J. Condensed Matter Nucl. Sci. 8 (2012) 115–123

Research Article

Electrochemistry and Calorimetry of Ruthenium Co-deposition

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Abstract

The electrochemical co-deposition of ruthenium (Ru) proved challenging due to the numerous possible oxidation states of this metal. Ruthenium (III) nitrosylnitrate, $Ru(NO)(NO_3)_3$, was investigated in the $NH_4Cl + NH_4OH/H_2O$ and $ND_4Cl + ND_4OD/D_2O$ electrolytes. The ruthenium solution had an intense red color that remained unchanged during extensive electrolysis at constant currents of 6, 10, 20 and 100 mA. However, at a constant current of 400 mA, the solution became completely clear overnight with a black deposit of ruthenium metal covering the copper cathode. The collapsed cyclic voltammetric trace indicated a large electrode capacitance (1–2 F) and a large ruthenium surface area (10^5 cm^2) similar to the previous observations for palladium co-deposition in this ammonia system. Extensive calorimetric studies using a constant current of 200 or 300 mA produced no measureable excess power in H_2O or D_2O for this ruthenium system. The very stable calorimetry allowed the determination of the effect of the electrolyte level on the cell constant at 0.0008 W/K mL for both the Ru/H_2O and the Ru/D_2O systems. The mean cell constants were 0.1318 ± 0.0025 W/K for the Ru/H_2O study and 0.1312 ± 0.0025 W/K for the Ru/D_2O experiment. There was no chemical excess power or shuttle reactions due to the nitrate ions present in these ruthenium solutions. In contrast to the palladium co-deposition studies, there was no detection of chlorine or nitrogen trichloride formation in any ruthenium co-deposition study. Based on out-gassing observations when the current was turned off, there was no absorption of hydrogen or deuterium within the bulk of the deposited ruthenium metal. Preliminary results are also reported for co-deposition studies of rhenium (Re), iridium (Ir), and nickel (Ni). Based on these new experiments with various metals, both palladium and D_2O are essential for excess power in co-deposition studies.

Keywords: Absorption, Capacitance, Cell constants, Oxidation states, Vacancies

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1. Introduction

Previous co-deposition calorimetric experiments in the $ND_4Cl + ND_4OD/D_2O$ electrolyte have focused solely on the Pd/D system [1,2]. However, if the anomalous excess power is due to near surface effects or vacancies, then other metals may also be active in producing excess power in co-deposition experiments. The use of other metals will also allow for the testing of the calorimetric system under conditions similar to those for the Pd/D co-deposition system. Ruthenium was selected because this metal was previously investigated as a supercapacitor material [3]. It has been proposed

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that the large electrochemical capacitance effects observed for ruthenium may involve hydrogen ion absorption into the metal as well as adsorption at the surface [3]. Similar to platinum and palladium, ruthenium is also an excellent catalyst for water electrolysis, fuel cells and other processes. Ruthenium has the electronic configuration $[Kr]4d^7 5s^1$ and exhibits various oxidation states in its compounds. The most common oxidation state is 3+ as found for $Ru(NO)(NO_3)_3$. This is explained by the loss of two electrons from the 4d level and one electron from the 5s level to give the more stable electronic configuration $[Kr]4d^5 5s^0$. Other oxidation states for ruthenium are 4+ as illustrated by RuO_2, 8+ as found for the toxic RuO_4, as well as 2+, 5+, 6+, and 7+ oxidation states [4]. The seven oxidation states for ruthenium are tied with osmium as the most for any metal [4]. Another major reason for this ruthenium experiment is that it may serve as a control regarding possible chemical excess heat due to shuttle reactions in the $ND_4Cl + ND_4OD + D_2O$ co-deposition system [5–7]. This study will also provide a comparison between the similarities and differences encountered in palladium and ruthenium co-deposition systems.

