

In-Situ Investigation of the Growth of Silver Oxy-Iodide Popsicles: Part III

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In one week beam time assigned to this experiment, we could finalize the project and complete the previous experiments in order to determine the relative locations of AgI and Ag₂O and their reaction mechanisms [1-3]. In the two previous experiments we discovered that a: the silver oxide (Ag₂O) grown by anodic oxidation was extremely rough accompanied by partial metal (Ag) dissolution into the electrolyte and b: that the charge transferred during the oxidation was not only stoichiometrically proportional to the mass of the Ag₂O formed at the Ag/electrolyte interface but also it was potential dependant. In the current work we took the reverse approach in which the silver thin film electrode was first placed in KI solution and after growing AgI at different polarizations (from -0.1 to +0.1V_{SCE}), it was anodically oxidized at +0.25V_{SCE} for 120s.

The open circuit potentials at different experimental stages are shown in Figure 1. As seen, the E_{OC} monitored immediately after adding KI solution and before potentiostatic voltage application (black line) is ~-0.2V whereas the E_{OC} after applying -0.1V for 20 minutes increased slightly to ~-0.17V and remained constant afterwards (red line). This small increase in E_{OC} could be attributed to the incorporation of Cl⁻ ions released from the reference electrode and partial formation AgCl at the Ag electrode. Under the current condition the E_{OC} for Ag/AgCl (measured versus SCE) system was expected to appear in ~0.11 to 0.15V region [2]. According to the open circuit potential monitored before and after anodic oxidation at +0.25V, the dominant system after immersing Ag thin film electrode in 10⁻³M KI solution was Ag/AgI (black line in figure 1) with E_{OC}~-0.2V while after anodic oxidation (120s at +0.25V_{SCE}) the Ag/Ag₂O system with E_{OC}~+0.15V_{SCE} (Figure 1, blue line) was the main RedOx system. The stabilized E_{OC} monitored after anodic oxidation at +0.25V_{SCE} was measured +0.15V (blue line) which then dropped to ~+0.11V after 12 hours. This drop can also be assigned to the incorporation of Cl⁻ into the Ag₂O/Ag system and formation AgCl. After the first and second cathodic stripping voltammetry (CSV1 and CSV2) in which the

potential was scanned from +0.2 to -0.4 V_{SCE}, the E_{OC} was measured ~-0.17 V_{SCE}. This value indicated that the Ag₂O was reduced and replaced by AgI.

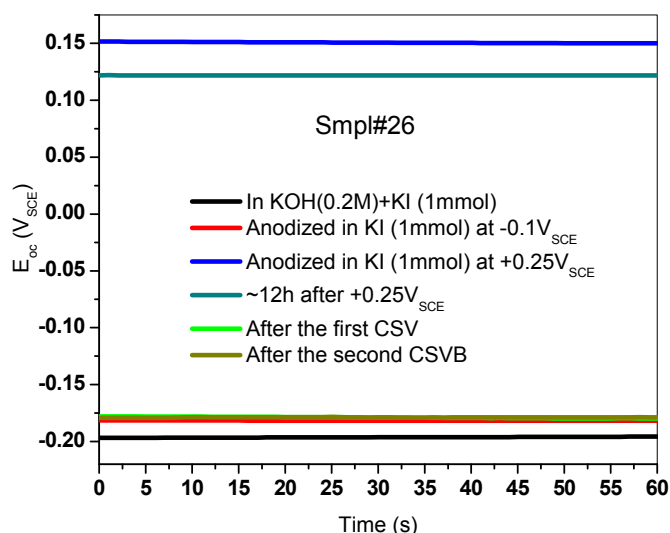


Figure 1 The open circuit potential (E_{OC}) of the silver electrode (sample #26) monitored at different experimental stages. The expected E_{OC} for the Ag/Ag₂O system at this experimental condition is ~0.15V_{SCE} whereas for the Ag/AgI is ~-0.2 V_{SCE}.

