Dimethylpyrrolidinium-Mercury and Tetramethylphosphonium-Mercury.
Electrodeposition of an Initial Layer

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The complete sequence of the electrodeposition process for dimethylpyrrolidinium-mercury was identified using cyclic voltammetry and chronoamperometry. Experimental evidence clearly demonstrates the formation of an initial layer of monomolecular thickness prior to the three-dimensional growth of a bulk phase. The corresponding charge density for the initial layer formation equals 46.5 μC cm⁻². The initial layer formation is triggered by the reorientation of adsorbed dimethylpyrrolidinium (Me₂Py⁺) ions at mercury/solution interface. This two-dimensional non-faradaic phase transition involves 2.5-3.0 μC cm⁻² for the complete monolayer. The initial layer formation of tetramethylphosphonium-mercury is remarkably similar. The charge associated with the reorientation of the adsorbed tetramethylphosphonium (Me₄P⁺) monolayer equals 5 μC cm⁻² while the initial layer formation involves 43 μC cm⁻². It was suggested that the similarity in the deposition process reflects a similar spatial arrangement of the organic cations and negatively charged mercury clusters in Me₄P-mercury and Me₂Py(Hg₃).

1 INTRODUCTION

Tetraalkylammonium-metals (R₄N-metals) are formed by the reduction of tetraalkylammonium (R₄N⁺) salts at a variety of post-transition metal cathodes¹). They comprise of the cation (R₄N⁺), metal (M) from the cathode and electrons. The stoichiometric composition of 1R₄N⁺/1e/5M was determined for several R₄N⁺ reduced at mercury²,³), and lead⁴,⁵) and the general empirical formula R₄N(M₅) was proposed. The cation remains relatively unperturbed and it acts as the counter-ion to (M₅)⁺. R₄N-metals constitute a new class of organometallic materials but should be related to other materials that contain anionic clusters of post-transition metals such as Zintl salts and phases⁶).

R₄N-metals are highly reactive solids capable of heterogeneous electron-transfer to the organic molecules acting as a catalyst for organic electroreductions⁷,⁸).

During the electrochemical formation of R₄N-metals, the cathode is consumed and the product is electrodeposited at the cathode surface. The process involves intriguing phase changes when dissolved cations, metal atoms from the cathode and electrons combine to generate an ordered solid. It must be a sequence of reorganizations at the surface and recrystallization.

For Pb, Sn and Hg, that have been studied⁹,¹⁰) in more detail it was established that the formation of the bulk product proceeds via three-dimensional nucleation and growth process. The deposition and stripping of R₄N(M₅) bulk phase (C₃b/A₁b in Fig. 1) was observed by cyclic voltammetry. An example of R₄N⁺ (dimethylpyrrolidinium, Me₂Py⁺) at Pb cathode is shown in Fig. 1.
The main goal of this work was to study the initial stages of \( R_4N(Hg_3) \) generation and to determine if the general mechanism of the initial layer followed by bulk deposition pertains to this system. Mercury also provides a homogenous, atomically smooth surface on which the adsorption of organic is pronounced. Our second goal was to search for surface reorientation preceding the electrodeposition.

We have also performed a preliminary study of the cathodic behaviour of tetramethylphosphonium cations at \( Hg \) using the tools and understanding developed in the studies of \( R_4N(Hg_3) \).

### 2 EXPERIMENTAL

#### 2.1 Materials

Tetrabutylammonium tetrafluoroborate \( (Bu_4NBF_4) \) was prepared by the reaction of tetrabutylammonium bromide \( (Bu_4NBr) \), Southwestern Analytical, and aqueous fluoroboric acid \( (HBF_4, Aldrich) \), recrystallized from 5% pentane in ethyl acetate. Dimethylpyrroldinium tetrafluoroborate \( (Me_2PyBF_4) \) was prepared by a reported procedure, and recrystallized from ethanol. Tetramethylphosphonium iodide was obtained from Lancaster and recrystallized twice from acetonitrile. 1,1-Dimethylphospholanium iodide \( (Me_2Ppl) \) was synthesized by the alkylation of dimethylphosphine with excess 1,4-diodobutane in DMF. The alkyl phosphine concentration was 0.05 M. In addition, 1 eq of 2,6-dimethylpyridine (Aldrich) was present to deprotonate the intermediate tertiary phosphonium species. The resulting precipitate was recrystallized from acetonitrile to afford 1,1-dimethylphospholanium iodide in 12% yield \( \text{[H NMR (D}_2\text{O)}(\delta_{ppm}) 1.95 (6H, d), 2.14 (4H, m), 2.36 (4H, m)] \). All salts were dried in vacuum before use and stored in a vacuum desiccator.