2. Experimental

Calorimetric studies used a new isoperibolic design as previously reported [8,9]. Electrochemical experiments such as cyclic voltammetry (CVA) and electrochemical impedance spectroscopy (EIS) were performed using the Princeton Applied Research PARSTAT 2272 with the appropriate software as described elsewhere [6]. The deuterated chemicals used were Cambridge Isotope Laboratories D_2O (99.9 atom % D), ACROS ND_4Cl (98 atom% D), and ACROS ND_4OD (99 atom% D). Alfa-Aesar ruthenium (III) nitrosylnitrate, $Ru(NO)(NO_3)_3$, was used for the electrochemical deposition of ruthenium metal. The actual solution concentrations were 0.02534 M $Ru(NO)(NO_3)_3$, 0.1468 M ND_4Cl, and 0.45 M ND_4OD for the Ru/D_2O study and 0.02158 M $Ru(NO)(NO_3)_3$, 0.1502 M NH_4Cl, and 0.45 M NH_4OH for the Ru/H_2O study.

3. Results

3.1. Electrochemical deposition of ruthenium

The electrochemical deposition of ruthenium from the $Ru(NO)(NO_3)_3 + NH_4Cl + NH_4OH/H_2O$ solution proved to be much more difficult than the deposition of palladium from this ammonia system. This was likely due to the multiple of oxidation states for ruthenium. The $NH_4Cl + Ru(NO)(NO_3)_3$ dissolved readily in H_2O to form a dark red solution with pH = 2.53. This acidic ruthenium solution was stable towards displacement reactions for all metals that were tested (Cu, Ni, Co, Al, Ta, Mo, Hf, Ag and Pt). Therefore, metal ion impurities due to chemical reactions should not be a concern in these ruthenium solutions. The addition of 0.15 M NH_4OH did not produce the expected precipitate, thus the NH_4OH concentration was increased to 0.45 M. The solution remained dark red and gave no precipitate with the pH = 9.67. The intense red color of the ruthenium solution remained unchanged during extensive electrolysis at constant currents of 6, 10, 20 and 100 mA. Finally, at a constant current of 400 mA, the ruthenium solution became completely clear overnight with a robust deposit of black ruthenium metal covering the copper cathode. The measured pH of the solution also decreased to pH = 2.02. This is similar to the pH effects observed for palladium co-deposition [6]. The acidic solution produced (pH = 2.02) is due to the cell reaction

$$2Ru^{+++} + 3H_2O \rightarrow 2Ru + 3/2O_2 + 6H^+, \qquad (1)$$

where each Ru^{+++} ion deposited is replaced by three hydrogen ions to maintain charge neutrality. Furthermore, the electrolysis gases at high currents drive off the ammonia. There was no detection of chlorine evolution or the related formation of nitrogen trichloride, NCl_3, as previously observed for palladium deposition in this ammonia electrolyte [5,6]. However, this Cl_2/NCl_3 phase may have been passed through quickly overnight at 400 mA. Based on the initial Ru^{+++} concentration in H_2O (0.02158 M), the expected final pH would be 1.19. The higher measured pH = 2.02 could

