Electrochemistry

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Heat-Assisted Electrodissolution of Platinum in an Ionic Liquid**

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Noble metals (especially Pt) are interesting catalytic materials that offer an unusually high catalytic activity for many chemical reactions, particularly for hydrogen oxidation and oxygen reduction reactions in fuel cells.[1] This unique ability has also attracted much attention for several potential applications, which include electronics, sensing, and energy.[2] Noble metals are also scarce. To date, Pt metal and its alloys remain the best cathode catalysts for proton-exchange membrane (PEM) fuel cells; however, one major factor that limits the large-scale commercialization of PEM fuel cells is the high Pt content in the layers of the electrode catalyst. The ultimate goal is to decrease the Pt content of the catalyst or to use catalysts that do not contain noble metals without sacrificing the performance of the fuel cell.[1a,3] The growing demand for pure Pt metal and its alloys makes it necessary to develop efficient and environmentally friendly processes for recycling Pt and other precious-metal catalysts. The recycling of Pt is a challenging and complicated process,[4] the first step of which requires the dissolution of Pt. Platinum is considered to be one of the “noblest” among noble metals. Thus far, the highly corrosive agent aqua regia (HNO_3/HCl) or the strong oxidative agent piranha acid (H_2SO_4/H_2O_2) have been used to dissolve Pt or other noble metals.[4b,5] Although electrochemical methods are a possible solution to this challenge, there are major concerns around the use of highly toxic electrolytes or corrosive solutions and the evolution of toxic gases. This approach to the efficient recovery of Pt is also limited by low current densities and the passivation of the electrode that typically occurs in electrochemical processes.[4b,5a]

Herein, we report a basic 25:75 mol% $ZnCl_2$/1-ethyl-3-methylimidazolium chloride ionic liquid ($ZnCl_2$/EMIC IL) that serves as a solvent system for the electrodissolution of large amounts of Pt metal. As well as the primary goal of dissolving Pt metal, we also demonstrate that Pt metal can be recovered directly and effectively through simple reduction at the cathode in the same solvent system. ILs are defined as salts that melt below 100 °C and the compounds are attracting increasing attention as “environmentally friendly” solvents for electrochemical and synthetic applications. Some of the remarkable properties of ILs include low vapor pressure, high thermal stability, and high ionic conductivity.[6] The $ZnCl_2$/EMIC IL is an air- and water-stable IL.[7] It has been reported that the solvation properties and electrochemical windows of ILs strongly depend on their Lewis acidity, which, in the case of $ZnCl_2$/EMIC, can be adjusted by varying the $ZnCl_2$/EMIC molar ratio.[7a] It has also been demonstrated that free Cl^- ions are one of the major components in the $ZnCl_2$/EMIC IL.[7a] Pt metal is a popular working electrode material and has been used for several electrochemical studies in ILs or other solvent systems as a result of its noble properties.[8] In a well-known basic $AlCl_3$/EMIC IL, the anodic window at a Pt working electrode is limited by the oxidation of Cl^- ions, and the cathodic window is limited by the reduction of the imidazolium cation.[9] Similar results have also been reported for the basic 25:75 mol% $ZnCl_2$/EMIC IL.[7a,10] Although Pt electrodes have been widely used in several electrochemical studies, very little attention has been directed towards examining the extent of the dissolution of the Pt electrode.

In this study, we found that the continuing electrodissolution of the Pt electrode occurs with an increase in the working temperature of the IL. The temperature-dependent electrochemical windows of a Pt electrode in the basic 25:75 mol% $ZnCl_2$/EMIC IL are shown in Figure 1a. At low temperature (70 °C), the anodic potential limit has been assigned as the anodic oxidation of Cl^- ions to Cl_2, and the cathodic limit was from the reduction of the imidazolium cation and $ZnCl_4^{2-}$.[7a] In general, an increase in the temperature of this IL could promote the mass transport of Cl^- ions and cause the voltammetric currents to increase further. Surprisingly, upon heating the ionic liquid to temperatures greater than 80 °C, we observed an exceptionally significant increase in the anodic current and a negative shift in the anodic limiting potential. This implies that new anodic reactions can be induced by an increase in temperature. To determine the nature of the thermally induced reactions, the electrode potential was maintained at 1.25 V for 120 min in the IL at 100 °C. The Pt electrode quickly sharpened to a needle-shaped structure (Figure 1b, inset image). Because the electrode potential was greater than 1.2 V, it was apparent that a significant amount of the Pt electrode had dissolved into the warm IL; however, dissolution of the Pt electrode was not observed at the same electrode potential at lower temperatures.

