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Oxygen Reduction Reaction monitoring at Iron Single Site Catalyst: Electrochemical Scanning Tunnelling Microscopy of Iron Octaethylporphyrin

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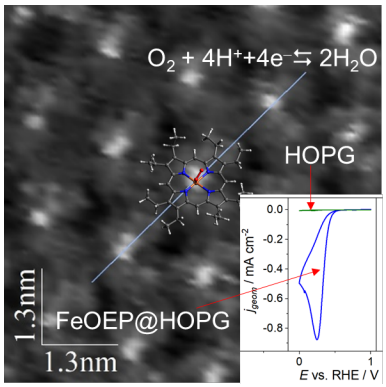
Porphyrins and phthalocyanines can accommodate transition metals giving birth to MN_4 sites, where M is the metal surrounded by four pyrrolic nitrogen atoms (N_4) located on the porphyrin ring. Metal porphyrins are herein exploited as mimicking systems of MN_4 active sites, which are currently employed in carbonaceous materials as valid alternative catalyst for oxygen reduction reaction (ORR) in PEM-fuel cells, in H_2O_2 electrogeneration or O_2 electrochemical sensors [1].



In this paper, iron(III) octaethylporphyrin chloride (FeOEP) and the parent free-base ligand are characterized by means of *in situ* electrochemical scanning tunnelling microscopy (EC-STM). The FeOEP adlayer was found to be stable when adsorbed on HOPG, even in the presence of an electrolyte (0.1 M $HClO_4$). The FeOEP@HOPG was employed as working electrode in a typical three electrode configuration cell, and at the same time the STM tip was allowed to scan the surface for monitoring the electrocatalysis of O_2 on metal-porphyrins active site. FeOEP@HOPG resulted active versus ORR and, guided by voltammetric measurements, it was possible to observe, through the STM, i) the stability of the FeOEP at different applied potential, ii) the Fe^{III}/Fe^{II} redox transition and iii) the phenomena of adsorption and reduction of oxygen at the metal center. In particular O_2 is visible as a bright spot in shifted position with respect to molecular center, indicating the adsorption of a O_2 in an end-on configuration onto the Fe-catalytic site. The number of transferred electrons and the energetics of ORR intermediates at FeOEP@HOPG were determined by rotating ring disk electrode and DFT / MD analysis, respectively.

[1] G. Wu, Current challenge and perspective of PGM-free cathode catalysts for PEM fuel cells, Frontiers in Energy. 11 (2017) 286–298.