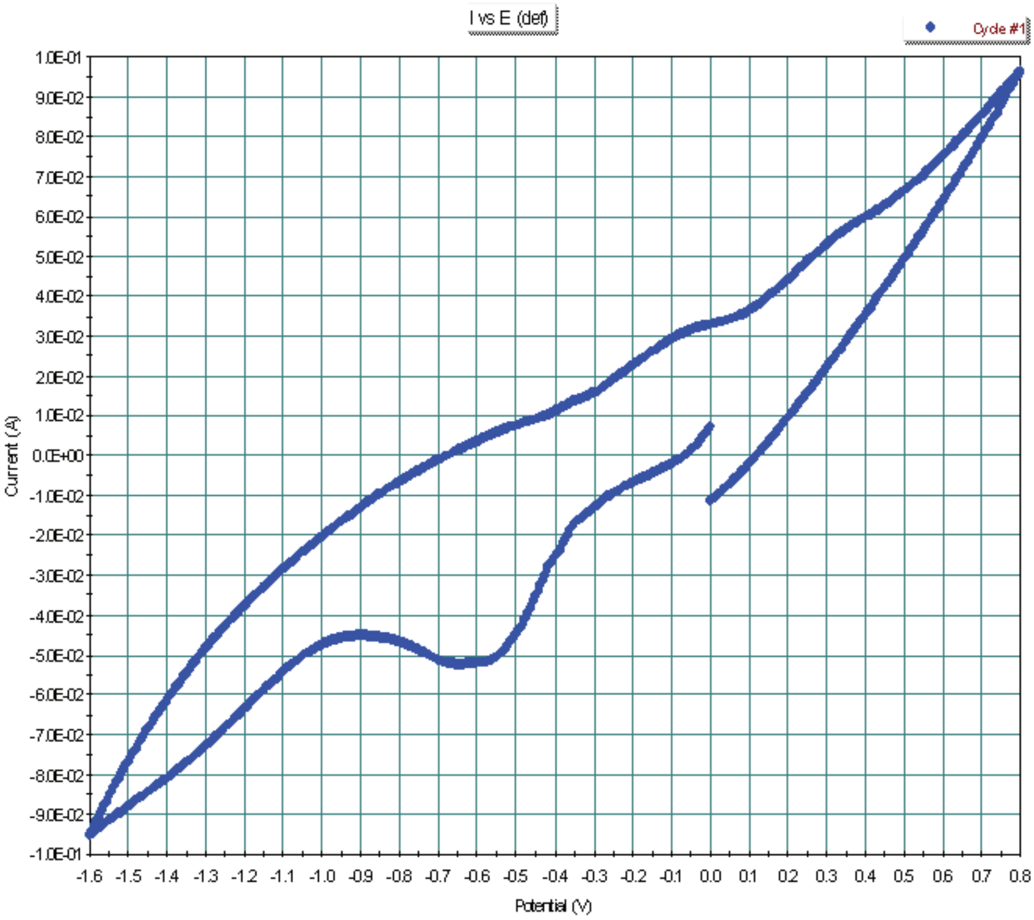

Figure 1. Cyclic voltammetric study prior to the completed ruthenium deposition. The potential sweep rate was 50 mV/s.

be due to some chlorine evolution. Another possibility is the oxidation of small amounts of ruthenium ions to form the volatile and toxic RuO_4 that may exit the cell.

3.2. Electrochemical investigations

The cyclic voltametric study of the cathode before the completed ruthenium deposition is shown in Fig. 1. The solution was still dark red in color, but the copper cathode was completely black due to the partial ruthenium deposition. This study was made following the application of a constant current of 100 mA for 24 h. The reduction peak at -0.63 V may be due to the reduction of Ru^{+++} ions to Ru^{++} or Ru metal. The small oxidation partial peak at -0.05 V could be due to Ru^{++} oxidation back to Ru^{+++}. However, this cyclic voltammogram appears to be partially tilted and collapsed

