

Electrochemical Deposition of Silver on Gold Electrodes in the Presence of Halogen Ions

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Electrochemical reactions of silver in the presence of chloride and bromide ions were examined using cyclic voltammetry (CV) and electrochemical quartz-crystal microbalance measurements. In the presence of chloride ions, repeated CV cycles caused AgCl to deposit on the electrode. In contrast, reduction of silver ions in the presence of bromide ions to form metallic silver was very slow, and AgBr was not deposited on the gold electrode.

The electrochemistry of silver is important because of its numerous applications. In the presence of halogen ions (X^-), silver ions can form several kinds of complexes: AgX , AgX_2^- , and AgX_3^{2-} . In the case of a chloride or bromide solution of moderate concentration, for example, 0.1 M KCl, the major species present in the solution is $AgCl_2^-$ (see Figure S1 in the Supporting Information; SI¹¹). AgX is insoluble in aqueous solution but dissolves if AgX_2^- is formed. The influence of these complexes should be taken into account to understand the electrochemical properties of silver. The electrochemistry of silver has been examined with regard to its use in metal plating.^{1–3} However, little is reported about the electrochemical reactions of Ag, AgX , and AgX_2^- . Skompska et al. obtained cyclic voltammetry (CV) and electrochemical quartz-crystal microbalance (EQCM) measurements for silver in the presence of chloride ions.⁴ The EQCM measurements provided quantitative information about the complicated redox reactions in acetonitrile that contained formation of $AgCl$, its dissolution as $AgCl_2^-$, and reduction of these species to deposit metallic silver.

We previously reported that uniform silver shells could be formed on gold nanorods in chloride solution.⁵ In contrast, in bromide solution, the reduction of silver ions was very slow, and the shapes of the shells could not be controlled.^{5,6} Thus, the electrochemical reactions of silver were significantly affected by the halogen ions. Another important factor is adsorption of halogen ions on an electrode surface. It is known that halogen ions interact strongly with gold surfaces.^{7,8} Quantitative evaluation of the redox reactions of silver on a gold electrode can provide basic information to understand the deposition of metallic silver on gold electrodes and nanoparticles in the presence of halogen ions.

In this work, we studied the effects of chloride and bromide ions on the redox reactions of silver on gold and glassy carbon (GC) electrodes in aqueous solutions. The deposition and dissolution processes of metallic silver and $AgX \cdot AgX_2^-$ were revealed by in situ EQCM measurements.

An electrochemical analyzer equipped an EQCM system (HZ-5000, Hokuto Denko) was used for electrochemical

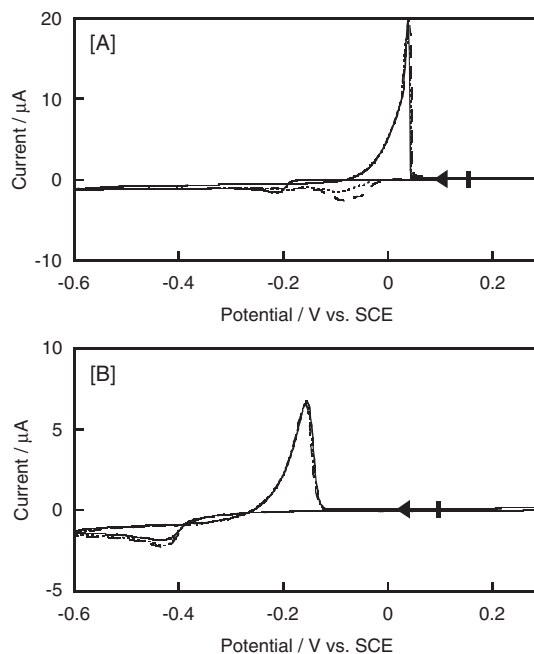


Figure 1. CVs using a GC disk electrode in 1 M KCl (A) and KBr (B) solutions containing 0.1 mM Ag ions.

measurements. In situ EQCM measurements were performed using a 10 MHz AT-cut quartz tip. All reagents were commercially available and used without further purification.

