

Investigations of co-deposition systems

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Abstract. Electrochemical studies of co-deposition show that the palladium deposited onto a copper substrate produces very high capacitance values (370 Farads/g) equal to those of supercapacitor materials. This large electrode capacitance causes a collapsing and tilting of the cyclic voltammograms that approaches Ohm's Law behavior. Results for the electrochemistry, chemistry, and calorimetry of the 0.025 M PdCl₂+0.15 M NH₄Cl+0.15 M NH₄OH system and its deuterium analog are reported.

1. Introduction: selection of co-deposition systems

The observation of Fleischmann-Pons effects (FPE) for co-deposition systems was first reported by Szpak and Mosier-Boss using the PdCl₂+LiCl/D₂O system [1, 2]. Improved reproducibility of the excess power effect was obtained with the PdCl₂+ND₄Cl+ND₄OD/D₂O system [3-5]. In fact, all three initial experiments using this ammonia-based system produced large excess power effects [3]. This system was selected because the H₂O analog is commonly used for commercial palladium plating [6]. However, the extended electrolysis at the higher currents required for FPE studies leads to a black dendritic hydride deposit, large pH changes, chlorine evolution, and other unknown processes in this ammonia-based co-deposition system.

2. Experimental methods used for investigations of co-deposition systems

Electrochemical studies included cyclic voltammetry (CVA), electrochemical impedance spectroscopy (EIS) and various galvanostatic methods. The solution pH was periodically measured using a pH meter (± 0.01 pH units). Commercial chlorine detectors were used to monitor the gases escaping from the cell. A new isoperibolic calorimeter was used to determine any excess power produced by the electrochemical cell [7].

3. High capacitance produced by co-deposited palladium

The 0.025M PdCl₂+0.15M NH₄Cl+0.15M NH₄OH/H₂O system was investigated at various stages of the co-deposition onto a copper cathode. Figure 1 shows the cyclic voltammogram after the initial co-deposition at -6.00 mA for two hours (43 coulombs). This trace shows the normal features of a palladium surface with PdO formation at 0.25V and PdO reduction at -0.48V along with probable palladium deposition at -0.90V. Hydrogen and oxygen evolution occurs at the negative and positive vertexes, respectively.

Further electrolysis at -6.00 mA for 28.45 hours, I= -20 mA for 22.70 hours, then I= -50 mA for 22.95 hours (6423 coulombs total) gradually gave the completely tilted and collapsed cyclic voltammogram presented in Figure 2. Furthermore, the pH changed from pH=8.87 for the initial solution to pH=1.25, and chlorine evolution was readily detected at this electrolysis stage.

The striking contrast between Figure 1 and 2 has been previously observed for supercapacitor materials [8]. As shown in the Appendix, the exact equation for cyclic voltammetric studies yields Ohm's Law, $I \approx E/R_s$, for extremely high electrode capacitances ($R_s C_d \gg t$). From the EIS measured cell resistance ($R_s=0.9945 \Omega$) and

the time for a single scan in Figure 2 ($t=38$ s), it is estimated that the electrode capacitance (C_d) must be at least 50 Farads (F) or about 370 F/g for the deposited palladium. Typically, electrode capacitances are about $50 \mu\text{F}/\text{cm}^2$, thus the deposited palladium has an effective surface area of 10^6 cm^2 . Chronopotentiometry was used to confirm the unusually large RC time constant for the palladium deposited onto the copper cathode [8]. Similar experiments were conducted on the $\text{PdCl}_2+\text{LiCl}/\text{H}_2\text{O}$ co-deposition system and similar high capacitance values were observed. The electrochemical literature today relating to supercapacitor materials does not generally realize how large RC time constants distort cyclic voltammograms as shown in Figure 2 and explained in the Appendix.

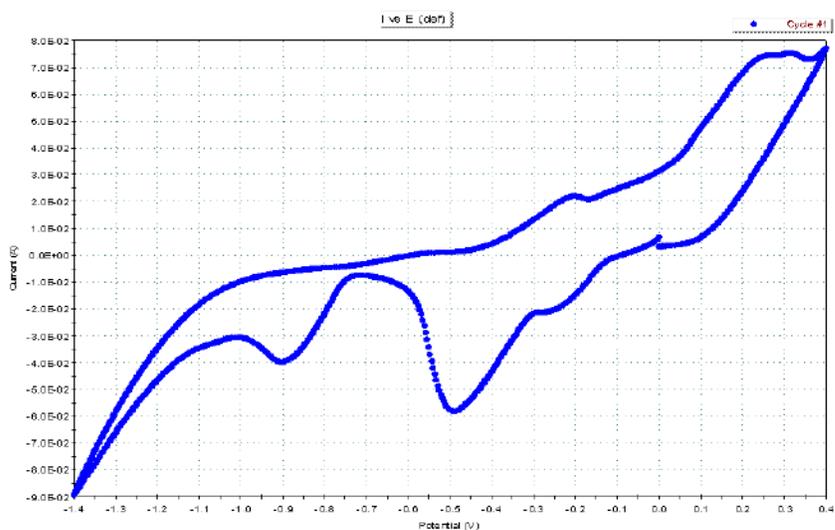


Fig. 1 - Early cyclic voltammetric study of co-deposition ($v = 50$ mV/s).

