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Environmentally friendly recycling of fuel cell's membrane electrode assembly using ionic liquids

Maxime Balva ^[a,b], Sophie Legeai ^[*,a], Nathalie Leclerc ^[a], Emmanuel Billy ^[c] and Eric Meux ^[a]

Abstract: The platinum nanoparticles used as catalyst in Proton Exchange Membrane Fuel Cells (PEMFCs) could represent around 46 % of the total price of the cells¹ for a large scale production which is one of the limitation of their commercialization. The recycling of this platinum catalyst can then be the best alternative to limit the production cost of PEMFCs. Usual recovery routes for spent catalysts containing platinum are pyro-hydrometallurgical processes in which a calcination step is followed by aqua regia treatment, generating fumes and NO_x emission, respectively. An electrochemical recovery route is proposed here, more environmentally friendly, performed in "soft" temperature conditions and without any gases emission. It consists in the coupling of electrochemical leaching of platinum in chloride-based ionic liquids (ILs), followed by its electrodeposition. The leaching of platinum was studied in pure ionic liquids and in ionic liquids melts, at different temperatures and chloride contents. By modulating the composition of the ionic liquid melts, it is further possible to leach and electrodeposit the platinum from fuel cell electrodes in a single cell process, under inert or ambient atmosphere.

Introduction

Platinum group metals (PGMs) play a key role in our world, as they are used as catalysts in varied fields of applications. Their unique properties make them more suitable than any other metals for catalytic activity. Indeed, platinum based catalysts can be used for example as car catalytic converters, to reduce the toxic gases emission of vehicles², as catalyst for oxidation of ammonia to nitrogen oxide³ or as catalyst for reforming and isomerization⁴. Platinum group metals used for catalytic activities are often immobilized on solid substrates such as alumina, in the field of automotive and reforming⁵, and carbon, in the field of fuel cell⁶. The platinum demand is constantly increasing due to its versatile applications in various industries, but platinum reserves are limited : 7905 tons in 2013, equivalent to 44 years of production with the actual use of platinum⁷. This explains the large interest to recycle the spent catalysts from different sources of waste.

The platinum nanoparticles used as catalyst in Proton Exchange Membrane Fuel Cells (PEMFCs) could represent

around 46 % of the total price of the cells¹ for a large scale production, which is one of the limitation of their commercialization. Studies have been realized to reduce the platinum content or replace the platinum with other catalysts but performances reached are then not equivalent to those obtained with pure platinum catalysts⁸. Recycling of platinum used in fuel cells can then be the best alternative to limit the cost of fabrication without sacrificing the performances of fuel cells.

The usual way to recover platinum from spent catalysts is a pyro-hydrometallurgical process. The spent catalysts are first calcined to produce ashes mainly containing PGMs^{2, 5a, 9}. The ashes are then leached in aqua regia solution with high temperature, up to 100 °C¹⁰. The use of aqua regia leads to the emission of toxic gases, such as NO_x. The replacement of nitric acid has been studied with other oxidants, as Cl₂ or H₂O₂¹¹. Some authors also tried to replace chloride by other halide ions, such as fluoride¹², bromide¹³, or iodide¹⁴, but the leaching performances are not comparable to those obtained with aqua regia. The leached platinum can further be recovered from the leachate using either Liquid/Liquid Extraction - usually with Alamine 336, Aliquat 336, or tri octylamine extractants^{10b, 15}- or by ion exchange, usually with AM-2B, Amberjet 4200 or Chelex 100 resins¹⁶. Main stripping agents used are thiourea or thiosulfate solution for Liquid/Liquid Extraction and sodium hydroxide for ion exchange. The final step of these different processes is the recovery of platinum by precipitation, using ammonium chloride as a reagent, to obtain solid (NH₄)₂PtCl₆^{10b}. The common way to recover platinum from spent catalysts is then very long, constituted by multiple steps which induce the use of organic solvents and strong acidic solutions, and is not in agreement with the green chemistry's principles. It is then needed to find a treatment route which is more environmental friendly, without the use of organic solvents or strong acid solutions and without toxic gases emission.

Some authors¹⁷ have studied the leaching of platinum nanoparticles contained in MEA's electrode by electrochemical dissolution in aqueous solutions. As the platinum is already immobilized on an electrode, its electrochemical dissolution seems to be a promising way, avoiding the use of an oxidant such as HNO₃. In these works, dissolution experiments have been performed in HCl 1 M, due to the coordinating properties of chlorides toward platinum ions that decrease the oxidation potential of platinum. Results obtained show the possibility to dissolve electrochemically platinum in aqueous chloride media. The leached platinum is then recovered by precipitation with ammonium chloride. Unfortunately, the leaching rate and the quantity of platinum dissolved are extremely low (0.25 mg.h⁻¹.cm⁻²) compared to what is obtained with conventional aqua regia treatment (4 mg.h⁻¹.cm⁻²).

Ionic liquids (ILs) represent an alternative to aggressive and toxic aqueous solutions for the leaching of platinum-based catalysts. ILs are salts that melt below 100°C, usually composed

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of a big organic cation and an organic or inorganic anion. ILs are promising due to their unique properties such as an extremely low volatility, a relatively good electric conductivity and a wide electrochemical window, usually more than 2 V¹⁸, that could allow an electrochemical leaching of platinum by oxidation, and without degradation of the ionic liquid. The wide electrochemical window can also allow the recovery of metallic platinum by electrodeposition.

Among ILs, chloride-based media are particularly promising for the electroleaching of platinum due to their high chloride content (typically 6 – 10 M). Some authors have already studied the electrochemical dissolution of platinum and other metals in chloride-based deep eutectic solvents (DES), and particularly in a mixture of 1:3 ZnCl₂-EMIM Cl¹⁹, but there is no study in typical ionic liquids. Electrochemical dissolution of platinum in DES has been demonstrated but the major drawback of the use of halometallate DES for the recovery of platinum is that the presence of a zinc salt can interfere with the platinum electrodeposition by forming ZnPt alloys.

The aim of this work is to study the feasibility of electrochemical dissolution and electrodeposition of platinum in imidazolium-based ILs containing chloride ions (RMIM Cl), and to apply this method to the recovery of platinum nanoparticles immobilized on the carbon substrate of fuel cell electrodes.

Results and Discussion

1) Electrochemical leaching of platinum in RMIM Cl ionic liquids

a) Electrochemical studies

Imidazolium-based ILs were selected because of their relatively low viscosity and good cathodic stability^{18, 20}. Several platinum complexing anions were selected, and tested in association to BMIM⁺ cation for the electroleaching of platinum: Cl⁻, Br⁻, I⁻, SCN⁻ and N(CN)₂⁻. It appeared that only chloride ions lead to the anodic dissolution of the platinum anode. Three chloride-based ionic liquids have then been chosen for further studies, with three different chain lengths: MIM Cl, BMIM Cl and HMIM Cl.

Melting point (T_m)²⁰⁻²¹, density (d), viscosity (η) and electrochemical window on glassy carbon disk (EW) of these 3 ionic liquids are given in Table 1.

Table 1. Physico-chemical properties of the 3 chloride-based ionic liquids selected

Ionic liquid	T _m (°C)	d _{80°C}	η _{80°C} (mPa.s)	EW _{80°C} (V)
MIM Cl	75 ²⁰	1.18567	114.8	2.3
BMIM Cl	65 ²⁰	1.05409	162.5	2.8
HMIM Cl	5 ²¹	1.00917	169.8	2.8

Prior to electrochemical leaching of platinum, anodic linear sweep voltammetry (LSV) experiments were performed using the three selected ionic liquids at 80 °C (T > T_m of MIM Cl). LSV curves obtained on glassy carbon and platinum electrodes are given in Figure 1.

