Interaction of Aqueous Iodine Species with Ag<sub>2</sub>O/Ag Surfaces

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The chemical conversion of Ag<sub>2</sub>O films on Ag surfaces to AgI in aqueous iodide solutions has been studied electrochemically. Ag<sub>2</sub>O films were grown potentiostatically and then exposed to I<sup>−</sup> solutions. The chemical conversion process was followed at open-circuit potential (E<sub>OC</sub>) using cathodic stripping voltammetry performed after various exposure periods. The E<sub>OC</sub> showed a sudden drop at the completion of the conversion of Ag<sub>2</sub>O to AgI, reaching a steady-state value close to the equilibrium potential for AgI/Ag and the iodide solution. This sudden drop in E<sub>OC</sub> allowed easy determination of the total reaction time required for complete conversion of Ag<sub>2</sub>O to AgI. Distinctly separated current peaks were observed for the cathodic reduction of Ag<sub>2</sub>O and AgI to Ag, and the charges associated with these peaks provided a measure of the amount of Ag<sub>2</sub>O converted. The conversion reaction was 100% efficient. The total reaction times from the E<sub>OC</sub> measurements and the cathodic stripping results were used to determine the reaction order and rate constant required for the development of nuclear reactor safety assessment codes.

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One of the safety issues of nuclear power plants is the potential radiation dose to the public in the unlikely event of a severe accident. From the perspective of public safety, radionuclides are one of the most important fission products from the uranium fuel because of its large fuel inventory, high volatility, and radiological hazard. Such an accident would lead to fuel and fuel channel damage, and it is assumed that a significant fraction of the radioiodine fuel inventory would be released from the reactor core into the containment building.3,4 It has been established that most of the released iodine would quickly dissolve and remain in the water ubiquitous throughout the containment building following an accident.2 However, a small fraction could be released to the gas phase due to the continuous conversion of nonvolatile to volatile iodine species under the management.6,7

A complication is the pseudo steady state that exists between I<sup>−</sup> and I<sub>2</sub> in the aqueous solution8

\[
\text{I}^- \rightleftharpoons \text{I}_2
\]

However, these studies have not unambiguously established detailed mechanisms and kinetics of the individual reactions.

Equilibria 5 and 6 are achieved thermally even in the absence of radiation. Furthermore, the effects of oxide and iodide film morphologies on the reaction kinetics have not been examined.

In this study, Ag<sub>2</sub>O film growth on Ag was controlled, and the effect of the film on the reaction of I<sup>−</sup> with Ag<sub>2</sub>O (Reaction 1) examined, using electrochemical and surface analytical techniques. The reduction potentials for AgI/Ag and Ag<sub>2</sub>O/Ag are well separated and the open-circuit potentials of Ag and Ag<sub>2</sub>O in I<sup>−</sup> solutions very different, allowing the kinetics of the chemical reaction 1 to be followed by electrochemical methods. To our knowledge, this is the first time electrochemical techniques have been used to quantitatively monitor the kinetics of an aqueous anion induced chemical transformation between two insoluble solids. From these measurements, the rates of individual reactions required for the development of nuclear reactor safety assessment codes can be extracted.

Experimental

Electrochemical cell and electrodes.— 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 disk, 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 polishing residue was 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, an SCE. A Solartron model 1240 potentiostat was used to control and measure potentials and to record current responses. Corrware and Corrview software (supplied by Scribner and Associates) was used to control experiments and analyze data.

Solutions.— Experiments were conducted at room temperature in Ar-purged 0.02 M NaH<sub>2</sub>PO<sub>4</sub> with the pH adjusted to 12 with NaOH. Phosphate solutions were used to control the local pH within pores in the growing oxide film. Solutions were prepared with water purified using a NANOpure Diamond UV ultrapure water system from...
was then transferred to a 0.02 M NaH₂PO₄ solution containing KI at E₀. Dispersive X-ray spectroscopy and the composition of products analyzed with energy-dispersive X-ray (EDX) spectroscopy.

The onset of AgI reduction at potentials very close to the equilibrium potential, Ag₂O/Ag, is also possible, but galvanostatic reduction of the potential less than (E')Ag₂O/Ag has been attributed to the chemisorption process

\[ \text{Ag} + \text{OH}^-(\text{ad}) \rightleftharpoons \text{AgOH} + e^- \]  

In stage 2, where potentials are slightly more positive than (E')Ag₂O/Ag, the current rises steeply with potential. If the scan was reversed in this region, the current on the reverse scan is larger than that on the forward scan, consistent with a rapid oxide nucleation and growth process.

