide, and graphite oxide as reference, are reported as biocompatible electrodes for the neural system. An electrodeposition process based on dynamic potential sweeps, allows an optimal adherence of coatings to the platinum substrate. The resulting electrochemical properties evidence an order of magnitude increase in charge capacity with respect to iridium oxide, and a quasi reversible cyclability for the electrode that expands to more than a thousand cycles for the graphene oxide case. Such stability upon cycling is also an order of magnitude larger than that of IrOx. Neuronal cell cultures show full biocompatibility even in absence of growth factors, and sustain near 100% survival rates and optimal development of neurites. Together with previously reported hybrid IrOx-carbon nanotubes, IrOx-graphene oxide hybrids open the field of materials to be used in the neural system.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Neural system electrostimulation or repair through the use of electric fields using implanted electrodes is nowadays a significant frontier research in terms of the biomaterials used. The development of implanted electrodes in the neural system require a new generation of electroactive and biocompatible materials that are able to render applied electric fields without the secondary effects related to charge transfer at the electrode-liquid interface, usually related with heating, radical formation and oxidation of the nearby tissue. The electrode must have good conductivity and low impedance, and allow minimal faradic reactions at the surface involving the biological ionic media. The materials used now as electrodes in the neural system [1–8] are mostly noble metals: gold, platinum, glassy carbon, platinum-iridium, or capacitive electrodes such as titanium-nitride. On the other hand, pseudo-capacitive (intercalation electroactive materials that undergo a redox reaction themselves during electron exchange) are being tested. Conducting polymers such as PEDOT with PSS counterions have become popular for its easiness of preparation but cell cultures on it are no reproducible unless they are functionalized or used in presence of NGF. On the other hand, Iridium oxide shows

full biocompatibility and the best overall results in cell culture, being optimal in terms of charge capacity along the polymers. However, coatings based on this oxide have significant drawbacks, and although dynamic electrodeposition methods have given a very good adhesion and reproducibility of the material [7], there is room for improvement. In fact, those properties such as high electrochemical efficiencies, good bio-stability and significant biocompatibility, have turned IrOx into one of the most promising materials for neural recording and stimulation electrodes.[1–7] These superior characteristics are mainly a consequence of the faradaic (pseudo-capacitive) charge-injection properties of iridium oxide, instead of the sole capacitive character of other materials as TiN.[8] During an electrical stimulation pulse within safe potential working limits, IrOx can undergo reversible redox changes itself, with the corresponding ion-intercalation processes, yielding to high charge capacity values and preventing side reactions. All faradaic contributions are therefore assumed as coming from the material itself. This redox-intercalation capability prevents electrode alteration/degradation or tissue damage by possible radical formation or irreversible reactions. [9] Because of its electrical conductivity and intercalation processes, carbon may offer the formation of composites or hybrids, depending on the nanostructuring and chemical interactions achieved with IrOx, as proven by IrOx-carbon nanotubes. [10] In the case of nanotubes, a significant improvement was observed beyond IrOx itself, thanks to the nanostructuring in which they act as a scaffold sustaining

the electrode material, while at the same time being embebed in the hybrid without any release to the media. Such synergy yields one order of magnitude larger values in charge capacity and a ciclability above 1000 cycles, ten times more than the pure oxide coating. [10]

Carbon is usually part of electrodes in batteries for example, because it increases conductivity and connectivity between grains of the main phase material, and it also conveys significant practical benefits in lithium anodes. On the other hand, graphene itself has a significant range of properties that could add up to the conductivity and charge capacity of electrodes that need to be implanted in the neural system, without adding the extra hardness of platinum. [11] Although biocompatibility studies have been started on graphene phases (oxide or bare graphene), an anti-inflammatory effect has been reported [12] but also an inflammatory one [13], axonal guidance when used as Si-coated nanoparticles [14], and also its use in recording electrodes [15,16] among others. In that sense, nanostructuring graphene within a known material, yielding a hybrid material could render more stability within biological systems, without the usual phagocytosis found in nanoparticles. [17]

This work shows how hybrids of IrOx with graphite and graphene materials offer a different nanostructuring and evidences the larger charge capacity values when acting as electrodes, as compared with IrOx or IrOx-nanotubes hybrid, while being biocompatible for neural systems. The need to favor hydrophillicity for interaction with IrOx and with cells, has involved the use of graphite and graphene oxide. The results shown here apply also to other electrochemical devices. Also, this study is an example of the interaction of graphene with metals, a focus in the fundamental research in graphene.

