INTERACTION OF AQUEOUS IODINE SPECIES WITH AG/AG_2O SURFACES

Sarah Danielle Stewart
Undergraduate Student
Department of Chemistry, The University of Western Ontario
London, Ontario

Abstract

One of the safety issues of nuclear power plants is radioiodine volatility in the reactor containment building in the unlikely event of an accident [6]. One important reaction for iodine volatility is that of I_2/I^- with Ag in either the reduced metallic form or an oxidized state [6]. It has been suggested that the oxidation state of silver could play a significant role in iodine sorption on silver. However, a detailed mechanism and the kinetics for iodine-silver interactions are not well established. In our study, the effect of the oxide film on the adsorption kinetics of iodine species on silver and silver oxides is examined using various electrochemical methods. The Ag_2O growth on silver is electrochemically controlled, and the reaction kinetics of the controlled surface with aqueous iodine species is followed using various electrochemical methods.

1. Introduction

Nuclear energy contributes ~12% of electricity generation in Canada and ~40% in Ontario, and is expected to remain as an important component of future energy sources. As the prevalence of nuclear reactors is expected to remain high, it is evident that reactor safety is an important aspect to be considered in order to improve this valuable energy source. One issue pertinent to reactor safety is the potential exposure of radiation to the public in the event of a severe accident, particularly exposure to radioiodines, one of the main products from fission of the uranium fuel. There is a possibility that in an accident a significant amount of iodine may be released from the reactor core into the containment building [6]. Radioiodines are radiologically hazardous because they can easily be absorbed by the thyroid glands.

One of the iodine reactions of interest for its volatility assessment is that of I_2/I^- with silver surfaces. Silver is used in control rods, for neutron flux, in some nuclear reactor designs, and is assumed to be released into the containment building environment in some accident scenarios [6]. Complicating this interaction is the presence of high radiation fields, where the reactions of the water radiolysis products with iodine species would result in I_2 and I^- being in a pseudo-steady state [7]. The reactivity of I^- and I_2 with silver surfaces varies depending on the oxidation state of silver, further complicating the kinetic analysis of the silver-iodine system [6]. The differing reactivity means that in order to determine the volatility of iodine under changing post-accident containment conditions, we need to establish the mechanism and kinetics of the individual reactions of aqueous iodine species with silver surfaces, particularly:

$$\mathbf{Ag_2O + 2\,I^- + 2\,H^+ \rightarrow 2\,AgI + H_2O} \quad \mathbf{(1)}$$

$$\mathbf{2\,Ag + I_2 \rightarrow 2\,AgI} \quad \mathbf{(2)}$$

Early studies, which monitor the total iodine uptake by silver/silver oxide as a function of extent of silver oxidation, however, fail to establish detailed mechanisms and rates of these individual reactions. The main reason has been the difficulties in separating the contributions from these two reactions to forming AgI and in characterizing the oxide film. Our research on the silver-iodine interaction has taken advantage of electrochemical analyses techniques, in conjunction with surface and aqueous analyses. Because the oxidation stages of Ag (Ag, Ag^{I}, Ag^{II}) are well-seperated electrochemically, the growth of the Ag_2O film can be controlled, and the effect of the oxide film on the adsorption kinetics of iodine species can be examined. Also, the reduction potentials of AgI to Ag and Ag_2O to Ag are well-separated, therefore the reactant, Ag_2O, and the product, AgI, can also be monitored using electrochemical analysis techniques. Furthermore, Reaction (1) is a purely chemical reaction, whereas Reaction (2) is an electrochemical reaction in which the oxidation state of silver changes. Therefore, electrochemical responses during the AgI formation from these two reactions will be very different.