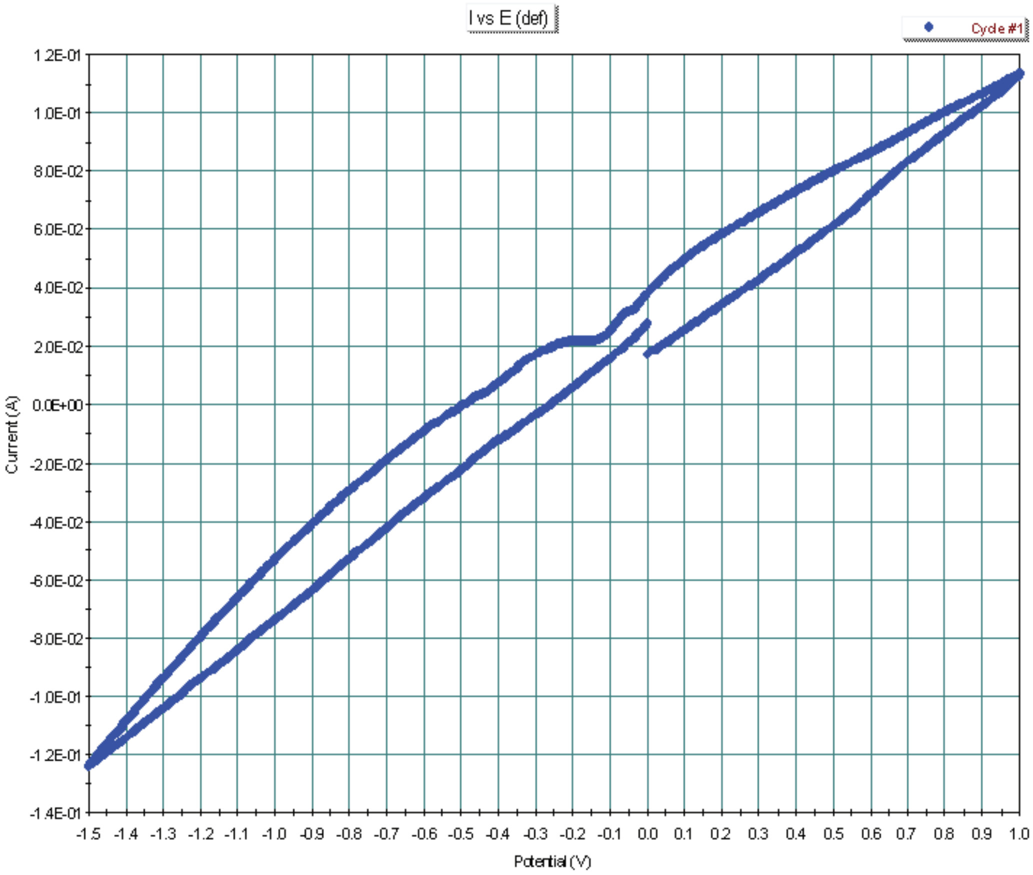

Figure 2. Collapsed and tilted cyclic voltammetric trace following the complete deposition of ruthenium (50 mV/s).

towards Ohm's law behavior due to a large capacitance effect as previously reported for palladium deposition [5]. A reasonable cell resistance of 8.312 Ω can be calculated from the cell currents and voltages at the end points.

Figure 2 presents the cyclic voltammetric study following the complete deposition of ruthenium at a constant current of 400 mA. The cyclic voltammogram is now almost completely tilted and collapsed into a featureless Ohm's law behavior as found for palladium deposition [5,6]. A cell resistance of 10.52 Ω is calculated from the end points for the cell currents and voltages using Ohm's law. This result indicates a capacitance of about 1–2 F for the ruthenium cathode and a surface area of about 10^5 cm^2 (Refs. [3,5]).

Figure 3 presents the Nyquist plot for an EIS study after further electrolysis at 50 mA over the weekend. A reasonable semicircle is observed followed by the beginning of a larger semicircle at lower frequencies. The EIS results suggest good electrode kinetics due to the larger surface area and also provides an accurate value of 14.25 Ω for the cell resistance. From the measured charge transfer resistance ($R_{\rm ct}$) of 3.30 Ω, an exchange current of 4×10^{-3} A is calculated for the electrode reaction at open circuit.