As well as the rapid anodic current increase, an unusual hysteresis was detected (Figure 1a, inset graph). The oxidation current on the forward scan was lower than that on the backward scan. This indicated that an impurity had been adsorbed onto the Pt electrode, possibly an insoluble platinum chloride complex, which hindered the anodic dissolution of the electrode during the forward voltammetric scan.[9,11] After anodic treatment of the Pt electrode in the forward scan, a “clean” Pt surface was obtained, which give a more negative anodic limiting potential and a gradual

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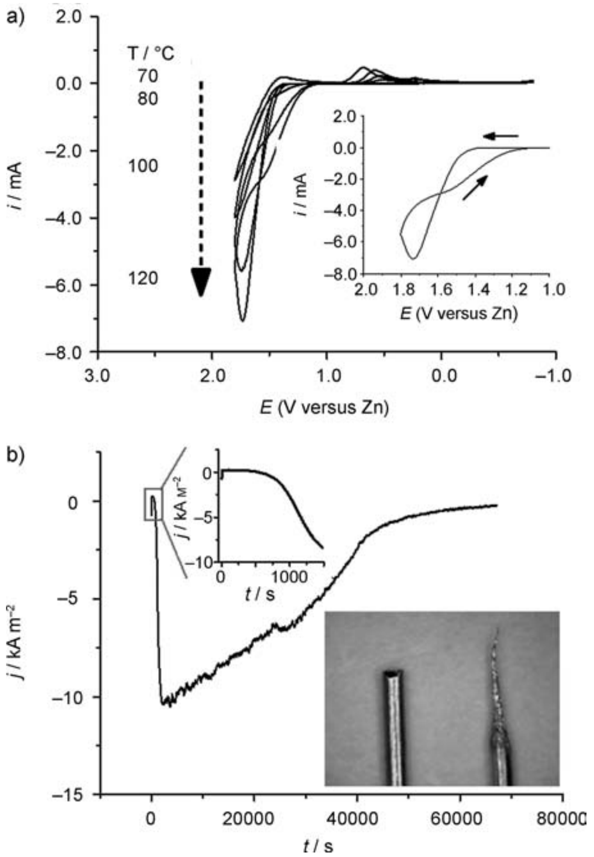

Figure 1. a) Temperature-dependent electrochemical windows of a Pt electrode in the 25:75 mol% $ZnCl_2$/EMIC IL. Inset: magnification of a cyclic voltammogram of the 25:75 mol% $ZnCl_2$/EMIC IL at the Pt electrode at 120°C. The scan rate was 50 mV s^{-1}. b) The current/time transient from the chronoamperometry experiment at $E = 1.25$ V for the Pt anodic dissolution process in the basic 25:75 mol% $ZnCl_2$/EMIC IL at 120°C. Upper inset: magnification of the current/time transients in the 0–1500 s range. Lower inset: image of Pt wires before (left) and after (right) the anodic oxidation at $E = 1.25$ V and 100°C.

increase in the anodic current. Similar behavior has been reported for other metallic systems, for example, Pd, Ag, and Sn,[11a,12] in which metal chloride complexes adsorb onto the electrode surface. To confirm that the dissolved Pt ion was Pt^{4+}, we introduced Pt ions into the ionic liquid through the controlled-potential oxidation of a Pt wire. The weight loss of the Pt electrode was determined after the passage of a certain charge through the system. The results of this verification and the related data are listed in Table S1 in the Supporting Information. In accordance with Faraday's laws of electrolysis, the results of these experiments confirmed that Pt^{4+} ions were the major anodization product.[8b]

Figure 1b shows the current/time transients from the chronoamperometric anodic dissolution of the Pt electrode in the $ZnCl_2$/EMIC IL. The transient that was obtained after an induction period of around 500 s, when the redox current was almost zero, shows that the anodic current increased rapidly as a result of the initiation of the dissolution process. This rising current eventually reached a maximum current density of $j_m = -10.5$ kA m^{-2}, and the maximum rate of dissolution of the Pt electrode was approximately 98 mol m^{-2} h^{-1}. This value was greater than previously reported values of 0.004–0.8 mol m^{-2} h^{-1} at room temperature for noble metals such as Au, Ag, and Pd, which were measured by using chemical leaching agents.[13] In these previous studies, Pt electrodes were shown to be inert to these chemical agents. In another report, Pt metal was shown to dissolve from the anode during the electrolysis of chloride in aqueous acid, and Pt(IV) compounds were formed only at very low current densities (below 10 A m^{-2}), which is much lower than in the IL in this study because of surface passivation.[4b,5a]