The current study focuses on Reaction (1). The initial amount of silver oxide was controlled by potentiostatically growing the oxide on a silver working electrode. The electrode was then transferred to an aqueous solution containing I^- for the reaction to occur. The reaction kinetics were followed by monitoring the open circuit potential, E_{OC}, and by analyzing the amounts of AgI and Ag_2O using cathodic stripping voltammetry as a function of reaction time. Surface analysis was performed using Scanning Electron Microscopy in conjunction with Energy Dispersive X-Ray Spectroscopy (SEM/EDX).

2. Experimental

A three-electrode system consisting of a silver working electrode, a saturated calomel reference electrode, and a platinum counter electrode is used for all experiments. The reactions of interest occur on the silver working electrode that has a 7mm diameter and is encased in a plastic sheath. Prior to each experiment this electrode was polished manually with 600 and 800 grit silicon carbide papers. All experiments were conducted in Ar-purged, 0.02M NaH_2PO_4 solution adjusted to pH 12.0 with NaOH. This pH was chosen because Ag_2O dissolution is at a minimum at pH 12.0. A potential of –1.1V was then applied to the silver working electrode in order to cathodically clean the silver surface. The Ag_2O film was subsequently grown on the silver surface by applying a potential of +0.6V until the total charge reached a desired value, typically 0.2 Coulombs. The input of this amount of charge was controlled using the Solatron Potentiostat.

The Ag_2O covered electrode was then transferred to a 0.02M NaH_2PO_4 solution containing $5x10^{-4}$M KI. The open circuit potential of the electrode system was then monitored while the reaction between Ag_2O and I^- occurred. In this particular system the open circuit potential shows a sudden drop at the completion of the reaction. At various reaction times, the reaction was terminated by removing the electrode from the 0.02M NaH_2PO_4 + $5x10^{-4}$M KI solution and placing it back into the 0.02M NaH_2PO_4 solution where cathodic stripping was performed. All experiments were performed at room temperature unless otherwise indicated.

3. Results and Discussion

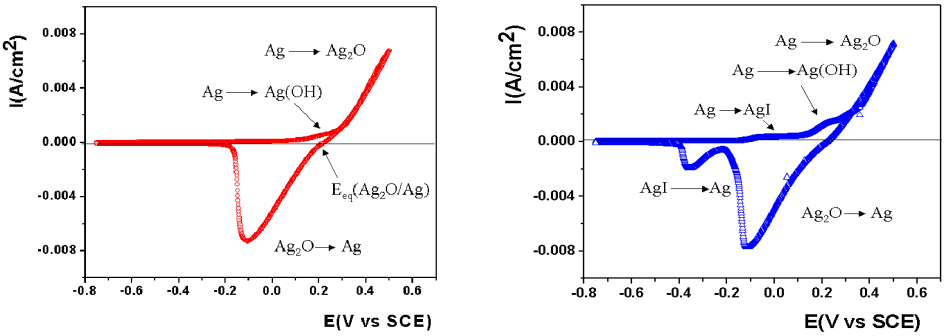


Figure 1. Cyclic Voltammogram Recorded with a Silver Electrode at pH 12.0 in Ar-Purged 0.02M Na_2HPO_4 Aqueous Solutions, containing; (a) KI-free; (b) 5 x 10^{-4}M KI; Potential Sweep from –1.1V to +0.5V and Back at a Scan-Rate of 100mv/s

Figure 1a shows the cyclic voltammogram obtained on a silver electrode in a de-aerated 0.02M Na_2PO_4 solution of pH 12.0. Following cathodic cleaning at –1.1V for 300s, the electrode potential was scanned from –1.1V to +0.5V and back to –1.1V at a scan rate of 100 mV/s. On the forward scan the observed anodic current indicates the electrochemical formation of Ag_2O according to the half-reaction [2]:

$$2\,Ag + 2\,OH^- \rightarrow Ag_2O + 2\,e^- + 2\,H_2O \qquad (3)$$

This reaction is balanced by a reduction reaction that occurs at the platinum counter electrode, mainly:

