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Galvanically coupled process for the conversion of Ag_2O to AgI

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Abstract

The conversion of Ag_2O, grown ~~in~~ Ag substrates, to AgI has in been investigated, using open-circuit potential, linear polarization, and potentiostatic control measurements. Three distinct reaction stages were clearly identified from the time-dependent behaviour of the open-circuit potential, E_{OC}, and the corrosion currents measured by linear polarization. In the early stages, when the silver surface was covered with a coherent Ag_2O film with low porosity, $E_{OC} \sim (E^e)_{Ag_2O/Ag}$ and only chemical conversion of Ag_2O to AgI was observed. As Ag_2O was consumed and the area of Ag exposed to I^- solution increased, galvanic coupling of Ag_2O reduction to Ag and the oxidation of the Ag substrate to AgI also occurred. Once all the Ag_2O has been reduced, AgI formation stopped and E_{OC} fell to $(E^e)_{AgI/Ag}$. Chemical conversion was shown to produce fine particulate AgI whereas that formed anodically via galvanic coupling was in the form of large crystals. Since few larger crystals were observed, conversion via galvanic coupling appeared to be a minor process.

Keywords: A. Silver; B. SEM; C. Anodic film

1. Introduction

We have previously reported on the conversion kinetics of Ag_2O to AgI in aqueous iodide solutions at pH 12 [1]:

$$Ag_2O + 2I^- + H_2O \rightarrow 2AgI + 2OH^- \quad (1)$$

The reaction kinetics were followed by electrochemically growing a known amount of oxide on Ag in iodide-free solution and subsequently following the reaction in an iodide-containing solution on open-circuit, and periodically determining the amounts of oxide and iodide on the surface using cathodic stripping voltammetry. Complete conversion was indicated by an abrupt transition in the open-circuit potential from a value close to the equilibrium potential for Ag_2O/Ag, $(E^e)_{Ag_2O/Ag}$, to a value close to the equilibrium potential for AgI/Ag, $(E^e)_{AgI/Ag}$. This abrupt change in E_{OC} allowed an easy determination of the total reaction time, τ_f, required for complete conversion of Ag_2O to AgI. The total reaction time as a function of iodide concentration and initial Ag_2O inventory, and the amounts of AgI and Ag_2O as a function of reaction time, t_{rxn}, determined by cathodic stripping voltammetry, were used to determine rate parameters for the chemical conversion. The rate was found to be first order in both iodide concentration and oxide surface area.

This first study was primarily aimed at the determination of kinetic parameters that can be used in models developed to predict the fate of radioiodine in various proposed nuclear reactor accident scenarios [2], and the mechanistic details of the reaction were not studied in detail.

Two possible mechanisms were identified; (i) a direct chemical process (Reaction 1); and (ii) a galvanically coupled process in which the cathodic reduction of oxide to Ag is coupled to the anodic oxidation of Ag to iodide:

$$\text{Cathodic Reaction}: Ag_2O + H_2O + 2e^- \rightarrow 2Ag + 2OH^- \quad (2a)$$

$$\text{Anodic Reaction}: 2Ag + 2I^- \rightarrow 2AgI + 2e^- \quad (2b)$$

In this paper we describe a more detailed investigation of the mechanism.

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2. Experimental

2.1. Electrochemical cell

A three-electrode system, consisting of a silver working electrode, a reference electrode and a counter electrode, was used for all experiments. The working electrode was a 7-mm (in diameter) Ag disc set in resin so that only the flat front face was exposed to the solution. Prior to each experiment, this electrode was manually polished with 600 and 800 grit silicon carbide papers, and any polishing residue removed by sonication in an acetone/methanol mixture for 5 min. The reference electrode was a saturated calomel electrode (SCE) and the counter electrode was platinum mesh. All potential measurements were made with, and are quoted against, a saturated calomel reference electrode (SCE). A Solartron model 1480 potentiostat was used to control and measure potentials and to record current responses. Corrware™ and Corrview software (supplied by Scribner and Associates) were used to control experiments and analyze data.

Experiments were conducted at room temperature in Ar-purged 0.02 M NaH_2PO_4 with the pH adjusted to 12 with NaOH. Solutions were prepared with water purified using a NANOpure Diamond UV ultrapure water system from Barnstead International to remove organic and inorganic impurities. Prepared in this manner, the water had a resistivity of 18.2 MΩ cm.

2.2. Experimental procedure

All experiments were preceded by a cathodic cleaning of the electrode at a potential of −1.1 V for 300 s. An Ag_2O film was then grown potentiostatically at +0.6 V until the total oxidation charge reached 0.2 C (or $0.52\ \mathrm{C\,cm^{-2}}$). Reaction with iodide was initiated by transferring the Ag_2O covered electrode to a 0.02 M NaH_2PO_4 solution containing a known concentration of KI, and following the progress of the reaction by measuring the open-circuit potential (E_{OC}) as a function of time. Completion of the reaction was indicated by a sudden decrease in E_{OC} to $(E^e)_{AgI/Ag}$.