\( N,N\)-Dimethylformamide (DMF, Burdick and Jackson, high purity) was distilled under vacuum \( (60-65°C, 30 \text{ Torr}) \). The middle 60 percent was collected and stored over activated 4Å molecular sieves. Standard solutions of 0.1 M \( Bu_4NBF_4 \) were prepared under a nitrogen atmo-
sphere using a cannula. The DMF was passed through a column of activated alumina into a volumetric flask containing Bu₄NBF₄ which had been purged with nitrogen. The solution was then transferred through another column of activated alumina into a nitrogen purged storage container.

Triply distilled Hg was used as the cathode materials. Platinum wire (1.0 mm dia.) served as the anode material. The reference used was an aqueous saturated calomel electrode (SCE) modified for use in DMF. The SCE was in contact with the electrolysis solution via two bridges; 1.5% w/v agar in saturated aqueous NaCl, and 5% w/v methylcellulose in DMF containing 0.5 M Bu₄NBF₄.

2.2 Instrumentation

The cell used in cyclic voltammetry and chronoamperometry experiments was a four necked 25 ml round bottom flask equipped with a working electrode consisting of either a sessile mercury drop (approximately 0.025 cm²) or a mercury film (0.008 cm²) on a platinum disk, a platinum wire counter electrode, a reference electrode, and an argon inlet adapter. Mercury film electrodes were prepared by depositing mercury from a solution of 0.05 M Hg₂(NO₃)₂·2H₂O in 0.1 M HClO₄ onto a polished platinum disk. A constant current of 30 μA was used for deposition. The electrode was then washed with water followed by electrolyte solution.

The cell was oven dried prior to use, and cooled in an argon atmosphere. In a typical experiment, 10 ml of the stock electrolysis solution was introduced via volumetric pipette. The experiments were performed using a PAR-173 potentiostat with a PAR-175 universal programmer. CVs were recorded on an omnigraphic 2000 x-y recorder, and the potential step experiments were recorded on a Tektronix 5111 storage oscilloscope.

3 RESULTS AND DISCUSSION

Dimethylpyrrolidinium was chosen as the cation to study because of the extensive information available and the stability of the product. It was used in the form of tetrafluoroborate salt. Since the very early stages of the reaction were of interest, low concentrations of Me₂Py⁺ were employed. The methods used were cyclic voltammetry and chronoamperometry. Subsequently, tetramethylphosphonium ion and phosphorous analog of dimethylpyrrroolidinium were examined in the same manner.

3.1 Cyclic voltammetry of dimethylpyrrolidinium cation

Cyclic voltammograms of Me₂Py⁺ at various concentrations, in the range of 0.00-1.00 mM, were recorded. The ones that provided useful information are shown in Figs. 2-4. The lowest concentration of Me₂Py⁺ that affected CV of the supporting electrolyte (Fig. 2a) was 0.05 mM (Fig. 2b). It caused a slight positive shift of the background decomposition potential.

![Fig. 2 Cyclic voltammetry of Me₂Py⁺ at a mercury film electrode; 0.1 M Bu₄BF₄ in DMF; v=20 mV/s; (a) background electrolyte, (b) a+0.05 mM Me₂PyBF₄, (c) a+0.10 mM Me₂PyBF₄, (d) a+0.15 mM Me₂PyBF₄. At the concentration of 0.10 mM Me₂Py⁺ (Fig. 2c) the positive shift of the decomposition process now shows an anodic peak upon reversal of the potential scan. At the concentration of 0.15 mM Me₂Py⁺ (Fig. 2d) the cathodic shoulder appeared.](image-url)
on the background decomposition current while the anodic peak grew.

The concentration of Me$_2$Py$^+$ was further increased to 0.2 mM and the CV was recorded at a ten times higher current sensitivity (Fig. 3a). The cathodic shoulder appears as a well defined spike (C$_s$) at -2.795 V. At this concentration two well defined anodic peaks, A$_{m}$ and A$_{b}$, are also observed. The first anodic peak, A$_{m}$, is larger than the second anodic peak, A$_{b}$.