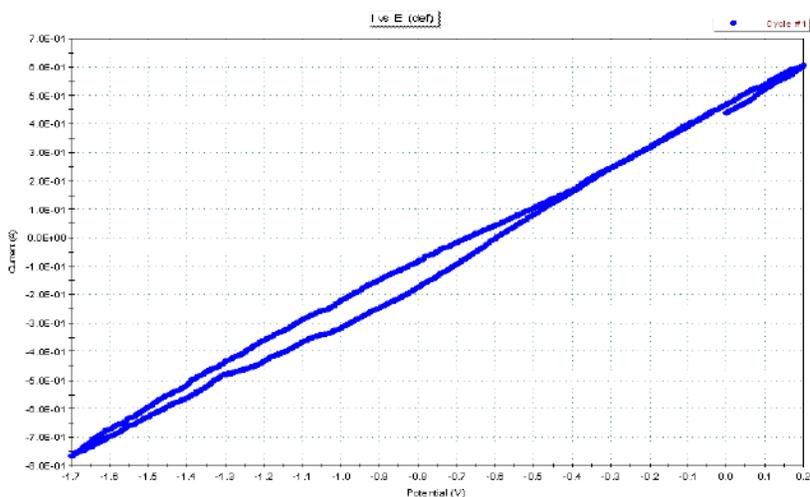


Fig. 2 - Later cyclic voltammetric study of co-deposition ($v = 50$ mV/s).

4. Complex chemistry of ammonia co-deposition system

Solution pH measurements were the key to unraveling the complex chemistry of the 0.025 M PdCl₂+0.15 M NH₄Cl+0.15 M NH₄OH co-deposition system. The electroneutrality expression for molar (M) ionic concentrations



along with the equilibrium $\text{NH}_4\text{OH} = \text{NH}_4^+ + \text{OH}^-$, $K_b = 1.81 \times 10^{-5}$ M, were also very useful. The reaction of palladium ions with NH₄OH produces insoluble palladium hydroxide



thus Pd⁺⁺ ions are initially replaced by additional ammonium ions (Eq. 1). The resulting low activity of palladium ions explains the stability of the copper cathode and other metals towards displacement reactions such as $\text{Cu} + \text{Pd}^{++} \rightarrow \text{Cu}^{++} + \text{Pd}$ in this initial solution. The cell reaction for the palladium deposition can be expressed as



with the solution remaining basic as observed experimentally. However, the generated electrolysis gases (H₂, O₂) gradually drive off the ammonia by the net reaction $\text{NH}_4^+ \rightarrow \text{NH}_3 + \text{H}^+$ and the solution becomes acidic, $[\text{H}^+] = 0.050$ M, pH = 1.30 from Eq. 1. Acidic solutions make chlorine evolution thermodynamically more feasible, and a portion of the cell reaction becomes



instead of H₂O electrolysis. A readily observable decrease in the cell voltage magnitude clearly defines when the solution becomes acidic and chlorine evolution commences as also shown by chlorine detectors.

The introduction of chlorine into an acidic NH₄Cl solution is known to produce nitrogen trichloride, $\text{NH}_4\text{Cl} + 3 \text{Cl}_2 \rightarrow \text{NCl}_3 + 4 \text{HCl}$. The net electrochemical cell reaction for this NCl₃ production is



with hydrogen formed at the cathode. The enthalpy change for this reaction is 864 kJ/mol, thus the thermoneutral potential for Eq. 5 is nearly the same as for water electrolysis (1.49 V vs. 1.48 V). The consumption of acidic HCl by both Eqs. 4 and 5 produces an increase in the pH and an end to the Cl₂ and NCl₃ production. Therefore, only normal water electrolysis occurs after the first few days, and this is marked by a significant increase in the solution pH and an observable increase in the cell voltage as well as the end of any chlorine detection. In previous experiments, most of the excess power was observed after the third day when the chlorine evolution and NCl₃ production had ceased [3-5].

5. Calorimetric measurements of co-deposition systems

The PdCl₂ + NHCl + NH₄OH system was developed for palladium plating [6] and was not designed for the extended electrolysis at high currents required for the Fleischmann-Pons effect (FPE). However, this ammonia system can readily be converted to a very stable electrolysis system with no Cl₂ or NCl₃ formation if sufficient LiOH is added following the palladium co-deposition to maintain a basic pH. The required amount of LiOH or LiOD is given by $[\text{LiOH}] > [\text{NH}_4\text{Cl}] + 2[\text{PdCl}_2]$, or a LiOH concentration greater than 0.20 M in these experiments. Following the LiOH addition, all NH₃ is driven off by the electrolysis gases, and the solution consists of only LiCl + LiOH. Initial studies of the PdCl₂ + NH₄Cl + NH₄OH system with the LiOH

addition produced a very stable electrolysis process that was used in calibration of a new isoperibolic calorimeter [7].

