

Full Length Article

Morphological changes of porphine films on graphite by perchloric and phosphoric electrolytes

An electrochemical-AFM study



Rossella Yivlialin^{a,*}, Marta Penconi^{b,c,d}, Gianlorenzo Bussetti^{a,b,c,d}, Alessio Orbelli Biroli^{b,c,d}, Marco Finazzi^a, Lamberto Duò^a, Alberto Bossi^{b,c,d}

^a Department of Physics, Politecnico di Milano, p.za Leonardo da Vinci 32, I-20133 Milano, Italy

^b Institute of Molecular Science and Technologies of the CNR (ISTM), PST via G. Fantoli 16/15, I-20138 Milano, Italy

^c Institute of Molecular Science and Technologies of the CNR (ISTM), via Golgi 19, 20133 Milano, Italy

^d SmartMatLab Center, via C. Golgi 19, I-20133 Milano, Italy

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ABSTRACT

Organic molecules have been proposed as promising candidates for electrode protection in acidic electrolytes. The use of tetraphenyl-porphines (H₂TPP) as graphite surface-protecting agents in sulphuric acid (H₂SO₄) is one of the newest. With the aim of unveiling the mechanism of such a protective effect, in this paper we test the stability of a H₂TPP thin film immersed in perchloric and phosphoric acid solutions that differently interact with porphyrins.

The protective role of H₂TPP is tested in the electrochemical potential range where the pristine graphite undergoes an oxidation process that erodes the surface and eventually exfoliate the stratified crystal. The electrochemical analysis is performed in a three-electrode cell, while the surface morphology is monitored *ex-situ* and *in-situ* by atomic force microscopy. Electro spray mass analysis is also employed to investigate the presence of H₂TPP fragments in the solution. We find that the organic film is not stable in perchloric solution, while it is stable and avoids graphite surface corrosion in phosphoric acid solution. These results provide a rationale for the role played by free-base porphines in graphite protection.

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1. Introduction

Graphite is a long-established electrode material in batteries thanks to its good mechanical properties and chemical stability [1–3]. Nevertheless, improving next-generation electrodes in terms of cost reduction, stability, high performances, and life span remains a strategic task. In this frame, organic molecules have been proposed as candidates for the realization of protective layers on the electrode surfaces [4]. Notably, organic molecules can be deposited on a surface by exploiting different techniques, some of which are cheap and easy to implement in an industrial process (e.g. drop casting) or to integrate in a production chain involving high vacuum systems [5]. Moreover, organic molecules can be specifically designed and functionalized to optimize the protection of electrodes (e.g. graphite), working in different electrochemical solutions. Nevertheless, only few results are available in this research topic: in particular, the existence of a class of molecules with a

clear protective role has not yet been proven and researchers are still exploring a broad range of possible candidates. Among them, porphine and porphyrinoid compounds attracted the attention because the porphyrin/graphite interface shows interesting assembling [6–12], optical [7], electronic [8], and chemical [9] properties, and, most important, because of the high chemical stability of porphine structures. Recently, the authors proved that metal-free tetra-phenyl porphine (H₂TPP, Fig. 1) grows following a Stran-sky–Krastanov mode on graphite [13] and they succeeded in controlling the selective stabilization of either 2-D or 3-D phases [14,15]. In all cases, the H₂TPP 2-D phase covers almost uniformly the graphite surface.

Despite the electrochemical properties of porphines have been widely investigated in solution [16,17], their stability when deposited onto an electrode surface is still under debate. We recently showed that the H₂TPP 2-D phase acts as a protective film for a graphite electrode in a conventional three-electrode cell [18]. In that work, a highly-oriented pyrolytic graphite (HOPG), with or without a protective porphine overlayer, was immersed in a sulphuric acid (H₂SO₄) solution, which is the typical electrolyte employed

* Corresponding author.

E-mail address: rossella.yivlialin@polimi.it (R. Yivlialin).



Fig. 1. Free-base tetra-phenyl-porphine (H_2TPP). A meso phenyl substituted tetrapyrrolic macrocycle (carbon atoms: black spheres; hydrogen atoms: silver spheres; nitrogen atom: blues spheres). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

in lead-acid batteries. On pristine HOPG, H_2SO_4 intercalates between graphite planes and produces CO , CO_2 and O_2 gases during carbon oxidation, leading to the swelling (blistering) of the basal plane of graphite, as reported in the literature [19–22]. The presence of the 2-D porphine wetting layer on the electrode surface inhibits this process [18]. The protective role of H_2TPP is noticeable considering that sulphuric acid solutions can be used as “solvents” to dissolve free-base porphine aggregates [23].