At various intervals a linear polarization experiment was conducted by scanning the potential ±30 mV above the E_{OC} value at a scan rate of 0.17 mV/s (10 mV/min). The anodic and cathodic currents measured during the linear polarization were used to obtain relative corrosion rates using the Stern–Geary equation [3,4]. Additional potentiostatic experiments were conducted at distinct times during the open-circuit transient. The potentials applied were the open-circuit values prevailing at that time in the transient.

The morphology of silver electrode surfaces at various stages of the reaction were obtained with a Leo 440 Scanning Electron Microscope, and the composition of products analyzed with energy dispersive X-ray (EDX) spectroscopy.

3. Results and discussion

3.1. Open-circuit potential behaviour during the reaction

The value of E_{OC} shows three distinct features as a function of time, Fig. 1. In stage I, E_{OC} remains close to the value established on first exposing the Ag_2O/Ag electrode to iodide-containing solution. Eventually, a transition to a second stage (II) occurs, and after a steady decrease a final transition to stage III occurs. As previously demonstrated using cathodic stripping voltammetry [1], the transition between stages II and III signals the completion of the oxide–iodide conversion and no further AgI is formed thereafter.

In stage I, $E_{OC} \sim (E^e)_{Ag_2O/Ag}$ and is independent of $[I^-]$ and the initial oxide inventory ($(Q_{Ag_2O})_o$, the anodic charge consumed in growing the oxide). This would be consistent with the occurrence of a chemical reaction, as specified by Reaction 1. The transition to stage II (∼40 mV) and the slow decrease in E_{OC} with time throughout this stage indicates a polarization of the potential away from the equilibrium value. Given the demonstrated reversibility of the Ag_2O/Ag redox process (Reaction 2a) [1], this introduces the possibility that the cathodic reduction of Ag_2O to Ag is coupled to the anodic oxidation of Ag to AgI. For such a coupling to occur, exposure of the underlying Ag surface to the iodide-containing solution would be required. This suggests that the transition between stages I and II marks the time at which the chemical transformation has progressed sufficiently to expose the Ag substrate.

Fig. 2 presents evidence in support of this claim. In this figure the transition times between stages I/II and the final transition to stage III are plotted (logarithmically) against $(Q_{Ag_2O})_o$ which is proportional to the oxide film thickness. These values were recorded in a solution with

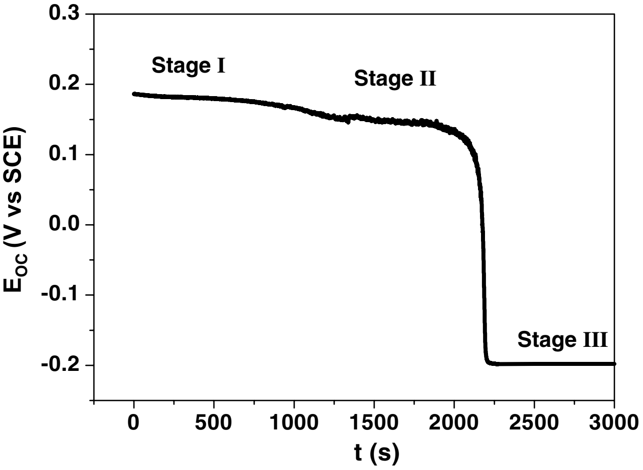

Fig. 1. Open-circuit potential (E_{OC}) as a function of time during the reaction of Ag_2O/Ag with I^-, exhibiting three distinc~~tive~~ reaction stages. The oxide was grown at 0.6 V (vs. SCE) to a total anodic charge $(Q_{Ag_2O})_o$ of 0.2 C in iodide-free solution, and then the oxide covered electrode was transferred to 5×10^{-4} M I^- solution to initiate the conversion reaction.

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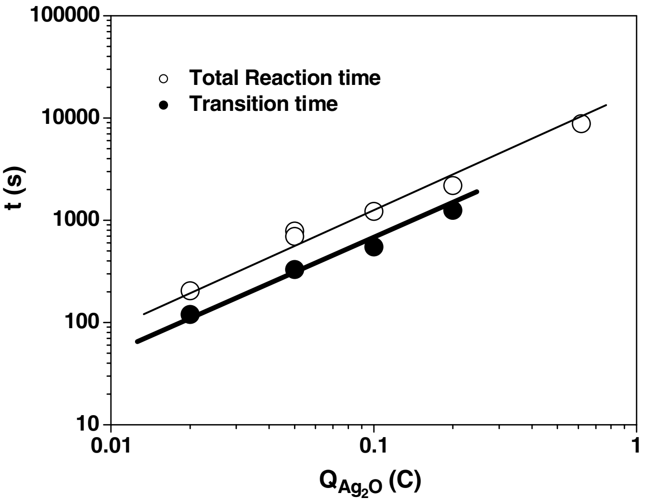

Fig. 2. Total reaction time (open circles) and the transition time from stage I to II (solid circles) observed as a function of the initial oxide inventory.

