Research Article

Investigations of Possible Shuttle Reactions in Co-deposition Systems

Melvin H. Miles*

Dixie State College, St. George, UT 84770, USA

Abstract

Experiments in the 0.025 M $PdCl_2$ + 0.15 M ND_4Cl + 0.15 M ND_4OD/D_2O co-deposition system produced anomalous excess power in three out of three prior experiments in Japan. Completely new experiments have produced even larger excess power effects for this deuterated co-deposition system. The largest excess power effect in D_2O produced 1.7 W or about 13 W/g of palladium (160 W/cm^3). These large excess power effects were absent in extensive studies of H_2O controls. Excess power was also absent in various experiments involving the co-deposition of ruthenium (Ru), rhenium (Re), and nickel (Ni) in both H_2O and D_2O ammonia solutions. The statistical analysis of all 18 co-deposition experiments yields a probability of greater than 99.9989 % that the co-deposition excess power effect requires both palladium metal and D_2O. Shuttle reactions have been proposed to explain the reproducible excess power effect in this ammonia co-deposition system. However, various electrochemical studies show no evidence for any shuttle reactions in this ammonia system. Nevertheless, the initial chemistry for the Pd system is complex leading to large pH changes, chlorine (Cl_2) evolution, and the formation of nitrogen trichloride (NCl_3) during the first few days. However, the large excess power effects are observed later in the experiments after this chemistry is completed. A better understanding of the chemistry should be helpful in the reproduction of anomalous excess power in co-deposition systems.

Keywords: Ammonia, Calorimetry, Electrochemistry, Excess Power, Palladium

1. Introduction

Anomalous energy or power observed in the Pd/D system is often called the Fleischmann–Pons Effect (FPE) to avoid the controversy of labeling this as a nuclear process. However, the term Chemically Assisted Nuclear Reactions (CANR) is also used to stress the important role of chemistry. The understanding of the chemistry involved is especially important for this study of the FPE in Pd/D co-deposition systems.

Anomalous effects for Pd/D co-deposition were first reported by Szpak and Mosier-Boss using the $PdCl_2$ + $LiCl/D_2O$ system [1,2]. However, commercial electroplating baths for palladium are often based on $Pd(NH_3)_2Cl_2$ in aqueous NH_4Cl/NH_3 at pH 7–10 [3]. This related $PdCl_2$ + ND_4Cl + ND_4OD/D_2O ammonia system previously produced large

*E-mail: melmiles1@juno.com

excess power (FPE) in all three experiments conducted in 1998 at the New Hydrogen Energy (NHE) laboratory in Japan [4–6]. Features observed in this new co-deposition system such as the effect of thermal perturbations (positive feedback) and the effect of cell current perturbations (heat-after-death) were similar to anomalous effects observed in other Pd–D systems [6]. Nevertheless, the reproduction of co-deposition effects by other groups has proven to be illusive, hence a better understanding of the chemistry is needed. Recent studies [7] have shown that each Pd^{++} ion deposited is replaced by two H^+ (D^+) ions to maintain electroneutrality, and the electrolysis gases gradually drive off the ammonia, thus large pH changes occur (pH = 8.87–1.25) during the first few days of electrolysis. Chlorine evolution and the formation of yellow nitrogen trichloride (NCl_3) are observed with Pd under acidic conditions, but these chemical effects dissipate within the first three days in an open system [7]. The large excess power effects measured in D_2O, but not in H_2O, occur after the yellow solution coloration due to the NCl_3 has cleared. Although the Naval Research Laboratory (NRL) reproduced an excess power effect for this $PdCl_2 + ND_4Cl + ND_4OD/D_2O$ system in 2009 using an open Seebeck calorimeter [8], they proposed that the effect may be due to chemical and electrochemical shuttle reactions (a form of recombination) involving nitrates or chlorates that may form in this system [9,10]. We report here various electrochemical studies designed to test for possible shuttle reactions involving nitrates, nitrites, and chlorates. Previous calorimetric experiments showed no excess power effects for either the potassium nitrate (KNO_3) electrolyte [11,12] or the sodium chlorate ($NaClO_3$) electrolyte [11].