In this work we investigate the stability of a H_2TPP thin film deposited on graphite and exposed to a different acidic environment, constituted by a solution of either perchloric or phosphoric acid. Perchloric acid ($HClO_4$, typically employed to exfoliate graphite) is usually reported to affect the conjugated structure of pyrrole rings or methin bridges of the H_2TPP molecule [24]. Phosphoric acid, on the other hand, is able to corrode the pristine graphite basal plane (without showing a clear blistering) [25,26] and it also behaves as a porphine “solvent”, similar to H_2SO_4 [23,24]. Comparing the behaviour of protected HOPG in these three mineral acids (H_2SO_4 , $HClO_4$, H_3PO_4), where only the perchloric one should be able to destroy the porphine system, allows acquiring more insight into the chemistry of graphite protection in acid solutions. To this end, we test a thin (nominally 12 Å-thick) H_2TPP film on graphite, immersed in an electrochemical cell containing a 2 M solution of either $HClO_4$ or H_3PO_4 . The 12 Å-film shows a widespread porphine 2-D phase, covered by 3-D crystals [18]. We observe that the porphine film is compromised after a single electrochemical scan performed by cyclic-voltammetry (CV) in the $HClO_4$ solution: some areas of the sample result exposed and blisters immediately appear on the graphite surface. Conversely, the porphine 3-D phase is still present on the sample surface after immersion in the H_3PO_4 solution. In this case, the CV treatment precluded a direct “*in-situ*” analysis of the porphine film due to the formation of tars caused by phosphates [26]. Nonetheless, a comparison of morphological images with electrospray mass analysis, employed to investigate the presence of H_2TPP fragments in the solution (see the [Supplementary Information](#)), allows concluding that the porphine film is preserved in phosphoric electrolyte.

2. Experimental section

z-grade HOPG (Optigraph) is mechanically exfoliated with adhesive tape. H_2TPP is grown by physical vapour deposition (PVD) from a Knudsen Cell (KC) fitted on a Kenosistec KE500 system. The KC is filled with 30 mg of H_2TPP powder purchased from Sigma–Aldrich. The powder is degassed in vacuum until the base

pressure of the PVD chamber ($1-2 \times 10^{-6}$ mbar) is restored. The graphite substrate is kept at room temperature during H_2TPP deposition. A quartz-microbalance monitors the molecular flux, which is kept constant at 0.6 Å/s. The detailed characterization of the film growth is described elsewhere [18].

The $HClO_4$ and H_3PO_4 electrolyte solutions (2 M) are prepared and deaerated by bubbling argon for several hours prior the use. The electrolyte solution is placed in a three-electrode cell where the HOPG is the working electrode (WE), a Pt wire acts as counter electrode (CE) and a second Pt wire is used as a quasi-reference electrode (QRef). The WE is inserted in the cell and immersed in the electrolyte solution without any contamination [27]. Being a single Pt wire, the QRef is not at thermodynamic equilibrium, which can in principle shifts the reference potential [27]. We tested the stability of the Pt-QRef electron in the present experimental conditions (time, temperature, solvent, etc.) and found a fixed and stable shift of $+0.740 \pm 0.010$ V with respect to the normal hydrogen electrode [22].

A single cyclic-voltammetry (CV; scan rate 25 mV/s) sweep is acquired on the samples. In CV, the current flowing through the WE is measured as the WE electrochemical (EC) potential is ramped linearly in time. A good compromise between charge transfer and mass transport is obtained with a scan rate of 25 mV/s, as reported in the literature [19–22].

Electrochemical atomic force microscopy (EC-AFM) has already proven its potentialities and versatility when *in-situ* analysis of surface electrode is required [28,29]. In particular, EC-AFM is used in combination with HOPG electrodes [30,31] and/or with organic molecules at the liquid/solid interface [32,33]. In this study, a commercial 5500 Keysight system is used for the *ex-situ* and *in-situ* atomic force microscopy (AFM) measurements. The AFM images are acquired in non-contact mode, to preserve the quality of the organic film. For *ex situ* measurements, the sample is extracted from the electrochemical cell and accurately dried with a stream of pure nitrogen.

3. Results and discussion

After the deposition of a nominal 12 Å-thick film of H_2TPP on HOPG, the surface topography is characterized by 3-D structures with sharp edges on top of a 2-D porphine wetting layer (see Fig. 2a) [13]. The 3-D crystals are stable in air and their thickness

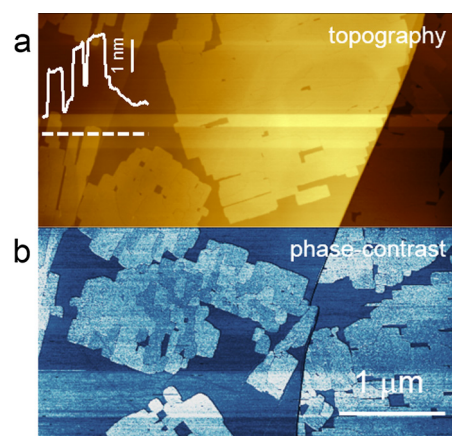


Fig. 2. AFM non-contact image ($4 \times 4 \mu m^2$) of the nominal 12 Å-thick porphine film before the electrochemical treatment. (a) Topography ($4 \times 2 \mu m^2$). The profile scan (white line) of the 3-D structures is reported in the image. (b) Phase-contrast image ($4 \times 2 \mu m^2$). We attribute the light blue areas to the 3-D phase, while the dark blue parts can be ascribed to the 2-D phase. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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