2. Experimental Methods

2.1. Synthesis of materials as coatings

Synthesis of IrOx hybrids films containing graphite and graphene oxides (IrOx-GK and IrOx-GO) was carried out by dynamic electrodeposition methods, using a three-electrode electrochemical cell, basing the preparation on the reported iridium pre-deposition solutions reported before. The working electrode where the sample is deposited, is a transparent soda-lime glass slide ($38 \times 12 \, mm^2$, AFORA) coated with 5 nm of titanium (as adhesion phase) and 12 nm of platinum by thermal evaporation. A Platinum sheet (Goodfellow 99.9%) of the same geometric area was used as counter electrode, placed in a parallel arrangement with a separation of 1 cm from the working electrode. A platinum wire, 0.5 mm in diameter (Goodfellow 99.9%) was used as pseudo-reference electrode, its potential versus Ag/AgCl being 0.02 V [18,19]. Thin films were obtained by a potentiodynamic sweep involving 25 potential cycles. Cyclic potential sweep rate was 5 mV/s, and the potential limits were from equilibrium (near 0.0 V) to 0.70 V vs Pt for graphite or 0.85 V for graphene hybrids. The maximum potential in cycling was optimized empirically since the potential used for bare IrOx did not yield any deposit. A VMP potentiostat (Biologic) was used for electrodeposition control. Bare IrOx coatings used for comparison, were synthesized using the same substrates and with a similar potentiodynamic protocol: scan rate of 10 mV/s, potential limit to 0.55 V and 50 cycles, using a pre-deposition solution described by Ana M. Cruz et al. [7].

The pre-deposition solution for hybrid preparation is a modification of the one used by for pure IrOx [7], and was prepared from 5.5 mg/mL of oxidized graphene or graphite precursors dispersed by sonication during 30 minutes in 10 mL of milliQ water, and the posterior addition of 0.2 mmol $IrCl_3.H_2O$ (Aldrich 99.9%) and 5 mmol of K_2CO_3 (Aldrich 99%), with a final

pH of 10. The solution was kept at 37 °C for 7 days and stored at 4 °C until use. Graphite oxide (GK), and Graphene oxide (GO) were prepared as previously reported: Graphite oxide (GK) was prepared by oxidation of Kish graphite coarse powder (100 mesh, 0.15 mm) provided by Nanomagnetics Ltd following the method described in the article of G. Tobias et al. [20] by treating the graphite with nitric acid (HNO_3, Fisher Chemical, 65%). Around 200 mg of graphite were added to a round-bottomed flask with 100 mL of 3 M HNO_3 and refluxed at 130 °C during 45 h in order to ensure the mild oxidation. Then, the mixture was filtered with a 0.2 μm Millipore polycarbonate membrane and rinsed with distilled water until pH = 7. The black powder is then dried in air. Quantification of functional groups was performed by X-Ray Photoelectron Spectroscopy (XPS) on pre- and after-treated graphite, yielding an atomic relation O/C around 0.08.

Graphene oxide (GO) was prepared following a previously reported protocol [21] via a modified Hummer's method [22]. Briefly, 5 g of graphite powder ($< 20 \, \mu$m, Sigma–Aldrich) was treated with 115 mL of H_2SO_4 (Panreac, 98%) and 2.5 g of $NaNO_3$ (Sigma–Aldrich, < 99%). This mixture was cooled down to 0 °C and left for 30 min. Next, 15 g of $KMnO_4$ (Panreac 99%) were added slowly. After stirring for 30 min, 230 mL of distilled water was slowly added maintaining the reaction temperature at 98 °C for 2 h. Then, additional water (1 L) and 5 mL of H_2O_2 (Acros Organic, 30%) were added and the reaction mixture was cooled down. The resulting graphene oxide was purified by subsequent centrifugation and washing with distilled water until the pH of the solution was neutral. GO obtained in this case was characterized by XPS, showing a 30 atomic % of oxygen, that is, O/C around 0.4. The final GO has been proven by AFM studies to have most particles with 1.1 nm profiles [22].

Carbon phases without iridium do not deposit in the same conditions.

2.2. Coatings characterization

IrOx-carbon hybrids were characterized using several techniques. Scanning electron microscopy (SEM) using a FEI Magellan 400L High Resolution SEM at 10–30 kV in high vacuum conditions, was performed for all samples. The thickness of the coatings was measured also by SEM, placing the transversal fractured substrate in parallel with the electron beam. TEM experiments, after scratching the coatings, were performed on a 120 KV JEOL 1210 with a double tilt specimen holder GATAN 646 and a camera Orius 831 SC600 (GATAN).

AFM experiments failed for the range of roughness observed. Confocal Microscopy was performed using a Leica DCM 3D instrument with a 100x lens and ambient conditions of temperature and pressure, to get information on the surface microstructure. The data acquisition was repeated twice for each of the samples and the area captured was $128 \times 95 \, \mu m^2$. Subsequently the data was processed with the MountainsMap Premium Software to obtain the roughness factor RMS. Optical microscopy was performed with a Olympus BX51 Optical Microscope (BX2 Series) and a 20x magnification lens. The contrast and resolution were optimized manually.

X-ray photoelectron spectroscopy (XPS) measurements were performed at room temperature using an PHI 5500 Multitechnique System (from Physical Electronics) with a monochromatic X-Ray source (Aluminum K α: 1486.6 eV energy and 350 W) placed perpendicular to the analyzer axis. The analyzed area was a circle of 0.8 mm diameter, and the selected resolution for the spectra was 187.5 eV of Pass Energy with 0.8 eV/step for the general spectra, and 11.75 eV of Pass Energy and 0.05 eV/step for the high resolution spectra.