$[I^-] = 5 \times 10^{-4}$ mol dm^{-3}. As noted previously, the final transition time, indicating completion of the reaction, is directly proportional to the oxide film thickness, and Fig. 2 shows that the time to the first transition (I–II) has the same direct dependence on $(Q_{Ag_2O})_o$; i.e., the time to break through of the solution to the Ag surface is also directly related to the film thickness. Based on these results and those in our previous paper [1], we could claim that the reaction in stage I is purely chemical and first order in $[I^-]$ whereas in stage II both the chemical reaction and a galvanic coupling reaction (2) are occurring simultaneously.

To determine whether or not the galvanic process contributed significantly to the overall reaction, linear polarization measurements were performed at regular intervals throughout the open-circuit transient. Fig. 3a shows the currents measured on an Ag_2O/Ag electrode in iodide-free solution, Fig. 3b the currents measured during the conversion in a solution containing 5×10^{-4} mol dm^{-3} I^-, and Fig. 3c the currents measured in the iodide solution after all oxide has been converted to iodide. Fig. 4 shows the corresponding E_{OC} values recorded and the corrosion currents obtained from the linear polarization plots using the Stern–Geary equation to fit in the range of about 15 mV around E_{OC}. It is acknowledged that the corrosion currents measured in this manner may not be correct absolute values since E_{OC} is close to $(E^e)_{Ag_2O/Ag}$. However, as relative values, they remain very instructive.

In the iodide-free solution, E_{OC} remained constant with time and close to $(E^e)_{Ag_2O/Ag}$. The stability of the oxide-metal system is confirmed by the negligible corrosion current observed, Fig. 4a. On transfer of the electrode to the iodide-containing solution E_{OC} remained close to $(E^e)_{Ag_2O/Ag}$ and the corrosion rate was negligible during stage I, Fig. 4b. As discussed previously [1], cathodic stripping voltammetry showed that the oxide to iodide conversion was proceeding in stage I. These observations confirm the absence of galvanic coupling in the early stages of reaction and that the conversion process is proceeding chemically via Reaction 1.