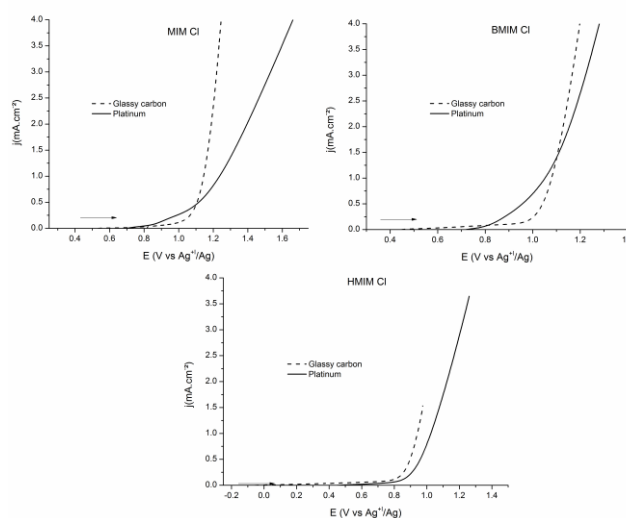
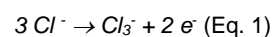


Figure 1. LSV obtained in MIM Cl, BMIM Cl and HMIM Cl at 80 °C on glassy carbon and platinum working electrodes. Scan rate = 20 mV.s⁻¹.

On glassy carbon electrode, an oxidation signal is observed at 1.0 V vs Ag⁺/Ag, 0.9 V vs Ag⁺/Ag and 0.8 V vs Ag⁺/Ag respectively for MIM Cl, BMIM Cl and HMIM Cl, which corresponds to the oxidation of chloride ions according to the following reaction²²:



Using the platinum electrode, an oxidation signal is observed at 0.88 V vs Ag⁺/Ag, 0.83 V vs Ag⁺/Ag and 0.86 V vs Ag⁺/Ag respectively for MIM Cl, BMIM Cl and HMIM Cl. For BMIM Cl and MIM Cl, this oxidation signal is observed at less positive potentials on platinum than on glassy carbon, contrarily to what is observed in HMIM Cl. This can be due to either a kinetics enhancement of chloride oxidation on platinum substrate or to the oxidation of platinum, according to the reaction:



Electrochemical dissolution experiments were first performed by applying a constant potential of 1.4 V vs Ag⁺/Ag and a coulometric charge of 30 C. The chronoamperograms obtained are given in Figure 2.

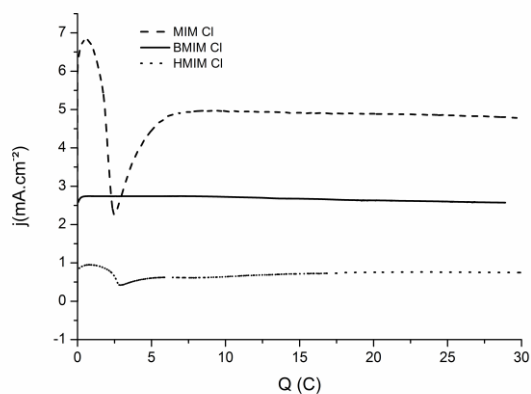


Figure 2. Chronoamperograms obtained during electrochemical dissolution of platinum in imidazolium-based chloride ionic liquids at 80 °C, $E = 1.4$ V vs Ag⁺/Ag, and $Q = 30$ C.

The leachates were analyzed by AAS. Gravimetric data are not presented here due to the formation of an interfacial blocking layer that impedes the dissolution in MIM Cl and HMIM Cl, which impact the gravimetric estimation of leached platinum. Results obtained are given in Table 2, as well as the leaching rate values, calculated from AAS results. Up to date, the oxidation state (+II or +IV) of leached Pt is not known and the development of analytical methods for the speciation of platinum in ILs is under study. As a consequence, the faradaic yields corresponding to the Pt leaching cannot be calculated yet. However, as the leaching experiments were performed for a constant coulombic charge applied (30 C), the comparison of the amount of Pt leached in each IL can represent an evaluation of the performances of the leaching in each medium and each set of experimental conditions.

Table 2. Results obtained during electrochemical dissolution of platinum in imidazolium-based chloride ionic liquids at 80 °C $E = 1.4$ V vs Ag⁺/Ag, $Q = 30$ C.

Ionic liquid	[Pt _{dissolved}](g.L ⁻¹) determined by AAS	Leaching rate (mg.h ⁻¹ .cm ⁻²)
MIM Cl	0.73	4.1 <i>Passivating layer</i>
BMIM Cl	0.93	6.9
HMIM Cl	-	<i>Passivating layer</i>

Platinum dissolution is observed in MIM Cl and BMIM Cl, but not in HMIM Cl. In the ionic liquid BMIM Cl, the anodic

dissolution leads to the highest leaching rate of platinum, of the same order of magnitude as the one obtained with aqua regia at 25 °C (4 mg.h⁻¹.cm⁻²). In MIM Cl and HMIM Cl, a thin layer containing chloride is observed by SEM-EDX analysis on the electrode surface, revealing a passivation of the electrode which hinders the oxidation of platinum. This is confirmed by the decrease of the oxidation current in MIM Cl and HMIM Cl observed on Figure 2 at the beginning of the anodic polarization, which is characteristic of a passivation process. This passivation phenomenon during an anodic polarization of a metallic electrode has already been observed by Abbot et al.^{19c} in a chloride-based DES media (1:2 mixture of choline chloride and ethylene glycol). Huang and al.^{19a} have also observed the formation of a passivating layer during the anodic dissolution of platinum in a ZnCl₂/EMIM Cl DES. Below 100 °C, the authors did not observe any platinum dissolution, due to a possible formation of a Pt-Cl blocking film. We can observe that a current is still circulating for MIM Cl and HMIM Cl after this passivation phenomenon. In the case of HMIM Cl, as no platinum has been dissolved during the experiment, the current is likely linked to the oxidation of chloride ions. In MIM Cl electrolyte, a higher current than the one measured in BMIM Cl is recorded, although the electrode is partially passivated. After the experiment, however, a lower amount of platinum dissolved is present in MIM Cl than in BMIM Cl. This could be linked to a higher contribution of the oxidation on chloride ions to the overall current in MIM Cl. The difference observed in the mean current value recorded in MIM Cl and BMIM Cl could also be partially due to the difference of viscosity between both ionic liquids (Table 1).

b) Influence of temperature

The influence of temperature on the leaching rate and on the formation of the passivating layer has been studied at 80, 100 and 150 °C. As the viscosity of ionic liquids decreases strongly with temperature, the current density measured by the application of a given potential increases consequently with temperature. So, in order to make a better comparison of the leaching rate and of the amount of dissolved platinum obtained at different temperature values, we chose to perform electrochemical dissolution experiments in a galvanostatic mode, applying the same current density in the three ILs. Similar leaching rates were obtained in the potentiostatic and the galvanostatic modes in BMIM Cl at 100°C. Potentiostatic dissolution tests were performed at 1.4 V vs Ag⁺/Ag, and galvanostatic ones were performed at 5.4 mA.cm⁻², which is the value corresponding to the average current density obtained during potentiostatic dissolution at 1.4 V vs Ag⁺/Ag. In both cases, 1.04 g.L⁻¹ of Pt was dissolved for 30 C, with a leaching rate of 16.7 mg.h⁻¹.cm⁻². The feasibility of the leaching in galvanostatic mode is important to further perform the leaching of the platinum without the use of a reference electrode, which is industrially more convenient.

Dissolution experiments were then performed in the three ionic liquids at 100 and 150°C, by applying a constant current density of 5.4 mA.cm⁻². The concentration of platinum dissolved and the leaching rates obtained are given in Figure 3.

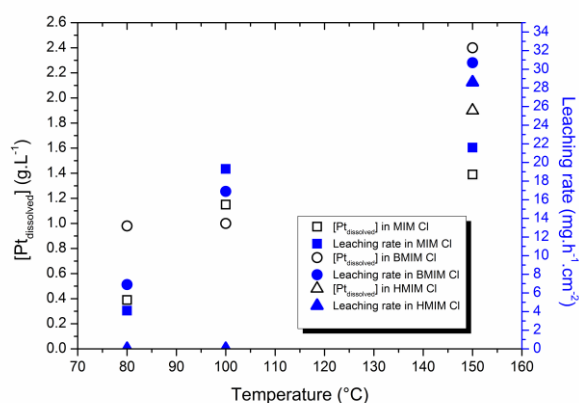


Figure 3. Influence of temperature on the leaching of platinum obtained after galvanostatic dissolution in MIM Cl (square), BMIM Cl (circle) and HMIM Cl (cross) ILs

As observed on Figure 3, the leaching rate and the concentration of platinum dissolved increase with temperature. This can be explained by the decrease of the viscosity with the increase of temperature that promotes mass transport of complexing anions and dissolved platinum species, and by the kinetics enhancement of platinum oxidation at highest temperature. One can also observe that the passivating layer is not observed anymore at 100 and 150 °C in MIM Cl, and at 150°C in HMIM Cl. As observed by Huang et al. in DES, temperature plays a major role in the formation of passivating layer^{19a}. The corresponding chronopotentiometric curves are in good agreement with this observation (Figure 4).