2. Experimental

Electrochemical studies such as cyclic voltammetry (CVA) and electrochemical impedance spectroscopy (EIS) were performed using the Princeton Applied Research (PAR) PARSTAT 2273 with the appropriate software (PowerCV, PowerPULSE, PowerSINE). Calorimetric studies used a new isoperibolic design as previously reported [11,12]. Temperatures were measured to within ±0.005 K using a Cole Parmer Thermistor Thermometer unit consisting of five thermistor probes. The bath temperature was controlled to within ±0.005 K by use of a Techne TE-100 unit. The constant current used in calorimetric studies was provided by the PAR Model 363 Potentiostat/Galvanostat or by the PAR Model 362 Scanning Potentiostat. The solution pH was monitored using a Oakton pH 6 Acorn Series pH/mV/°C meter (±0.01 pH units). Commercial chlorine detectors (Chromair System) were used to monitor the gases escaping from the cell. The deuterated chemicals used were ACROS D_2O (99.8 atom% D), ACROS ND_4Cl (98 atom% D), and ACROS ND_4OD (99 atom% D) while Alfa-Aesar Premion $PdCl_2$ (99.999% metals basis) was the palladium source. A copper cathode (0.318×2 cm, 99.999%) from Alfa-Aesar (Puratronic) served as the substrate ($A = 2.1$ cm^2).

3. Results

3.1. Reactivity of various metals with the solution

The 0.025 M $PdCl_2$ dissolves in the 0.15 M ND_4Cl to give an orange solution. However, the addition of 0.15 M ND_4OD produces an orange colored precipitate by the proposed reaction

$$PdCl_2 + 2\,ND_4OD \rightarrow Pd(OD)_2 + 2\,ND_4Cl, \tag{1}$$

where Pd^{++} ions removed by precipitation are replaced by additional ND_4^+ ions. The exact nature of this precipitate is unknown, but the addition of alkali to aqueous solutions of palladium ions (Pd^{++}) produces a precipitate of the hydrous oxide [13]. Nevertheless, the resulting low activity of palladium ions explains the stability of the copper cathode towards the displacement reaction, $Cu + Pd^{++} \rightarrow Cu^{++} + Pd$, in this initial solution. It was found experimentally that the metals Cu, Ag, Ni, Co, Fe and Al all showed displacement reactions with the $PdCl_2 + NH_4Cl$ solution prior to the addition of NH_4OH or ND_4OD that precipitates palladium ions (Eq. (1)). The displacement reaction involving the various metal wires could be visually observed by the darkening of the metal surface by the palladium deposit. These displacement

reactions can be a source for metal ion impurities in co-deposition systems that may affect the FPE reproducibility. No reactions were observed for these metals following the addition of the ammonia solution to give the precipitation reaction. However, placing the copper substrate directly into the orange colored precipitate where there was a higher palladium ion activity led to a gradual darkening of the copper. There were several metals (Pt, Mo, Ta and Hf) that gave no reactions before or after the palladium precipitation. Stable oxide films likely protect Mo, Ta, and Hf while Pt is an unreactive noble metal similar to Pd.

3.2. The palladium deposition step

A low current of 6.00 mA (2.86 mA/cm^2 based on the initial copper cathode area) was used for 24 h or more for the palladium deposition and gave a cell voltage of about 2 V. The net cell reaction for the palladium deposition step can be expressed as

$$Pd(OD)_2 \rightarrow Pd + {}^1/_2 O_2 + D_2O. \qquad (2)$$

Deuterium gas is also formed at the cathode and is co-deposited as PdD_X. Theoretically, the deposition of all of the palladium onto the copper cathode would require only 11.2 h at 6.00 mA if all of the cathodic current were used for the reduction of palladium ions. Thus, more than half of the cathodic current during the first 24 h is used for the reduction of D_2O to form D_2 gas at the cathode, $2 D_2O + 2 e^- \rightarrow D_2 + 2 OD^-$, rather than palladium deposition, $Pd(OD)_2 + 2 e^- \rightarrow Pd + 2 OD^-$.

The deposition of palladium onto the copper substrate gradually produces a very large electrode capacitance (C). As reported previously [7], this increasing capacitance effect can be seen by the gradual tilting and collapsing of the cyclic voltammogram traces during the palladium deposition step. The black dendritic palladium deposit produces capacitance values equal to those of supercapacitor materials (370 F/g). The measured electrode capacitance indicates that the deposited palladium gives an effective surface area of 10^6 cm^2 (Ref. [7]). The deposited dendritic black palladium is in the form of nanoparticles that have an unusually large capacitance [7]. The resulting large RC time constant, where R is the cell resistance, distorts the cyclic voltammograms into approximately Ohm's law behavior [7,14].

The $PdCl_2 + NH_4Cl + NH_4OH/H_2O$ system serves as a buffered solution, hence there are only slight pH changes during the palladium deposition step at 6.00 mA. In one H_2O experiment, the initial pH was 8.87 while the pH was measured at 8.70 when the palladium deposition was complete. However, the application of higher currents drives off the ammonia, the buffering capacity is lost, and large pH changes are observed. The replacement of 0.025 M Pd^{++} ions by 0.050 H^+ to maintain electroneutrality would give a measured pH of 1.30. This transition to an acidic solution at higher currents is always marked by a noticeable decrease in the magnitude of the cell voltage because H^+ ions are reduced more readily than H_2O molecules. An example of this cell voltage change observed in a H_2O control cell is shown in Fig. 1. The initial pH for the electrolysis at 20 mA (Fig. 1) was 8.70 and the final pH was 1.75. The sharp change in the cell voltage near 70,000 s mirrors the sharp transition to an acidic solution (pH = 8 to pH = 2).