After around 100 min, the current started to gradually decay because of the decrease in the size of the working electrode. We strongly believe that the long induction period that is needed to induce the dissolution of the Pt electrode is a result of platinum chloride complexes, which initially protect the electrode surface. The dissolution of the Pt electrode should be initiated after the adsorbed complexes are transformed into their soluble forms and subsequently leave the electrode surface. A possible mechanism to illustrate this phenomenon is outlined in Figure 2. The adsorption of the $PtCl_x^{(x-2)-}$ complex $PtCl_2$ or $PtCl_4^{2-}$ occurs on the Pt substrate at the lower working temperature and protects the electrode from continuous anodic dissolution. When the IL is warmed to higher temperatures, for example 80°C, the anodic dissolution of Pt is initiated upon the formation of a Pt(IV) complex that has higher solubility, such as $PtCl_6^{2-}$.[4b,5a]

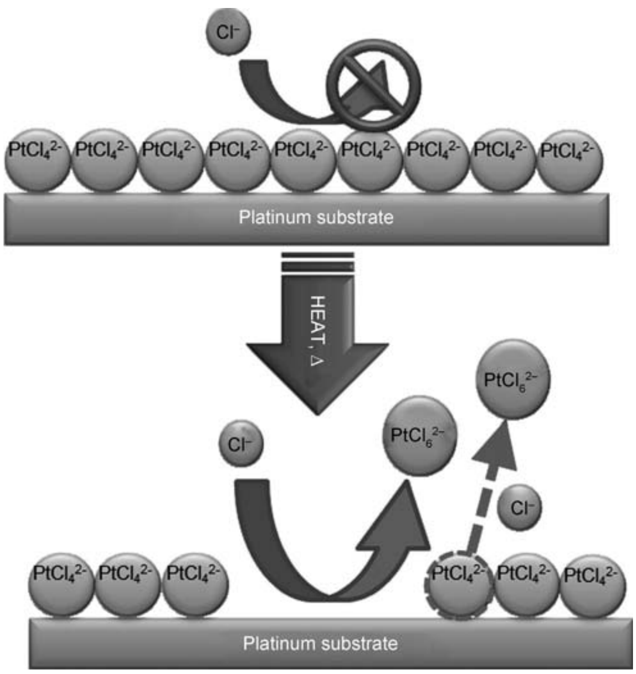

Figure 2. Illustration of the Pt electrode dissolution process.

We also sought to characterize the electrochemical behavior of the IL after the introduction of Pt^{4+} ions by controlled-potential oxidation. The anodic oxidation of Pt metal and Cl^- ions could occur concurrently at the anodic potential limit at lower temperatures, which makes it difficult to track these two reactions separately. Fortunately, we found that the indium–tin oxide (ITO) electrode has a much wider