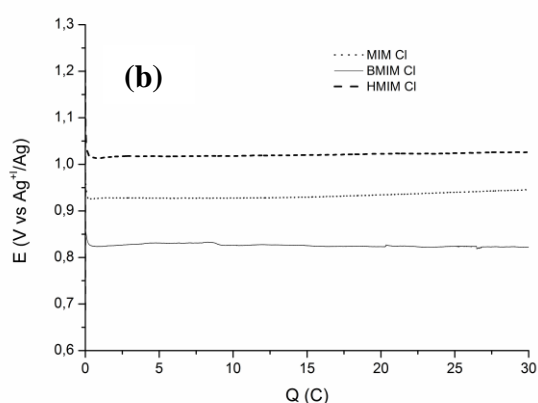
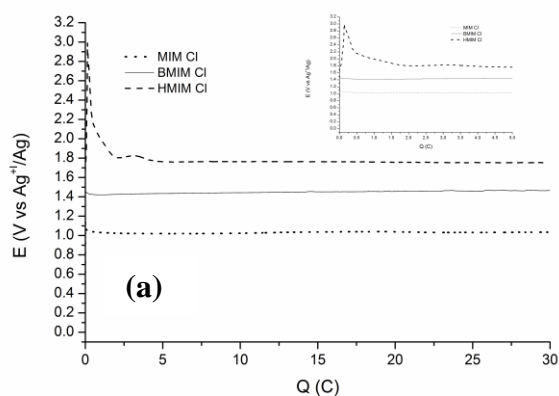


Figure 4 a and b. Chronopotentiometric curves obtained during galvanostatic leaching of platinum in RMIM Cl ionic liquids : 100°C (a) and 150 °C (b); j applied = 5.4 mA.cm⁻²; Q = 30 C

The Figure 4a shows that the potential measured is almost constant during leaching in BMIM Cl and MIM Cl at various temperatures, while a significant potential variation is observable at 100°C in HMIM Cl during the first 15 min of the dissolution (inset of Figure 4a). This variation of potential is characteristic of a passivation process²³, and corroborates the presence of a passivating layer after the experiment performed in HMIM Cl. At 150 °C, no variation of potential was recorded during leaching in the three ionic liquids, and no passivation was observed. As observed by Huang et al. ^{19a}, the temperature plays a major role on the passivation of the electrode, and consequently on the electrochemical dissolution of platinum.

c) Influence of applied potential

The influence of applied potential was first studied in MIM Cl and HMIM Cl at 80 °C to see if it has an influence on the formation of the blocking film observed previously. Results obtained show us that the passivating layer is present whatever the potential applied, which leads us to eliminate this two ionic liquids of this study and focus on BMIM Cl ionic liquid.

The influence of applied potential on electroleaching experiments was then studied in BMIM Cl. As the leaching rate increases with temperature, the study was performed at a higher temperature value, namely 100°C. The temperature at 100 °C was selected to keep reasonable in terms of energetic consumption and to be comparable to what could be obtained in aqueous media.

The study was performed at 100 °C for potential values ranging from the intersection potential $E_{\text{intersection}}$ defined in Figure 5, to $E_{\text{intersection}} + 1\text{V}$.

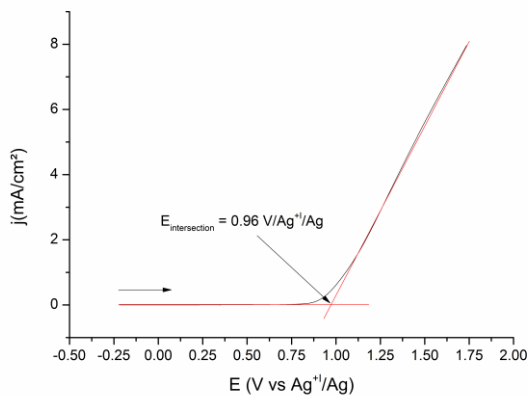


Figure 5. LSV obtained in BMIM Cl at 100 °C on platinum. Scan rate = 20 mV.s⁻¹.

Concentrations of platinum and weight loss of platinum electrode obtained after electroleaching experiments are given in Figure 6.

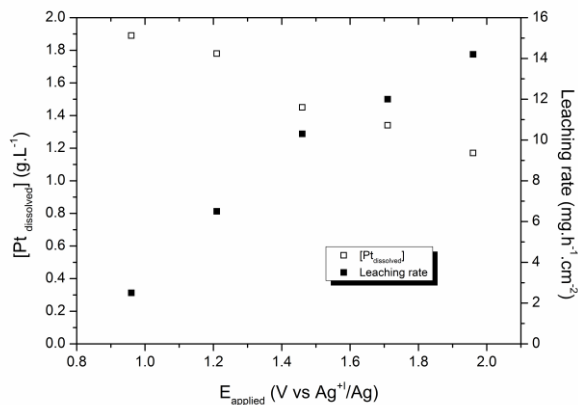


Figure 6. Influence of applied potential on the electroleaching of platinum in BMIM Cl at 100°C, Q = 30 C.

As we can see in Figure 6, the amount of platinum dissolved decreases with the increase of potential. This means that chloride oxidation is promoted when the potential increases in accordance with the linear voltammograms presented in Figure 1. On the contrary, the leaching rate increases with the potential.

d) Electrodeposition attempts

Electrodeposition attempts have been performed in BMIM Cl and MIM Cl ionic liquids containing 7.5 mM of platinum electrochemically dissolved according to previous dissolution experiments ($T = 100\text{ °C}$, $Q = 30\text{ C}$). A typical cyclic voltammogram obtained on a glassy carbon electrode in BMIM Cl containing 7.5 mM of leached platinum is given in Figure 7. Similar voltammograms were recorded in MIM Cl and HMIM Cl.

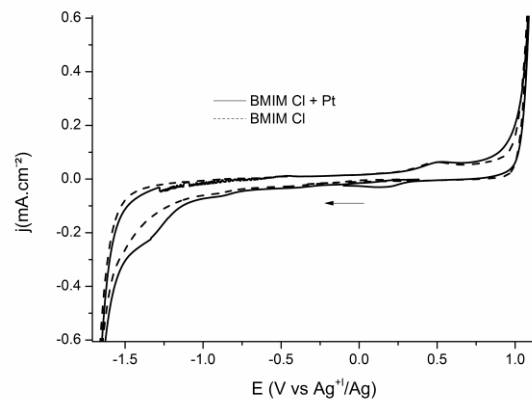
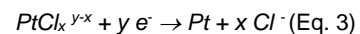


Figure 7. Cyclic voltammogram obtained on a glassy carbon disk electrode in BMIM Cl containing 7.5 mM of leached platinum, $T = 100\text{ °C}$, Scan rate = 20 mV.s⁻¹.

