Phase-separation between conductive and insulative materials under the static electric field: Modeling for Ag and Sb spatiotemporal patterns on the electrode surface

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In the Ag and Sb co-electrodeposition system, in which Ag and Sb atoms consistently accumulate on an electrode surface from a solution during electrodeposition [1, 2], various spatiotemporal patterns are formed on the electrode surface depending on the experimental conditions. All of the patterns consist of light and dark stripes. According to our static element analysis [3], the light and dark stripes of the pattern have been reported to be rich in Ag and Sb, respectively. It indicates that the phase separation of Ag and Sb in the electrodeposition system was suggested as a plausible pattern formation mechanism.

Moreover, to validate the phase separation as a main mechanism, in this study, the difference between resistivities of Ag and Sb is considered. The resistivity for Sb is 25 times larger than that of Ag. The results suggest that the spatiotemporal pattern is composed of two types of stripes with different resistivities (the Ag-rich "conductive" light stripe and the Sb-rich "insulative" dark stripe).

From this view point, assuming the mixed system of the conductive and the insulative materials under the steady electric field, dynamics of the concentration distribution was investigated through the numerical simulation. For such a dissipative system, the extended Cahn-Hilliard equation was formulated using the Onsager's variational principle [4].

$$\frac{\partial C_A(x,t)}{\partial t} = L\nabla^2\left(-\varepsilon^2\nabla^2 C_A(x) + \frac{dW}{dC_A(x)}\right) + L\nabla^2 \frac{d\bar{f}(\{C_A(x)\})}{dC_A(x)}$$

$$\int \bar{f}(\{r(x)\},t)dx = R \cdot I^2$$

C_A is a concentration for an insulative material. L and ε are constants. For W, the Ginzburg-Landau style is used. $\bar{f}$ is a function which spatially averages the local resistance. R and I are an entire resistance and a current, respectively.

The calculation result shows that the phase separation of the conductive and the insulative materials is induced under the constant current mode, but is suppressed under the constant voltage mode.

According to our experimental observation in the Ag and Sb electrodeposition system, the pattern emerges in the wide range of the current values under the constant current mode. On the other hand, under the constant voltage mode, the pattern rarely appears. This experimental tendency is coincident with my calculation result of this study with the extended Cahn-Hilliard equation.

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