Figure 1 shows CVs of solutions containing $AgNO_3$ and either KCl or KBr using a GC disk electrode. In these solutions, silver ions form AgX_2^- (and $AgX_n^{(n-1)-}$) complexes (see SI¹¹). No precipitate formed in either solution. In the case of the KCl solution, potential sweeps were started at +0.17 V vs. SCE in the negative direction using a sweep rate of 80 mV s^{-1} . The first sweep (solid line) gave cathodic and anodic peaks at -0.20 and $+0.04$ V vs. SCE, respectively. The cathodic peak corresponded to the reduction of $AgCl_2^-$ to form a metallic silver layer on the GC electrode. The anodic peak arose from the oxidation of this silver layer. In the second and third sweeps, the anodic peak remained at $+0.04$ V vs. SCE, but new peaks appeared at around -0.1 V vs. SCE in the cathodic sweeps. These are the reduction peaks of $AgCl$ formed by oxidation of the metallic silver on the GC electrode.⁴

In the case of the KBr solution, the sweep was started at $+0.1$ V vs. SCE in the negative direction. No peak was found at the position corresponding to reduction of $AgBr$, even for the

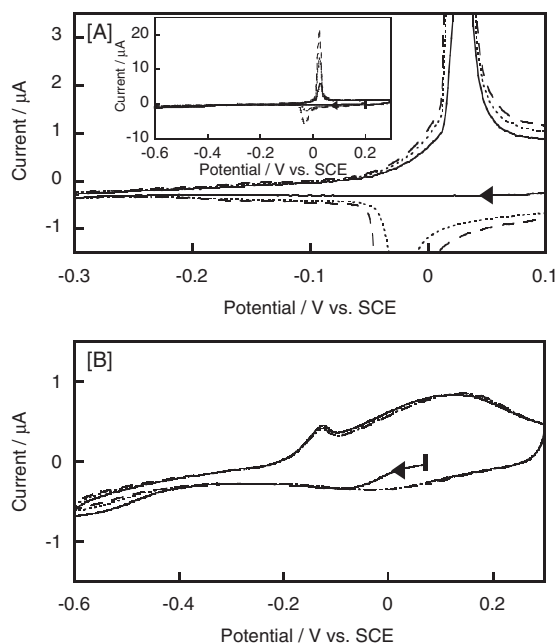
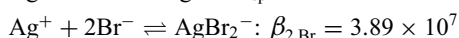
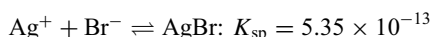
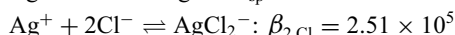
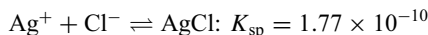


Figure 2. CVs using a gold disk electrode in the 1 M KCl (A) and KBr (B) solutions containing 0.1 mM Ag ions. The inset in (A) shows full range of CVs.

second and third sweeps. The solubility products of AgX and stability constants of AgX_2^- are listed below.^{9,10}



The large $\beta_{2,\text{Br}}$ indicates that the water-soluble AgBr_2^- readily formed in the presence of 1 M KBr, and insoluble KBr did not accumulate at the electrode surfaces. In the case of the KCl solution, $\beta_{2,\text{Cl}}$ is smaller than $\beta_{2,\text{Br}}$. Therefore, soluble AgCl_2^- hardly formed at the electrode surface when silver ions were provided at once at the oxidation potential of metallic silver.⁴ Due to the limited diffusion of the ions at the electrode surfaces, the silver ions formed AgCl instead of AgCl_2^- during the oxidation of the silver layers. Thus, the repeating sweeps in KCl solution caused AgCl to deposit on the electrode.

Figure 2 shows CVs of silver in KCl and KBr using a gold disk electrode. In the KCl solution, the sweep started at 0.2 V vs. SCE in the negative direction. The first sweep (solid line) did not show a significant cathodic peak, but an anodic peak was found at 0.03 V vs. SCE. This indicated that reduction of silver ions was controlled by electrical charge transfer at the electrode. In the second and third sweeps, cathodic peaks arising from the reduction of AgCl appeared at -0.03 V vs. SCE. No significant reduction peak was observed in KBr solution. This indicates that the redox reactions of silver ions at a gold electrode in the presence of KBr were very slow. It is known that bromide ions interact strongly with gold.^{7,8} The bromide anions form a static layer on gold surface and suppress the reduction of anionic AgBr_2^- through electrostatic repulsion. In contrast, chloride ions