There is a much higher overvoltage at the cathode for the reduction of H_2O molecules, $2H_2O + 2e^- \rightarrow H_2 + 2 OH^-$, than there is for the direct reduction of hydrogen ions, $2 H^+ + 2e^- \rightarrow H_2$. Molecular bonds must be severed for H_2O reduction but not for H^+ reduction. As soon as the reduction of H^+ can carry a significant fraction of the cathodic current, a net decrease in the magnitude of the cell voltage is observed. This effect has been seen in every experiment involving this system including the NRL experiments [8–10]. Previous studies have established that the reduction of hydrogen ions is the charge-transfer reaction in the acidic pH range, and the direct reduction of water is the predominant charge-transfer mechanism at higher pH values [15].

The observed change in pH can be simply explained by the equilibrium reaction

$$NH_3 + H^+ \leftrightarrow NH_4^+. \qquad (3)$$

The presence of ammonia (NH_3) gas dissolved in water is often represented as NH_4OH, but this is not an actual compound. The dissolved ammonia acts as a buffer and converts the H^+ ions produced to NH_4^+ as shown in Eq. 3. However, when the dissolved NH_3 gas is driven off by the electrolysis gases, then this NH_4^+ reverts back to H^+. Thus, the simple chemistry of Eq. (3) readily explains the large pH change observed in this system at the higher currents. The measured pH of 1.25 following the palladium deposition and the loss of the ammonia is in close agreement with the net cell reaction

$$Pd^{++} + H_2O \rightarrow Pd + {}^1\!/_2O_2 + 2H^+, \tag{4}$$

where Pd deposits at the cathode and oxygen forms at the anode and each deposited Pd^{++} ion is replaced by two H^+ ions. Thus, the 0.0272 M $PdCl_2$ actually used in this experiment becomes 0.0544 M HCl (pH = 1.26) when the palladium deposition in the H_2O experiment is completed and all the ammonia is driven off. This large pH change is the normal behavior expected for any palladium co-deposition system. Similar pH changes will occur for the deposition of other metals.

3.3. Production of chlorine and nitrogen trichloride

The transformation to acidic solution (HCl or DCl) shown in Fig. 1 makes chlorine evolution thermodynamically more competitive with the oxygen evolution at the anode, $2\,Cl^- \rightarrow Cl_2 + 2e^-$ versus $H_2O \rightarrow {}^1\!/_2\,O_2 + 2\,H^+ + 2e^-$ ($E_o =$ 1.3583 V for Cl_2 and 1.2288 V for O_2 in acid at standard conditions). Although oxygen evolution is still favored in acidic solutions by thermodynamics, the electrode kinetics are slow due to the breaking of bonds in the H_2O molecule to form oxygen. Therefore, the formation of chlorine as well as oxygen occurs at the anode in acidic solutions. This was shown by the use of chlorine detectors [7]. The introduction of chlorine gas into an acidic NH_4Cl solution is known to produce nitrogen trichloride

$$NH_4Cl + 3Cl_2 \rightarrow NCl_3 + 4HCl. \tag{5}$$

Nitrogen trichloride is a volatile, yellow oily liquid of high density (1.653 g/cm^3), only slightly soluble in water, and explosive in pure form. The formation of NCl_3 could be readily observed experimentally as a yellow solution
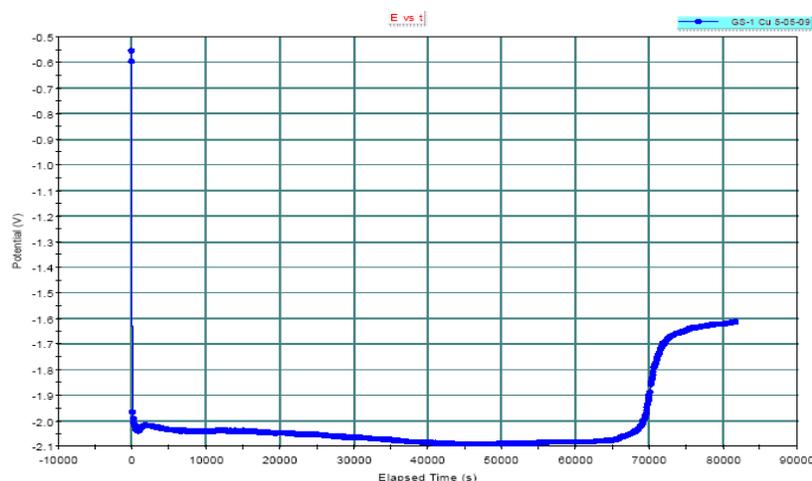