At a concentration of 0.35 mM Me$_2$Py$^+$ (Fig. 3b) the spike (C$_s$) shifts to -2.76 V. It is immediately followed by a peak at approximately -2.78 V, C$_m$, and yet another, C$_b$, which appears as a shoulder on the background current. As the scan is reversed, the two anodic peaks are observed, but in this case, the second anodic peak, A$_b$, is larger than A$_m$. Both peaks are shifted positively.

The voltammogram for the 0.40 mM Me$_2$Py$^+$ solution (Fig. 4a) shows further change: relative size of the spike is decreased and the second cathodic peak, C$_b$, grows and begins to obscure peak C$_m$. As for the anodic peaks, the first peak (A$_m$) remains constant and the second peak (A$_b$) grows appreciably. As the concentration is increased to 0.60 mM (Fig. 4b), the cathodic spike becomes even smaller and shifted positively, and C$_b$ totally obscures C$_m$. The second anodic peak (A$_b$) continues to grow and first (A$_m$) remains constant and still well separated from peak A$_b$. The CV at 0.60 mM Me$_2$Py$^+$ is similar to previously reported CV$_S$ at higher concentration. The C$_b$/A$_b$ couple is typical of the deposition and stripping of bulk Me$_2$Py(Hg$_5$). On the other hand, the size and shape of the first anodic peak, A$_m$, remains constant after 0.30 mM Me$_2$Py$^+$ and well separated from the growing stripping peak A$_b$.

Fig. 3 Cyclic voltammetry of Me$_2$Py$^+$ at a mercury film electrode; 0.1 M Bu$_4$NBF$_4$ in DMF; v=20 mV/s; (a) 0.20 mM Me$_2$PyBF$_4$, (b) 0.35 mM Me$_2$PyBF$_4$.

Fig. 4 Cyclic voltammetry of Me$_2$Py$^+$ at a mercury film electrode; 0.1 M Bu$_4$NBF$_4$ in DMF; v=20 mV/s; (a) 0.40 mM Me$_2$PyBF$_4$, (b) 0.60 mM Me$_2$PyBF$_4$. 
Therefore it seemed that the peak $A_m$ represents the stripping of an initial layer. This was confirmed by the amount of charge associated with it. Integrating the charge of the peak $A_m$ at its maximum growth shows 46.5 $\mu$C cm$^{-2}$. This charge corresponds to a surface concentration of 4.8x10$^{-10}$ mol cm$^{-2}$ or 0.345 nm$^2$ per deposited unit in the monolayer. This value corresponds well to the area of one $\text{Me}_2\text{Py(Hg}_5\rangle$, (0.35 nm$^2$) calculated by means of computer modeling$^3$.

The peaks $C_m/A_m$ seemed to represent a redox couple. But, the area of $C_m$ could not be accurately measured and the CV of $C_m/A_m$ couple could not be completely isolated because of the overlap of $C_m$ and $C_b$. Nevertheless, the relationship between $C_m$ and $A_m$ shows when the potential scan of the CV was reversed at -2.788 V (Fig. 5). The peak current of $C_m$ was studied as a function of the potential scan rate (2-20 mV s$^{-1}$), to further confirm that $C_m/A_m$ represent the deposition and stripping of a monolayer. As expected, the relationship was linear. This is typically observed for the reduction of an adsorbed species$^{14}$.

The appearance of spike $C_S$ at the rising portion of $C_m$ is an indication of a phase transition process$^{15}$. The sharp peaks in linear sweep voltammetry are known to be associated with the peaked current-time transients obtained by the application of a potential step. Therefore the nature of $C_S$ was studied using chronoamperometry.

### 3.2 Chronoamperometry of dimethylpyrroli-dinium cation

The current-time (i-t) transients were recorded in 0.30 mM solution of $\text{Me}_2\text{Py}^+$. At a pulse width ($\tau$) of 20 ms, the potential is stepped from a value of no reaction ($E_1$=-2.73 V) to various values where the reaction takes place ($E_2$). The peak shaped i-t transients (Fig. 6) correspond to a phase transition which differs from the process observed at higher concentrations of $\text{Me}_2\text{Py}^+$ (Fig. 7 in ref. 10).