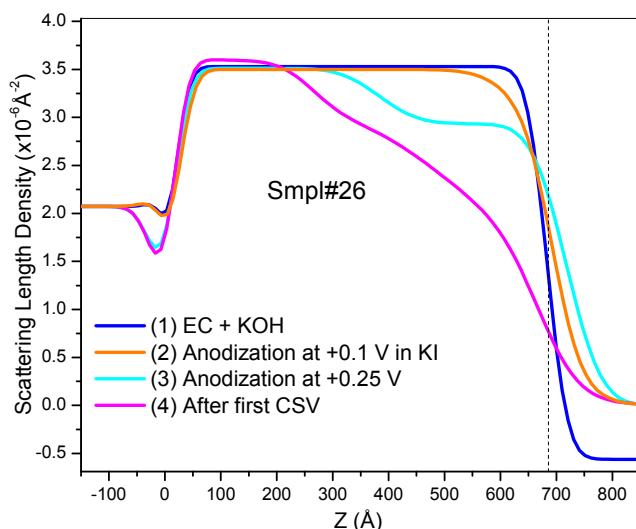


Figure 2 The SLD profiles proposed after fitting the NR data obtained from silver electrode (sample #26) at different experimental stages. Unless otherwise mentioned, the measurement was performed in empty electrochemical cell after draining solution.

The results of the Neutron Reflectometry (NR) data obtained at each step of the experiment are shown in Figure 2 as the overlay of their SLD profiles. The comparison between the SLD profiles in Figure 2 revealed that no significant change in the thickness of the Ag film was observed after applying -0.1 and +0.1V to the thin film Ag electrode in KI solution (comparison of the blue and orange curves). Although the change in the Ag film was not detected by NR, the roughness of the Ag/electrolyte interface increased significantly. This roughness is defined by the slope of the transition from one phase (in this case Ag layer) to another (electrolyte) in the SLD profile. If the AgI (SLD= $1.63 \times 10^{-6} \text{ \AA}^{-2}$) was formed with interfaces (e.g. Ag/AgI and AgI/electrolyte interfaces), the corresponding SLD profile would show a step at Ag/electrolyte interface. The absence of such distinct layer indicated that the formation of AgI at Ag electrode created a rough Ag/AgI interface where AgI diffused into both Ag and electrolyte layers. As the thickness of the Ag layer (orange curve) did not show any significant change, one could conclude that the less soluble AgI formed at the interface remained attached to the electrode and protected the Ag surface from further oxidation or dissolution. The SLD profile after anodic oxidation at +0.25V (cyan curve) showed a step with lower SLD at above $\sim 350 \text{ \AA}$. As the +0.25V was suitable for the formation of silver oxide [2,3], the lower SLD step in the corresponding SLD curve is assigned to the formation of Ag_2O . The change in the E_{OC} from -0.11V to $\sim +0.15\text{V}$ after anodic oxidation not only indicated that the Ag_2O was formed but also showed that the Ag_2O was formed underneath the AgI layer in contact with Ag metal. A similar value for E_{OC} was observed in our previous experiments (part I and II) where the $E_{\text{OC}} \sim +0.15\text{V}$ was measured for the Ag/ Ag_2O system in the absence of I^- and AgI. Interestingly, in this work where I^- was present (cyan curve in Figure 2), the Ag metal was not significantly dissolved during the anodic oxidation at +0.25V. This observation contradicted with the result in the absence of I^- (two previous experiments) where the Ag was dissolved into

the electrolyte during the anodic oxidation at +0.25V. In this work in accord with two other experiments, the charge transferred during the reactions was not exactly proportional to the formation of the RedOx species. When the orange and cyan curves are compared in Figure 2, a small increase in the total thickness of the Ag+ Ag_2O layers can be seen after anodic oxidation. This might be due to the presence of the AgI formed at Ag surface which could protect Ag electrode from dissolution during the anodization.