Figure 1. Change in cell voltage with time at a constant current of $I = 20$ mA for the $PdCl_2 + NH_4Cl + NH_4OH /H_2O$ system.

coloration during the Cl_2 evolution period as well as by an unpleasant pungent odor. Sometimes the NCl_3 could be seen as a small yellow pool at the cell bottom. Although no incidents have been observed, the reported explosive nature of NCl_3 makes it mandatory to keep the cell behind a safety shield. A possible positive feature of NCl_3 formation is that this substance may react with and remove solution impurities and electrode poisons that block the FPE. This would explain the greater reproducibility in this ammonia co-deposition system.

3.4. Chemical excess power due to nitrogen trichloride

In every palladium co-deposition experiment in H_2O or D_2O, a chemical excess power effect is observed for about one day when the yellow coloration due to NCl_3 is present. The dissolved NCl_3 that gives the yellow solution coloration likely reacts with the hydrogen generated at the cathode. This reaction

$$NCl_3 + 3H_2 \rightarrow NH_4Cl + 2HCl \tag{6}$$

is exothermic with an enthalpy change of -864 kJ/mol.

Figure 2 shows the calorimetric excess power effect measured in a H_2O control for this chemical reaction of NCl_3 with H_2. The measured chemical power effect was near zero when the current was increased from 6 to 100 mA and then rose to a peak power of 112 mW. This chemical power effect was gone within 24 h. A similar chemical excess power effect was observed by NRL early in their experiment that used an open Seebeck calorimeter [8–10].

The total chemical enthalpy measured in Fig. 2 was -5.40 kJ that corresponds to the reaction of 0.00625 mol of NCl_3. Theoretically, the chemical excess power for Reaction 6 can be expressed as

$$P = (1 - \gamma)I E_H, \tag{7}$$

where γ is the fraction of the electrogenerated hydrogen that does not react and escapes the cell, I the current in Amperes, and E_H is the thermoneutral potential for Reaction 6 (1.49 V at standard conditions). Initially, the dissolved NCl_3 may react with all of the electrogenerated hydrogen ($\gamma = 0$) to give a maximum theoretical peak power of 149 mW at $I = 0.100$ A, assuming $E_H = 1.49$ V. As more and more of the NCl_3 is consumed, γ approaches unity and P decreases as described by Eq. (7) and illustrated in Fig. 2. The chemical excess power due to NCl_3 is zero in less than 24 h. The yellow coloration due to NCl_3 is also gone at this point. In contrast to Pd, no chemical excess power or evidence for NCl_3 was found in the co-deposition of Ru, Re, and Ni in H_2O or D_2O solutions.

3.5. Anomalous excess power

Anomalous excess power (FPE) has been observed for the Pd/D_2O co-deposition system but not for the Pd/H_2O system. Including the NHE (Japan) studies, six out of six studies using the $PdCl_2 + ND_4Cl + ND_4OD/D_2O$ system have now given the FPE. The largest excess power effect in D_2O produced 1.7 W or about 160 W per cubic centimeter of palladium (13 W/g). This recent experiment is shown in Fig. 3.

A small excess power effect was observed when the current was increased to $I = 100$ mA at 5.56 days. This FPE increased to more than 600 mW when the current was increased to $I = 200$ mA at 6.80 days. The largest FPE in this experiment was more than 1700 mW (1.7 W) after increasing the cell current to $I = 400$ mA at 8.80 days. This is the largest excess power observed in any of our Pd/D co-deposition experiments. Erroneous excess power due to shuttle reactions or recombination could not exceed the thermoneutral potential times the current (1.5267 I). This could only explain 305 mW at 200 mA and 610 mW at 400 mA, even if the shuttle reaction consumed 100% of the current.

