Squaric acid adsorption and oxidation at gold and platinum electrodes

William Cheuquepán, Jorge Martínez-Olivares, Antonio Rodes, José Manuel Orts

PII: S1572-6657(17)30725-7
DOI: doi:10.1016/j.jelechem.2017.10.023
Reference: JEAC 3583

To appear in: *Journal of Electroanalytical Chemistry*

Received date: 28 July 2017
Revised date: 6 October 2017
Accepted date: 10 October 2017

Please cite this article as: William Cheuquepán, Jorge Martínez-Olivares, Antonio Rodes, José Manuel Orts , Squaric acid adsorption and oxidation at gold and platinum electrodes. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. Jeac(2017), doi:10.1016/j.jelechem.2017.10.023

Squaric acid adsorption and oxidation at gold and platinum electrodes

William Cheuquepán[b], Jorge Martínez-Olivares, Antonio Rodes[a,b,*], José Manuel Orts[a,b]

[a] Departamento de Química Física and [b] Instituto Universitario de Electroquímica

Universidad de Alicante

Apartado 99, E-03080 Alicante, Spain

*Corresponding author

E-mail: Antonio.Rodes@ua.es

Phone and fax: 965909814

Abstract

The adsorption and oxidation of squaric acid (3,4-dihydroxycyclobut-3-ene-1,2-dione, $H_2C_4O_4$, SQA) at platinum and gold electrodes were studied spectroelectrochemically in perchloric acid solutions. Voltammetric experiments demonstrate that reversible adsorption takes place at gold electrodes in the double-layer region. As a difference with platinum electrodes, no dissociative adsorption processes leading to the blocking of the electrode surface are detected. ATR-SEIRAS experiments show potential-dependent adsorbate bands at potentials below 1.20 V RHE that, according to DFT calculations, can be assigned to adsorbed squarate. For platinum electrodes, the potential-dependent adsorption of squarate anions is coupled with the oxidative stripping of adsorbed carbon monoxide, which is formed upon dissociative SQA adsorption. Bonding of squarate species to the platinum and gold surfaces involves two oxygen atoms in a bidentate configuration, with the molecular plane perpendicular to the metal surface. The ATR-SEIRA spectra obtained for gold electrodes in the SQA oxidation region show bands for adsorbed bicarbonate anions formed from dissolved carbon dioxide molecules. In the case of platinum, distinct bands are observed for adsorbed oxidation products which probably are formed upon opening of the SQA ring.

Keywords: squaric acid; squarate anions; platinum; gold; thin film electrodes; ATR-SEIRAS; DFT