$$2\,H_2O + 2\,e^- \rightarrow 2\,OH^- + 2\,H_2 \qquad (4)$$

Upon closer inspection of the forward scan a small anodic current can be observed at a potential slightly below the equilibrium potential of Ag/Ag_2O. This current has been attributed to OH^- adsorption on the silver surface [2], whose mechanism does not concern us. The equilibrium potential for the Ag/Ag_2O redox equilibrium (Reaction (3)) at a pH of 12.0 was calculated from the Nernst equation and the standard potential for Ag/Ag_2O:

$$E_{eq}\,(Ag/Ag_2O) = -0.216\ (vs\ SCE)$$

The exponential dependence on potential is only observed over a small potential range. Outside this Butler-Volmer region, the anodic and cathodic currents increase linearly over a wide range of potentials [1]. The linear i – E dependence provides some insight into the Ag_2O film growth and its impact on the reaction kinetics of the AgI formation. However, due to the space limitation, detailed discussion on this subject will not be discussed here.

Integration of the anodic and cathodic currents with time reveals that the anodic charge, Q_A, is equal to the cathodic charge, Q_C [1]. Therefore, the oxidation of Ag to Ag_2O and reduction of Ag_2O to Ag in 0.02M Na_2PO_4 at pH 12.0 is a reversible process; i.e. there is no measurable dissolution of silver oxide as the reaction progresses [3], and all of the silver oxide formed on the forward scan is being reduced on the reverse scan.

Figure 1b shows the cyclic voltammogram obtained with a silver electrode in the aqueous solution containing $5x10^{-4}$M KI. Again, following a cathodic cleaning at –1.1V for 300s a potential sweep from –1.1V to 0.5V and back to –1.1V was performed. In the presence of I^-, oxidation of Ag to both AgI and Ag_2O is possible. The first onset potential observed for the anodic current is due to the formation of AgI. As for the onset potential of Ag_2O, it compares well with the equilibrium potential for the half-reaction:

$$\mathbf{Ag(s) + I^- = AgI(s) + e^-} \qquad \mathbf{(5)}$$

where the calculated equilibrium potential for the redox couple at $[I^-] = 10^{-4}$M is:

$$\mathbf{Eeq\ (Ag/AgI) = -0.277V\ (vs.\ SCE)}$$

On the reverse scan, the reduction of Ag_2O and AgI back to Ag metal occurs, and the total cathodic charge, Q_C, is the same as the total anodic charge, Q_A. These electrochemical characteristics allow us to follow the amounts of the reactant, Ag_2O, and the product, AgI, from the reaction of Ag_2O and I^- as a function of time. In addition, the reduction peaks for Ag_2O to Ag and AgI to Ag are well separated (the slower the scan rate, the better the separation, see Figure 5).

For the following experiments Ag_2O film growth was investigated as a function of applied potential. After a brief cathodic cleaning at –1.1V for 300s, in 0.02M Na_2PO_4 at pH 12.0, a constant potential ranging from + 0.2V to +0.6V was applied, and the anodic current was monitored as a function of time. The results are plotted as the total anodic charge (i.e. the current integrated over time) as a function of time in Figure 2. The total anodic charge is related to the total number of moles of Ag_2O formed:

$$\mathbf{Q^o_{Ag2O} = \eta \bullet F \bullet N^o_{Ag2O}} \qquad \mathbf{(6)}$$

where η is the number of electrons involved in the oxidation; F is the Faraday constant and N^o_{Ag2O} is the amount of Ag_2O in units of moles [1].

