Graphene derivatives as positive electrode materials in a vanadium redox flow battery

Zoraida González, Cristina Botas, Silvia Roldán, Patricia Álvarez, Clara Blanco, Ricardo Santamaría, Marcos Granda and Rosa Menéndez

Instituto Nacional del Carbón, CSIC, Francisco Pintado Fe, 26, 33011 Oviedo, Spain

zoraidag@incar.csic.es

Graphene derivatives have been extensively studied for energy storage devices such as supercapacitors [1], lithium-ion batteries [2], and more recently for a vanadium redox flow battery (VRFB) [3]. This is because these carbon materials exhibit peculiar properties such as a high specific surface area, an excellent electrical conductivity and remarkable mechanical strength [4], which make them promising electrochemical active materials.

The objective of this work is to evaluate the use of different graphene derivatives as electrode materials in the positive half-cell of a VRFB, taking into account their textural and physico-chemical properties and comparing them with commercial multi-walled carbon nanontubes (MWCNT).

Graphene oxide (GO5) was prepared by a modified Hummers method and characterized by transmission electron microscopy (TEM) and atomic force microscopy (AFM) analysis. Subsequently, it was thermally reduced at different temperatures (700, 800 and 1000º C) generating three different graphene samples (GO5TR700, GO5TR800 and GO5TR1000). The surface chemistry of all the samples were studied by temperature programmed desorption (TPD).

The electrochemical characterization was performed on a Swagelok-type three electrodes cell, consisting of: carbon material (graphene derivative or MWCNT) in a coin-type design as working electrode, a Pt wire as the counter electrode and a saturated calomel electrode as the reference one. The electrolyte used was a 1M H_2SO_4 + 0.5 M $VOSO_4$ solution. Cyclic voltammetry (CV) was carried out using a Biologic VMP Multichannel Potentiostat.

Accordingly to the TEM and AFM images shown in Figure 1, monolayers of graphene oxide with size of ~1 μm are obtained. In addition to the samples structure, the decisive influence of surface chemistry on the electrochemical properties of graphene materials, mainly on the electrical conductivity, made it essential to carry out an analysis of the carbon surface groups [4]. As can be seen in Table 1, the amount of oxygen-containing functional groups on the surface of the graphene oxide sheets is significantly high for the graphene oxide and decreases as a result of thermal treatment, which is in agreement with the TPD results.

Figure 2 presents the CV curves of V(IV)/V(V) redox couple on the graphene derivatives and MWCNT based electrodes tested. Both the oxidation and reduction peak currents are significantly larger on GO5TR1000, which is in agreement with the higher electrical conductiviy of this material. On the other hand, MWCNT and GO5TR800 present the smallest peak potential separation (ΔEp) and peak currents ratio respectively, indicating that these samples exhibit the best reversibility. In the case of GO5TR700, its higher oxygen content explain its electrochemical performance.

The selection of graphene materials suitable as electrodes in the positive half-cell of the VRFB has to be made taking into account their textural and physico-chemical properties. The ideal active material would present mainly high electrical conductivity. In this way, GO5TR1000 is a promising material for this application.

Aknowledgements: The authors thank the Ministry of Science and Innovation (CONSOLIDER CSD2009-00500, and Ramon y Cajal Program) and “Fundación para el Fomento en Asturias de la

Investigación Científica Aplicada y la Tecnología" –FICYT (postgraduate grant) and Hidroeléctrica del Cantábrico for their financial support.

References

[1] S.R.C. Vivekchand, C. Sekhar Rout, K.S. Subrahmanyam, A. Gouindaraj and C.N.R. Rao, J.Chem. Sci., **120** (2008) 9..
[2] P. Guo, H. Song, X. Chen, Electrochem. Commun., **11** (2009) 1320.
[3] P. Han, H. Wang, Z. Liu, X. Chen, W. Ma, J. Yao, Y. Zhu, G. Cui, Carbon, **49** (2011) 693.
[4] C. Liu, Z. Yu, D. Neff, A. Zhamu, B.Z. Jang, Nanoletters, **10** (2010) 4863.
[5] D. Pantea, H. Darmstadt, S. Kaliaguine, C. Roy, Appl. Sur. Sci., **217** (2003) 181.