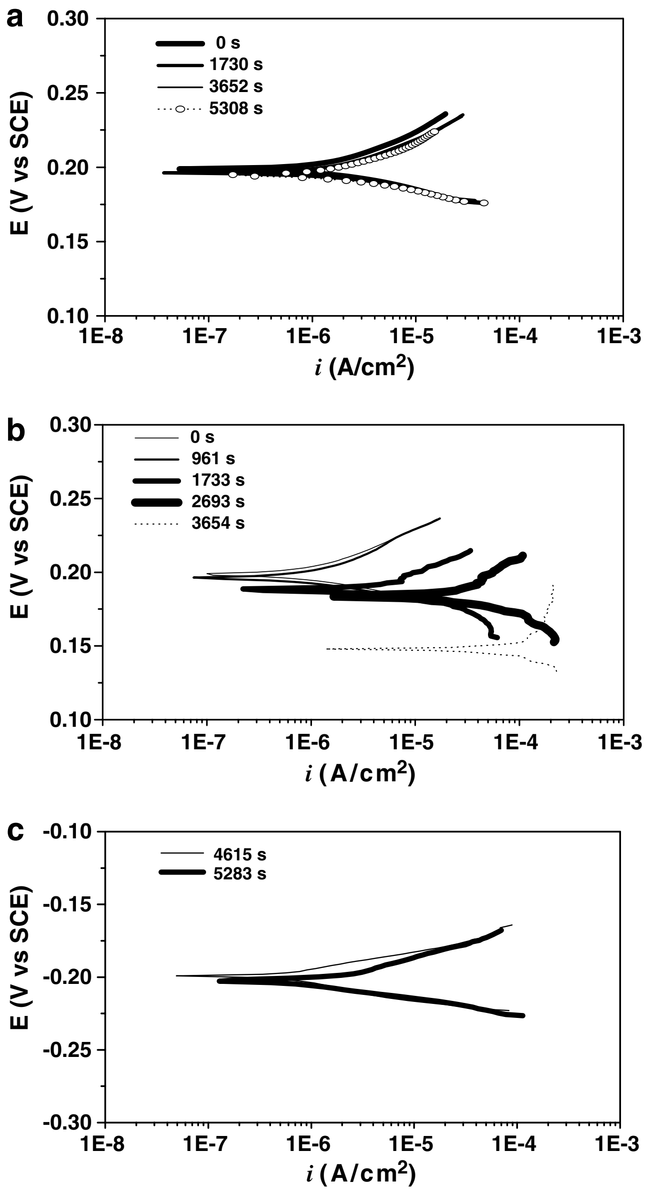

Fig. 3. Anodic and cathodic currents during linear polarization over the potential range $E_{OC} \pm 30$ mV; (a) Ag_2O/Ag in iodide-free solution, (b) during the conversion of Ag_2O to AgI in 5×10^{-4} M I^-, and (c) after completion of the conversion in 5×10^{-4} M I^-.

Once the potential transition to stage II occurs a measurable corrosion rate is observed, indicating the onset of conversion by galvanic coupling, as well as the on-going chemical reaction. The rate (current) of the galvanic reaction accelerates as E_{OC} decreases throughout stage II, but collapses to an insignificant value once the transition to stage III, indicating complete oxide conversion, occurs. The absence of a significant galvanic current in stage III confirms the stability of the AgI/Ag redox system and demonstrates the need for Ag_2O to sustain the galvanic process.

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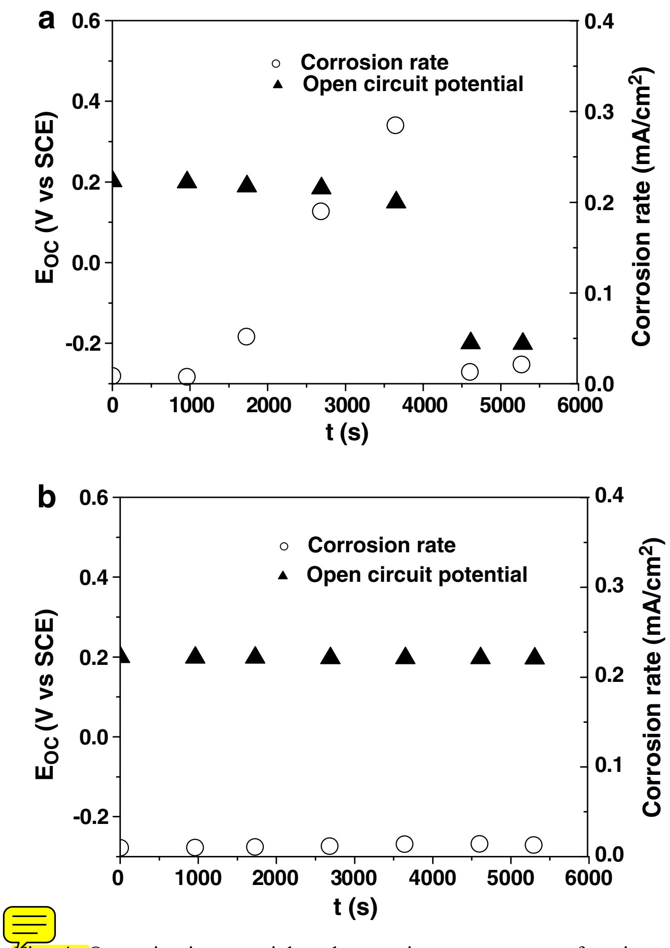

Fig. 4. Open-circuit potential and corrosion current as a function of reaction time; (a) Ag_2O/Ag in a KI-free Solution, and (b) during the conversion of Ag_2O to AgI in 5×10^{-4} M I^-.

The proximity of E_{OC} to $(E^e)_{Ag_2O/Ag}$ (as opposed to $(E^e)_{AgI/Ag}$ throughout stage II indicates that the rate determining step in the galvanic process is the anodic reaction, Reaction 2b. This is confirmed by the currents measured in the linear polarization experiment which show an increase in anodic current throughout stage II while the cathodic current (for Reaction 2a) remains constant. The most likely rate limiting process is the diffusion of I^- to the exposed metal surface to support anodic reaction (2~~a~~). This would occur through pores in the oxide deposit and would be compounded by the consumption of I^- by the chemical reaction (1) at the Ag_2O/I^- solution interface. The increase in anodic current, and hence the rate of the galvanic reaction (2), as stage II progresses can be attributed to a combination of an increased area of exposed Ag and an accompanying increase in the surface concentration of iodide as the chemical consumption of Ag_2O proceeds and the flux of I^- through shortened pores accelerates. The absolute value of E_{OC} throughout stage II will be determined partly by these kinetic features and partly by the change in $(E^e)_{AgI/Ag}$ as the surface concentration of I^- changes.