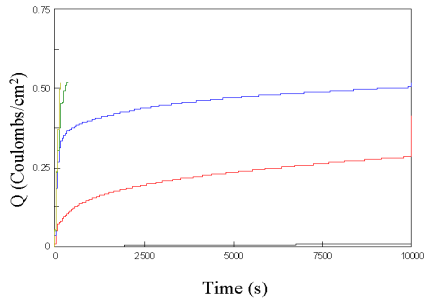


Figure 2. Plot of the Anodic Charge vs. Time for a Number of Applied Potentials (0.2V, 0.3V, 0.4V, 0.5V, 0.6V)

The rate of increase in the total anodic charge is initially rapid, but soon reaches a slow and linear increase. The rate of the initial increase strongly depends on the applied potential [1]. This dependence can be interpreted, as an increase in the number of nucleation sites and the rate of increase in the initial coverage of the surface [3], with an increase in the applied potential. However, once the surface is covered by a certain thickness of the Ag_2O layer, the rate of increase becomes independent of potential [1]. Since the Ag_2O film is growing, the constant current indicates that the resistive component of the film remains constant [1], and the films presence on the silver surface is not impeding further Ag_2O film growth; therefore the Ag_2O film must be extremely porous or highly conducting.

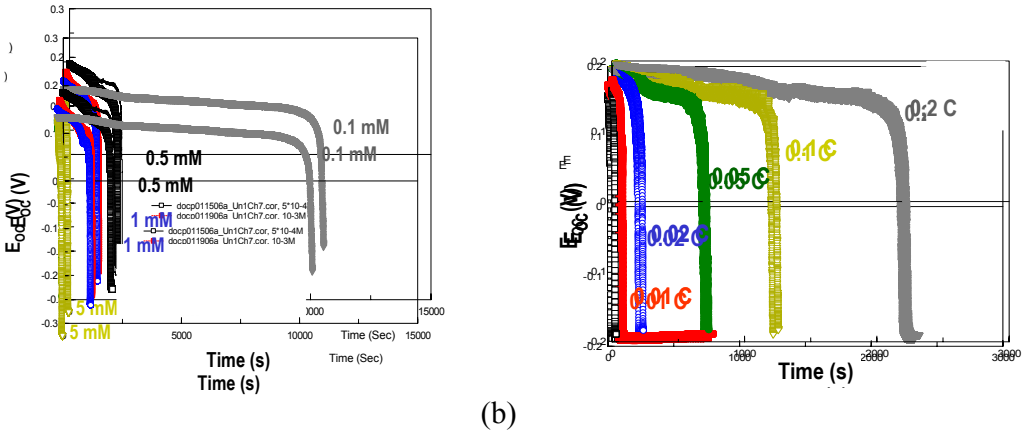


Figure 3. Open-Circuit Potential (E_{OC}) Behaviour Observed During the Reaction of Ag/Ag_2O with I^- in 0.02M Na_2HPO_4 Solution at pH 12.0; (a) at various KI concentrations where the total anodic charge used to grow the initial amount of Ag_2O was constant at 0.2C; (b) at various initial amounts (anodic charges) of Ag_2O at a constant KI concentration, 5×10^{-4}M.

Following the controlled formation of the Ag_2O film, the electrode was transferred to an aqueous solution containing KI. The open circuit potential as a function of reaction time observed (a) at various KI concentrations and (b) with various initial amount of Ag_2O is shown in Figure 3. For the KI dependence study, the Ag_2O film was formed in the 0.02M Na_2PO_4 solution by applying +0.6V until the total anodic charge reached +0.2C, while the I^- concentration ranged from 0.1mM to 5mM. For the Ag_2O dependence study, the I^- concentration was kept constant at 0.5mM, while the total anodic charge used to grow the initial Ag_2O film at +0.6V was varied from 0.01 to 0.2C

In all cases studied, the time-dependent behavior of the open-circuit potential showed three distinct stages. The initial E_{OC} was the same, ~0.2V, after a certain time at this value, E_{OC} decreased slowly, followed by a sudden drop to a new steady-state. This abrupt change in the E_{OC} indicates that the chemical reaction $Ag_2O + I^- \rightarrow AgI$ is complete, and the Ag surface became fully exposed to the I^- solution. The time to reach the lower steady-state corresponds to the total reaction time, T_{RXN}, which was observed to increase with the initial amount of Ag_2O and decrease with the I^- concentration. The completion of the reaction was confirmed by transferring the electrode back to the KI free solution, and performing cathodic stripping of the

electrode. No cathodic peak corresponding to the reduction of Ag_2O was observed and the cathodic charge used to reduce all AgI to Ag equaled the anodic charge used to grow the initial Ag_2O film. The cathodic stripping was also performed at a long time after the reaction was complete to ensure that no additional AgI was formed due to the reaction of Ag and I^-.

