EIS study on Copper Electrodepositon -Roles of MoO_4^{2-} as an Additive into Electrolyte Solution-

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The copper electrodeposition has been used to fabricate the microscopic trace and electronic devices. The solutions which contain $CuSO_4$ and H_2SO_4 were the most common solution for the copper electrodeposition. Some additives are generally mixed in this solution to control the electrodeposition on the electrode [1, 2]. Recently, there were a lot of reports regarding the effect of inorganic additives on the electrodeposition of copper [3, 4]. However, the details of the roles of the copper electrodepositon in the acid solutions containing inorganic additives have not been clarified yet. In this study, the copper electrodeposition in the acid solutions which contain MoO_4^{2-} was investigated by EIS to reveal the effect of MoO_4^{2-} on the electrodeposition of copper.

The electrochemical measurements were carried out using RDE. The working electrode was the Cu which was electrodeposited on the Pt disk electrode using RDE with two electrode system. The counter electrode was a Pt wire and reference electrode was a KCl-saturated silver/silver chloride electrode (SSE). All measurements were carried out at 25 ^oC. The cathodic polarization curve was measured from the open circuit cell potential to -0.4 V vs. SSE. The scan rate was 100 mV s^{-1} and the rotating speed of RDE was 500 rpm. The compositions of test solutions were 5×10^{-5} mol/cm^3 $CuSO_4$ and 2×10^{-3} mol/cm^3 H_2SO_4 contanig various concentrations of Na_2MoO_4 (1×10^{-5} mol/cm^3, 1×10^{-6} mol/cm^3 1×10^{-7} mol/cm^3, 1×10^{-8} mol/cm^3 Na_2MoO_4) to evaluate the effect of MoO_4^{2-}. Impedence spectra were measured in the frequency range from 10 mHz to 10 kHz at five frequencies per decade with AC amplitude of 10 mV. The applied DC potential difference was -0.05, -0.10, -0.20 and -0.25 V vs. SSE. The concentrations of test solutions were 5×10^{-5} mol/cm^3 $CuSO_4$ and 2×10^{-3} mol/cm^3 H_2SO_4 contaning 1×10^{-6} mol/cm^3 Na_2MoO_4.

The cathode polarization curves of Cu electrode are shown in Fig. 1. The current densities measured in the acid solutions containing MoO_4^{2-} is larger than that without additives from open circuit potential to -0.2 V. However, the current densities which were measured in those solutions are same from -0.2V to -0.4 V. It indicated that MoO_4^{2-} enhanced the Cu electrodeposition from open circuit potential to -0.2 V and didn't enhance from -0.2 V to -0.4 V.

The impedance spectra of Cu electrodeposition at -0.2 V were shown in Fig. 2. The impedance spectra which were measured in the solution containing no additives shows capacitive loop related to the time constant of charge transfer resistance and electric-double layer capacitance in the high frequency range and straight line (gradient 45^o) related to diffusion of Cu ion in the intermediate frequency range. The loop in the low frequency range is related to adsorption of Cu ions on the electrode.

On the other hand, the impedance spectra which were measured in the solution containing MoO_4^{2-} in Fig. 2 show capacitive loop related to the time constant of charge transfer resistance and electric-double layer capacitance in the high frequency range. The loop in the low frequency is related to adsorption of Cu ion and MoO_4^{2-} on the electrode. Impedance spectra which were measured in the solution containing MoO_4^{2-} show negative resistance.

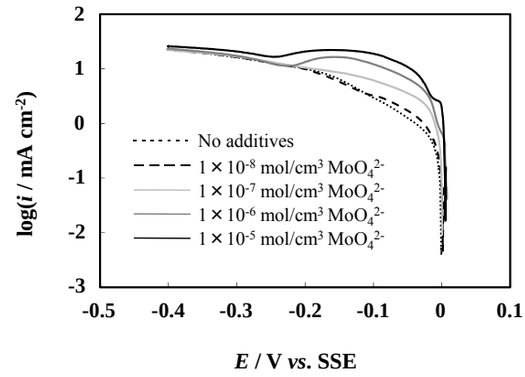

Fig. 1 The cathodic polarization curves of Cu electrode.

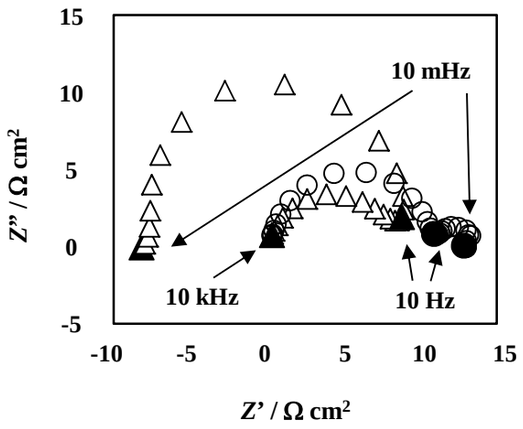

Fig. 2 The impedance spectra at -0.2 V in no additives and 1×10^{-6} mol/cm^3 MoO_4^{2-} solutions;
○: No additives, △: MoO_4^{2-} 1×10^{-6} mol/cm^3

References

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