![Fig. 5 Cyclic voltammogram of 0.35 mM $\text{Me}_2\text{Py}^+$ at a mercury film electrode; 0.1 M $\text{Bu}_4\text{NBF}_4$ in DMF; $v=20$ mV/s.](image)

![Fig. 6 Cathodic i-t transients recorded during potential step experiments. 0.30 mM $\text{Me}_2\text{PyBF}_4$; 0.1 M $\text{Bu}_4\text{NBF}_4$ in DMF; mercury film electrode; $\tau=20$ ms; $E_1$=-2.730 V; $E_2$/V: (a) -2.848, (b) -2.850, (c) -2.852.](image)

![Fig. 7 Reduced variable plot for experimental and theoretical 2D nucleation and growth. Experimental data from Fig. 6.](image)
After initial charging, current has decayed substantially, the current increases once again, reaches a maximum, and then falls. For the three overpotentials indicated the peak maximum occurs at shorter times as the potential is stepped at more negative values. The peaks are symmetrical, and they become taller and narrower at more negative potentials. The area under each of the three curves is the same. These properties are characteristic of two-dimensional (2D) nucleation and growth.

In order to further characterize this process, experimental data were compared to theoretical dimensionless plots (Fig. 7) for 2D instantaneous and progressive nucleation and growth. They perfectly fit the curve for 2D progressive nucleation and growth. The charge under the peak ranges from 2.5 to 3 μC cm⁻² which is typical for a non-faradaic phase transition in adsorbed organic layers. Therefore, the process reflects reorientation of Me₂Py⁺ in the adsorbed layer prior to the deposition of initial layer and most likely corresponds to the spike C_s in the reduction voltammogram.

3.3 Voltammetry and chronocoulometry of tetraalkylphosphonium cations

The dimethylphospholanium cation (Me₂P⁺), the phosphorous analog to Me₂Py⁺, is not able to form a stable composit under the conditions of our experiment. Cyclic voltammetry was performed at a variety of scan rates, concentrations, and temperatures. No reversible redox couple was detected for Me₂P⁺. The signal was erratic indicating that the surface was being altered or disrupted in some way.

In contrast, the cyclic voltammogram for the simple phosphonium cation Me₄P⁺ (5.00 mM) in Fig. 8 is remarkably similar to the complex cyclic voltammogram observed for Me₂Py⁺ at a low concentration (0.35 mM). Reversal of the potential scan just after peak C_m reveals a redox couple (dashed curve) similar to that of the monolayer found for Me₂Py⁺. The peak A_m was integrated and it had a charge density of 43 μC cm⁻². Again, this is remarkably close to the charge density obtained for the Me₂Py(Hg₅) monolayer formation (46.5 μC cm⁻²). The peak current for C_m was studied as a function of the scan rate (2-20 mV s⁻¹). As in the case of Me₂Py⁺ the peak current of C_m is directly proportional to the potential scan rate.

![Cyclic voltammogram of 5.00 mM Me₄P⁺](image)

The i-t transients in Fig. 9 illustrate distinct processes in the formation of tetramethylphosphonium-mercury: initial layer formation (C_s and C_m) and the bulk deposition (C_b). In 5.00 mM Me₄P⁺ solution and pulse width of 50 ms, the formation of initial layer is well separated from the deposition of the bulk phase. The peak C_s was integrated and a charge of 5.4 μC cm⁻² was obtained, which is similar to that observed for i-t transients of Me₂Py⁺ at low concentrations.

In comparison to Me₂Py(Hg₅), the initial layer formation of Me₄P-mercury is remarkably similar. The reorientation of
adsorbed $\text{Me}_4\text{P}^+$ monolayer proceeds through two-dimensional nucleation and growth within the first 20 ms involving 5 $\mu$C cm$^{-2}$ while the initial layer formation involves 43 $\mu$C cm$^{-2}$. However, the multiple phase transitions of $\text{Me}_4\text{P}^+$ can be detected at much higher concentrations than of $\text{Me}_2\text{Py}^+$.

4 CONCLUSIONS

The reduction of $\text{R}_4\text{N}^+$ at Hg begins with the deposition of a monolayer of $\text{R}_4\text{N(Hg)}_2$. Only then can the three-dimensional nucleation and growth of bulk $\text{R}_4\text{N(Hg)}_2$ take place. The initial layer formation is triggered by the reorientation of adsorbed $\text{Me}_2\text{Py}^+$ ions at mercury/solution interface. This two-dimensional phase transition involves 2.5-3.0 $\mu$C cm$^{-2}$ for the complete monolayer.

The initial layer formation of phosphonium analog $\text{Me}_4\text{P}$-mercury is remarkably similar. Such similarity in the deposition process indicates a similar spatial arrangement of the organic cations and negatively charged mercury clusters in $\text{Me}_4\text{P}$-mercury and $\text{R}_4\text{N(Hg)}_2$.

REFERENCES