Further measurements were not possible because of an overload problem for the PAR Model 363 instrument. Initially, a defective electrode contact was believed to be the problem, but this did not check out. Eventually, it was found that the electrolyte had become nearly depleted such that the cell could not sustain the 400 mA current. Follow up
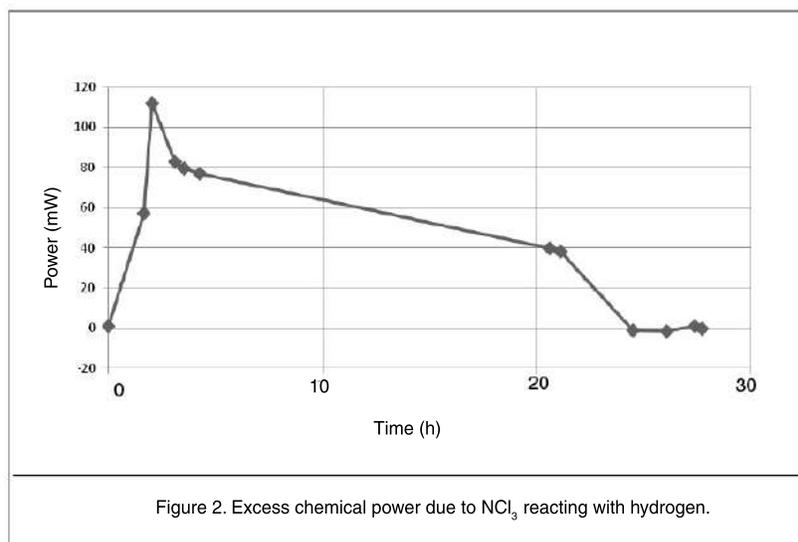
Figure 2. Excess chemical power due to NCl$_3$ reacting with hydrogen.

Figure 2.

experiments showed that a solution of 0.01 M NH$_4$Cl gave about the same cell voltage effect. This indicates a depletion of 95% of the 0.20 M NH$_4$Cl present following the precipitation reaction (Eq. (1)). A possible electrolyte depletion reaction is

$$2ND_4Cl \rightarrow 2ND_3 + D_2 + Cl_2, \tag{8}$$

where the ND$_4^+$ ions hydrolyze with water to form ND$_3$ that is driven off and D$_2$ and Cl$_2$ are formed at the cathode and anode, respectively. This reaction depleting the electrolyte is considerable more endothermic than D$_2$O electrolysis ($\Delta H° = 507.11$ kJ/mol, $E_H^o = -2.6279$ V for the NH$_4$Cl reaction at standard conditions) and could not contribute to any excess power effect. However, this electrolyte depletion effect for the D$_2$O experiment could not be reproduced in an exhaustive H$_2$O control study of PdCl$_2$ + NH$_4$Cl + NH$_4$OH. Perhaps the higher cell temperatures (over 70°C) for the D$_2$O study (Fig. 3) were needed to produce this electrolyte depletion effect. The cell temperature in the H$_2$O study, in contrast, never exceeded 43°C despite the use of currents up to 500 mA. There were two earlier China Lake experiments using D$_2$O that produced small excess power effects of 70 to 100 mW [7]. Both studies involved LiOD additions to avoid NCl$_3$ formation and had problems with the detachment of most of the palladium from the copper cathode early in the experiment [7].

Large increases in the cell voltages with time during electrolysis at constant current were observed in all three NHE D$_2$O studies that produced large excess power effects [4–6]. An even larger increase in the cell voltage with time was observed in the China Lake D$_2$O study (Fig. 3). These unusual increases in the magnitude of the cell voltage with time during electrolysis in the D$_2$O experiments that produced larger excess enthalpy effects suggest a gradual depletion of
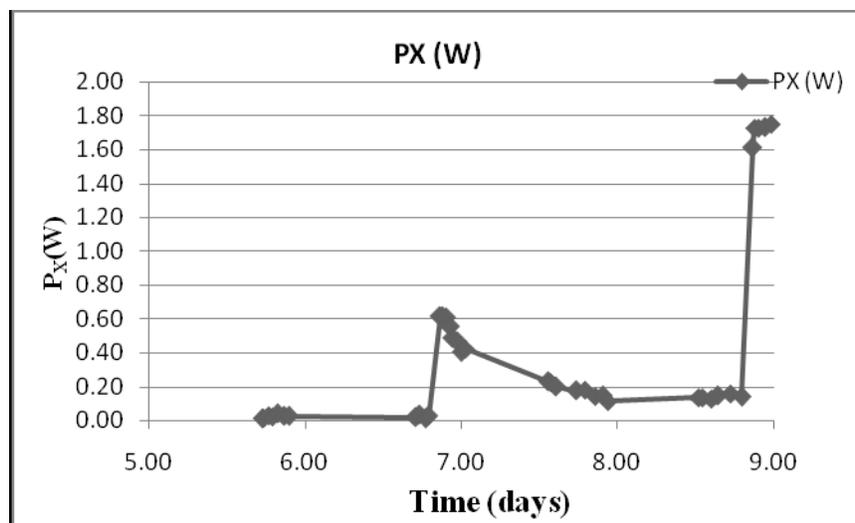
Figure 3. Large anomalous excess power effects for the $PdCl_2 + ND_4Cl + ND_4OD / D_2O$ system.

the electrolyte by some reaction such as Eq. (8). Normally, the cell voltage will decrease with time during electrolysis because the electrolyte becomes more concentrated due to the loss of D_2O by the electrolysis. The normal decrease of the cell voltage with time was always observed for the exhaustive China Lake H_2O control study. It is not known exactly why this electrolyte depletion occurs in the D_2O cells but not in the H_2O cells. The higher cell temperatures due to excess power in the D_2O cells could be an important factor. Hot spots on the deposited palladium [16] or anomalous radiation [17] in the D_2O systems could also be involved.