In stage 3, the anodic current increases more slowly and, for a short range, indicated by the tangential line, a near linear i – E relationship is observed at potentials < +0.3 V. A similar linear i – E relationship is maintained during the cathodic scan. The slope of this line yields a resistance value of ~58 Ω, which is close to the resistance of the solution, suggesting film growth is controlled by ion migration in water-filled pores. The eventual occurrence of the current peak shows that the thickening of the layer eventually impedes its growth. This behavior is similar to that observed in borate buffered solutions. If the voltammogram is recorded in the absence of the phosphate buffer, then the current continues to increase with increasing potential, indicating the presence of the film does not impede its further growth. This is most likely due to pH variations within the pores of the growing film.

The current recovery for potentials ≥ 0.5 V suggests an open structure allowing the three-dimensional (3D) growth of an outer layer, in agreement with previous claims that a dual-layer porous oxide is produced. In this high potential range, the oxidation of Ag₂O to AgO is also possible, but galvanostatic reduction of the potentiostatically grown film at +0.6 V (these results are not shown) does not show behavior that can be clearly identified as the reduction of AgO. The variability of the current peak around +0.4 V from one scan to another is also an indication of the change in transport behavior rather than the oxidation behavior.

Figure 2 shows voltammograms recorded in aqueous solutions containing 10⁻⁴ M and 10⁻³ M KI with the anodic limit confined to a value less than (E')Ag₂O/Ag to avoid the possibility of oxide formation. The onset of AgI formation

\[ \text{Ag} + \Gamma \rightleftharpoons \text{AgI} + e^- \]  

occurs at potentials immediately above the equilibrium potential, (E')Ag₂O/Ag given by

\[ (E')_{\text{AgI/Ag}} = -0.396 - 0.0592 \log(\Gamma^+) \text{ (V vs SCE)} \]

\[ = -0.159 \text{ V (vs SCE) (at } 10^{-3} \text{ M}\Gamma^+) \]

\[ = -0.218 \text{ V (vs SCE) (at } 10^{-3} \text{ M}\Gamma^+) \]  

The potential-independent current at positive potentials can be attributed to control of AgI formation by \( \Gamma^- \) diffusion in solution. No attempt was made to control convective conditions: the noise shows the influence of Ar purging. No current peak for \( \Gamma^- \) adsorption was observed, probably due to the lower \( \Gamma^- \) concentration and higher pH.

The onset of AgI reduction at potentials very close to (E')Ag₂O/Ag, and the equality in anodic (AgI formation) and cathodic (AgI reduction) charges, confirms that the AgI/Ag reaction is as (more) reversible as (that) the Ag₂O/Ag reaction. The linear i – E relationship

\[ \text{Ag} + 2 \text{OH}^- \rightleftharpoons \text{Ag}_2\text{O} + 2e^- + \text{H}_2\text{O} \]  

given by the Nernst equation (at pH 12)
Ag₂O is complete, the current returns to the diffusion-limited value confirming both phases are present. Once the cathodic reduction of AgI from the initial inventory of oxide present prior to exposure to KI solution was obtained by integrating the current–time transient recorded at 5 mV s⁻¹ on a Ag electrode in Ar-purged 0.02 M NaH₂PO₄ solutions containing I⁻ at pH 12 to an anodic scan limit of 0.4 V, for [I⁻] of 10⁻⁴ and 10⁻³ M. The vertical broken lines indicate the equilibrium potentials for AgI/Ag for the two [I⁻].

for AgI reduction (≈0.25 V to the reduction peak) suggests a reaction involving ion migration. The slope of this relationship is −150 Ω, which is slightly greater than the solution resistance, suggesting the reaction is partially controlled by the resistance of the pore structure in the AgI film. Extension of the forward scan to +0.4 V shows both AgI and Ag₂O formation (Fig. 3). The observation of two cathodic reduction peaks at the potentials for Ag₂O (Fig. 2) and AgI (Fig. 3) reduction confirms both phases are present. Once the cathodic reduction of Ag₂O is complete, the current returns to the diffusion-limited value for AgI anodic formation (in the potential range −0.05 to −0.2 V), indicating that the two film formation processes may occur independently.

Potentiostatic growth of initial Ag₂O films.—To provide a starting point for the study of I⁻ with Ag₂O, a known amount of oxide was grown potentiostatically (at (E_{Ag₂O}₀)) on Ag in an Ar-purged KI-free solution. The anodic charge associated with oxide growth was obtained by integrating the current–time transient recorded at (E_{Ag₂O}₀). Since negligible oxide dissolution occurs during film growth at pH 12, this anodic charge, referred to as (Q_{Ag₂O}₀), is the initial inventory of oxide present prior to exposure to KI solution.