The initial value of E_{OC} was observed to be the same, ~0.2V, independent of the total anodic charge to grow the Ag_2O film and of the I^- concentration. This initial E_{OC} value is very close to the equilibrium potential of [2]:

$$\mathbf{2\ Ag\ +\ H_2O\ \Leftrightarrow\ Ag_2O\ +\ H_2} \qquad \mathbf{(7)}$$

On the other hand, the final E_{OC} is still independent of the initial Ag_2O amount, but depends on iodide concentration. The final E_{OC} is close to the equilibrium potential for:

$$\mathbf{2\ Ag\ +\ 2\ I^- + H_2O \Leftrightarrow 2\ AgI\ +\ OH^-\ +\ H_2} \qquad \mathbf{(8)}$$

where the E_{eq} is determined by the Nernst equation [1]:

$$\mathbf{E_{eq} = E_o + \left(\frac{RT}{F}\right) log\ [I^-]} \qquad \mathbf{(9)}$$

That the open-circuit potential is close to the E_{eq} for a given $[I^-]$ solution is a further indication that at the end of the reaction, no Ag_2O remained on the silver electrode and the Ag surface is fully exposed to the I^- solution [5].

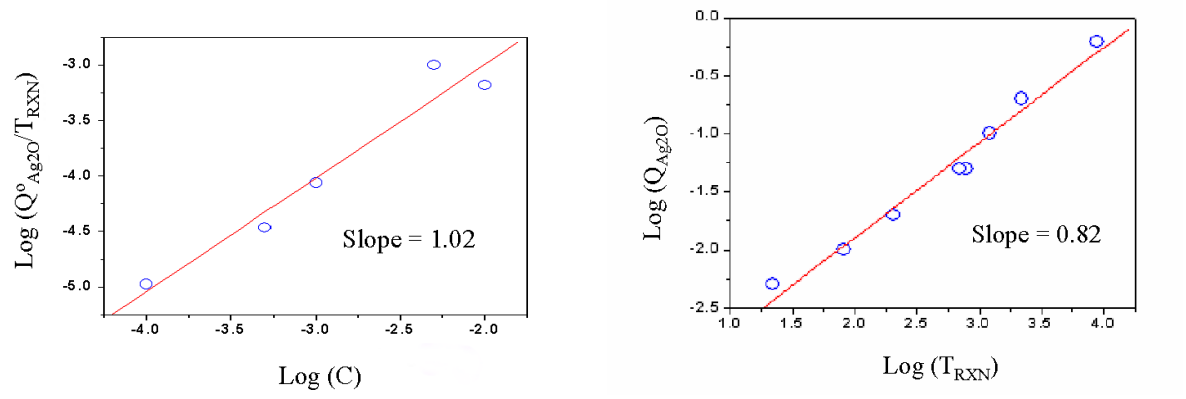


Figure 4. Reaction Rate Dependence on (a) $[I^-]$ and(b) Q^o_{Ag2O}, yielding the Reaction Orders from the slope

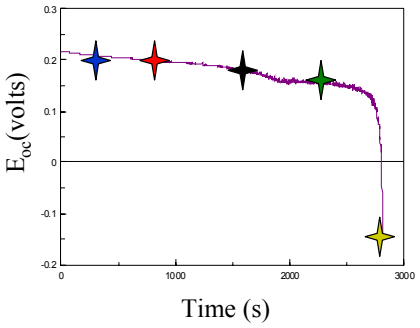
The reaction order dependence on $[I^-]$ and Ag_2O can be obtained from the total reaction time, T_{RXN}, as a function of $[I^-]$ and the initial Ag_2O amount. A kinetic analysis shows that the slope of the plot of the log $\frac{[Q^o_{Ag2O}]}{T_{RXN}}$ vs. log $[I^-]$ provides the reaction order on $[I^-]$. The observed slope of 1.02 (Figure 4a) indicates the reaction has a first order dependence on $[I^-]$.

