

A comprehensive study of electrochemical HOPG intercalation with HClO₄ and H₂SO₄ electrolytes by photoemission spectroscopy and atomic force microscopy.

Madan. S. Jagadeesh^{1*}, A. Calloni¹, R. Yivlialin¹, D. Alliata², L. Duò¹, F. Ciccacci¹, G. Bussetti¹.

¹ *Department of Physics, Politecnico di Milano, piazza Leonardo da Vinci 32, I-20133 Milano, Italy.*

² *UnitySC, 611 Rue Aristide Berges 38330 Montbonnot-Saint Martin, France*

* e-mail: madan.sangarashettyhalli@polimi.it

Graphitic materials are employed in many technological applications, from the realization of electrodes in batteries to the production of graphene foils by electrochemical (EC) procedures [1]. In particular, the processes characterizing graphite oxidation have attracted researches in view of optimizing battery duration and quality-rate ratio in graphene production protocols [2]. In this context, highly oriented pyrolytic graphite (HOPG), with its well-defined layered structure, is generally considered a model system to elucidate the mechanisms of the EC oxidation of graphite electrodes, and in particular the intercalation process that occurs at oxidative EC potential ranges.

Recently, we demonstrated that anion intercalation can be detected not only at high (within 1.9 and 2.1 V vs SHE) EC potential values, i.e. above literature-reported intercalation stages, but also at lower potentials and allowing for a faster dynamics [3]. Here, we compare the results obtained on HOPG by using two different EC techniques for ion intercalation, namely cyclic voltammetry (CV) and normal pulsed voltammetry (NPV), with two different aqueous electrolytes (i.e. perchloric and sulfuric acid). The samples were analysed in-situ by atomic force microscopy (EC-AFM) and ex-situ by X-ray photoemission spectroscopy (XPS), where ion intercalation results in a shift of the XPS core levels towards lower binding energies, as previously highlighted by one of us [4].

We detect comparable XPS lineshapes after intercalation at high potentials, both with CV and NPV and for both electrolytes. Intercalation of perchlorate ions at lower potentials (namely, at the oxygen evolution potential) surprisingly shows a similar spectral evolution, where much stronger modifications are obtained by applying NPV, compared to CV. Finally, we investigated the effect of increasing the CV scan rate on both sample morphology and chemical surface condition. Our results show that, in spite of a similar XPS behaviour, fast CV scans prevent the development of extended surface defects (such as blisters) usually observed on HOPG due to the formation of gases seeded by ion intercalation [5].

References:

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