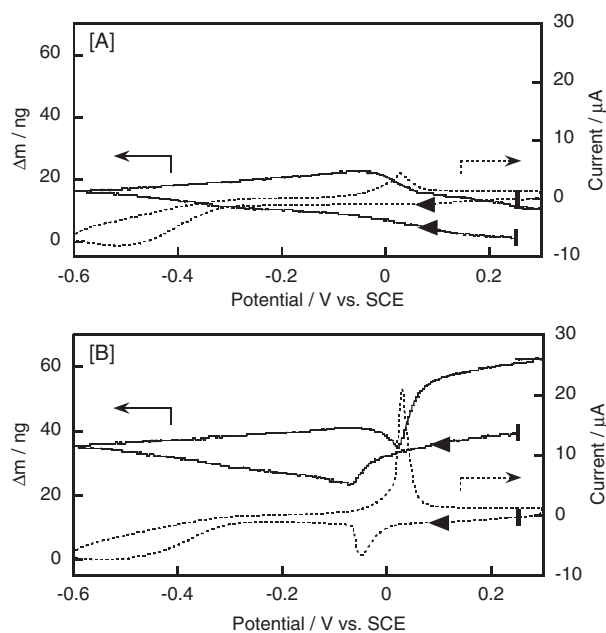


Figure 3. Changes in the mass of a gold electrode studied by EQCM measurements (solid lines) and CVs (dotted lines) in 1 M KCl solution containing 0.1 mM Ag ions. First (A) and third (B) sweeps are shown.

are probably dynamic on gold surface and do not form a static layer that suppresses the reduction of anionic AgCl_2^- .

Figure 3 shows EQCM measurements of the redox reactions of silver in the presence of KCl (1 M). The first sweeps (a set of cathodic and anodic sweeps) Figure 3A and the third sweeps Figure 3B are shown with the corresponding CVs. The solid lines are the changes in mass during CV experiments, while the dotted lines are the CVs. The initial potential was +0.25 V vs. SCE, and the sweeps started in the negative direction. Total mass changes are shown in Figure S2 (SI).¹¹ In the first cathodic sweep, the mass of the electrode increased almost monotonically until -0.6 V vs. SCE. This increase was about 120 g F^{-1} and indicates deposition of metallic silver on the electrode. Because the deposited metallic silver worked as an electrode, the reduction proceeded continuously during the cathodic sweep. The peak in the CV at around -0.5 V vs. SCE does not originate from the reduction of silver ions because it does not change the mass of the electrode. In the anodic sweep, the mass also increased until -0.05 V vs. SCE because of the successive reduction of silver ions. The deposited metallic silver was not oxidized in this potential range. The same silver deposition in anodic sweeps was reported in the previous work.⁴ In the following sweep, the mass decreases after -0.05 V vs. SCE, and an anodic peak is observed at +0.03 V vs. SCE. These changes correspond to the oxidation of the metallic silver layer. The charge of the anodic peak was 130 pF, and the decrease of the mass was 65 pmol. This inconsistency indicates that some silver ions remained on the electrode as AgCl. The subsequent decrease of the mass in the anodic sweep from +0.08 to +0.3 V vs. SCE probably originates from the dissolution of AgCl by conversion into AgCl_2^- . The rate of the decrease of mass would be controlled

by the diffusion of Cl^- onto the electrode from the bulk solution.