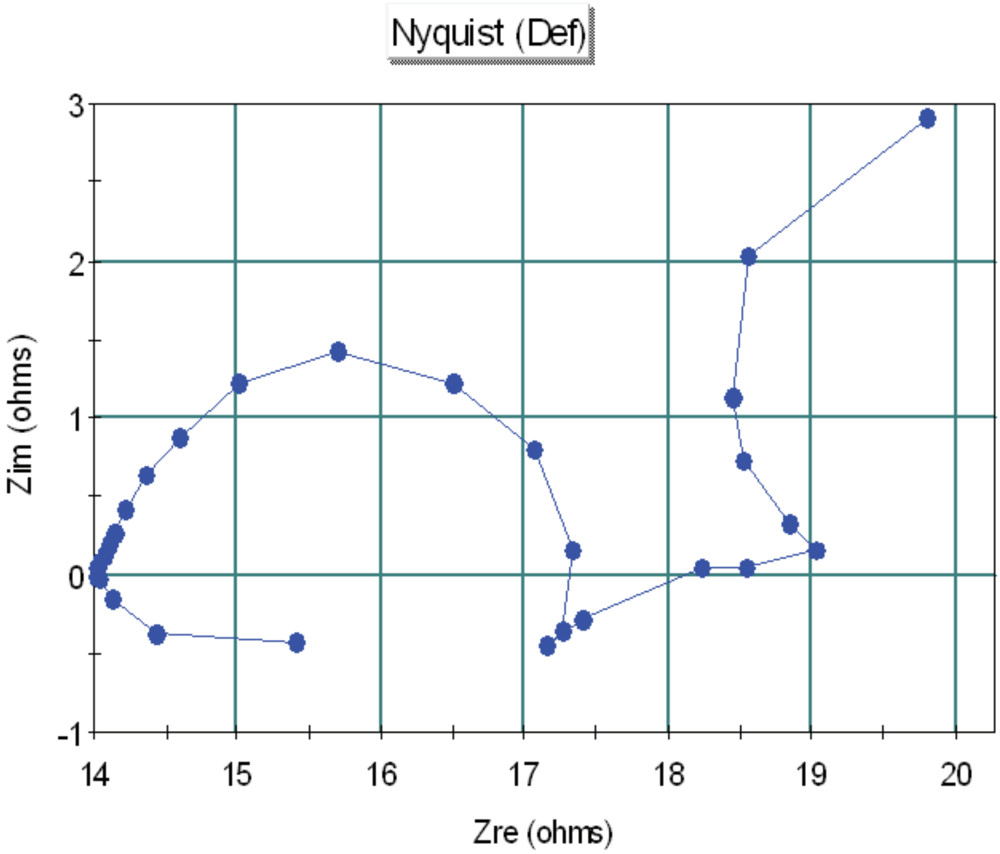

Figure 3. Nyquist plot for an EIS study after further electrolysis. The frequency range was from 100 kHz to 10 mHz.

3.3. Calorimetry

The simplest starting point for calorimetric measurements is (Refs. 8–10)

$$P_x = (k_C - k'_C)\Delta T, \tag{2}$$

where P_x is the excess power, k_C is the true conductive heat transfer coefficient, k'_C is the lower bound conductive heat transfer coefficient obtained by assuming $P_x = 0$. Obviously k_C and k'_C would be identical if there were actually no excess power. The advantage of this simple equation is that all other calorimetric power terms cancel in this derivation [8–10]. For the calorimeter used in this study, the true conductive heat transfer coefficient has been established as 0.1340 W/K when the electrochemical calorimetric cell is filled with 50.0 mL of electrolyte. This cell constant will decrease as the electrolyte level decreases during electrolysis.

