In-Situ Investigation of the Growth of Silver Oxy-Iodide Popsicles (Part II)

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This experiment is the follow up to the previous experiment in order to determine the relative locations of AgI and Ag_2O in films grown by oxidizing iodide-covered silver metal, and compare them to those grown by conversion of Ag_2O to AgI [1-3]. In the previous experiment we noticed that if the anodic oxidation at +0.25 V_{SCE} (voltages were measured versus Standard Calomel Electrode (SCE)) takes longer than 120 s, the oxide layer became extremely rough and part of the Ag film was dissolved in KOH solution during the oxidation. In this experiment we aimed to control the charge transfer/oxidation time to manage the interfacial roughness.

The Figure 1 shows the current-time profiles measured during the anodic oxidation for an old sample #22 and new sample #25. Both samples were prepared under the same condition and the only difference was 36 hours extra time that sample #25 remained in the KOH solution before anodic oxidation. The delay imposed by an unexpected reactor shut down due to the technical problems. As seen in Fig.1, the charge transferred during the anodic oxidation for sample #25 is approximately three times higher that sample #22. This difference may be due to the formation of hydrated layer (AgOH) at Ag/electrolyte interface which facilitates the charge transfer during the anodic oxidation.

The overlay of the Neutron Reflectivity (NR) curves at different experimental stages is shown in Figure 2. The measurements were done in empty cell after draining and purging it with Argon except the black one which was measured in KOH solution. As expected, when water is present, the background of the NR curve is significantly higher than the NRs measured in Argon. However, the only difference is after adding KI solution for 20 minutes. The higher unexpected background after KI reaction may assign to the trapped colloidal AgI compound in the pores of Ag_2O rough layer which acts as a water reservoir.

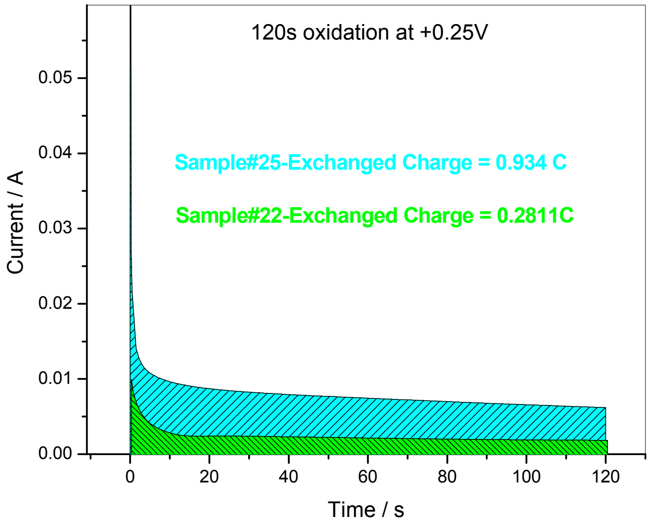

Figure 1 The comparison between the charge transferred during the 120 s anodic oxidation for two different thin film Ag samples #22, #25 in two different experiment. The sample #25 stayed in solution for extra 36 hours during an unexpected reactor shut down.

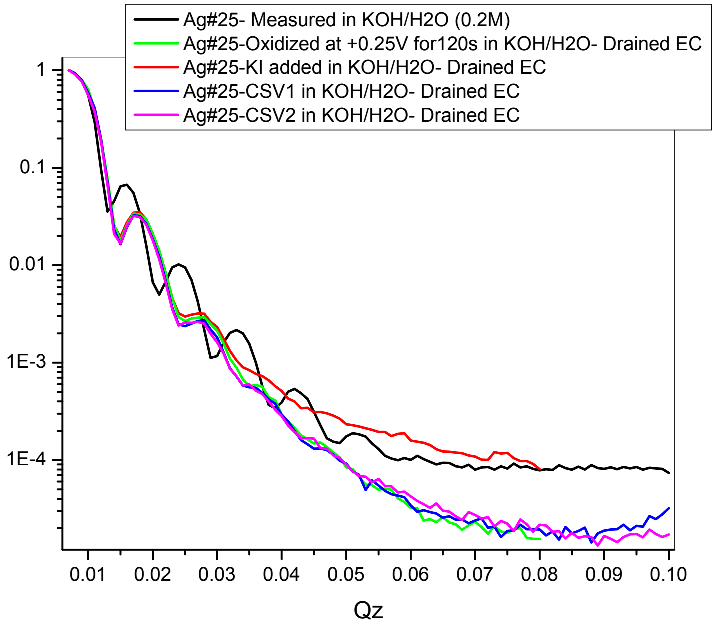

Figure 2 The comparison between the charge transferred during the 120 s anodic oxidation for two different thin film Ag samples #22, #25 in two different experiment. The sample #25 stayed in solution for extra 36 hours during an unexpected reactor shut down.