A reduction signal is observed between -1.0 and -1.5 V vs Ag^+/Ag , but unfortunately, no deposition of platinum occurs for potential values lower than -1 V vs Ag^+/Ag , meaning that this signal cannot be related to platinum deposition. The impossibility to electrodeposit Pt in RMIM Cl electrolytes is probably due to the high concentration of chloride ions (10 M in MIM Cl, 6 M in BMIM Cl and 5 M in HMIM Cl), that makes the platinum chloride complex non reducible in the electrochemical window of the RMIM Cl ionic liquids. To electrodeposit platinum at more positive potential values, the amount of complexing anions in the electrolyte must be decreased. This can be achieved by diluting RMIM Cl in another ionic liquid composed of a low coordinating anion, such as TFSI⁻. By decreasing the chloride concentration, the reduction potential of leached platinum will then increase, according to Nernst relation (Eq. 4):



$$E = E^0 + \frac{2.3 RT}{y F} \log \frac{a(\text{PtCl}_x^{y-x})}{a(\text{Cl}^-)^x} \text{ (Eq. 4)}$$

2) Electrochemical leaching of platinum and electrodeposition in ionic liquid melts

The electrochemical leaching and electrodeposition of platinum was studied in BMIM TFSI containing different amounts of BMIM Cl. BMIM TFSI was chosen as ionic liquid solvent due to its weak coordinating properties against platinum and its cathodic stability (-1.8 V vs Ag⁺/Ag) which should allow the electrodeposition of leached platinum. Moreover, BMIM TFSI presents a relatively low viscosity (9.84 mPa.s at 80°C), that will promote mass transport compared to RMIM Cl media, and a high anodic stability that prevents TFSI⁻ oxidation during platinum leaching. Finally, BMIM TFSI has a low hygroscopic character (3280 ppm of water for a saturated ionic liquid²⁴) compared to RMIM Cl ionic liquids, that should allow platinum electroleaching and electrodeposition in ambient atmosphere with negligible water oxidation and reduction secondary reactions. The first attempts of electroleaching were performed in BMIM TFSI containing BMIM Cl 0.1 M at 100°C. The influence of temperature and BMIM Cl content were then studied.

a) Electrochemical leaching of platinum plate in BMIM TFSI + BMIM Cl 0.1 M

Prior to electroleaching experiments, the electrochemical behavior of the platinum electrode in BMIM TFSI and BMIM TFSI + BMIM Cl 0.1 M was studied by linear sweep voltammetry (Figure 8).

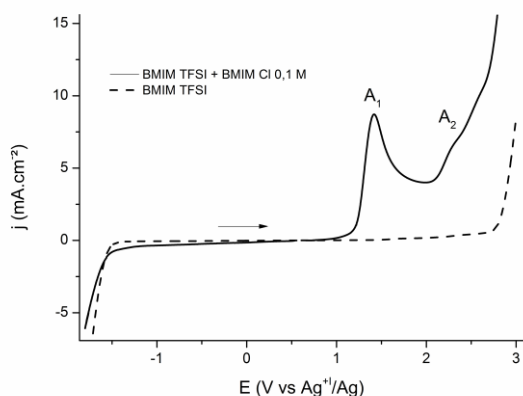


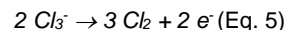
Figure 8. LSV of Pt disk electrode performed in BMIM TFSI and BMIM TFSI + BMIM Cl 0.1 M, T = 100 °C, Scan rate = 20 mV.s⁻¹.

An oxidation signal is observed in BMIM TFSI starting at 2.8 V vs Ag⁺/Ag which corresponds to the oxidation of the TFSI⁻ anion according to literature²⁵. No oxidation of platinum was detected by AAS in pure BMIM TFSI after a potentiostatic polarization at 3 V vs Ag⁺/Ag for a coulometric charge of 30 C.

In the BMIM TFSI + BMIM Cl 0.1 M melt, an oxidation peak A₁ is observed at 1.2 V vs Ag⁺/Ag, which can correspond to the oxidation of chloride and/or platinum, according to Eq. 1 and 2 previously given. The oxidation of Pt occurs at potential values

lower than the values corresponding to the oxidation of the TFSI⁻ anion, so the degradation of BMIM TFSI will not occur at the anode during Pt leaching.

A second oxidation signal A₂ is observed at 2.3 V vs Ag⁺/Ag that could be due to the oxidation of Cl₃⁻ to Cl₂, as observed in other halogen ILs, like bromide²⁶ or iodide-based ILs²⁷, according to the following equation :



First dissolution experiments were performed by applying a constant potential of 1.2 V vs Ag⁺/Ag, corresponding to the potential of A₁ peak, and a 30 C coulometric charge. Unlike experiments performed in pure RMIM Cl, the dissolution experiments were conducted potentiostatically, to avoid an ionic liquid degradation due to the oxidation of TFSI⁻ anion in the galvanostatic mode. The corresponding chronoamperogram is given in Figure 9a, and compared to pure BMIM Cl experiment. The Figure 9b represents the evolution of the ratio j/j_{final} , j_{final} being the final current density recorded in each electrolyte.

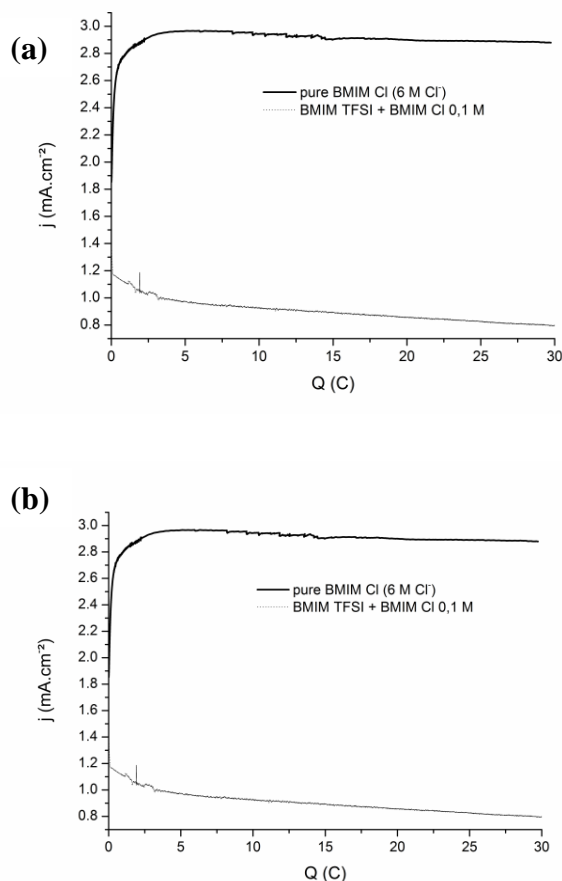


Figure 9a and b. Chronoamperograms obtained during potentiostatic dissolution of platinum in BMIM TFSI + BMIM Cl 0.1 M and BMIM Cl ($j=f(Q)$ (a) and $j/j_{\text{final}}=f(Q)$ (b)), T = 100 °C, E_{applied} = 1.2 V vs Ag⁺/Ag, Q = 30 C.

We can see in the Figure 9a that the mean current density recorded during the electrochemical dissolution in BMIM TFSI + BMIM Cl 0.1 M is roughly three times lower than the one obtained in pure BMIM Cl. Dissolution experiment is then longer in IL mixture than in pure BMIM Cl, although the viscosity of the IL melt is 16 times lower than the one of BMIM Cl (162.5 mPa.s in BMIM Cl and 10.6 mPa.s in BMIM TFSI + BMIM Cl 0.1 M). This can be attributed to the limitation of the leaching by the mass transport of chloride ions, as their concentration is 60 times lower than in pure BMIM Cl. Indeed, the Figure 9b clearly evidences a diminution of the current density during the experiment in the BMIM TFSI + BMIM Cl 0.1 M melt, characteristic of a limitation by mass transport, which is not the case in pure BMIM Cl.

The platinum electrode leached in BMIM TFSI + BMIM Cl 0.1 M was rinsed off with acetone and water and weighted. A weight loss of 11.6 mg was measured for 30 C applied, which correspond to a leaching rate of 1.47 mg.h⁻¹.cm⁻². It is then possible to dissolve massive platinum in ionic liquids melts, although the amount of dissolved platinum and the leaching rate are lower than in pure BMIM Cl (18.6 mg and 6.5 mg.h⁻¹.cm⁻² respectively in pure BMIM Cl at 1.2 V vs Ag^{+/}Ag). The lower amount of platinum dissolved could be due to a lower faradaic yield (competition with chloride oxidation) or to a difference in the oxidation state of leached Pt. Indeed, the first UV-visible spectroscopy analyses revealed the presence of Pt^(III) and Pt^(IV) in IL melts whereas mainly Pt^(II) is observed in pure BMIM Cl. A systematic study is under progress to determine the proportion of Pt^(III) or Pt^(IV) in the leachate as a function of electrolyte composition and applied potential.

After the leaching experiment in BMIM TFSI + BMIM Cl 0.1 M, a deposit was observed on the surface of the glassy carbon counter electrode. Corresponding SEM and EDX analysis of the deposit are given in Figure 10.