The progress of the chemical reaction at the oxide/solution interface was previously followed by observing the changes in surface morphology by SEM [1]. The initial oxide was composed of an irregular array of ill-defined crystals approximately 0.3 by 1 μm in dimension, Fig. 5a. As the oxide to iodide conversion proceeded, the electrode surface became progressively covered by small AgI particulates, Fig. 5b. Although not shown here, the micrograph recorded at the onset of stage II showed the coexistence of oxide crystals and iodide particulates, confirming that the chemically formed AgI did not form a reaction-blocking layer on the surface of the oxide.

This large difference in size between the electrochemically grown Ag_2O and the AgI product allows the conversion to proceed unimpeded, and can be attributed to the difference in size of the iodide and oxide anions. The chemical reaction can be considered an anion-replacement process with the greater size of I^- precluding its incorporation into the Ag_2O lattice. Consequently, reaction between I^- and the oxide leads to significant surface stresses causing a rapid detachment of the AgI product which limits the growth of the particulates and allows the conversion reaction to proceed to completion.

The SEM micrograph of the AgI present on completion of the experiment, Fig. 5b, also shows a small number of larger facetted crystals to be present. These crystals possess a similar morphology to AgI crystals grown elec-

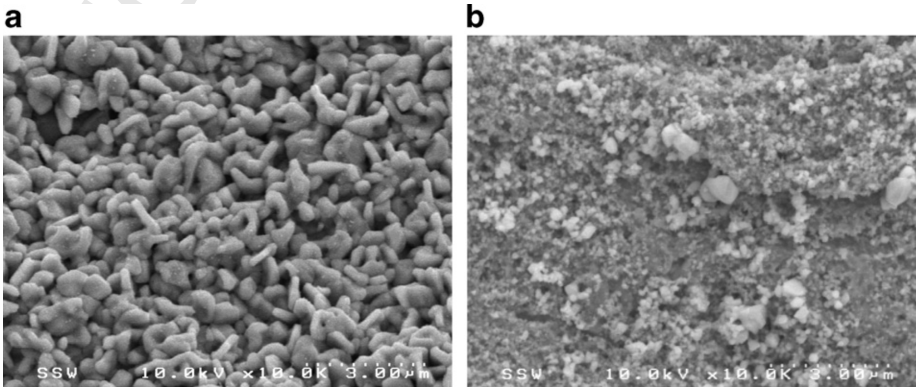

Fig. 5. Scanning electron micrographs (SEM) of: (a) the Ag_2O/Ag electrode, where the oxide film was grown potentiostatically at 0.6 V to a total anodic charge of 0.2 C (or 0.52 C cm^{-2}); (b) the electrode following termination of the reaction (i.e., stage III).

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trochemically on a clean Ag surface, Fig. 6, suggesting they are the products of the galvanic process occurring in stage II. The minor amount of these crystals indicates that the conversion of oxide to iodide via galvanic coupling is probably a minor reaction compared to the chemical conversion process. Previous studies [1,5] have shown that the anodic formation of AgI on Ag in iodide solution is controlled by the diffusion process in a wide potential range, and not inhibited by the build-up of AgI. ~~The~~ highly conductive nature of the electrochemically grown AgI films, evidenced by the linear increase in the total anodic charge with time observed during potentiostatic growth of AgI at 0.0 V in 10^{-3} M KI solution, Fig. 6a. A typical SEM image of the electrochemically grown AgI is shown in Fig. 6b.

To confirm the differences in mechanism between stages I and II, additional experiments were conducted with partial potentiostatic control. These experiments were conducted on electrodes with identical amounts of pregrown oxide to that used in the experiments described above. In the first experiment, a potential of 0.2 V was applied immediately after immersing the electrode in a 5×10^{-4} mol dm^{-3} KI solution. This potential was applied for time, τ_F, that would have been required for the E_{OC} transition between stages II and III marking completion of the conversion. Subsequently, the electrode was switched to open-circuit and E_{OC} followed until it decreased to $(E^e)_{AgI/Ag}$; i.e., until the electrode achieved the final iodide-covered equilibrium state.

In the second experiment, the conversion reaction was allowed to proceed on open-circuit for the time required to complete stage I, and then a potential of 0.15 V (equal to the prevailing E_{OC} value) was applied and maintained for the total time (τ_F) to complete the reaction. Fig. 7 shows the potential profiles, including both the controlled and measured segments, for both experiments. The currents observed and the corresponding SEM micrographs are shown in Figs. 8 and 9, respectively.