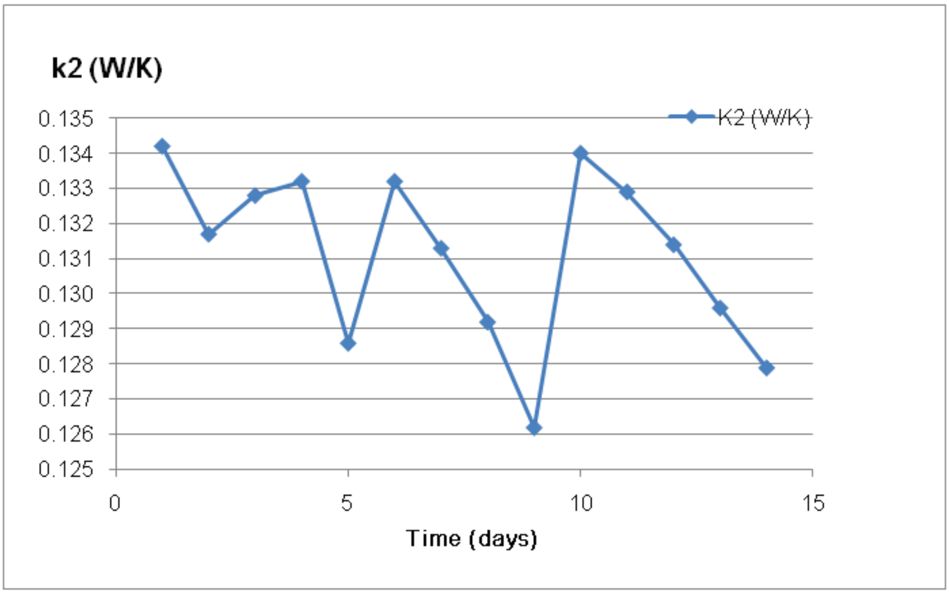

Figure 4. Calorimetric lower-bound conductive heat transfer coefficient (k_2) versus time for the Ru/H_2O experiment in the NH_4Cl + NH_4OH/H_2O electrolyte.

Figure 4 presents the lower-bound conductive heat transfer coefficient (k_2) measured using Thermistor 2 for the Ru/H_2O experiment in the ammonia (NH_4Cl + NH_4OH/H_2O) electrolyte.

This calorimetric study at a constant current of 300 mA shows only the expected changes of the cell constant due to changes in the electrolyte level. The peaks show where make-up H_2O was added to the cell. These results are for Thermistor 2 used in the calorimeter. A second thermistor (Thermistor 4) positioned on the opposite side of the electrochemical cell provided results (k_4) similar to those of Fig. 4.

Figure 5 shows the lower-bound heat transfer coefficient (k_2) for the Ru/D_2O experiment in the ND_4Cl + ND_4OD/D_2O electrolyte. This cell started with an over-filled electrolyte level of about 55 mL, thus the cell constant (k_2) is higher at the beginning. Also, lower currents of 200 and 250 mA were used during the first few days. Nevertheless, the results in Fig. 5 are very similar to those shown in Fig. 4. Both the Ru/H_2O and the Ru/D_2O studies were run longer than normal between cell re-filling in order to measure the effect of the electrolyte level in these stable calorimetric experiments. Much smaller changes in k_2 would occur with the normal cell filling every 1 or 2 days.

As shown in Figs. 4 and 5, there are no significant differences between the Ru/H_2O and the Ru/D_2O experiments because neither study produced excess power. In fact, the mean calorimetric cell constants are almost identical. For Ru/H_2O, the mean cell constant is $\langle k_2 \rangle = 0.1318 \pm 0.0030$ W/K while $\langle k_2 \rangle = 0.1312 \pm 0.0025$ W/K for Ru/D_2O. These mean cell constants are less than the true value of 0.1340 W/K because the mean electrolyte level is less than the initial filled volume of 50.0 mL. The error ranges given for $\langle k_2 \rangle$ reflect the larger than normal changes in the electrolyte volume rather than actual calorimetric errors. The calorimetric stability for these ruthenium studies allowed the measurements of the effect of the electrolyte level on the cell constant, $\Delta k_2/\Delta V$. For both Ru/H_2O and Ru/D_2O, the results were measured as $\Delta k_2/\Delta V = 0.0008 \pm 0.0001$ W/K mL.

3.4. Consumption of H_2O and D_2O

The H_2O or D_2O consumption has been measured in every co-deposition study using the ammonia system. These measured amounts are then compared with the theoretical calculations based on Faraday's law using −9.03 mL/F for H_2O electrolysis and −9.07 mL/F for D_2O electrolysis where F = 96,485 C/eq (C = A s). Previous results are presented elsewhere [6]. In these experiments, the Ru/H_2O study gave a measured H_2O consumption of 45.5 mL versus the theoretical value of 40.7 mL. For the Ru/D_2O study, the measured consumption of D_2O was 43.0 mL versus the theoretical value of 41.8 mL. The ratio of measured/theoretical is 1.12 for Ru/H_2O and 1.03 for Ru/D_2O. This is consistent, within error limits, of previous studies [6]. Including these ruthenium results with six previous palladium studies [6] yields a mean measured/theoretical ratio of 1.083 ± 0.099. None of these consumption measurements suggest any significant recombination of the electrolysis gases or any significant shuttle reactions [6]. This measured/theoretical ratio is expected to be somewhat larger than unity due to H_2O or D_2O evaporation where the vapor exits the cell with the electrolysis gases [10]. The exact value of this ratio is largely determined by the temperature of the vapor at the glass exit tube.

