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Electrochemical and Spectroelectrochemical Study of Reduction of Oxygen on Cobalt Phthalocyanines

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There is a vast amount of work on the modification of electrode surfaces using metal phthalocyanine due to their ability to catalyze electrochemical processes such as the reduction of oxygen. In this study, the electrochemical activity of cobalt phthalocyanine, as a monolayer adsorbed on gold (111) single crystal surface, was investigated in perchloric acid aqueous solution. The monolayers have an electrochemical activity similar to that reported for their thin films counterparts[1]. The reduction of molecular oxygen, on the modified gold (111) surfaces was probed by cyclic voltammetry (CV), in situ scanning tunneling microscopy (STM), and in situ Surface enhanced Raman spectroscopy (SERS). The voltammetric results revealed an enhancement in the reduction current in the presence of the adsorbed monolayers (Figure 1), which points to a significant catalytic role of the adsorbed molecules in the reduction reaction, over the bare gold surfaces, as reported previously[2,3]. While there are several reports of the structure of the adsorbed CoPc monolayer at electrode surfaces[2], there are no investigations of structure of the CoPc layer in the presence of O_2. STM imaging of the film in the presence and the absence of molecular oxygen shows changes in the image features when oxygen is present. The STM measurements show that for a 1:1 CoPc:H_2Pc adlayer, only the CoPc molecules undergo structural and/or electronic changes during course of the oxygen electrolysis. If these changes are structural, they could be due to the formation of adsorbed phthalocyanine intermediates containing neutral or protonated oxygen molecules[3]. The effect of the tip bias also needs to be considered to assess if the changes are electronic in origin. To help us understand this process, the proposed intermediates were treated theoretically by means of density functional theoretical (DFT) calculations. The CoPc intermediates were studied in the gas phase and in an aqueous-like medium, with the hope of obtaining frontier orbitals that can then be compared with the shape of electron densities observed in the STM measurements. This is based on the postulate that tunneling between the modified surface and the STM tip occurs via one of the frontier orbitals of the adsorbed intermediates[4].

In addition, in situ SERS at a roughened gold electrode were acquired. Raman spectra with and without oxygen were gathered from the same area on the electrode surface as a function of potential. The potential range was selected based on the CV obtained for a CoPc modified roughened polycrystalline gold electrode. Figure 3 shows the Raman spectra for a CoPc modified roughened gold electrode for one of the potentials studied, i.e., -200 mV_{SCE}, in the absence and presence of oxygen. The data supports the formation of a PcCo-OOH type intermediate but it is still unclear if oxygen reduction causes any reorientation of the CoPc molecules. Further analyses are on the way.

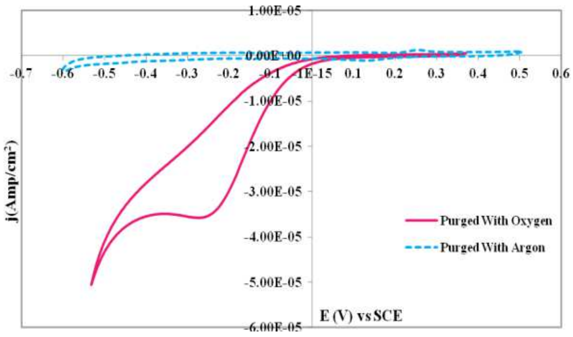

Figure 1: Cyclic Voltammograms of CoPc modified gold (111) electrode in 0.1 M $HClO_4$ aqueous solution, scan rate: 50 mV s^{-1}.

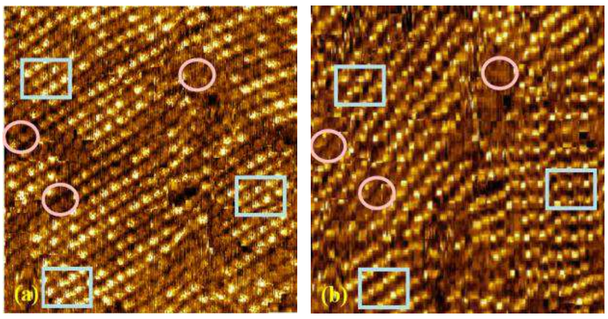

Figure 2: 30 x 30 nm^2 STM image of 1:1CoPc (indicated with squares):H_2Pc (indicated with circles) modified gold (111) electrode acquired in 0.1 M $HClO_4$ under a) argon, and b) oxygen.

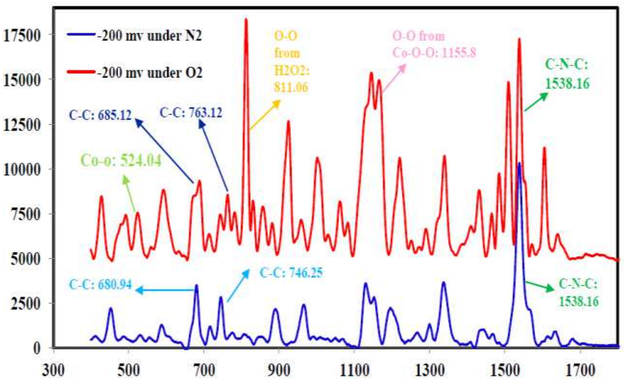

Figure 3: in-situ Surface Enhanced Raman Scattering spectra for CoPc modified roughened gold electrode at surface potential: -200 mv_{SCE} under argon (blue spectrum), and oxygen (red spectrum).

References

1 J. Zagal, M. Paez, A.A. Tanaka, J.R. Dos Santos Junior, C.A. Linkous, J. Electroanal. Chem. **1-2**, 13 (1992).
2 S. Yoshimoto, A. Tada, K. Suto, K. Itaya, J. Phys. Chem. B, **107**, 5836 (2003).
3 F.J. Beck, Appl. Electrochem. **3**, 239 (1977).
4 X. Lu, K.W. Hipps, X.D. Wang, U. Mazur, J. Am. Chem. Soc., **30** 7197 (1996).

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