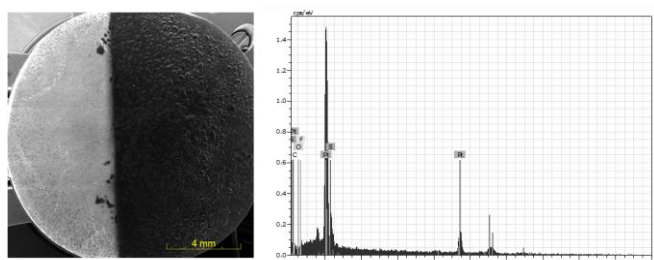


Figure 10. SEM-EDX analysis of the glassy carbon cathode after electrochemical leaching of massive platinum in BMIM TFSI + BMIM Cl 0.1M.

The deposit is mainly composed of platinum, with some traces of S and F which come from the perfluorinated anion TFSI⁻ of the ionic liquid BMIM TFSI. The traces of S and F can be removed with an appropriate acetonitrile rinsing of the electrode. It appears then that it is possible to deposit platinum dissolved in this ILs melt and that leaching and deposition of platinum can be run simultaneously in a single cell.

b) Influence of temperature on the leaching of platinum in BMIM TFSI + BMIM Cl 0.1 M

The influence of temperature on the leaching of massive platinum has then been studied, in the temperature range 30 - 100°C. Linear sweep voltammetry studies were first performed to determine A₁ peak potential value for each temperature (Figure 11), corresponding to the applied potential for leaching experiments.

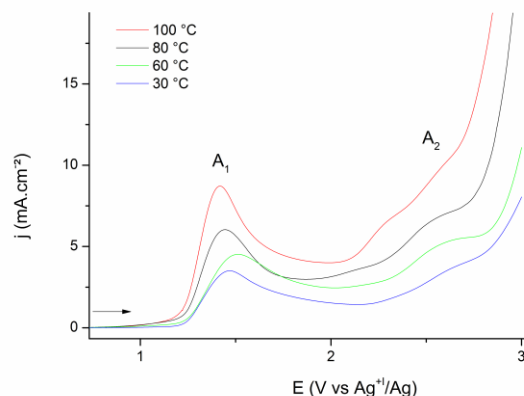


Figure 11. LSV of Pt disk electrode performed in BMIM TFSI + BMIM Cl 0.1 M at different temperatures, Scan rate = 20 mV.s⁻¹.

Two oxidation peaks, noted A₁ and A₂, are observed on Figure 11. A₁ corresponds to the oxidation of chloride/platinum and A₂ may correspond to the oxidation of Cl₃⁻ to Cl₂, as seen previously (Eq. 5). A slight negative shift of A₁ and A₂ peak potentials is observed with the raising of temperature, which is probably due to kinetics enhancement with temperature. Dissolution experiments were performed by applying a constant potential corresponding to A₁ peak and a coulombic charge of 30 C.

No platinum dissolution was observed for temperature lower than 100 °C, as already noticed by Huang et al.^{19a} in ZnCl₂/EMIM Cl DES.

c) Influence of chloride concentration

The influence of chloride concentration on platinum dissolution has been studied by varying the amount of BMIM Cl in the melt in the range 0.05 - 1 M. All experiments were performed at 100°C. As previously, dissolution experiments were conducted in a potentiostatic mode and linear sweep voltammograms were recorded in the different melts prior to leaching experiments to determine A₁ peak potential (Figure 12).

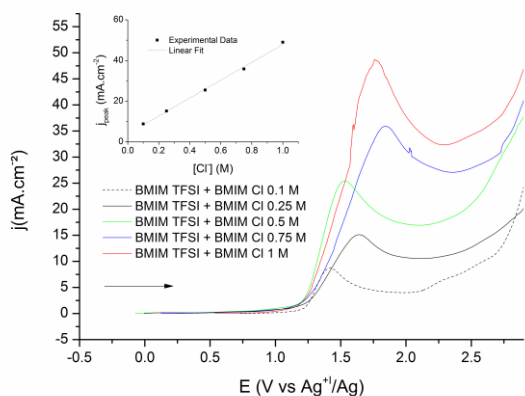


Figure 12. Influence of chloride concentration: LSV of Pt disk electrode performed in BMIM TFSI + BMIM Cl melts at 100 °C, Scan rate = 20 mV.s⁻¹. Inset: Influence of chloride concentration on the j_{peak} value.

The A_1 peak observed on Figure 12 is assigned to the oxidation of platinum and/or chloride. We can observe a linear increase of peak intensity with the increase of chloride concentration (inset of Figure 12). Dissolution experiments were conducted as previously by applying a constant potential corresponding to A_1 peak. Leaching rates obtained as a function of BMIM Cl content are reported in Figure 13.

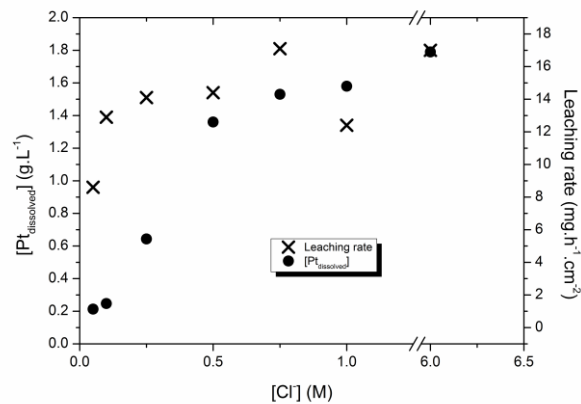


Figure 13. Leaching rate of platinum in BMIM TFSI + BMIM Cl melts at 100 °C; Q = 30 C. $[Cl^-] = 6\text{ M}$ corresponds to pure BMIM Cl

As expected from LSV presented in Figure 12, the leaching rate of platinum increases with the increase of chloride concentration. We can also see that for a chloride concentration of 1 M, the leaching rate is in the same order of magnitude than the one obtained in pure BMIM Cl ($[Cl^-] = 6\text{ M}$). A significant increase of the leaching rate is observed up to $[Cl^-] = 0.5\text{ M}$. For higher $[Cl^-]$ values, the increase of the leaching rate becomes less significant. This can be explained by the fact that the rate of the electrochemical leaching depends on 2 phenomena : the charge transfer kinetics and the chloride mass transport kinetics. At low

chloride content ($< 0.5\text{ M}$), the Pt oxidation seems to be limited by the chloride mass transport. At higher concentration values, the Pt oxidation is probably less limited by mass transport and the charge transfer becomes the rate limiting phenomenon, that would explain constant leaching rate for high chloride concentration values. It is then not necessary to use chloride concentration higher than 0.5 M to reach a concentration of 7.5 mM of leached Pt.

During electroleaching experiments, a platinum deposit was formed at the counter electrode in melts containing 0.05 and 0.1 M BMIM Cl, which is not observed for higher concentrations.

d) Electrodeposition experiments in ILs melts

Deposition experiments have been performed in ionic liquid melts BMIM TFSI + BMIM Cl for chloride concentration in the range 0.05 - 1 M, in melts containing 7.5 mM of Pt electrochemically dissolved. An example of LSV curves obtained in BMIM TFSI + BMIM Cl 0.1 M or 1 M containing 7.5 mM of Pt is given in Figure 14.

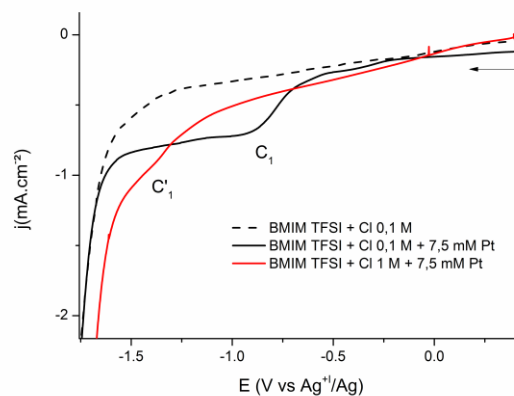
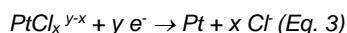


Figure 14. LSV of glassy carbon electrode performed in BMIM TFSI + BMIM Cl melts containing 7.5 mM Pt electrochemically dissolved, T = 100 °C, Scan rate = 20 mV.s⁻¹.

In the presence of leached platinum, a reduction signal C_1 is observed, that shifts towards more negative potential values (noted C_1' , at -1.4 V vs Ag^+/Ag for a chloride concentration of 1 M) as chloride concentration increases, according to Eq. 4. Electrodeposition experiments have been performed in the potential range corresponding to this potential signal and down to -1.8 V vs Ag^+/Ag .

