Electrodeposition of Palladium on Electrode Surfaces from Acidic, Neutral, Neutral—Buffered, and Basic AlCl₃—MEIC Molten Salts

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Abstract

The electrodeposition of palladium onto various electrode surfaces was examined in AlCl₃—MEIC molten salts at room temperature. The behavior of palladium electrodeposition was markedly dependent on the mole fraction of AlCl₃ in the molten salts. Shifting from basic to acidic melts, results in a 2.0 volt shift in the potential of palladium. Mole fractions from N=0.33 to N=0.67 AlCl₃ were examined. Nucleation overpotentials were evident in basic melts, and to a lesser extent in acidic and neutral melts.

Introduction

Room temperature molten salts are of interest due to their wide liquidus range and high conductivity. Of particular interest is aluminum chloride 1—methyl—3—ethylimidazolium chloride (AlCl₃—MEIC). Its wide liquidus range and its adjustable Lewis acidity make it a unique nonaqueous solvent. Variation of the Lewis acidity is accomplished by changing the mole ratio of AlCl₃ to MEIC. Therefore, basic melts contain excess Cl⁻ and acidic melts contain the Lewis acid Al₂Cl₇⁻ as the following equilibrium equation indicates.

$$2\text{AlCl}_4^- = \text{Al}_2\text{Cl}_7^- + \text{Cl}^-$$

This equation is similar to water, where, like the hydronium ion, Al₂Cl₇⁻ is the acidic species and, like the hydroxide ion, Cl⁻ is the basic species.

Characterization of metals in this molten salt are important for its consideration as a possible battery electrolyte. Several different metals have already been examined (see reference 1 for list). The idea is to take advantage of the molten salt’s wide electrochemical window. Various active metals have been studied as possible anodes with redox potentials close to the negative limit.2—3. This report is concerned with the study of metals useful at the positive melt limit. They must have a high theoretical energy density in relation to one of the active metals such as sodium. Several electrode combinations were looked at, but palladium coupled with sodium, which has a high energy density (>900 Watt—hours/Kg), looked the most promising.

The electrodeposition of palladium was originally examined in basic
AICI₃—MEIC molten salts at 40°C by Hussey et al. In this study, an attempt was made to examine the deposition–stripping process of palladium throughout the entire room temperature composition range, N=0.33 to N=0.67 AICI₃—MEIC.

Experimental

Synthesis and purification of melt components has been previously described. PdCl₂ (Aldrich, 99.999%) and NaCl (Aldrich, 99.999%) were used without further purification. Polycrystalline palladium, platinum and tungsten metal electrodes were made by sealing the wire in glass tubes. The palladium and platinum electrodes are 1mm diameter disks. The tungsten electrode is a 0.5mm diameter disk. The glassy carbon (3mm diameter) and gold (1.65mm diameter) electrodes were purchased from BAS and Sargent Welch. Polishing was accomplished using a Struers DAP-V grinder–polisher producing a highly polished disk electrode. The rotating disk glassy carbon, palladium, and platinum electrodes were reported by the manufacturer to have a geometric surface area of 0.1964cm². The geometric areas of the rotating disk tungsten electrodes were 0.2815cm² and 0.2822cm². All rotating disk electrodes were purchased from Pine Instrument Co.

All experiments were performed in a UHP helium atmosphere using a Vacuum Atmosphere drybox at room temperature. The counter electrode was a platinum foil or tungsten wire and the reference electrode consisted of Al wire immersed in either a N=0.67 or N=0.60 AICI₃—MEIC melt contained in separate glass fritted or asbestos fiber compartment. Cyclic voltammetry and chronocoulometry were performed on an EG&G PAR model 273 potentiostat/galvanostat using the M270 Version 3 software environment with a Zenith 248 computer.

All melts were prepared by adding known amounts of AlCl₃ to weighed MEIC to achieve the desired mole fraction. All melts received approx. 70mg PdCl₂/30g AlCl₃—MEIC. Protonic impurities were removed by addition of EtAlCl₂. Care was taken to not use too much or the PdCl₂ would be reduced by the excess EtAlCl₂ to palladium metal. The melt compositions examined were N=0.33, N=0.44, N=0.49, N=0.50, N=0.55, N=0.67, and the neutral buffered melt of AICl₃—MEIC—NaCl (1:0.78:0.22).

Results and Discussion

Addition of PdCl₂ (brick red) to a basic AICl₃—MEIC melt results in an yellow–orange solution. Addition of PdCl₂ to an acidic melt results in a red solution. The basic melts have PdCl₂ at a concentration of 1.7x10⁻² molar. PdCl₂ is not very soluble in acidic melts at room temperature, so the concentrations were at saturation. Heating the melts at 95 °C for one week helps dissolve more PdCl₂. The order of solubility is: all basic melts >> N=0.67 > N=0.55 > N=0.50.