In the third sweep (Figure 3B), a continuous decrease of mass that can be assigned to the reduction of AgCl was observed from $+0.22$ to -0.07 V vs. SCE. From -0.05 to -0.08 V vs. SCE, the mass decreased rapidly. This decrease originated from the reduction of AgCl on the electrode and the release of Cl^- from the electrode. The following sweep from -0.08 to -0.6 V vs. SCE showed monotonic deposition of metallic silver from AgCl_2^- in the bulk solution. In the anodic sweep, the deposition of metallic silver was also observed as a monotonic increase of the mass until -0.05 V vs. SCE. From -0.05 to $+0.01$ V vs. SCE, the mass decreased rapidly. This is caused by the oxidation of metallic silver into AgCl_2^- .⁴ The following increase of mass was assigned to the deposition of AgCl . Because of the lack of Cl^- at the electrode interface, the Ag^+ ions formed insoluble AgCl instead of AgCl_2^- , and the AgCl was deposited on the electrode surface. Thus, the mass changes after the oxidation of the metallic silver ($> +0.08$ V vs. SCE) were controlled by the diffusion of chloride ions at the electrode surfaces. The increase of mass is assigned to the deposition of AgCl ($\text{AgCl}_2^- + \text{Ag}^+ \rightarrow 2\text{AgCl}_2$), whereas the decrease is assigned to the dissolution of AgCl ($\text{AgCl} + \text{Cl}^- \rightarrow \text{AgCl}_2^-$). After finishing the third sweep at $+0.25$ V vs. SCE, 60 ng of AgCl was deposited on the electrode. The deposition of AgCl contributed the large peak current.

In the case of bromide (Figure 4), the CV measurements were started at $+0.18$ V vs. SCE in the negative direction. In the first cathodic sweep (shown in Figure 4A), the mass increased monotonically in the range from $+0.1$ to -0.6 V vs. SCE. This indicated deposition of metallic silver at the electrode. The cathodic current observed in the range from -0.4 to -0.6 V vs. SCE did not originate from the deposition of metallic silver. In the anodic sweep, deposition occurred until -0.2 V vs. SCE. The continuous decrease of the mass from -0.2 to $+0.25$ V vs. SCE was assigned to the oxidation of metallic silver and its dissolution as AgBr_2^- . In the third sweep (shown in Figure 4B), similar profiles were obtained in the EQCM and the CV measurements. It should be noted that the mass at $+0.18$ V vs. SCE did not change in the third sweep (see also Figure S2 in SI¹¹). This indicated that AgBr did not accumulate on the electrode; instead AgBr_2^- formed in the anodic sweeps and diffused in the solution.

The EQCM measurements allow the redox reactions of silver on gold electrodes to be understood more clearly. In the presence of chloride ions, AgCl was deposited on the electrode. Because bromide has a larger complex formation constant for the formation of AgBr_2^- than chloride does for AgCl_2^- , AgBr was not deposited on the electrode. The redox reactions of silver on gold electrodes were much slower than those on GC electrodes. This probably originates from the adsorption of halogen ions on gold surfaces. Bromide suppressed the electrochemical reaction of silver on a gold electrode because of the lack of deposition of AgBr and the presence of adsorbed Br^- on the electrode. Such information regarding the redox reactions of silver in aqueous solutions containing halogen ions will contribute to allowing electrochemical reshaping or stabilization of silver nanoparticles on electrodes.

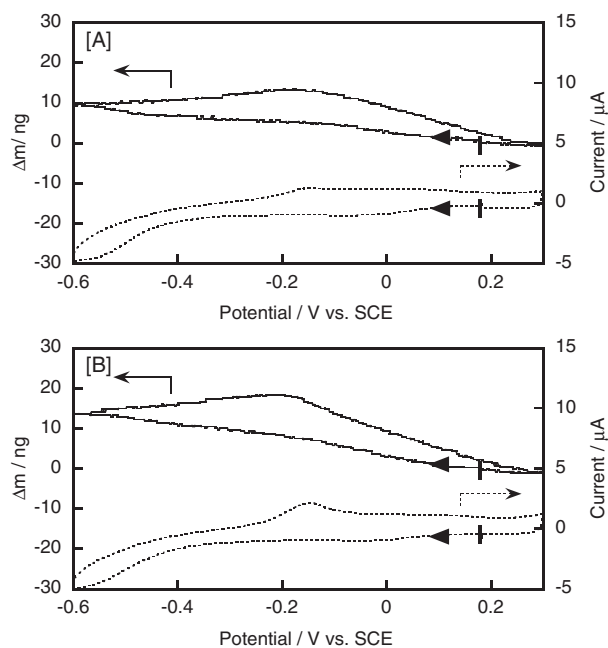


Figure 4. Changes in the mass of a gold electrode studied by EQCM measurements (solid lines) and CVs (dotted lines) in 1 M KBr solution containing 0.1 mM Ag ions. First (A) and third (B) sweeps are shown.

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