3.6. H_2O and D_2O consumption studies

It is always necessary to measure the amount of H_2O or D_2O consumed in every experiment to determine if the consumption is consistent with water electrolysis as the main electrochemical reaction. Any recombination or shuttle reactions would lower the measured consumption of H_2O or D_2O. This measured consumption can always be compared to the theoretical consumption based on Faraday's law.

Table 1 presents measured and theoretical consumptions of D_2O or H_2O for various experiments using this ammonia co-deposition system. The three experiments producing large excess power effects at NHE in Japan are also included.

Table 1. Measured and theoretical consumptions of D_2O or H_2O in ammonia co-deposition experiments.

Experiment	Measured (mL)	Theoretical (mL)	Ratio
NHE A-1 (D_2O)	7.4	8.1	0.91
NHE A-2 (D_2O)	7.7	7.2	1.07
NHE A-3 (D_2O)	8.7	8.1	1.07
China Lake (H_2O)	6.0	5.0	1.20
China Lake (D_2O)	8.2	6.7	1.22
China Lake (H_2O)	42.5	40.8	1.04

The China Lake (D_2O) experiment produced the largest excess power effect as shown in Fig. 3. The first China Lake (H_2O) control experiment produced no anomalous excess power, yet it produced a similar measured/theoretical ratio. In most of these experiments, the experimental error in volume measurements was ± 1.0 mL. For the NHE A-3 (D_2O) experiment, 82 kJ of excess enthalpy was produced. If this excess enthalpy were due to recombination, the measured volume of D_2O consumed would be less by 5.0 mL and would be easily measurable. The NHE A-1 (D_2O) was the only experiment that did not consume more D_2O than the theoretical, yet this NHE experiment had the smallest excess power effect [4–6]. The exhaustive, long-term China Lake (H_2O) study consumed 42.5 mL versus 40.8 mL theoretical. The measured/theoretical ratio of 1.04 is identical to that of a previous long-term experiments using a Pd-B cathode in D_2O that produced significant excess power [18]. This China Lake H_2O experiment was the failed attempt to reproduce the electrolyte depletion effect observed in the China Lake (D_2O) study (Fig. 3). No anomalous excess power was observed in this exhaustive H_2O experiment. There are always about 4% extra amounts of H_2O or D_2O that are evaporated and carried out of the cell by the electrolysis gases. This can vary with the geometry and temperature of the gas outlet tube. The effect of evaporation is included in the calorimetric equations [18].

There is a small recombination effect due to the reaction of NCl_3 with H_2 as shown in Fig. 2. The measured chemical enthalpy (5.40 kJ) corresponds to the reaction of 0.00625 moles of NCl_3. This reaction (Eq. (6)) would reduce the H_2O consumption by only 0.34 mL. The postulated endothermic electrolyte depletion reaction (Eq. (8)) would lower the D_2O consumption by only 0.18 mL assuming the complete reaction of all of the NH_4Cl (0.010 mol) present in the 50 mL of solution.

3.7. Electrochemical studies

Various electrochemical studies were conducted to determine if there were any shuttle reactions involving chlorates, nitrates, or nitrites. These studies included cyclic voltammetric (CVA) measurements, galvanostatic power pulse methods, and electrochemical impedance spectroscopy (EIS).

The CVA measurement at 50 mV/s using a platinum working electrode in the 0.156 M NH_4Cl + 0.150 M $NaNO_3$ + 0.0311 M $NaClO_3/H_2O$ system is shown in Fig. 4. The reduction of H_2O to form H_2 ($2H_2O + 2e^- \rightarrow H_2 + 2\,OH^-$) begins near -0.7 V vs. AgCl/Ag while the oxidation of H_2O to form O_2 ($H_2O \rightarrow \frac{1}{2}\,O_2 + 2\,H^+ + 2\,e^-$) begins near 1.1 V. The small oxidation peak at -0.75 V is due to the oxidation of adsorbed hydrogen ($H_{ads} \rightarrow H^+ + e^-$) and the small reduction peak near 1.0 V is the reduction of PtO formed during the oxygen evolution. It is clearly obvious from Fig. 4 that the nitrates and chlorates present in this solution do not support any significant electrode reactions. The only significant electrode reactions even in the presence of chlorates and nitrates are the reduction of H_2O to form hydrogen (H_2) and the oxidation of H_2O to form oxygen (O_2).