The dependence on the Ag_2O film surface area can be obtained from the plots of the log of the charge required to grow the initial Ag_2O film (Q^o_{Ag2O}) vs. the log of the reaction time (T_{RXN}). The slope of the plot is 0.82. The slope observed is the product of the dependence of the initial Ag_2O surface area on Q^o_{Ag2O} and the reaction order with respect to the Ag_2O surface area. The initial surface area of Ag_2O is related to the total anodic charge needed to grow the oxide (Q_{Ag2O}) by the following relationship:

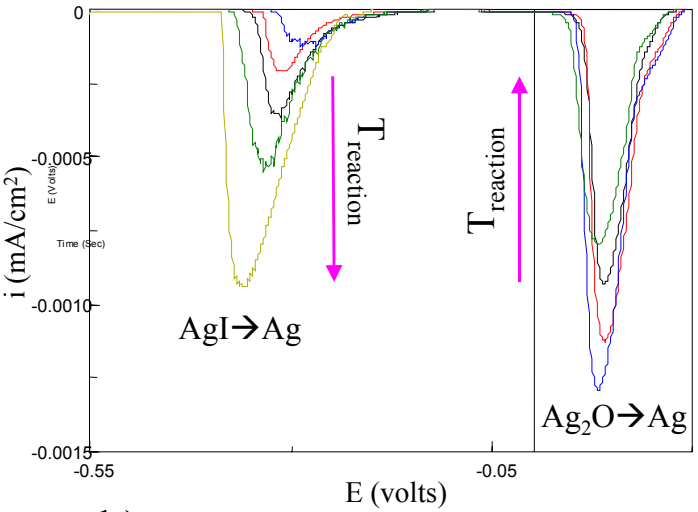
$$(Q_{Ag2O})_0 \propto (A_{Ag2O})_0 \cdot (d_{Ag2O})_0 \qquad (10)$$

where d_{Ag2O} is the thickness of the Ag_2O film and the subscript 0 indicates the initial value at reaction time zero [1]. The relationship between the initial Ag_2O surface area and Q^o_{Ag2O} is not known. If the Ag_2O film grows uniformly and flat on the silver electrode, the surface area of Ag_2O would be the same as the geometric surface area of the electrode, A_E. However, it does not grow uniformly in one dimension [3]. Therefore the surface area of the Ag_2O film is proportional to the power between 1/3 and 0 of A_E or 2/3 and 1 of Q_{Ag2O}. The observed slope of 0.82 is thus considered to be mainly due to this dependence of the initial Ag_2O surface area on Q_{Ag2O}. The reaction of Ag_2O and I^- to form AgI is thus considered to be first-order with respect to Ag_2O film structure.

To determine the rate constant the reactant (Ag_2O) and the product (AgI) concentrations were analyzed as a function of reaction time, this was accomplished by performing cathodic stripping of the electrode at various reaction times. The total charge used to grow the Ag_2O film was 0.2C, for all experiments. Once the Ag_2O film was formed it was transferred into the I^- + phosphate solution and the open-circuit potential was monitored as a function of time. In all cases, the iodide concentration was $5x10^{-4}$M. The reaction was terminated at various reaction times (Figure 6) by transferring the electrode back into the KI-free phosphate solution. This was followed by cathodic stripping from the open-circuit potential back to –1.1V at a scan rate of



a)



b)

0.17mV/s.

Figure 5. a) Shows the Potential at Which the Reaction was Terminated
b) The Cathodic Stripping Voltammograms recorded after termination of the reaction and transfer to the I^- - free solution.