With a potential of 0.2 V applied immediately on immersion, the current was initially negligible despite the large overpotential ($\eta = E_{APP} - (E^e)_{AgI/Ag}$) for the anodic formation of AgI, Fig. 8. This indicates that the Ag surface is not exposed to the iodide solution at the beginning of the reaction. The current remains negligible for a period of ~1000 s; i.e., for the duration of stage I when open-circuit conditions from the first immersion prevail. This is consistent with our claim that only chemical conversion of oxide to iodide is occurring at the oxide/solution interface during stage I and that the E_{OC} transition to stage II represents the first exposure of the substrate Ag to the iodide-containing solution. Once solution contact with Ag is made, and pores in the oxide film begin to open, the current for the anodic formation of AgI increases steadily, Fig. 8. Since the anodic formation of AgI is rapid and does not lead to formation of a passive layer, Fig. 6, it consumes I^- and the chemical conversion becomes slow. On terminating the anodic oxidation by switching to open-circuit, the chemical (and galvanic) process(es) resume with E_{OC} close to $(E^e)_{Ag_2O/Ag}$ until all the oxide is converted after an open-circuit period of 1500 s, Fig. 7a.

When the chemical conversion reaction was allowed to proceed through stage I and the transition to stage II prior to application of an applied potential of 0.15 V (~the E_{OC} that prevails at the onset of stage II), Fig. 7b, the current immediately increases as would be expected if the Ag substrate was already exposed to the iodide-containing solu-

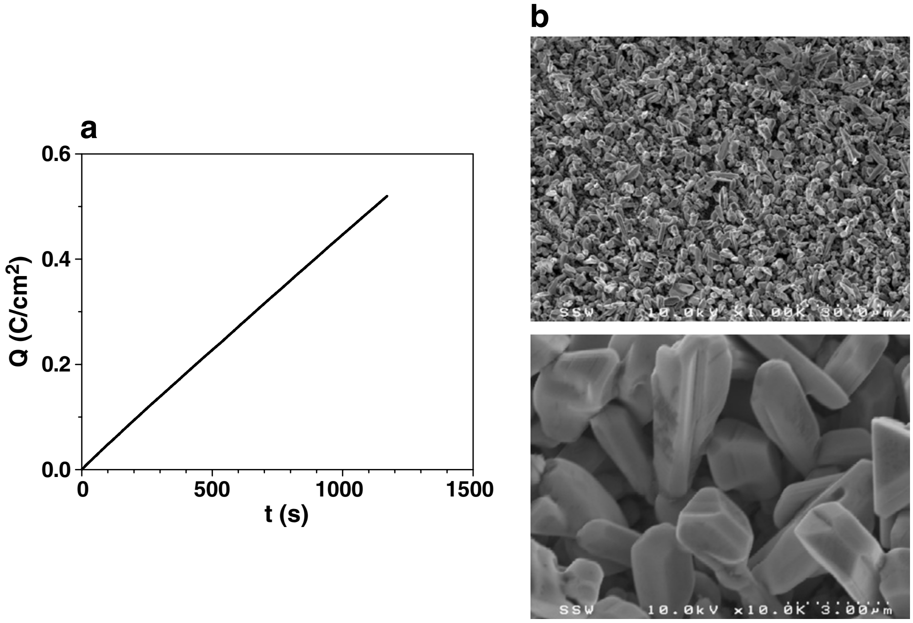

Fig. 6. (a) Anodic charge observed during potentiostatic growth of AgI at 0.0 V (vs. SCE) in $[I^-] = 10^{-3}$ M (pH 12); (b) SEM micrograph of the film formed for a total charge of 0.2 C.

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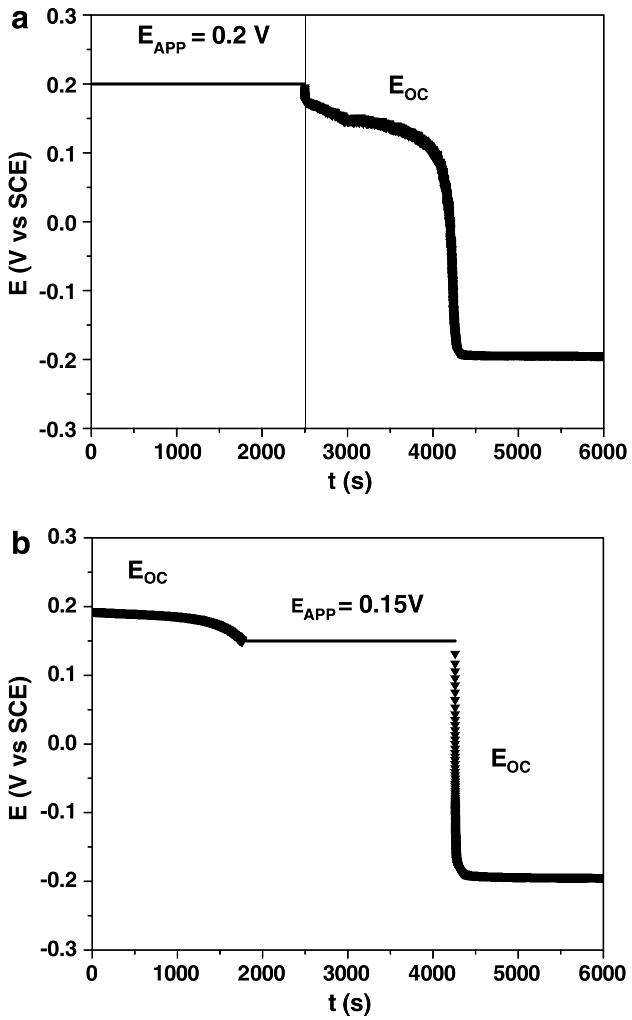