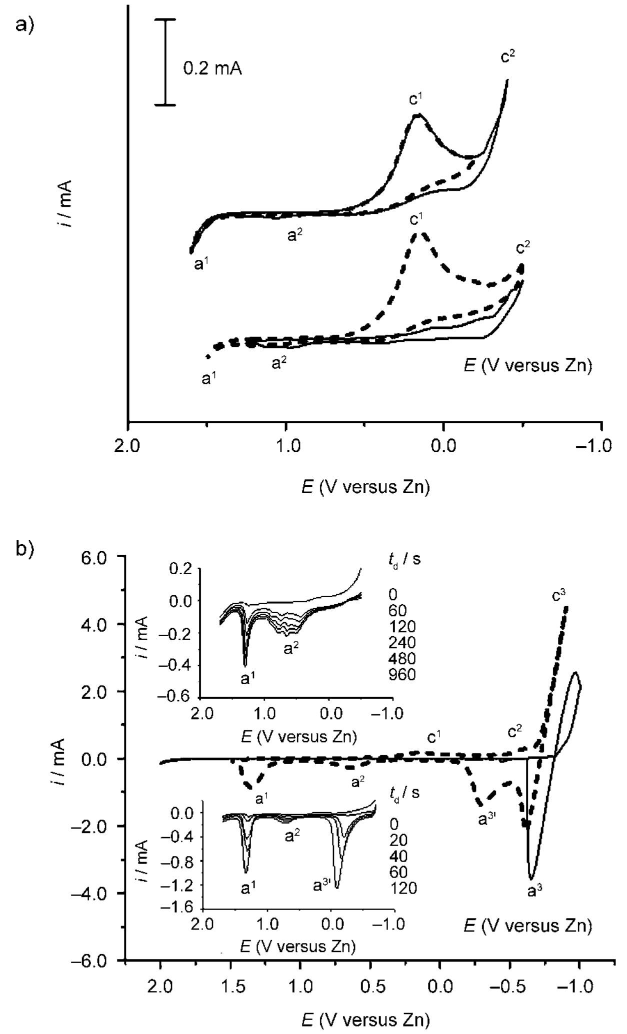

Figure 3. a) Cyclic voltammograms for $PtCl_4$ (34.2 mM, upper solid line), $PtCl_2$ (34.6 mM, lower solid line), and Pt^{4+} ions (35.0 mM, lower dashed line, from the electrodissolution of Pt wire in the 25:75 mol% $ZnCl_2$/EMIC IL) recorded at ITO electrodes at 100 °C. The scan rate was 50 $mV s^{-1}$. The cyclic voltammogram of Pt^{4+} (35.0 mM) was recorded at a more positive cathodic reversed potential than peak c^2 (−0.2 V, upper dashed line). b) Cyclic voltammograms of the 25:75 mol% $ZnCl_2$/EMIC IL (solid line) and of a solution of Pt^{4+} ions (35.0 mM) in the same IL recorded at ITO electrodes at 100 °C. Linear scan stripping voltammograms for a solution of Pt^{4+} ions (35.0 mM) at an ITO electrode after cathodic deposition at −0.5 V (upper inset) and −0.8 V (lower inset) for different deposition periods. The scan rate was 50 $mV s^{-1}$.

anodic potential limit than a typical glassy carbon (GC) electrode (Figure 3b, see also Figure S1 in the Supporting Information). This was assumed to be because anodic oxidation of Cl^- ions is kinetically slower on the surface of the ITO electrode.[8b] The voltammogram for an ITO electrode also had a sharp reduction current (c^3) at −0.80 V and a well-defined oxidation wave (a^3) because of the electrochemical deposition and stripping of bulk Zn.[8a,11a] The ITO slide (5.0 mm × 5.0 mm) was selected as the working electrode to study the electrochemical behavior of Pt^{4+} ions in the IL because of this unique electrochemical property. Platinum chloride salts, for example $PtCl_2$ and $PtCl_4$, served as sources of Pt^{2+} ions and Pt^{4+} ions, respectively, and were introduced into the 25:75 mol% $ZnCl_2$/EMIC IL separately. Cyclic voltammograms of these two solutions were recorded at the ITO electrode at 100 °C (Figure 3a). The cyclic voltammograms of the solution of Pt^{4+} ions exhibited two couples in the redox waves (c^1/a^1 and c^2/a^2) in the potential range of 1.0 to −0.5 V. The peak currents of all of the redox waves varied linearly with the concentration of Pt^{4+} ions in the IL (Figure S2 in the Supporting Information). The cyclic voltammogram of the solution of Pt^{2+} ions showed only one reduction wave (c^2) and the reduction wave c^1 disappeared in the cathodic scanning. A film was deposited on the electrode surface after setting the electrode potential to −0.5 V, which is more negative than that of the reduction wave c^2. Energy dispersive spectrometry (EDS) and XRD analyses of the film deposit indicated that it contained Pt metal with no trace of other elements, apart from a background signal from the ITO electrode surface (Figure 4a, see also Figure S5 in the Supporting Information). A solid deposit was not obtained on the electrode surface when the electrode potential was set to a more positive value (0.0 V).

The reduction wave c^1 can be assigned to the reduction of Pt^{4+} ions to Pt^{2+} ions, and then the Pt^{2+} ions are further reduced to Pt metal at the reduction wave c^2. On the return anodic sweep, Pt metal is oxidized to Pt^{2+} ions at the oxidation wave a^2 and further oxidized to Pt^{4+} ions at the oxidation wave a^1. It is important to note that the broadness of the oxidation over the oxidation wave a^2 is consistent with the formation of

