Mass Transport on a Clay-modified Electrode as Studied by Quartz Crystal Microbalance Method

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The quartz crystal microbalance method was applied to examine mass transport processes in the redox reactions of $[Ru(bpy)_3]^{2+}/[Ru(bpy)_3]^{3+}$ (bpy=2,2'-bipyridyl) in a clay modified electrode, and it was concluded that the oxidation of three $[Ru(bpy)_3]^{2+}$ molecules in a clay film was accompanied with the elimination of one $[Ru(bpy)_3]^{3+}$ molecule.

An electrode coated with a thin clay film (a clay-modified electrode) has been investigated because of its potential utility for electrocatalytic reactions.[1] A clay-modified electrode becomes electroactive after the incorporation of a metal complex which undergoes a redox reaction. One of the unsolved problems is that only a small fraction of a bound species (2-7%) is electroactive when a metal complex such as $[M(phen)_3]^{2+}$ (phen=1,10-phenathroline) and $[M(bpy)_3]^{2+}$ (bpy=2,2'-bipyridyl) is incorporated in a film.[1b] In the present study, the electrochemical quartz crystal microbalance (EQCM) method was applied to elucidate mass transport processes during cyclic voltammetry.[2]

A clay-modified electrode was prepared by casting 60μl of an aqueous suspension of synthetic saponite (Smecton; Kunimine Ind.Co.(Japan)) (0.35g/L) on a gold coated quartz crystal (0.43 cm^2), and dried at room temperature for 24h. The EQCM measurements were performed at the fundamental frequency of 6MHz, using an instrument as described previously.[3] A platinum foil and a Ag/AgCl/NaCl (satd) electrode were used as a counter and a reference electrode, respectively. The decrease of frequency, Δf, was related to the increase of mass of the electrode as: $\Delta M(\text{ng cm}^{-2})=12.3(\text{ng cm}^{-2}\text{Hz}^{-1})\Delta f(\text{Hz})$.

The upper part of Figure 1 shows the results when a cyclic voltammogram was measured for a solution containing 0.01M of Na_2SO_4 and 5.00×10^{-5}M of $[Ru(bpy)_3]SO_4$ after the clay modified electrode had been soaked in the same solution for about 50h. The frequency change was measured simultaneously as shown in the lower part of Figure 1. As for the current change, the oxidation and reduction peaks were observed at 1180mV and 1080mV versus Ag/AgCl/NaCl(satd), respectively. These peak positions were almost in the same range using a bare glassy carbon electrode. Thus it was concluded that they corresponded to the reversible oxidation and reduction reactions of bound $[Ru(bpy)_3]^{2+}$, respectively:

$$[Ru(bpy)_3]^{2+} \rightleftarrows [Ru(bpy)_3]^{3+} + e^-$$

In the positive-going potential scan, the frequency increased monotonously in the potential range from 900mV to 1300mV. From the impedance measurement, we confirmed that the resistance of the equivalent circuit of the quartz crystal remained constant in this potential range. Thus the frequency increase was ascribed to the interfacial mass loss at the EQCM electrode. Figure 2 shows the plot of the frequency change against charge during the positive-going scan. At the maximum slope of the curve, the total mass change per mole of charge ($\bar{m}$pe) was calculated to be -194g/eq. It is noted that this value is close to

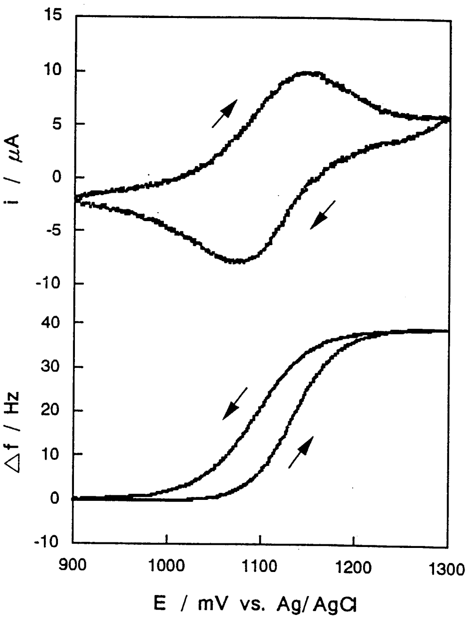

Fig.1. The cyclic voltammogram of a clay-modified electrode incorporated with $[Ru(bpy)_3]^{2+}$ (upper) and the simultaneously recorded frequency change (lower). Sweep rate was 10mV/s.

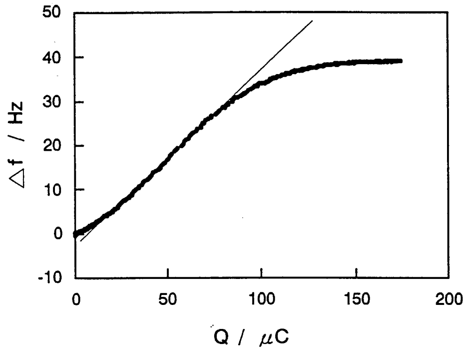

Fig.2. The plot of frequency versus charge for the cyclic voltammogram as shown in Fig.1.

one-third of the molecular weight of $[Ru(bpy)_3]^{2+}$ (569g/mole). We postulate that one $[Ru(bpy)_3]^{3+}$ molecule is eliminated from the electrode for each three oxidized $[Ru(bpy)_3]^{3+}$ ions. This ejection occurs in order to balance the excess positive charge generated in the film. Based on the present results, the redox reaction occurs only when a part of the oxidized metal complexes are eliminated from the film. This might be one of the reasons that only a small fraction of bound species is electroactive in a clay film.

References and Notes

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