Figure 2. Cyclic voltammograms recorded at 5 mV s⁻¹ on a Ag electrode in Ar-purged 0.02 M NaH₂PO₄ solutions containing I⁻ at pH 12 to an anodic scan limit of 0.15 V, for [I⁻] of 10⁻⁴ and 10⁻³ M. The vertical broken lines indicate the equilibrium potentials for AgI/Ag for the two [I⁻].

Figure 3. Cyclic voltammograms recorded at 5 mV s⁻¹ on a Ag electrode in Ar-purged 0.02 M NaH₂PO₄ solutions containing I⁻ at pH 12 to an anodic scan limit of 0.4 V, for [I⁻] of 10⁻⁴ and 10⁻³ M.

Figure 4 shows scanning electron microscopy (SEM) images of potentiostatically grown Ag₂O films after 700 and 1300 s (or total charges of 0.11 C (or 0.28 C cm⁻²) and 0.2 C (or 0.52 C cm⁻²), respectively.

Figure 4 shows scanning electron microscopy (SEM) images of potentiostatically grown Ag₂O films after 700 and 1300 s (or total charges of 0.11 and 0.2 C, respectively). The film grown for 700 s is composed of highly structured, tetrahedral crystals. The film grown for 1300 s is less structured with poorly defined crystals. This change in morphology is consistent with a transition from the 2D growth of a compact inner layer to the 3D growth of a more porous outer layer. Individual crystals ranged in size from 0.3 to 1 µm, depending on the growth potential and thickness. Different morphologies and crystal structures, depending on the potential applied, have been observed by others. EDX analysis and X-ray diffraction analysis (XRD) show that incorporation of phosphate into the oxide occurs. However, even after extensive film growth under potentiostatic conditions, the potential established on switching to open circuit (E_{OC}) always relaxes to (E’_{Ag₂O/Ag}) (see below), consistent with exposure of an Ag/Ag₂O interface to the pH 12 solution. Although presently unconfirmed, this suggests that despite the incorporation of phosphate, the film is behaving as an oxide.

Open-circuit potential behavior.—After immersion in an aqueous solution containing KI, the open-circuit potential (E_{OC}) of the Ag/Ag₂O electrode was followed as a function of reaction time, t_{rea}.

The dependence of the reaction kinetics on Ag/Ag₂O electrode was followed as a function of reaction time, t_{rea}.

The initial value of E_{OC} was independent of [I⁻] (Fig. 5a) and varied only marginally for different initial film thicknesses (Fig. 5b), and was very close to (E’_{Ag₂O/Ag}). With time, E_{OC} slowly decreased to a second plateau at a time dependent on the initial film thickness before undergoing a final abrupt transition to a much lower steady-state value. The time taken to reach the final transition decreased as [I⁻] increased and increased as (Q_{Ag₂O}) increased. The final steady-state value of E_{OC} is close to (E’_{Ag₂O/Ag}) as shown in Fig. 6 by a comparison of final E_{OC} values to calculated values of (E’_{Ag₂O/Ag}). Clearly, once the final potential transition has occurred, redox conditions on the Ag surface are dominated by the AgI/Ag reaction.

Amounts of reactant Ag₂O and product AgI as a function of reaction time.—There are two possible mechanisms by which oxide can be converted to iodide: (i) a direct chemical process via 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. Here we concentrate on the overall conversion process, and a detailed discussion of mechanistic details will be published elsewhere.

Figure 7a shows the times on the open-circuit potential transient when the reaction was stopped, the electrode transferred to a KI-free solution, and a cathodic stripping voltammogram (CSV) recorded. Figure 7b shows CSVs recorded for the reaction times indicated in Fig. 7a. The progress of the reaction is clearly monitored, the peak for AgI reduction increasing as that for Ag₂O reduction decreases.
Integration of the two reduction peaks in Fig. 7b yielded values of \((Q_{\text{Ag}_2\text{O}})_{t_f}\) and \((Q_{\text{AgI}})_{t_f}\) as a function of reaction time, \(t_{f}\) (Fig. 8). The values are inversely related, and \((Q_{\text{Ag}_2\text{O}})_{t_f} = 0 \) at \(t_f\), further confirming there is no residual oxide on the Ag surface at \(t_f\). The relationship

\[
(Q_{\text{Ag}_2\text{O}})_{t_f} + (Q_{\text{AgI}})_{t_f} = (Q_{\text{Ag}_2\text{O}})_{b}
\]  

is maintained throughout the potential transient, confirming the 100% efficiency of the conversion reaction, as well as the absence of both \(\text{Ag}_2\text{O}\) dissolution and the production of AgI by reaction between Ag and \(I^-\). The slopes of the two plots can be used to determine reaction rate constants, as described below.

