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A Study on the Affinity of Fe^{2+} and Zn^{2+} for Im-SH Self-Assembled Film on Piezoelectric Quartz Crystal

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In this work, the affinity of Fe^{2+} and Zn^{2+} for Im-SH group were investigated in the electrolyte solution of $FeCl_2$ and $ZnCl_2$ using quartz crystal analyzer (QCA). Imidazolyl-Alkanethiol (Im-SH) was coated on a side of quartz crystal electrode by the process of self-assembly. The result shows that the reaction of Zn^{2+} for Im-SH film is stronger them that of Fe^{2+} and the substitution reaction rises on (Im-SH)-Fe^{2+} film in the electrolyte solution of $ZnCl_2$, whereas the (Im-SH)-Zn^{2+} film is stable in the electrolyte solution of $FeCl_2$.

Keywords: Imidazolyl-Alkanethiol; QCA; self-assembly; affinity

INTRODUCTION

Self-assembled monolayers (SAMs) of alkanethiols on gold have been the subjects of numerous studies[1-2] because they have wide varieties of potential applications such as sensors, corrosion inhibition, biomolecular and molecular electronic devices. Although it is generally believed that SAMs of alkanethiols are formed as the result of the chemical bond between substrate atoms and sulfur atoms of thiols, and hydrophobic interaction between alkyl chains, their growth process is not studied well. Im-SH group, mainly

detected in histamine and histidine molecule, performs many important actions[3] in human-being. In this work, the affinity of Fe^{2+} and Zn^{2+} for an Im-SH self-assembled film on quartz crystal is compared by monitoring the electrochemical parameters such as frequency shift, potential and current.

EXPERIMENT

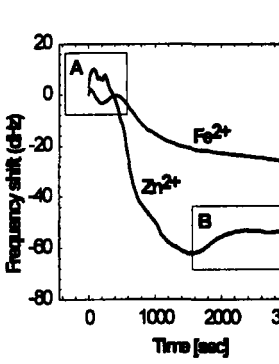

FIGURE 1 Comparison on the reaction of Im-SH film for Fe^{2+} and Zn^{2+} in phosporic buffer (pH 7).

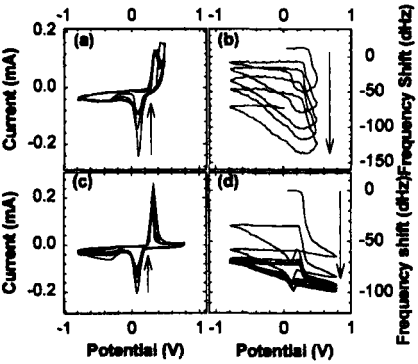

FIGURE 2 The cyclic voltammetry of (a), (b) (Im-SH)-Fe^{2+} film in 10^{-3} M $FeCl_2$/phosporic buffer (pH 7) and (c), (d) (Im-SH)-Zn^{2+} film in 10^{-3} M $ZnCl_2$/phosporic buffer (pH 7).

A 9 MHz, AT-cut quartz crystal with an Au electrode by the sputtering technique is used as a working electrode in a plastic resin cell exposing only one side of the electrode. Then, the quartz crystal is stabilized by the process of self-assembly in the solution of 0.03 g Im-SH and 20 ml N, N-dimethyl formamide under the condition of 30 °C and 300 rpm for 100 minutes. An

Ag/AgCl electrode and a platinum plate are used for a reference electrode and a counter electrode, respectively. All chemicals are obtained from Wako Pure Chemicals. A potentiostat (Solartoron, model 1286) and QCA (QCA917, Seiko, EG&G) are connected to a microcomputer (NEC, model PC-9801) to store the measured data and to control the apparatuses.

RESULTS AND DISCUSSION

Figure 1 compares the reaction of Fe^{2+} and Zn^{2+}, respectively, for an Im-SH film in phosporic buffer (pH 7) only using QCA. That the reaction of Zn^{2+} for the Im-SH film is stronger is shown by the comparison of the frequency shift on two different ions even though the molecular weight of Zn is a little larger than that of Fe. In the case of Zn^{2+}, the frequency shift is increased temporarily in the region of A and B. It is estimated that the combination body of Im-SH film and Zn^{2+} gets loose slightly on quartz crystal due to the weakness of bond force with the weight increase. Figure 2 shows the result of cyclic voltammetry of the (Im-SH)-Fe^{2+} film in 10^{-3} M $FeCl_2$ and the (Im-SH)-Zn^{2+} film in 10^{-3} M $ZnCl_2$, respectively for the stabilization of the (Im-SH)-Fe^{2+} film and the (Im-SH)-Zn^{2+} film. In Figures 2(a) and (b), the scale of reduction peak is decreased gradually with the cycle and the frequency shift is decreased by the effect of Cl^- at anion region. Figures 2(c) and (d) are the results of cyclic voltammetry in 10^{-3} M $ZnCl_2$/phosporic buffer (pH 7). If the redox peak is gradually decreased and the frequency shift is decreased, the (Im-SH)-Zn^{2+} film is more stable than the (Im-SH)-Fe^{2+} film. In order to identify the affinity difference of two different metal ions for the Im-SH film, the cyclic voltammetry of (Im-SH) film is established two times continuously in the mixture solution of 10^{-3} M $FeCl_2$ and 10^{-3} M $ZnCl_2$. In

Figures 3(a) and (b), the oxidation peaks of the two metal ions appear and the frequency shift varies about 140 Hz. The result of the continuous experiment in the same solution as shown in Figure 3(c) is nearly similar to the result of Figure 2(c). It can estimate that the binding force of Zn^{2+} and Im-SH film is not stronger than that of Fe^{2+}.

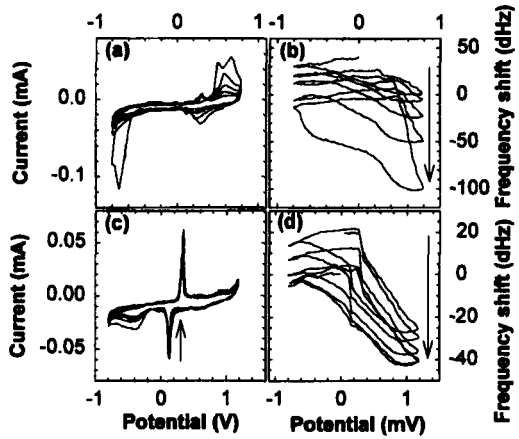

FIGURE 3 The cyclic voltammetry of (a), (b) (Im-SH) film in 10^{-3} M $ZnCl_2$ and 10^{-3} M $FeCl_2$, and (c), (d) repetiton in the same condition.

Acknowledgments

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