As shown in Figure 3, the open circuit potential monitored before and after each stage indicated that the dominant system before the anodic oxidation is Ag/AgOH/AgCl (E_{oc} ~ -0.07V) while after anodic oxidation (120 s at +0.25 V_{SCE}) Ag/Ag_2O (E_{oc} ~ 0.15 V_{SCE}) is pre dominant. Interestingly, after adding KI to Ag/Ag_2O system (for 20 minutes) no significant change was observed in E_{oc} and it remained at the same ~-0.15 V_{SCE} value. This unchanged E_{oc} indicates that not only KI cannot replace Ag_2O but also under the experimental condition no Ag/AgI system after anodic oxidation of Ag was formed. However, after the first cathodic stripping voltammetry (CSV1) (scanned from +0.2 to -0.4 V_{SCE}), the negative E_{oc} value (-0.07 V_{SCE}) indicated that the surface of Ag was reduced and there were no Ag_2O and AgI and the system was back to its initial condition. The more negative E_{oc} value -0.12 V_{SCE} after the second CSV indicates that Ag was partially oxidized to AgI.

The overlay of the SLD profiles after fitting the NR curves at different experimental stages is displayed in Figure 4. The comparison between the SLD profiles before and after anodic oxidation (Black and Green plots) indicates that part of the Ag film was dissolved during the anodic oxidation. However, the model proposed an extra layer with low SLD at the Ag/Solution interface which is displayed as a broad shoulder in the Green curve. This shoulder is most likely a porous Ag_2O layer formed and filled with solution after anodic oxidation. Two other interesting features which were also observed in the previous experiment are a small increase in the SLD of the Ag film and the increase in the roughness of the Si/Ag interface after anodic oxidation. As there is no strong base to argue, we assume that these two features are added by software to attain the best fit. After adding KI (Red curve in Fig. 4) the model proposed sharper interfaces between Ag/Ag_2O and Ag_2O/Solution. The sharp interfaces can be attributed to the penetration of KI into the Ag_2O pores and formation of distinct interfaces after draining the cell.

As one of the main difficulties in this experiment was to observe small changes at a very rough interface of Ag/Ag_2O, our next approach to understand the mechanism of the electrochemical reaction at Ag electrode should be either using contrast matching technique or creating an Ag_2O film by other method.

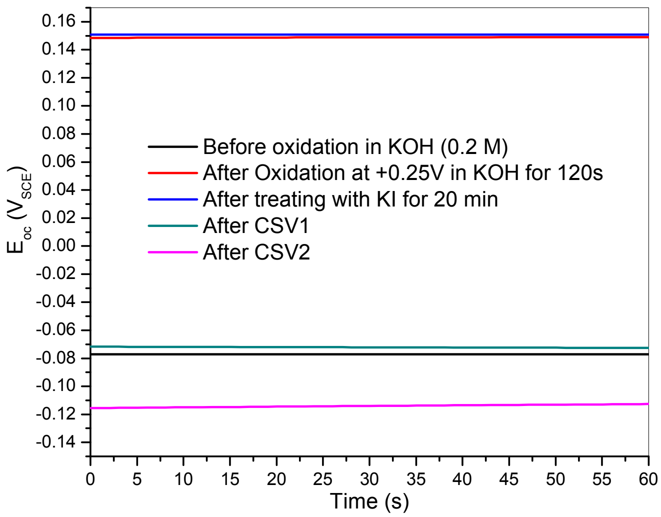

Figure 3 The open circuit potential (E_{oc}) of the silver sample #25 electrode monitored at different experimental stages. The expected E_{oc} for the Ag/Ag_2O system at this experimental condition is ~ 0.15 V_{SCE} whereas for the Ag/AgI is ~ -0.2 V_{SCE}.

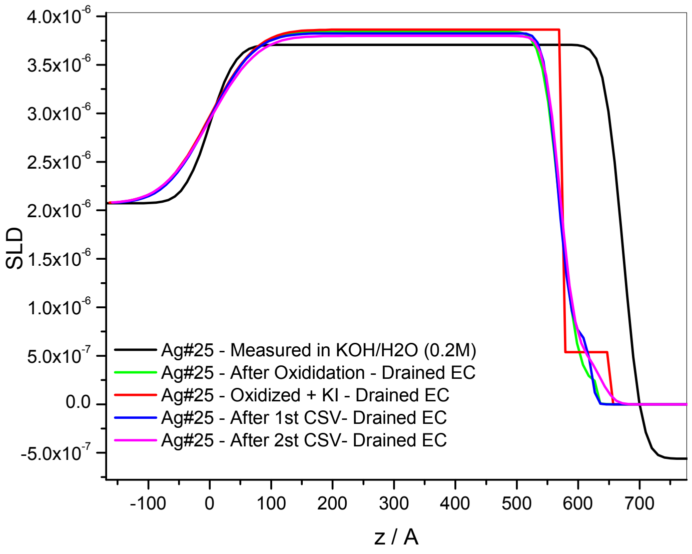

Figure 4 The SLD profiles of the silver sample #25 at different experimental stages. All the measurement obtained in empty electrochemical cell after draining solution except the Black curve which was measured in KOH solution.

References

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