Palladium deposition–stripping was unaffected by whether the electrode was platinum, tungsten, palladium, glassy carbon, or gold. The only exception is palladium in basic melts ( see figure 1 ). The peaks are broader and the oxidation of chloride at the positive limit is shifted negative by 600mV. This gives some
indication of palladium's increased reactivity towards chloride. Figure 2 is an example of the palladium deposition—stripping in basic melts on a glassy carbon electrode. An obvious feature is the nucleation effect present, causing the negative overpotential in the reduction wave. The crossover in potential is from the overpotential of palladium reduction on a non—palladium surface. This is followed by a potential shift in the positive direction, since the electrode is now palladium coated, hence the crossover. Also present are the two oxidation waves instead of the expected one. Hussey et al 4 calculated a Nernst plot of the reduction peak and found that the charge is representative of a two electron process. A plot of the peak current versus the scan rate indicates a diffusion dependence from the reduction wave and the more positive oxidation wave. The more negative oxidation wave does not fit for adsorption nor diffusion phenomena taking place, which may indicate some combination of the two. This phenomena of two oxidation peaks for a metal has been seen before (see reference 6 for Zn and reference 7 for Fe). There are a number of scenarios which may explain the two oxidation waves. 1) One may be bulk oxidation followed by a more strongly adsorbed underlayer. 2) The more positive oxidation peak may be the palladium complex and the more negative may be some protonic impurity. 3) Both peaks may be two complexes of palladium, and 4) Each may be one electron steps to complete oxidation.

In examining the above possibilities individually one may be able to, if not solve the problem, at least narrow the field. The first possibility should be eliminated, because the charge difference between the peaks is all wrong. The underlayer should be the smallest peak, since it represents a smaller charge than the initial bulk. Instead, the most positive peak is generally the largest of the two. The second possibility is negated in two ways. First, if the protonic impurity is present in the melt prior to PdCl2 addition, it would show up in the blank melt. It doesn't. Secondly, addition of MEIC—HCl (shown in figure 3) is made to a N=0.444 melt using platinum as a working electrode. Platinum is used because of its sensitivity to hydrogen. As the figure indicates, addition of protons causes new peaks to form, but doesn't effect the original peaks.

The third scenario Hussey et al 4 tried to eliminate by doing a Nernst plot of different concentrations PdCl2. The formal potentials from the intercepts shifted 124mV/pCl unit. This is what is expected for four chlorides present per palladium. UV—VIS spectroscopy (see table I) seems to indicate that in the basic melt PdCl4 2 is the only compound, which seems to contradict this scenario. If the fourth possibility was correct, I would have expected both oxidation peaks to be of equal charge, but the second or most positive peak is the largest.

This would seem to indicate that none of the possibilities presented are acceptable. Let's examine the neutral and acidic melt data. Figure 4 is of palladium deposition—stripping on a palladium electrode in neutral melt. Notice that there is only one oxidation peak instead of two. Also, the redox couple has shifted from —0.5 volts in basic melt to +1.5 volts in neutral melt. This is a tremendous shift in potential, which could be caused by a change in ligand on the palladium metal or due to a change in the chloride concentration of the melt. This shift in the redox potential of palladium is what makes it desirable as a cathode in the molten salt electrolyte.

Sometimes a second oxidative peak shows up as in the neutral buffered melt,
figure 5. The reason for it is explained below. Figure 6 shows the palladium redox in N=0.55 melt. Here is seen only one oxidation wave although two have been seen here as well. The oxidation is not as sharp as in the basic melt, because PdCl₂ is much more soluble in basic melt than any other. This means that when the palladium is reoxidized, it is forming a compound which is not very soluble and it shows a precipitation effect on the shape of the oxidation peak. The reduction peak is much sharper at the base than in the basic melt.

The final melt examined is the N=0.67 melt (see figure 7). It has only one oxidation peak and it has never shown two. The oxidation peak is broad as seen in other acidic melts for the same reason as before. Since this melt has shown only one oxidation peak, UV−VIS spectroscopy was done on it (see table I). The two dominate peaks and one shoulder are ~34nm further apart than the spectra in the basic melt. A spectra of PdAl₂Cl₈ has a longer wavelength d−d transition similar to the acidic melt, but it does not have present the 350nm shoulder, which exists in all of this reports data. It is unclear whether this is indicative of a different compound, since other data presented earlier seems to indicate that the basic and acidic compounds are similar. The Bronsted acid source MEIC−HC1 was added to this melt too. The protonic compound shows up right where the less positive oxidation peak in figure 5 shows it to be. This may indicate that, at least for acidic melts, the least positive oxidation peak is some protonic compound.