Platinum was successfully deposited at potential more negative than C_1 peak for BMIM Cl contents up to 0.5 M. However, it appeared that it is impossible to deposit platinum dissolved from a 7.5 mM leached platinum solution when the BMIM Cl content is higher than 0.5 M whatever the potential applied. The platinum complex formed for chloride concentration superior to 0.5 M is then too stable to be reduced in the electrochemical window of the ionic liquid. It is also important to notice that a dissolution of the platinum anode is always observed during the electrodeposition experiments.

C₁ signal is assigned to the reduction of Pt dissolved, according to the Eq. 3



The platinum reduction reaction will then release chloride anions, counter balancing the chloride consumption during anodic leaching of platinum.

3) Recovery of platinum contained in MEA's electrodes

Experiments on MEA's electrodes were then performed at 100 °C in BMIM TFSI + BMIM Cl 0.1 M in order to recover the platinum nanoparticles immobilized on the carbon substrate of the electrodes.

a) Electroleaching of MEA's electrodes

The MEA's electrode was placed as working electrode (anode) and a glassy carbon plate was placed as counter electrode (cathode). The Figure 15 presents the corresponding voltammogram, compared to those obtained on Pt and glassy carbon disk electrodes.

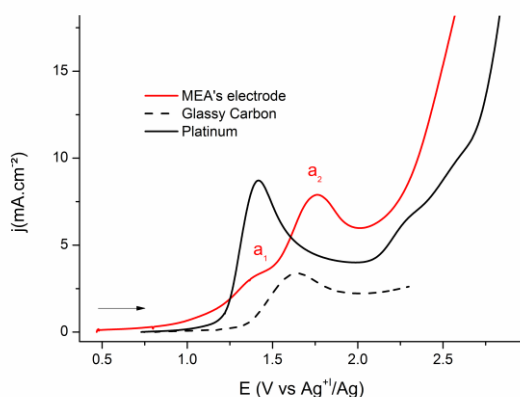


Figure 15. LSV obtained in BMIM TFSI + BMIM Cl 0.1 M on MEA's electrode, T = 100 °C, compared to voltammograms obtained on Pt and glassy carbon disk electrodes. Scan rate = 20 mV.s⁻¹, MEA's electrode immersed surface = 3.44 cm²

Two anodic signals are observed using the MEA's electrode, noted a₁ (1.1 V vs Ag⁺/Ag) and a₂ (1.4 V vs Ag⁺/Ag). We can suppose that the a₁ signal corresponds to the oxidation of platinum and/or chloride on the platinum nanoparticles surface, as observed previously on massive platinum electrode (Figure 8). a₂ probably corresponds to the oxidation of chloride on carbon substrate. The electrochemical dissolution of platinum was performed by applying to the MEA's electrode a constant potential corresponding to a₁ peak, namely 1.1 V vs Ag⁺/Ag. Electrode immersed surface was 3.44 cm², corresponding to a platinum theoretical weight of 0.258 mg, calculated from the average platinum loading of the MEA's electrodes used in this work. To ensure a complete leaching a Pt nanoparticles, a

coulombic charge of 0.85 C was applied, based on an hypothetical faradic yield of 60 % and on the basis of the dissolution of Pt by oxidation into Pt^(IV). The Figure 16 presents the SEM - EDX analyses of the MEA's electrode before (Figure 16a) and after (Figure 16b) the electroleaching.

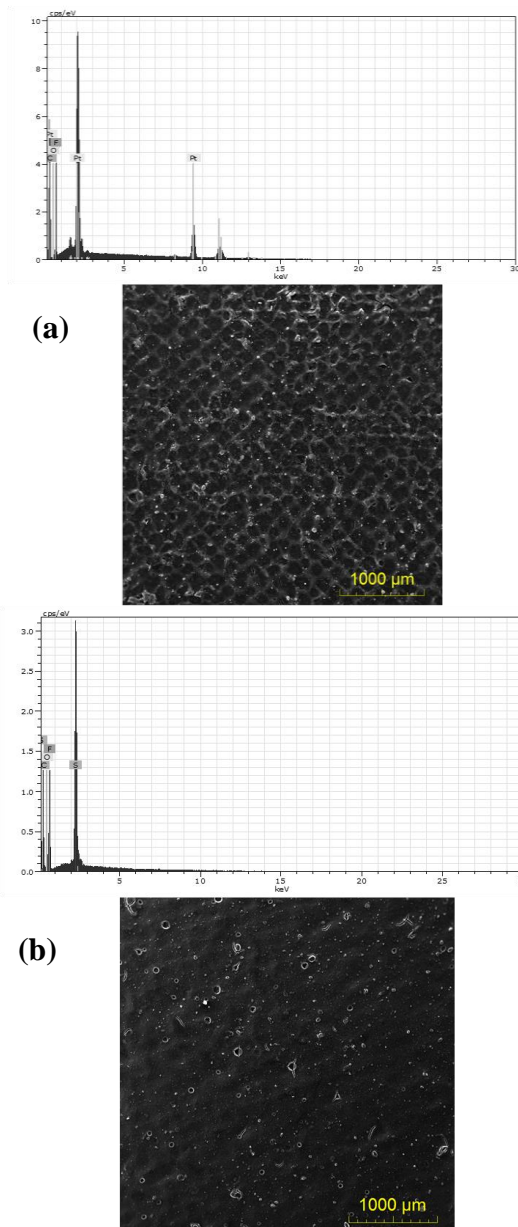


Figure 16 a and b. SEM-EDX analyses of the MEA's electrode before (a) and after (b) dissolution experiments in BMIM TFSI + BMIM Cl 0.1 M at 100 °C, E = 1.1 V vs Ag⁺/Ag, Q = 0.85 C, MEA's electrode immersed surface = 3.44 cm².

As the loading of the MEA's electrode is extremely low (75 μg.cm⁻²), the quantification of dissolved platinum was impossible by AAS (< limit of quantification). However, the EDX analysis of

the MEA's electrode after the experiment (Figure 16b) revealed no signal of platinum. Only C, F and S were detected, F and S coming from the perfluorinated anion of the IL. It is then clearly possible to dissolve platinum nanoparticles of end of life MEA's electrodes in this IL melt.

However, no platinum deposit has been observed at the counter electrode during MEA's electrodeleaching, contrary to previous results obtained with massive platinum in BMIM TFSI + BMIM Cl 0.1 M, probably because of the small amount of platinum in solution during the electrodeleaching of MEA's electrode.

b) MEA's electrodeleaching / Pt electrodeposition in a single cell

In order to study the feasibility of the simultaneous electrodeposition of platinum during the electrodeleaching of Pt nanoparticles contained in a MEA's electrode, a BMIM TFSI + BMIM Cl 0.1 M melt containing 7.5 mM of platinum was tested as leaching solution. The platinum was previously leached by electrochemical dissolution of a platinum plate, in the conditions previously defined in paragraph 2.a. A glassy carbon electrode was used as working electrode (cathode) and the MEA's electrode was placed as counter electrode (anode).

Based on the previous results obtained (paragraph 2.d), a constant potential corresponding to the C₁ peak was applied, namely -0.7 V vs Ag⁺/Ag, with a 5C coulometric charge. SEM and EDX analyses of the carbon cathode and the MEA's electrode after the experiment are given in Figure 17 and 18, respectively.