Figure 9 shows SEM images of the surface prior to the transfer of the electrode to an \(I^-\) solution (b), after the short potential transition (c), and on completion of the reaction (at \(t = t_f\)) (d). As the reaction proceeds the surface becomes progressively covered by small particulates of AgI. The micrograph in c shows the coexistence of oxide and iodide particles, confirming that AgI does not form a protective layer and that the underlying \(\text{Ag}_2\text{O}\) is continuously exposed.

**Reaction Kinetic Analysis**

**Reaction orders.**—The rate equation for the \(\text{Ag}_2\text{O}\) reaction with \(I^-\) (Reaction 1) can be expressed as

\[
\frac{d(m_{\text{AgI}})}{dt} = -\frac{d(m_{\text{Ag}_2\text{O}})}{dt} = k(10^{-3} \times [I^-]^p)(A_{\text{Ag}_2\text{O}})^q
\]

where \((m_{\text{AgI}})\) and \((m_{\text{Ag}_2\text{O}})\) are the number of moles of \(\text{Ag}_2\text{O}\) and AgI at reaction time \(t\); \([I^-]\) (in mol dm\(^{-3}\)) and \((A_{\text{Ag}_2\text{O}})\) (in cm\(^2\)) are the concentration of \(I^-\) and the surface area of \(\text{Ag}_2\text{O}\) at time \(t\), respectively; \(k\) is the reaction rate constant; and superscripts, \(p\) and \(q\), represent reaction orders with respect to \([I^-]\) and \((A_{\text{Ag}_2\text{O}})\), respectively. The units of \(k\) will depend on \(p\) and \(q\), and the factor of 10\(^{-3}\) is included to express \([I^-]\) in mol dm\(^{-3}\) (or M).

Because the \(\text{Ag}_2\text{O}\) surface area to solution volume ratio is very small, \([I^-]\) is constant. The number of moles of unreacted \(\text{Ag}_2\text{O}\) and AgI formed are given by the cathodic charges for reduction of \(\text{Ag}_2\text{O}\) to Ag, \((A_{\text{Ag}_2\text{O}})\), and AgI to Ag, \((Q_{\text{AgI}})\), by

\[
(m_{\text{Ag}_2\text{O}}) = \frac{(Q_{\text{Ag}_2\text{O}})}{2F}
\]

\[
(m_{\text{AgI}}) = \frac{(Q_{\text{AgI}})}{F}
\]

where \(F\) is the Faraday constant, and Eq. 13 becomes

\[
\frac{d(Q_{\text{AgI}})}{dt} = -\frac{d(Q_{\text{Ag}_2\text{O}})}{dt} = kF(10^{-3} \times [I^-]^p)(A_{\text{Ag}_2\text{O}})^q
\]

Figure 8 shows that this rate does not vary appreciably as the reaction proceeds, suggesting \((A_{\text{Ag}_2\text{O}}) = (A_{\text{Ag}_2\text{O}})_{b}\). This constant surface area is also indicated by the micrographs in Fig. 9. The rate equation can, therefore, be further reduced to

\[
\frac{d(Q_{\text{AgI}})}{dt} = kF(10^{-3} \times [I^-]^p)(A_{\text{Ag}_2\text{O}})^q
\]

and integrated to yield

\[
(Q_{\text{AgI}}) = kF(10^{-3} \times [I^-]^p)(A_{\text{Ag}_2\text{O}})^q
\]

The total reaction time, \(t_f\), is then determined by
where \( Q_{\text{AgI}} \) = \( Q_{\text{Ag}_2\text{O}_0} \), since all the initially available \( \text{Ag}_2\text{O} \) is converted to \( \text{AgI} \). The slope of a plot of \( \tau_f \) vs \( \log [I^-] \) yields a value of \( p = 1 \) (Fig. 10).