Fig. 7. Potential profiles recorded during partially controlled potentiostatic experiments; (a) 0.2 V (vs. SCE) was applied for 2500 s immediately after transfer of the Ag_2O/Ag electrode to the iodide solution, followed by an E_{OC} measurement; (b) E_{OC} was measured until the beginning of stage II, followed by potentiostatic control at E_{OC} (0.15 V vs. SCE) for 2500 s, followed by further measurement of E_{OC}.

tion. At this applied potential not only is there an overpotential for the anodic oxidation of Ag to AgI but there is also an overpotential for the cathodic reduction of Ag_2O to Ag ($\eta = E_{APP} - (E^{\circ})_{Ag_2O/Ag}$). Thus, the rapid increase in current to a large steady-state value can be attributed to the cathodic reduction of the oxide leading to exposure of the Ag substrate to higher concentrations of I^- and, hence, an enhancement of the anodic current for AgI formation. When the applied potential is subsequently removed, E_{OC} immediately falls to $(E^{\circ})_{AgI/Ag}$ confirming the absence of oxide on the Ag surface. The steady-state current density reached, Fig. 8 is approximately 30% lower than the value observed for the anodic formation of AgI on clean Ag at the same potential (0.15 V) and iodide concentration (5×10^{-4} mol dm^{-3}). This lower value can be attributed to the smaller effective surface area of Ag since a fraction of the surface is covered by chemically formed AgI.

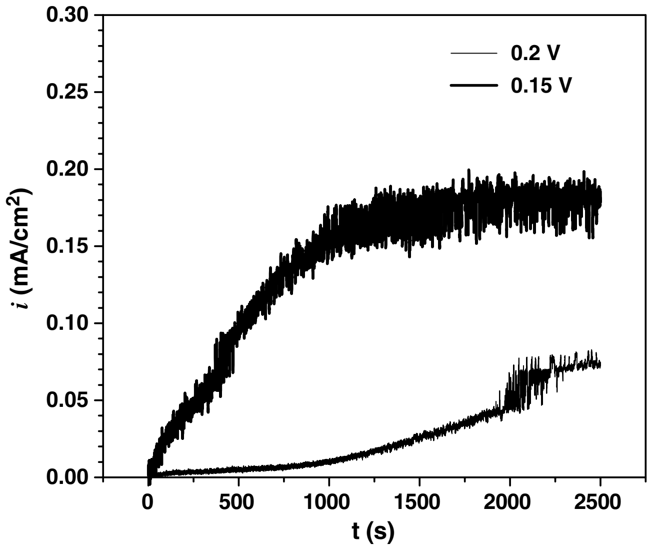

Fig. 8. Currents observed during the potentiostatic periods of the partial control experiments shown in Fig. 7.

The SEM images of the electrode surfaces obtained at the end of these experiments, Fig. 9, confirm the coexistence of small particulates formed chemically and large crystals formed electrochemically, and support our claim that the large crystals in Fig. 6b are formed by the galvanic coupling reaction. EDX analyses confirm that both are AgI.

3.2. Proposed mechanism for AgI formation from Ag_2O and I^-

The above observations indicate that the reaction between Ag_2O and I^- (Reaction 1) can occur chemically and/or electrochemically, depending on the relative areas of exposed Ag_2O and Ag. For a coherent Ag_2O film with low porosity, only the chemical reaction occurs. This happens at short times when available I^- is consumed by chemical reaction with Ag_2O, and $[I^-]$ at the Ag surface is low. As Ag_2O is consumed and the area of Ag exposed to I^- solution increases, galvanic coupling of $Ag_2O \rightarrow Ag$ and $Ag \rightarrow AgI$ can occur. The rate of the galvanically coupled reaction increases as Ag_2O is consumed, but $Ag \rightarrow AgI$ stops once all the Ag_2O is consumed. This proposed mechanism is schematically illustrated in Fig. 10.