Two calorimetric experiments have been completed using $\text{PdCl}_2 + \text{ND}_4\text{Cl} + \text{ND}_4\text{OD}/\text{D}_2\text{O}$ with LiOD addition following the completion of palladium deposition. Both experiments initially gave excess power effects of 70 to 100 mW at $I = -100$ mA. However, the excess power gradually diminished to near zero with further electrolysis. In both experiments, almost all of the deposited palladium somehow became detached from the cathode and settled to the cell bottom where it was electrochemically inactive. Further experiments are needed to determine if the LiOD addition destabilizes the palladium deposit.

Calorimetric studies of $\text{PdCl}_2 + \text{NH}_4\text{Cl} + \text{NH}_4\text{OH}/\text{H}_2\text{O}$ without the LiOH addition gave a chemical excess power effect reaching 50 mW during the acidic period of Cl_2 and NCl_3 formation. Nitrogen trichloride is a volatile, yellow oily liquid of high density (1.653 g/cm^3) and explosive in pure form. It could be observed experimentally as a small yellow pool at the cell bottom and as a yellow solution coloration during the Cl_2 evolution period. This NCl_3 substance is only slightly soluble in water, but this dissolved NCl_3 would readily react with the hydrogen generated by electrolysis to produce a chemical excess power effect by the reverse of Eq. 5. Because of the NCl_3 formation, it is recommended to keep the cell behind a safety shield with adequate ventilation and to wait until the chlorine evolution ceases and the yellow color clears before performing calorimetric measurements.

6. Investigations of chlorates, nitrates and nitrites

Chlorates, nitrates and nitrites are possible electrochemical products from the oxidation of chloride and ammonium ions. Therefore, effects of these substances on the electrochemistry and calorimetry were investigated. Cyclic voltammetric studies of 0.1505 M NaClO_3 using a platinum electrode showed only water electrolysis and no reversible reactions involving chlorates. The EIS studies showed that any chlorate reactions would be very slow with an exchange current density of $i_0 = 10^{-6} \text{ A/cm}^2$. Constant current pulse methods proved that any electrochemical reactions of chlorates could not sustain currents above 0.5 mA/cm^2 in 0.1505 M NaClO_3 . A calorimetric study of the 0.1505 M NaClO_3 in H_2O gave no measureable excess power effects. Based on pH measurements, it is estimated that more than 99.999% of the total current (48474 coulombs) was consumed by H_2O electrolysis. The volume of H_2O consumed in this chlorate calorimetric experiment was larger than calculated from Faraday's Law (6.5 mL vs. 4.5 mL). These studies all rule out any measurable shuttle reactions involving chlorates. Related investigations involving KNO_3 and NaNO_2 showed that there were no shuttle reactions involving nitrates or nitrites that would give false excess power effects [7].

7. Evidence for a palladium volume effect

Based on the measured capacitance of the deposited palladium, the effective surface area increased by a factor of 10^6 during co-deposition. The presence of H^+ or D^+ within the deposited palladium likely contributes to these high capacitance values. Because the excess power observed in co-deposition experiments scales much more closely with the palladium volume, it appears that the FPE is a volume effect in co-deposition systems. A secondary double layer consisting of D^+ within the deposited palladium is likely a region rich in both electrons and deuterons and a prime location for near surface fusion reactions.

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8. Appendix

The exact equation for a voltage scan for an electrical circuit of a resistor, R_s , and a capacitor, C_d , is given by

$$I = vC_d + (E_i/R_s - vC_d) \exp(-t/R_s C_d) \quad (\text{A.1})$$

where I is the current (A), v is the voltage scan rate (V/s), and E_i is the initial scan voltage at $t=0$ seconds [9]. Generally $R_s = 1 \Omega$ and $C_d = 50 \mu\text{F}$ (approximately) for electrochemical studies, thus the exponential term falls to zero within about 250 μs , and Eq. A.1 becomes $I = vC_d$. This simplified equation is generally used in cyclic voltammetric studies of supercapacitor materials [8]. However, $R_s C_d \gg t$ for high capacitance materials, thus $\exp(-t/R_s C_d) \approx 1 - t/R_s C_d$, and Eq. A.1 becomes

$$I \approx vC_d + (E_i/R_s - vC_d)(1 - t/R_s C_d) \quad (\text{A.2})$$

or

$$I \approx E_i/R_s - E_i t/R_s^2 C_d + vt/R_s \quad (\text{A.3})$$

Introducing $vt = E - E_i$ for a potential scan yields

$$I \approx E/R_s - (E_i/R_s)(t/R_s C_d) \quad (\text{A.4})$$

but $E > E_i$ and $R_s C_d \gg t$, hence $I \approx E/R_s$ which is Ohm's Law as observed experimentally in Figure 2.

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