Cathodic stripping reduces both the remaining Ag_2O reactant and the product AgI in two different potential ranges (Figure 5b). Integration of the reduction peaks shown in Figure 6b provides the total cathodic charges used for the reduction of both Ag_2O and AgI. As the reaction time, t_{RXN}, increased, the total cathodic charge used for the reduction of Ag_2O (Q_{Ag2O}) decreased, while the total cathodic charge used for the reduction of AgI (Q_{AgI}) increased. The total Q_{Ag2O} and Q_{AgI} as a function of reaction time are shown in Figure 6.

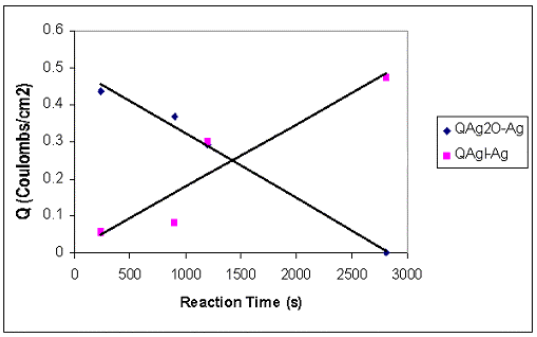


Figure 6. Reactant, Ag_2O and Product, AgI, Behaviour as a function of reaction time

For each reaction time the Q_{Ag2O} and Q_{AgI} terms added to a total of ~0.5C/cm^2 confirming that all of the anodic charge used to grow the initial Ag_2O film was retrieved when cathodically reducing the remaining Ag_2O and the product AgI [2,4]. The equal but opposite slopes indicate that the rate of loss of Ag_2O is equal to the rate of formation of AgI. It was established earlier that the reaction is first order with respect to [I^-] and the rate is directly proportional to the surface area of Ag_2O, thus the rate equation is:

$$\frac{d[AgI]}{dt} = \mathbf{k \,.\, [I^-] \,.\, (A_{Ag2O})} \qquad \mathbf{(11)}$$

Equation 11 was calculated under the experimental conditions, the rate constant was determined to be 4.15 x 10^{-6} (cm^2.s)$^{-1}$. A more extensive study is required to establish the uncertainties in this rate constant.

4. Summary and Conclusion:

- The kinetics of the chemical reaction $Ag_2O + I^- \rightarrow$ AgI can be determined using electrochemical techniques because the cathodic reduction potentials of Ag_2O to Ag and AgI to Ag are well separated and the E_{OC} is determined by $E_{eq}(Ag/H_2O)$ and $E_{eq}(Ag/AgI)$ which are very different.
- The linear increase in current with time for the electrochemical growth of Ag_2O shows that it is a porous film.
- Since the Ag_2O film growth is linear with time at a given applied potential and not impeded by the film formation, it is easy to control the initial amount of Ag_2O over a wide range prior to its reaction with I^-.

- The amounts of the reactant Ag_2O and product AgI on the silver surface were determined by cathodic stripping as a function of reaction time. The results were used to determine the kinetic parameters for the reaction.
- Since the time-dependent behaviour of the open circuit potential shows a sudden change upon the completion of the reaction, the total reaction time for the chemical reaction of Ag_2O to AgI can be easily measured. This total reaction time, measured as a function of the initial amount of Ag_2O $(Q_{Ag2O})_0$ and $[I^-]$, was used to determine the reaction orders.
- The results show that the reaction has a first order dependence on $[I^-]$, and a first order dependence on the initial Ag_2O surface area. The Ag_2O surface area remained constant during the reaction.

5. Future Work

- Investigating the effects of Ag_2O growth at lower potentials using our cathodic stripping method for analysis
- Examining the electrochemical formation of AgI by the reaction of $Ag + I_2$
- Investigating the $Ag_2O + I^-$ reaction in the presence of H_2O_2, as well as under radiolyisis conditions

6. Acknowledgement

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