The contribution of the galvanically coupled reaction to the overall AgI formation will depend on E_{OC} and $[I^-]$ at the Ag surface during the conversion of Ag_2O to AgI. Under the conditions used for the kinetic measurements reported in Ref. [1], the contribution of the galvanically coupled reaction is, however, considered to be negligible since the solution redox condition which influences the open-circuit potential is mainly determined by the iodide concentration and pH in the absence of other redox species. This is consistent with the absence of a significant number of larger AgI crystals. The influence of the relative

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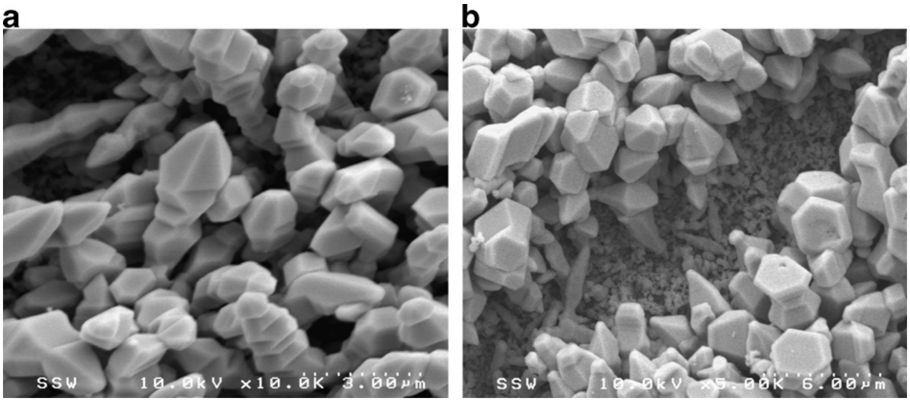

Fig. 9. SEM micrographs of AgI formed on Ag electrodes in the two different partial control experiments shown in Fig. 7.

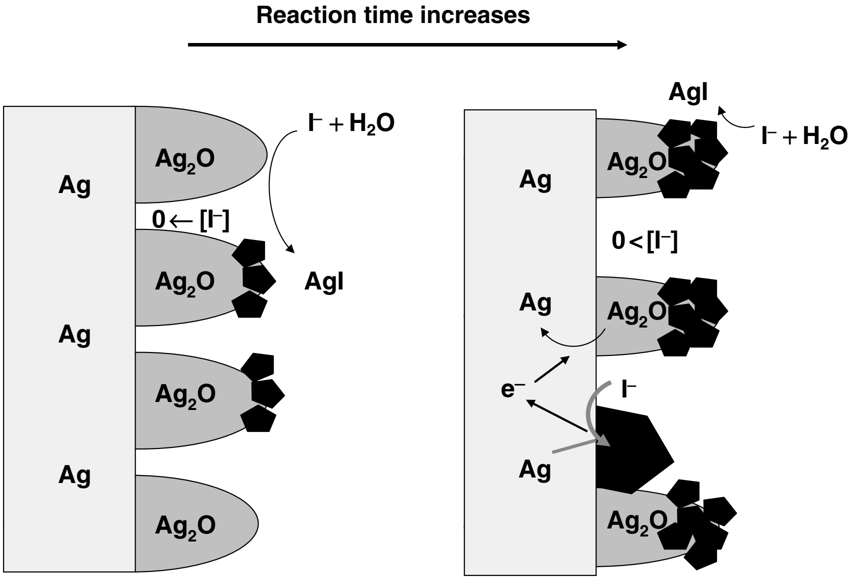

Fig. 10. Schematic representation of the mechanism for the conversion of Ag_2O on Ag to AgI.

surface areas of Ag_2O, AgI and Ag, iodide concentration, and the nature of supporting electrolyte, on the galvanic coupling process and its relative contribution to the overall reaction kinetics are presently under study.

4. Conclusions

The mechanisms for the conversion of Ag_2O/Ag to AgI/Ag in aqueous iodide solution on open-circuit potential was determined using linear polarization and potentiostatic measurements. Three distinct reaction stages were clearly identified from the time-dependent behaviour of E_{OC} and the corrosion currents measured by linear polarization. At short times, when the Ag surface is covered with a coherent Ag_2O film with low porosity, only the chemical conversion of Ag_2O to AgI occurs. As Ag_2O is consumed, and the area of Ag exposed to I^- solution increases, the galvanic coupling of $Ag_2O \rightarrow Ag$ and $Ag \rightarrow AgI$ occurs. Once all the Ag_2O is consumed, no~~t~~ further oxidation of Ag to AgI occurs. Experiments, in which the reaction was partially controlled electrochemically and followed by SEM showed that chemical conversion produced smaller particulates while AgI grown electrochemically formed well defined crystals. SEM images recorded on completion of open-circuit experiments showed the coexistence of small AgI particulates and large crystals, confirming that conversion occurred both chemically and electrochemically via galvanic coupling. Since only a small number of larger crystals were observed, the contribution of the galvanically coupled reaction appears to be minor.

Acknowledgements

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