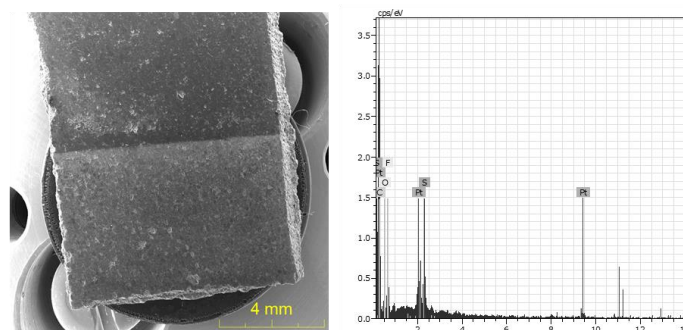


Figure 17. SEM-EDX analysis of platinum deposited on carbon working electrode in BMIM TFSI + BMIM Cl 0.1 M at 100°C, E_{applied} = - 0.7 V vs Ag⁺/Ag

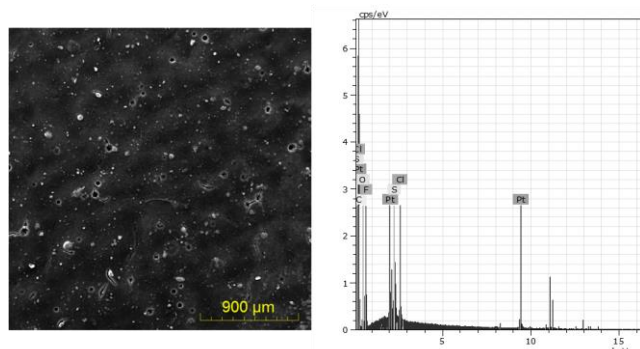


Figure 18. SEM-EDX analysis of the MEA's electrode used as counter electrode after deposition experiment in BMIM TFSI + BMIM Cl 0.1 M at 100 °C, E_{applied} = - 0.7 V vs Ag⁺/Ag. SEM and EDX analysis of Figure 17 highlight that platinum has been electrodeposited on the working electrode. Figure 18 shows that traces of platinum still remain on the MEA's electrode, but the leaching is almost complete. The platinum can be electrodeposited during MEA's electrode leaching by using a Pt containing leaching solution and controlling the cathode potential.

c) MEA's electrodeleaching / Pt electrodeposition in ambient atmosphere

In the perspective of an industrial application of the process, experiments were attempted under ambient atmosphere. First deposition experiments revealed that it is impossible to recover platinum by electrodeposition in BMIM TFSI + BMIM Cl 0.1 M in ambient atmosphere whatever the potential applied to the cathode. This is apparently due to the presence of water and oxygen in the solution which reduction occurs before the deposition of Pt, as shown in Figure 19²⁸.

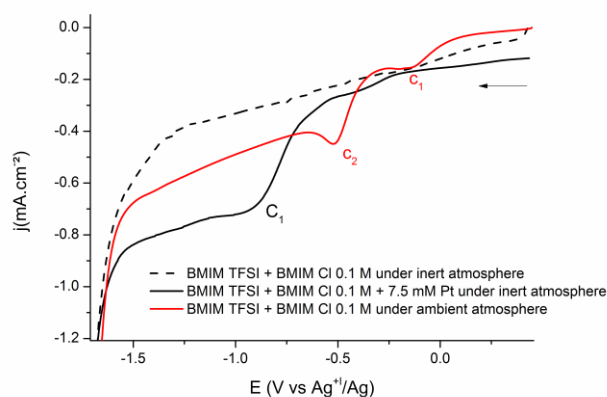


Figure 19. LSV curves obtained in BMIM TFSI + BMIM Cl 0.1 M under ambient and inert atmosphere, T = 100 °C, Scan rate = 20 mV.s⁻¹.

Two cathodic signals, c₁ and c₂, are observed in BMIM TFSI + BMIM Cl 0.1 M under ambient atmosphere at -0.1 and -0.5 V vs Ag⁺/Ag. As these two signals are not observed in this solution

under inert atmosphere, we can suppose that they correspond to the reduction of water and/or oxygen present in the ionic liquid melt. As observed on Figure 19, the reduction potential of platinum is lower than these two reduction signals, and consequently the presence of water and oxygen interferes with the electrodeposition of dissolved platinum.

To solve this problem, the chloride concentration of the ionic liquid was decreased to 0.05 M, to increase the reduction potential of the platinum complex, according to Eq.4. Corresponding LSV curves are given in Figure 20.

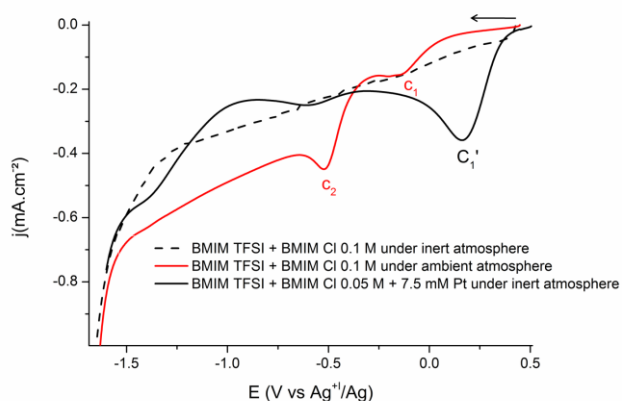


Figure 20. LSV curves obtained in BMIM TFSI + BMIM Cl 0.05 M + 7.5 mM Pt under inert atmosphere, $T = 100\text{ }^{\circ}\text{C}$, scan rate = $20\text{ mV}\cdot\text{s}^{-1}$.

A new signal C_1' , at $0.17\text{ V vs Ag}^+/\text{Ag}$, is observed in BMIM TFSI + BMIM Cl 0.05 M + 7.5 mM of platinum under inert atmosphere, which can correspond to the reduction of platinum complex in this ionic liquid. The reduction of platinum occurs then at a potential higher than the reduction of water and oxygen dissolved in IL under ambient atmosphere, which means that the presence of water and oxygen will not interfere with the electrodeposition of platinum. Deposition experiments have been performed under ambient atmosphere at C_1' peak potential. SEM and EDX analyses of the glassy carbon cathode are given in Figure 21.

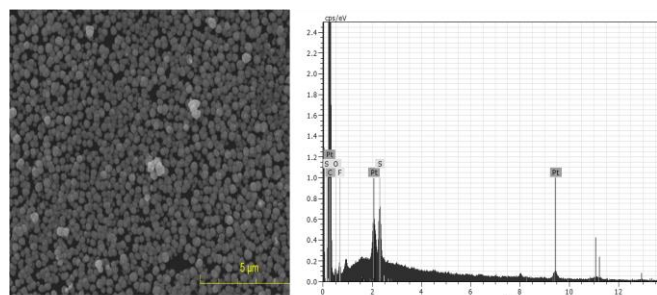


Figure 21. SEM-EDX analysis of platinum deposited on glassy carbon in BMIM TFSI + BMIM Cl 0.05 M at $100\text{ }^{\circ}\text{C}$ under ambient atmosphere.

SEM analysis highlights the electrodeposition of platinum on the glassy carbon electrode. The deposit is covering, composed of spherical particles of homogenous size of a few hundred of nanometers. EDX analysis shows that sulfur remains on the electrode, coming from the BMIM TFSI ionic liquid.

The MEA's electrode (anode), used as counter electrode, has also been analyzed by SEM-EDX (Figure 22).

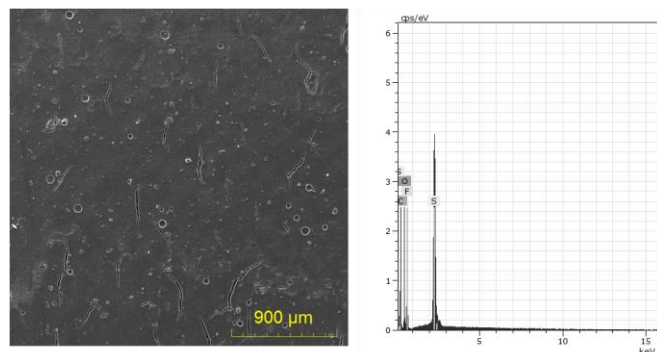


Figure 22. SEM-EDX analysis of the MEA's electrode used as counter electrode after deposition experiment in BMIM TFSI + BMIM Cl 0.05 M at $100\text{ }^{\circ}\text{C}$ under ambient atmosphere.

Figure 22 shows that all the platinum of the MEA's electrode has been leached under ambient atmosphere, contrarily to results obtained under inert atmosphere, where traces of platinum still remain on the electrode after the electrochemical leaching. This proves the feasibility of the recovery of Pt from MEA's electrode by simultaneous electroleaching / electrodeposition process in a single cell under ambient atmosphere.

