

ELECTROCHEMICALLY FORMED FILMS OF QUATERNARY PYRIDINIUM COMPOUNDS

Jennifer E. Wong, Viola I. Birss
and David T. Cramb

Department of Chemistry
University of Calgary
Calgary, AB Canada
T2N 1N4

INTRODUCTION

Quaternary pyridinium compounds, or "quats," are known to be effective corrosion inhibitors for the oil and gas industry¹ but little is established about the adsorption behaviour of these compounds.

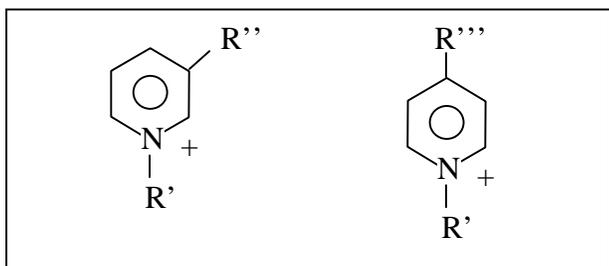


Figure 1 – General structure of quat inhibitors

In prior work, the adsorption of several standard quats was studied at Pt electrodes in slightly basic solutions, ca. pH 10-11.^{2,3} It was shown that exposure of these surfaces to solutions containing these quats led to the suppression of oxide film formation and of the adsorption of hydrogen. Also, it was shown that the chain length of the attached R group at the meta position of the pyridinium ring greatly influences the extent of adsorption of the quat on to a surface. It was also found that thicker quat overlayers could form as a result of their electrochemical reduction at potentials near -1.0 V vs. SSCE, and a mechanism was proposed for this process.^{2,3}

The kinetics of quat adsorption for a broader range of quats with varying lengths and positions of R groups was also reported⁴, as well as the effect of the substrate (oxide coated vs. metallic) on quat deposition. In general, quats that have alkyl side chains of C₈-C₁₂ deposited rapidly to completely suppress Pt electrochemistry. It was also reported that the presence of the oxide film is necessary for quat deposition.

In the present work, the morphology and structure of the quat overlayers was the main focus. The overlayers are formed by reduction of quats after initial blocking of the Pt electrochemistry. Figure 1 shows the basic structure of the quats tested in this work.

EXPERIMENTAL

The working electrodes consisted of Pt sputter-deposited onto a Ti-coated glass substrate (apparent area ca. 0.5 cm² or 0.75 cm²). The counter electrode consisted of Pt gauze while the reference electrode was a SSCE. Ellipsometry experiments were carried out on a Gaertner L116C ellipsometer. All AFM images were obtained by contact mode and MacMode in air and were obtained using a Molecular Imaging PICOAFM instrument.

RESULTS AND DISCUSSION

Quats deposit onto the Pt substrate to block the hydrogen evolution reactions (HER) as well as the Pt oxide formation process. The potential can be reduced further without interference by HER. A new redox couple is observed when the potential is decreased and is attributed to the reduction and oxidation of the quat. The reduction of the quat results in the formation of a thicker layer (the overlayer) of quat on top of the blocking layer. Only certain quats exhibit the ability to form overlayers on Pt in a pH 7 buffer solution. Holding at the peak potential of the reduction peak forms thicker overlayer films.

Ellipsometry, optical microscopy and atomic force microscopy (AFM) were used to study the films formed by the electrochemical reduction of the quat. Ellipsometry measured the average thickness of the film as it grew with holding time. Optical microscopy images were recorded periodically as the overlayer film was grown. From the images it is apparent that the film does not grow uniformly across the surface. Rather the film consists of many islands of quat with each island varying in diameter. The AFM images reveal the thickness of the quat islands. The thickness may give an indication of the extent of quat deposition as a function of holding time.

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