A galvanostatic power pulse study of this same solution is shown in Fig. 5. A cathodic current pulse of -0.45 mA (-1.0 mA/cm^2) is applied for 100 s followed by an anodic current pulse of 0.45 mA for 100 s and then repeated a second time. There is nothing in the solution capable of sustaining any electrode reactions except the reduction of H_2O near -0.8 V and the oxidation of H_2O near 1.1 V. There are no measurable reactions of chlorates or nitrates that can sustain even these relatively small currents (0.45 mA) compared to the 100 mA or larger currents used in the co-deposition studies that produced excess power. The small peaks in Fig. 4 due to the oxidation of absorbed hydrogen or the reduction of PtO are seen as slight shoulders in Fig. 5 when the polarity of the current is changed.

As expected, the addition of 0.0330 M $NaNO_2$ (sodium nitrite) to this same solution produced an electrode oxidation reaction. It is well known to electrochemists that while chlorates, perchlorates, and nitrates are electrochemically stable under most conditions, nitrites, in contrast, are easily oxidized. The CVA study with the sodium nitrite present gave a small irreversible oxidation peak of 6.6 mA at 0.85 V. This nitrite oxidation can be represented by $NO_2^- \rightarrow NO + \frac{1}{2}$ $O_2 + e^-$. The NO and O_2 gases produced evolve from the solution, hence there is no corresponding reduction peak. Therefore, any nitrate/nitrite shuttle reaction would quickly terminate by the oxidation of nitrite at the anode.
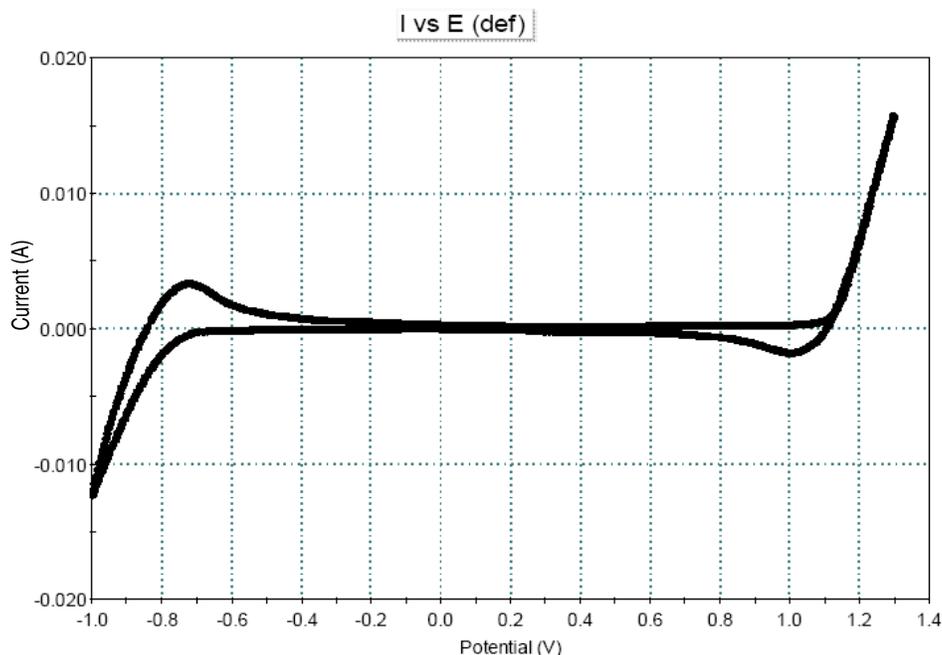
Figure 4.   Cyclic Voltammetry at 50 mV/s for the $NH_4Cl + NaNO_3 + NaClO_3/H_2O$ system.

Many other related solutions were studied by electrochemistry, but the results were always the same. There are no shuttle reactions involving chlorates, nitrates, or nitrites in these solutions. For example, various EIS studies show very slow kinetics for any electrochemical reactions involving chlorates or nitrates. The exchange current densities, i_o, measured by EIS are less than 10^{-6} A/cm^2 for any electrode reactions of chlorates or nitrates versus 10^{-3} A/cm^2 for the much faster hydrogen electrode reaction measured in the same solution.