Let us go back to the previously defined scenarios. With the addition of the acidic melt data it would seem that the third possibility needs to be reexamined. If there is only one compound in acidic melt and its spectra is similar to PdCl₄²⁻ not PdAl₂Cl₈ then the shift in potential must be due to the change in the activity of chloride in the different melts. This would also explain the precipitation effect experienced in the acidic melts on the oxidation peaks. PdCl₄²⁻ is much less soluble than PdAl₂Cl₈. This still leaves the two peaks in basic melt. Neither should be a complex of AlCl₄⁻ or it would form in acidic melt as well. The other oxidation peak could be some other chloro complex of palladium which is in equilibrium with the PdCl₄²⁻ in solution. This would explain the reason the Nernst plot derived formal potential shifts an amount equating to 4 Cl⁻'s per palladium. The other compound could have been consumed in the resulting change in equilibrium.

Conclusions

In summary, palladium deposition−stripping is possible in all examined mole fractions of MEIC−AlCl₃. There is a 2 volt shift in the couple when going from a free chloride source mole fraction (basic melt) to a chloride complexed mole fraction (all others). The Pd⁺²/Pd⁺⁰ couple is present near the positive limit of the melt, which is most desirable for use in a battery. Two oxidation peaks are present in basic melt, but only one is present in a neutral or acidic melt. This is, again, beneficial for the use of neutral melts as a battery electrolyte. Three dimensional nucleation is occurring in the reduction of palladium. Further nucleation studies are continuing to determine if progressive of instantaneous. Spectroelectrochemistry will be done to further identify the two oxidation peaks in basic melts. Battery tests will be ongoing.
Acknowledgements

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Table I: Absorption spectral data of PdCl$_4^{2-}$

|                  | aq soln | HCl$^a$ | Basic Melt$^b$ | Acidic Melt |
|------------------|---------|---------|---------------|------------|
| 223              | 280     | 336$^a$ | 474           | 619$^a$    |
|                  | 291     | 345-    | 480-          | 620$^a$    |
|                  | 278     | 350-    | 500-          | 504        |
|                  | 347$^a$h| 355$^a$h| 483           |            |
|                  |         |         | 483           |            |
|                  |         |         | 483           |            |
|                  |         |         | 483           |            |
|                  |         |         | 483           |            |

a) see ref 8, b) both n=0.33 and ref 4 data, c) MEIC absorbance interference
sh=shoulder, w=weak

Figure 1: Cyclic voltammogram of plating and stripping of palladium on palladium in basic melt with a scan rate of 1mV/sec. The reference electrode is an aluminum wire in 0.67 mole% AlCl$_3$ 0.33 mole% MEIC.
Figure 2 Cyclic voltammogram of plating and stripping of palladium on glassy carbon in basic melt with a scan rate of 1 mV/sec. The reference electrode is an aluminum wire in 0.67 mole% AlCl$_3$ 0.33 mole% MEIC.

Figure 3 Cyclic voltammogram of plating and stripping of palladium on platinum in basic melt with a scan rate of 1 mV/sec. The reference electrode is an aluminum wire in 0.67 mole% AlCl$_3$ 0.33 mole% MEIC. MEIC-HCL added, resulting in new peaks forming.
Figure 4 Cyclic voltammogram of plating and stripping of palladium on palladium in neutral melt ($N=0.50$) with a scan rate of 100mV/sec. the reference electrode is an aluminum wire in 0.60 mole% AlCl$_3$ 0.40 mole% MEIC.

Figure 5 Cyclic voltammogram of plating and stripping of palladium on palladium in neutral buffered melt with a scan rate of 100mV/sec. the reference electrode is an aluminum wire in 0.60 mole% AlCl$_3$ 0.40 mole% MEIC.
Figure 6 Cyclic voltammogram of plating and stripping of palladium on palladium in $N=0.55$ acidic melt with a scan rate of 100mV/sec. The reference electrode is an aluminum wire in 0.60 mole% AlCl$_3$, 0.40 mole% MEIC.

Figure 7 Cyclic voltammogram of plating and stripping of palladium on palladium in $N=0.67$ acidic melt with a scan rate of 100mV/sec. The reference electrode is an aluminum wire in 0.60 mole% AlCl$_3$, 0.40 mole% MEIC.