After the first cathodic stripping voltammetry CSV1 (the pink curve in Figure 2) a significant decrease in the SLD of the layer in contact with electrolyte and at above 300 \AA was observed. In addition, the total thickness of the Ag+ Ag_2O layers remained almost the same. By comparing the SLD of the Ag_2O (SLD= $3.28 \times 10^{-6} \text{ \AA}^{-2}$) and AgI (SLD= $1.63 \times 10^{-6} \text{ \AA}^{-2}$), one may conclude that the Ag_2O was reduced and replaced by AgI. This conclusion is confirmed with the open circuit potential measured after the first and second CSV. This $E_{\text{OC}} \sim -0.15\text{V}$ showed that the main compound in contact with the Ag electrode was AgI.

The summary of all three experiments are shown in Figure 3.

References

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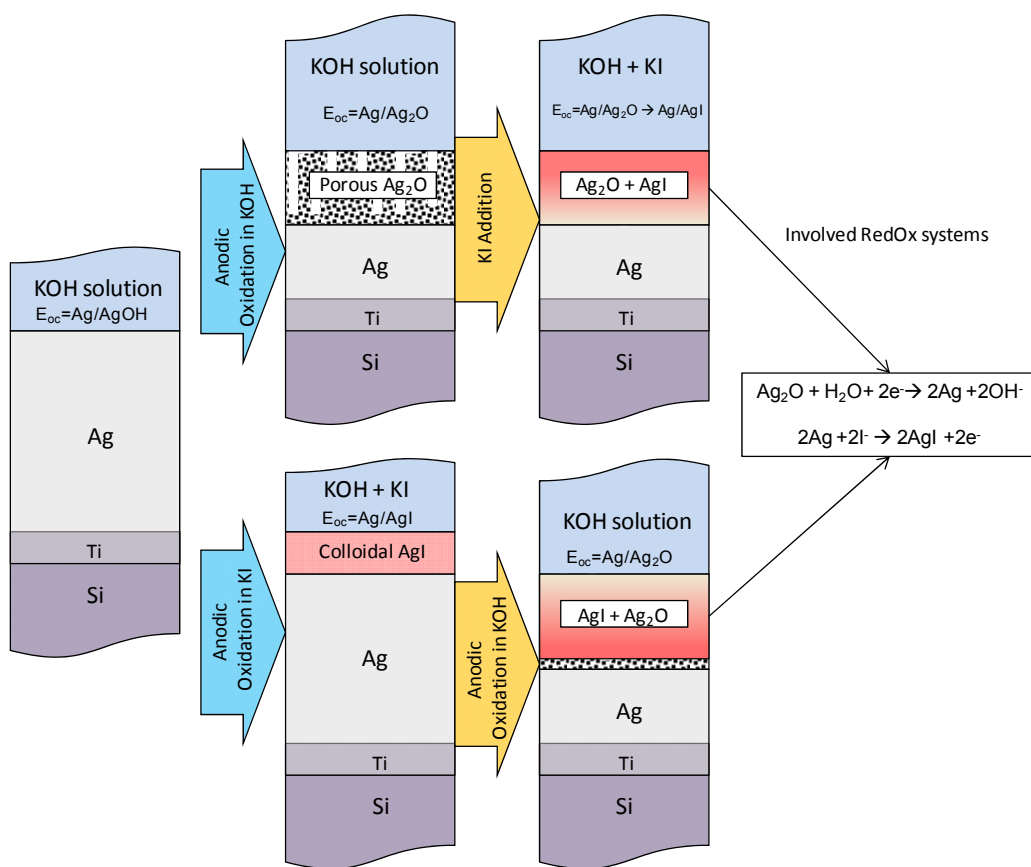


Figure 3 The schematic summary of the results obtained from the *in-situ* Electrochemical Neutron Reflectometry study on silver thin film electrodes in two different experimental conditions. Top row shows the experimental procedure in which the anodic oxidation of Ag film occurs before KI addition whereas the bottom row displays the experiment where silver film was first oxidized in KI solution then anodically oxidized at $+0.25V_{SCE}$ to form Ag_2O .