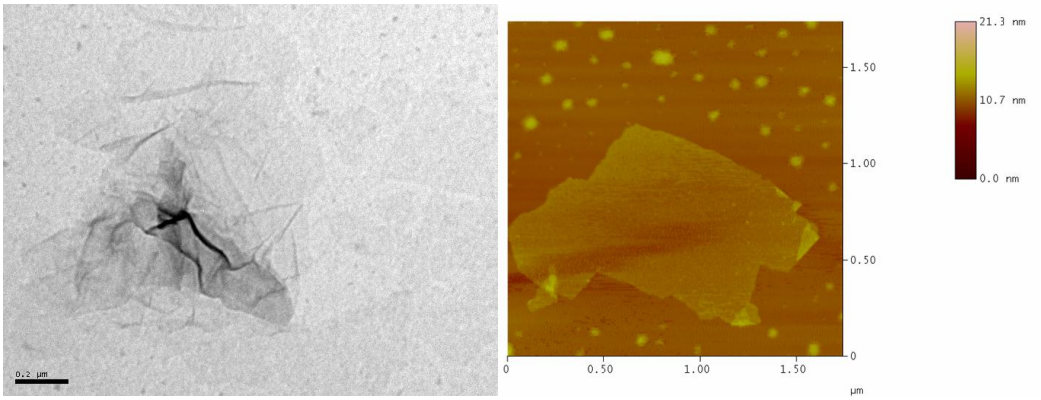

Figure 1: a) TEM image and b) AFM image of GO5

SAMPLE	TPD CO (mmol/g)	TPD CO_2 (mmol/g)
GO5	3,35	2,04
GO5TR700	2,06	0,22
GO5TR800	1,70	0,18
GO5TR1000	0,27	0,14
MWCNT	0,3	0,01

Table 1: TPD analysis of graphene materials and MWCNT

SAMPLE	$I_{p,a}$ / $I_{p,c}$	$E_{p,a}$ (V)	$E_{p,c}$ (V)	ΔE_p (V)
GO5	0,78	0,892	0,159	0,733
GO5TR1000	1,01	0,410	0,336	0,074
GO5TR800	0,95	0,395	0,352	0,043
GO5TR700	0,92	0,477	0,269	0,208
MWCNT	1,1	0,389	0,361	0,028

Table 2: Electrochemical parameters of graphene derivatives and MWCNT based electrodes.

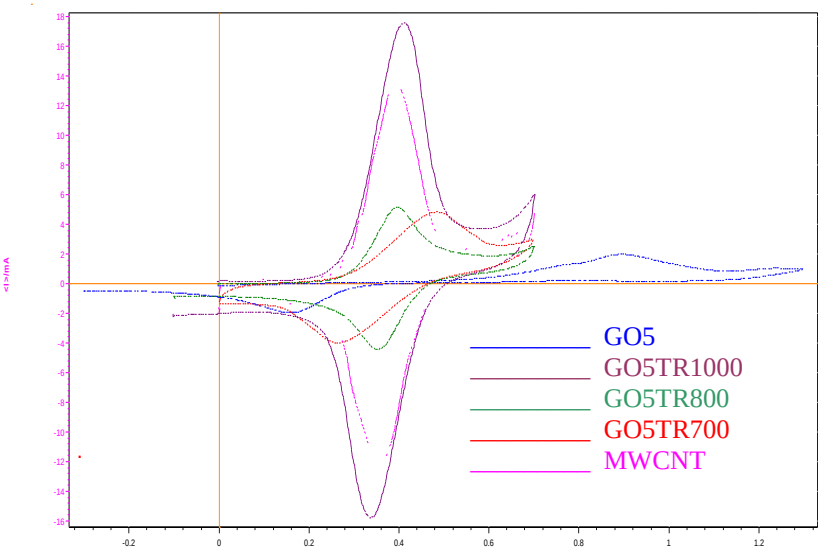

Figure 2: CVs of V(IV) / V(V) redox couple on graphene derivatives and MWCNT based electrodes.