Conclusions

We demonstrate in this work that the leaching of platinum can be performed in pure chloride ionic liquids and in ionic liquid melts containing chloride ions. Leaching rate values up to $15\text{ mg}\cdot\text{h}^{-1}\cdot\text{cm}^{-2}$ can be reached in pure BMIM Cl and in a BMIM TFSI-based ionic liquid melt containing 1 M chloride ions. This rate value is quite high compared to the $0.25\text{ mg}\cdot\text{h}^{-1}\cdot\text{cm}^{-2}$ value reported in literature in a HCl 1 M aqueous medium¹⁷. Moreover, from an environmentally point of view, chloride ions oxidation in aqueous media leads to Cl_2 evolution, which is a toxic and dangerous gas. In ionic liquid media, on the potential range applied for platinum leaching, chloride ions are oxidized into Cl_3^- , dissolved in the electrolyte. We also show that the electrodeposition of the leached platinum is only suitable in ionic liquids melts, due to the high concentration of the chloride anion in pure ILs. So, a high chloride concentration favors the leaching of platinum but can make its electrodeposition impossible. By adjusting the chloride content of the ionic liquid melts, Pt of MEA's electrode were successfully leached and recovered in an inert or an ambient atmosphere, at moderate temperature values.

Finally, we demonstrate that the simultaneous recovery of platinum by electrodeposition at the counter electrode during its electroleaching is possible. Further work will deal with the development and optimization of the electroleaching / electrodeposition single cell process that will allow performing platinum recovery with a negligible degradation of the ionic liquid and a negligible modification of the electrolyte composition. Indeed, if the potential is properly chosen, the reduction of platinum will be the only reaction performed at the cathode, releasing the chloride anions that are necessary for the leaching of platinum at the anode. At the anode, it could be possible to oxidize platinum with a negligible oxidation of chloride anions by a judicious choice of applied potential, as platinum seems to be oxidized at lower potential values than chloride anions, according to leaching rate decreasing with applied potential. So the use of ionic liquid melts to recover platinum nanoparticles from MEA's electrodes described in this work is an innovative and greener approach than usual routes for the recovery of platinum from spent catalysts. Indeed, this method induces no emission of toxic gases and is suitable in "soft" temperature conditions, unlike the usual process which consists of a calcination^{2, 5a, 9} and an aqua regia leaching of the platinum catalysts¹⁰.

Experimental Section

1) Chemicals

1-Butyl-3-Methyl Imidazolium Chloride (BMIM Cl) (99%), 1-Hexyl-3-Methyl Imidazolium Chloride (HMIM Cl) (>98 %), 1-Methyl Imidazolium Chloride (MIM Cl) (98 %), and 1-Butyl-3-Methyl trifluoromethanesulfonate (BMIM OTf) (98 %) were purchased from Iolitec®. Silver trifluoromethanesulfonate (Ag OTf) was purchased from ACROS®.

1-Butyl-3-Methyl Imidazolium Bromide (BMIM Br) was prepared according to the procedure described by Wu et al.²⁹. 1-Butyl-3-Methylimidazolium bis(trifluoromethyl)sulfonyl imide (BMIM TFSI) was also prepared according to Wu et al. procedure²⁹, slightly modified.

Briefly, 1.1 eq LiTFSI and 1 eq BMIM Br were mixed in ultra pure water during 16 h at room temperature. The solid obtained was then washed 4 times with ultra pure water and dried by evaporation under vacuum during 24 h at 80 °C.

Density and viscosity of ionic liquids were determined using respectively a DMA 4100 densimeter and a Lovis 2000 viscosimeter, both from Anton Paar®.

2) Electrochemical experiments

All electrochemical experiments were conducted using a Biologic® VSP-300 potentiostat controlled with EC-Lab software and a three electrodes cell. An Ag⁺/Ag reference electrode was used, prepared by immersing an Ag wire ($\varnothing = 1$ mm, Alfa Aesar®) in BMIM OTf containing 10 mM AgOTf. This reference electrode was used for all electrochemical experiments.

Voltammetric experiments were performed using glassy carbon or platinum disks ($\varnothing = 3$ mm and 2 mm, respectively) as working electrodes, and a glassy carbon disk ($\varnothing = 3$ mm) as counter electrode. The experiments were performed at 80, 100 and 150°C, with a sweep rate of 20 mV.s⁻¹. The disk electrodes were polished mechanically using 5 μ m and 0.3 μ m abrasive bands purchased from Radiometer Analytical® before each electrochemical experiment.

Electroleaching experiments were performed at 80, 100 and 150 °C, in potentiostatic or galvanostatic modes. A homemade platinum plate or a MEA's electrode (see paragraph 4) of this experimental section) was used as an anode. The platinum plate was made using a platinum plate (99.99 %) purchased from AMTS®. A large area glassy carbon disk (4.9 cm²) was used as a cathode. The volume of solution used was 8 mL.

Unless otherwise stated, the experiments were performed under inert atmosphere, in a MBraun® Labstar MB 10 Compact glove box, with O₂ and H₂O content below 0.5 ppm.

3) Determination of dissolved platinum concentration

The amount of leached platinum was determined by two methods: gravimetry and Atomic Absorption Spectrometry (AAS).

The platinum plate anode was weighted before and after its electrochemical dissolution, after rinsing with distilled water and acetone.

Besides, a quantification method was developed to determine platinum concentration by AAS. All AAS experiments were performed using a Varian® AA 240 spectrometer, controlled with the SpectrAA software. Two different procedures were used depending on electrolyte composition. The RMIM Cl (R corresponding to the cationic alkyl chain) samples were diluted in a 1 M HCl aqueous solution (1/10 (v/v)). The BMIM TFSI + BMIM Cl ILs melts samples were diluted (1/10 (v/v)) in a mixture of acetonitrile / 1 M HCl aqueous solution 1/1 (v/v). For RMIM Cl samples, LaCl₃ (1 g.L⁻¹) was added to the solution as releasing agent. A set of standard solutions was prepared for each medium, by dilution of a AAS standard Pt(IV) solution purchased from Sigma-Aldrich®. 10 wt. % of appropriated ILs was added in each standard solution to take into account the interferences due to ILs presence in samples.

The speciation of metallic ions in ionic liquids is very complex³⁰, and the speciation of platinum dissolved is at the moment still under study. The first results obtained by UV/visible spectroscopy in pure ionic liquids reveal that platinum has been mainly dissolved as Pt^{+II}, but the results obtained in ionic liquids melts show the presence of Pt^{+II} and Pt^{+IV}, in proportions depending on the chloride concentration of the leaching solution. It is then up to date difficult to compare performances of each set of experimental parameters in terms of coulombic efficiency. That is the reason why only the weight loss of platinum electrodes and their dissolution rate are presented here.

4) Leaching of platinum nanoparticles from MEA's electrodes

Leaching experiments of platinum nanoparticles from MEA's electrodes were performed on MEA's electrodes supplied by LITEN - CEA in Grenoble, the MEA's electrode being used as an anode. The electrode ink used is composed by Vulcan XC-72 Carbon with 47.3 wt. % of platinum and 26 wt. % of Nafion. The electrode ink is dispersed on the carbon paper (5 % Teflon) with a Micro Porous Layer (MPL). The average platinum loading of MEA's electrode is equal to 75 μ g.cm⁻². MEA's electrodes were characterized before and after dissolution experiments using a Tescan® Vega 3 SBU Easy Probe MEB with a Bruker® XFlash Detector 410 M driven by Espris Software to perform EDX analysis.

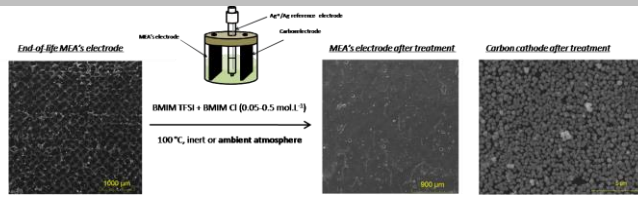
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Keywords: electrochemistry • electrodeposition • fuel cells • ionic liquid • platinum

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FULL PAPER



An electrochemical recovery route by coupling electrochemical leaching and electrodeposition in ionic liquids (ILs) is proposed here, performed in "soft" temperature conditions and without any gases emission. Imidazolium chloride ILs were selected for their complexing ability against platinum and their good electrochemical stability. They were used either pure or diluted in a low coordinating IL : BMIMTFSI. ILs melts were successfully used for platinum recovery from fuel cell electrodes. By further modulating the composition of the melt and the electrode potential control mode, it also appeared possible to simultaneously leach and electrodeposit platinum in a single cell process.

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**Environmentally friendly recycling of
fuel cell's membrane electrode
assembly using ionic liquids**