Similarly, a plot of \( \log \tau_f \) vs \( \log (A_{\text{Ag}_2\text{O}_0}) \) would yield the negative of the reaction order, \( q \). Since the surface area of the initial oxide film was not determined, a value of \( q = 0.82 \) was obtained from a plot of \( \tau_f \) vs \( \log (A_{\text{Ag}_2\text{O}_0}) \) (Fig. 11). If the initial oxide grew uniformly on the electrode, then the oxide surface area would be equal to its geometric area. Then, \( (A_{\text{Ag}_2\text{O}_0})_0 \) would be independent of \( (Q_{\text{Ag}_2\text{O}_0})_0 \) and the film thickness directly proportional to \( (Q_{\text{Ag}_2\text{O}_0})_0 \). However, the SEM micrograph in Fig. 4 shows three-dimensional oxide growth, and consequently, the surface area of the initial \( \text{Ag}_2\text{O} \) film is expected to have a small dependence on \( (Q_{\text{Ag}_2\text{O}_0})_0 \).
Rate constant.— Since the true surface area of Ag₂O has not been determined, the apparent rate constant, \( k_{\text{app}} \), was obtained using the geometric surface area of the electrode

\[
\frac{d(m_{\text{AgI}})}{dt} = 2 \frac{d(m_{\text{Ag}_2\text{O}})}{dt} = k_{\text{app}} (10^{-3} \times [\Gamma]) A_{\text{Elec}}
\]

where \( k_{\text{app}} = \frac{k C_{\beta} \left( \frac{Q_{\text{Ag}_2\text{O}}}{F} \right)^\beta}{A_{\text{Elec}}} \)

For small values of \( \beta \), \( k_{\text{app}} \) approaches \( k \).

A value for \( k_{\text{app}} \) can be extracted from the total reaction time observed as a function of \([\Gamma]^\beta\). From Eq. 18 \((p = q = 1)\)

\[
\tau_f = \frac{1}{k_{\text{app}}} \frac{1}{k_{\text{app}}} \frac{1}{k_{\text{app}}} (Q_{\text{Ag}_2\text{O}})^{\beta} F
\]

yielding a value of \( k_{\text{app}} = 5.4 \times 10^{-3} \text{ cm s}^{-1} \).

Alternatively, \( k_{\text{app}} \) can be obtained from \( (Q_{\text{Ag}_2\text{O}}) \) and \( (Q_{\text{AgI}}) \) as a function of reaction time. Equation 22 yields

\[
(Q_{\text{AgI}}) = (Q_{\text{Ag}_2\text{O}}) - (Q_{\text{Ag}_2\text{O}}) = k_{\text{app}} F(10^{-3} \times [\Gamma]) A_{\text{Elec}} t
\]

Hence, Fig. 7 yields \( k_{\text{app}} = 3.8 \times 10^{-3} \text{ cm s}^{-1} \), in good agreement (within 50%) with the \( k_{\text{app}} \) value obtained from the total reaction time.

A more rigorous kinetic study to determine the rate constant more accurately is presently underway. This includes a determination of whether the incorporation of anions into the electrochemically grown films exerts a significant influence on the kinetics of the film conversion reaction.

Conclusions

The chemical conversion of Ag₂O by \( \Gamma^- \) to AgI in aqueous iodide solutions (pH 12) has been studied by following the reaction on open circuit and periodically determining the amounts of oxide and iodide on the surface using CSV. The reaction was 100% efficient since both the oxide and the iodide are very insoluble under the experimental conditions employed.

Complete conversion was clearly indicated by an abrupt transition in the open-circuit potential from a value close to the equilibrium potential for Ag₂O/Ag to a value identical to the equilibrium potential for AgI/Ag. This abrupt change in \( E_{\text{OC}} \) allowed easy determination of the total reaction time required for complete conversion of Ag₂O to AgI. This time to complete the reaction was inversely proportional to the iodide concentration and was nearly proportional to the amount of oxide originally grown electrochemically on the surface.

The rate of the chemical conversion, determined by the CSV as a function of time, was constant, indicating that the effective surface area of Ag₂O available for the reaction was constant. This constant surface area was attributable to the fact that the AgI product did not form a protective layer on the Ag₂O surface.

A kinetic analysis established the relationship between the total reaction time and the reaction orders. From the total reaction times as a function of iodide concentration and initial Ag₂O inventory, the rate was found to be first order in iodide concentration and almost first order in oxide surface area, although the exact dependence on surface area remains to be determined.

The apparent rate constant, using the geometric surface area instead of the real surface area of Ag₂O, was obtained from both the total reaction time measurements based on the changes in \( E_{\text{OC}} \) and the cathodic charges for AgI and Ag₂O reduction to Ag using cathodic stripping voltammetry. The rate constants obtained by these two different procedures agreed to within 50%.

Based on the kinetic data obtained, rate equations were derived which can be used in models developed to predict the fate of radiiodine in various proposed nuclear reactor accident scenarios.
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