4. Discussion

4.1. Ruthenium red

The difficulty of the electrochemical deposition of ruthenium and the deep red solution color is likely due to the formation of the inorganic dye "Ruthenium Red" [4]. This substance, $[(NH_3)_5\text{–Ru-O-Ru}(NH_3)_4\text{-Ru}(NH_3)_5]^{6+}$ is produced by the treatment of "$RuCl_3$" with aqueous ammonia in air [4]. These conditions were certainly present in these experiments using the ammonia and ammonium chloride electrolyte and the production of oxygen at the anode. Two Ru atoms are in the 3+ oxidation and one is in the 4+ oxidation state in this substance. High over-voltages produced by high currents are likely needed to break up this stable substance and reduced the "Ruthenium Red" ruthenium ions to the metal. This

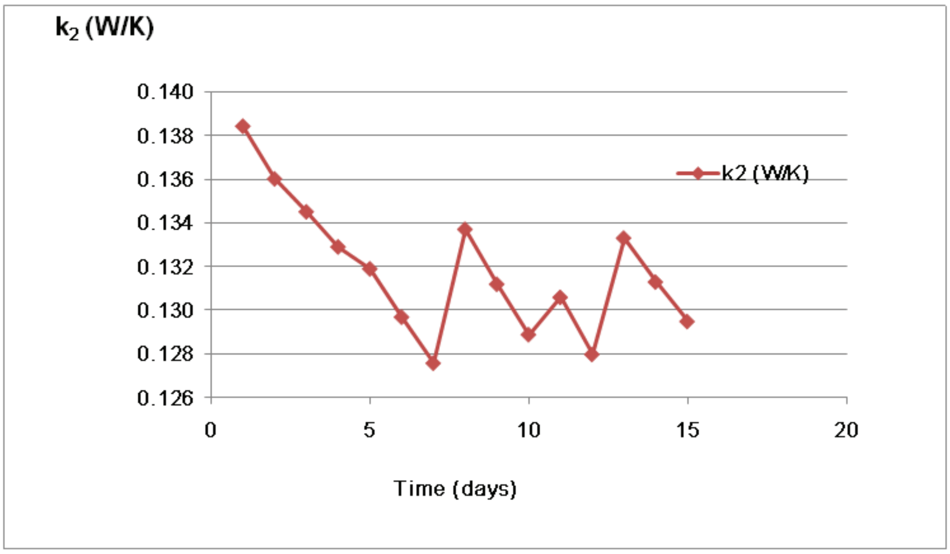

Figure 5. Calorimetric lower-bound heat transfer coefficient (k_2) versus time for the Ru/D_2O experiment in the $ND_4Cl + ND_4OD/D_2O$ electrolyte.

is very different from the palladium co-deposition system where the reduction of palladium ions occurs readily at low currents.

4.2. Nitrate ions

The 0.025 M $Ru(NO)(NO_3)_3$ dissolves to form 0.075 M NO_3^- in H_2O or D_2O solutions. It has been proposed that nitrate ions may form from the NH_4Cl + NH_4OH solutions and undergo shuttle reactions that give an excess power effect [5–7]. The lack of any excess power effect in these studies despite the presence of nitrate ions provides further evidence against proposed shuttle reactions in this ammonia based co-deposition systems [5,6].