4. Discussion

It is well known to electrochemists that electrode reactions cannot occur faster than solution mass transport or diffusion process that supplies the reactant to the electrode surface [19]. The mass transport process provides an equation for the limiting current, i_L (A/cm^2)

$$i_L = DnFC°/\delta, \tag{9}$$

where D is the diffusion coefficient (cm^2/s) of the reactant, $C°$ the bulk concentration of the reactant (mol/cm^3), n the number of electrons transferred per reaction (eq/mol), δ the diffusion layer thickness (cm), and F is Faraday's constant (96,485 A s/eq). Typically $D = 2 \times 10^{-5}$ cm^2/s and $\delta = 0.05$ cm (Ref. 19). According to the NRL group [8–10, 20], they detected a maximum of about 0.015 M (0.15×10^{-5} mol/cm^3) chlorate or nitrate ions in their co-deposition solution. Therefore, even if the chlorate or nitrate ions were extremely reactive electrochemically, the limiting current (i_L) would only be about 0.001 A/cm^{2}for such shuttle reactions assuming a typical two-electron transfer step. The experimental results shown in Fig. 5 prove that even at higher concentrations, chlorates and nitrates cannot sustain a current density of 0.001 A/cm^2. In contrast, the calculated limiting current from Eq. (9) for water electrolysis is 4.3

A/cm^2 due to the high concentration of H_2O (55.5×10^{-3} mol/cm^3). It could be debated that perhaps the diffusion layer thickness is 10 times smaller due to rapid stirring, but one cannot postulate simultaneously shuttle reactions occurring at the electrodes and rapid stirring by the electrogenerated hydrogen and oxygen gases due to H_2O or D_2O reactions.

For co–deposition experiments using ND_4Cl+ND_4OD/D_2O solutions, anomalous excess power (FPE) was measured in 6/6 experiments for the Pd/D_2O systems. There was no anomalous excess power measured for 2/2 Pd/H_2O experiment, 4/4 Ru/H_2O or D_2O experiments, 2/2 Re/H_2O or D_2O experiments or 4/4 Ni/H_2O or D_2O experiments. The statistical analysis of all 18 experiments yields a probability greater than 99.9989 % that the anomalous excess power effect in these co-deposition studies requires the presence of both palladium metal and D_2O[21].

5. Summary

Studies of the $PdCl_2 + ND_4Cl + ND_4OD/D_2O$ co-deposition system have produced anomalous excess power effects in three out of three experiments at NHE in Japan and now in three out of three experiments at China Lake, California. A recent experiment produced the largest effect of 1.7 W. The large excess power effects are accompanied by an unusual increase in the cell voltage due to the gradual depletion of electrolyte ions. There was no evidence for any proposed shuttle or recombination reactions involving chlorates, nitrates, or nitrites. There was also no excess power for the co-deposition of Ru, Re, or Ni in H_2O or D_2O solutions. The anomalous excess power was observed only for the Pd/ D_2O co-deposition system. This was also the only deposited metal that showed significant outgassing after the cell current was turned off. This result suggests the necessity of absorbed deuterium within the bulk of the palladium for the production of anomalous excess power in these co-deposition experiments. The increased inorganic chemical knowledge gained by this co-deposition study gives a much better understanding of this Pd/D system and may lead to
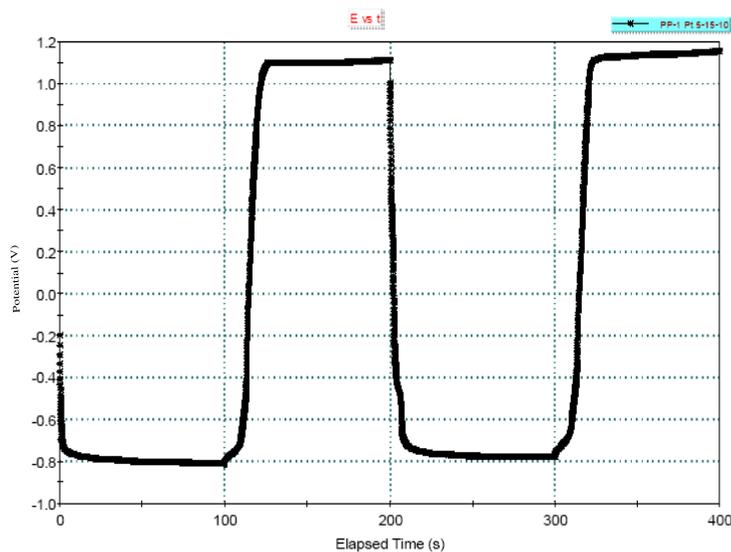

Figure 5. Galvanostatic power pulse study of the $NH_4Cl + NaNO_3 + NaClO_3/H_2O$ system using a platinum electrode ($A = 0.45$ cm^2).

reproducible excess power (FPE) experiments at other laboratories.

Acknowledgements

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