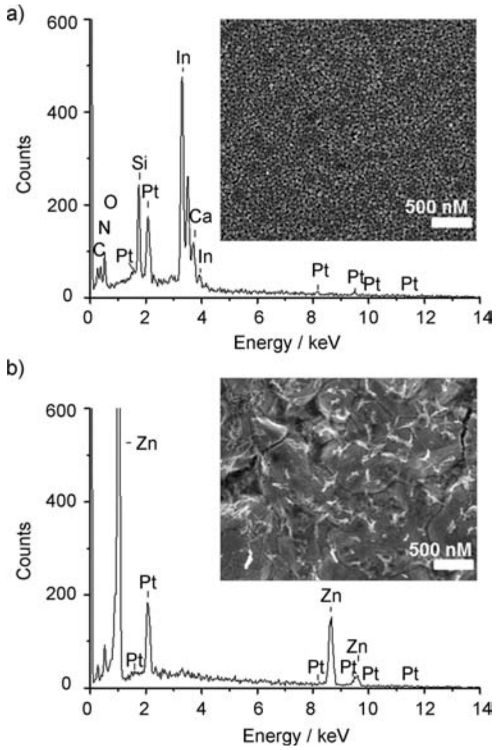

Figure 4. EDS plots of a) pure Pt metal and b) Pt–Zn deposits that were obtained on ITO substrates at a controlled potential of a) −0.5 V and b) −0.8 V at 100 °C in a solution of Pt^{4+} ions (35.0 mM) in 25:75 mol% $ZnCl_2$/EMIC IL. Insets: SEM images of a) a pure Pt deposit and b) a Pt–Zn deposit.

surface-bound platinum chloride complexes, such as $PtCl_2$ or $PtCl_4^{2-}$.[12a] In Figure 3a, the cyclic voltammogram of the solution of Pt^{4+} ions that were introduced by the electrodissolution of a Pt wire shows electrochemical behavior similar to that of $PtCl_4$ in the IL, which demonstrates that Pt^{4+} ions are the major anodization product of the electrodissolution of the Pt wire. In Figure 3b, the reverse potential is extended from −0.5 V to a more negative potential (−1.0 V), at which the reduction of bulk Zn occurs; the anodic oxidation waves (a^1 and a^2) increased, and a new anodic peak ($a^{3'}$) appeared at −0.2 V, as well as the original anodic peak (a^3) for the anodic stripping of bulk Zn. EDS composition analysis of the electrodeposits that were potentiostatically formed from the solution of Pt^{4+} ions at −0.8 V revealed the presence of both Pt^0 and Zn^0 in the deposits (Figure 4b). The presence of multiple stripping waves suggested that the deposits may contain different Pt–Zn alloy phases.[14] Linear scan stripping voltammograms that were recorded for the solution of Pt^{4+} ions showed that all of the stripping waves grew with increasing deposition time, and that the number of stripping waves was dependent on the deposition potential (−0.5 V for the upper inset and −0.8 V for the lower inset in Figure 3b). Two anodic stripping peaks, a^1 and a^2, were assigned after setting the deposition potential to −0.5 V for various deposition periods. When the deposition potential was set to −0.8 V, a third anodic stripping peak $a^{3'}$ appeared, and the peak current grew rapidly as the deposition time increased. These results demonstrate that pure Pt metal and Pt–Zn alloy, respectively, can be directly cathodically recovered from the IL solution that contains the Pt^{4+} ions at different deposition potentials.

The electrochemically reduced deposits were obtained on ITO substrates and the EDS and XRD analyses of the deposits indicated that the deposits consist of pure Pt metal and Pt–Zn alloy (Figure 4, see also Figure S5 in the Supporting Information). The Pt metal deposit was dark brown in appearance with good adhesion. The surface morphology was examined by SEM (Figure 4a, inset), which showed a thick and compact deposit that consisted of polygonal crystals of Pt metal with a homogeneous crystal size of 60–80 nm was obtained by using a controlled electrode potential of −0.5 V. Interestingly, nanopores with a uniform pore size of 40–50 nm were found to be widespread in the Pt deposit. The formation of these pores was a result of the aggregation of Pt nanoparticles. The major mechanism for the formation of these uniform nanopores is still not very clear. Because of the presence of these uniform nanopores on the surface, EDS and XRD surface analyses of the deposit showed the presence of the background signal from the ITO electrode surface along with the Pt metal signal from the deposits. When the deposition potential was even more negative than that required for Zn metal co-deposition, the surface morphology of the Pt–Zn alloy deposit lost its crystalline appearance and appeared as a sintered structure (Figure 4b).

In summary, we have demonstrated significant electrodissolution of a large amount of Pt metal in the basic 25:75 % $ZnCl_2$/EMIC IL at an ultrahigh dissolution rate. We have also reported the recovery of pure Pt metal, and the electrodeposition of Pt alloys, such as Pt–Zn, can be directly conducted in the same solution system without any treatment of the solution or exchange of the medium. This approach can readily be extended to the recycling of other noble metals. Furthermore, this method can be used to easily prepare a source medium that contains Pt ions for the synthesis of related materials. The preparation of catalysts that are made from Pt metal and its alloys, which were established on the ITO substrate, is popularly used in fields such as solar energy and biosensors, and may also be used to fabricate functional electrode materials for related energy or sensing applications.

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