4.3. Electrolyte level effect

The ruthenium experiments that gave the electrolyte level effect of $\Delta k_2/\Delta V = 0.0008$ W/K mL involved the usual 50.0 mL of the heat conducting fluid (Mobile-1 oil) surrounding the glass electrochemical cell within the calorimeter [8]. This heat conducting fluid was, therefore, always above the electrolyte level in the cell. In the next experiment with rhenium, only 35.0 mL of the heat conducting fluid was added. This simple change reduced the electrolyte level effect by about a factor of four to yield 0.0002 W/K ml. Maintaining the electrolyte level above the level of the heat conducting fluid maintains a constant surface area for the main heat transfer pathway from the electrolyte across the heat conducting fluid and cell insulation to the water bath. This principle is similar to the Fleischmann–Pons Dewar cell that is silvered at the top in the region of the electrolyte level to maintain a constant surface area for radiative heat transfer [10]. When properly filled, the electrolyte level is at the mid-point of the silvered region for the Dewar cell [10]. The silvered region does not support radiative heat transfer in the Dewar cell. Similarly, the regions filled with air or electrolysis gases in this copper calorimeter are not nearly as effective as the liquid phases for heat transfer by conduction. Providing a constant surface area for heat transport is an important feature for accurate isoperibolic calorimeters.

4.4. Role of vacancies

Metal vacancies created in co-deposition experiments may be important for the excess power effect [11]. The creation of vacancies during the co-deposition of metals mainly requires the absorption of hydrogen or deuterium into the metal lattice to give a high H/M or D/M ratio where M represents a metal [11]. Based on this study, ruthenium produces very little absorption of H or D into the metal. Unlike palladium, the outgassing of hydrogen from ruthenium stopped abruptly when the current was switched off. This observation agrees with ruthenium studies at high hydrogen pressures (90 kbar) that gave only very small ratios of H/Ru = 0.03 [12]. Therefore, the low level of acceptability of hydrogen into the ruthenium lattice and the resulting low level of vacancies may explain why there was no measurable excess power for the Ru/D co-deposition system.

4.5. Preliminary results for the co-deposition of other metals

Initial studies for the co-deposition of rhenium (Re), iridium (Ir), and nickel (Ni) have been completed using the same ammonia electrolyte as used for palladium and ruthenium. No measurable excess power was detected in the calorimetric studies. The compounds used were $ReCl_3$, $IrCl_3$, NiO, and $NiCl_2 \cdot 6\,H_2O$. Low cell currents (6–10 mA) were used for Re and Ir deposition as well as for the study using NiO. However, a much larger deposition current of 200 mA was used for the $NiCl_2 \cdot 6\,H_2O$ experiment. None of these metals showed any significant hydrogen absorption based on out-gassing observations. In fact, iridium is one of the most resistive metals to hydrogen absorption with H/Ir = 0.005 even at 90 kbar (90,000 atm) hydrogen pressure at 250°C [12].

It should be noted that the complete deposition of the metal was achieved in all studies except for the iridium solution where a black precipitate remained. However, about half of the iridium was deposited onto the cathode in the usual black form. The statistical analysis of all 19 co-deposition experiments involving Pd, Ru, Re, Ni and Ir in H_2O and D_2O yields a probability of greater than 99.9999% that the anomalous excess power effect in these co-deposition studies requires the presence of both palladium metal and D_2O. The probability that these results showing excess power only for the Pd/D co-deposition systems could be due to random errors calculates to be less than one in a million.

5. Summary

The electrochemistry and chemistry of the ruthenium co-deposition system varied markedly from the palladium system. However, the black metallic deposit, the high surface capacitance, the high electrode area produced, the H_2O and D_2O consumption, and the large changes in the solution pH were similar. However, no excess power was observed for the Ru/D system. This is likely due to the low level of acceptability of hydrogen or deuterium into the ruthenium metal lattice. The very stable calorimetry for the ruthenium co-deposition system permitted accurate measurements of the electrolyte level effect on the calorimetry.

Acknowledgements

The author thanks the New Energy Foundation, Concord, NH for a donation to purchase the PAR Model 362 Scanning Potentiostat used in the calorimetric studies. Financial support of this work was from an anonymous fund at the Denver Foundation. Dixie State College of Utah and the Dixie Foundation, especially Kalynn Larson, assisted in the administration of this fund.

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