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Recovery of Precious Metals from End of Life PEMFC Membranes – MbR Thesis

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Introduction

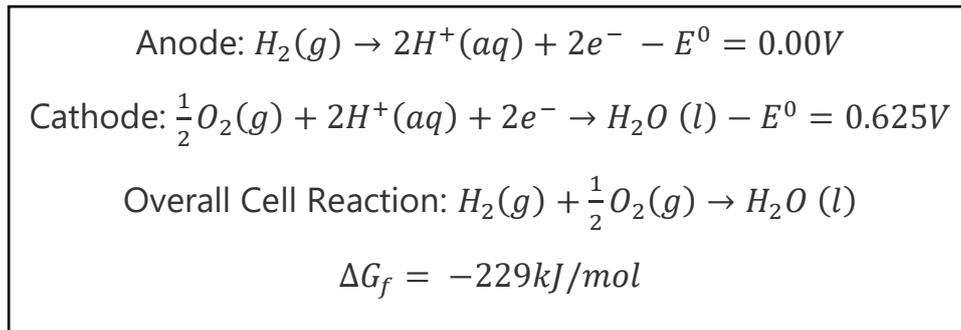
Fuel cells are electrochemical devices that produce a power output from the separation of two half-cell reactions thus creating current. This current is used to produce electrical power that can be applied to multiple differing industries. Proton exchange membrane fuel cells (PEMFC) have gained considerable attention in recent years due to the high efficiency, large fuel source and the clean production of energy. Proton exchange membranes fuel cells convert hydrogen to water, creating a relatively large current density in the process. This makes PEMFC's very attractive to the automotive industry, as it could be a viable alternative to petroleum-based vehicles in the future.

Hydrogen, with the development and feasibility of a hydrogen economy, receives attention due to the growing pressures, both environmental and political, placed upon governing bodies by the fossil fuel model currently in place. Issues raised include the growing effect on climate change, depletion of resources and air quality. These pressures have caused a shift towards increasing energy produced by renewable sources - causing hydrogen to be seen as a key energy carrier for a low carbon, low emission future.

Hydrogen is abundant as a resource and can be found in many differing resources. Large-scale examples of hydrogen production from feedstock include natural gas, coal, water electrolysis and biomass. Large-scale production in the United States comes from steam methane reforming. It is estimated that up to 95% of hydrogen produced in the US is formed this way. This production allows for up to 500 tonnes of hydrogen production per day, which can be converted into 800MW of continuous hydrogen based energy output (Ogden, 2015).

Other large-scale hydrogen producing techniques include coal gasification and thermochemical conversion of fossil fuels. Coal gasification is thought to be less energy efficient than methane but does have a smaller feedstock cost with similar capital and operating costs. Thermochemical conversion of fossil fuels is the least costly technique to create hydrogen but does rely on increasingly finite resources. Carbon emissions from such processes are expected to fall due to techniques such as carbon capture. Despite adding around 10-20% to the overall capital cost of a production plant, estimates suggest reductions of overall carbon emissions of the plant by 80-90% (Johnson et al., 2014 and Koornneef et al., 2012).

The operation of most PEMFCs is very similar and thus the configuration of each cell is similar. A hydrogen feed to the anode half-cell and an oxygen feed to the cathode half-cell is essential. Between each half-cell is a proton-conducting polymer that is surrounded by a precious metal catalyst. The catalyst allows for a faster rate of reaction at a reduced operating temperature. Reactions within the cell are displayed in equation 1.1.



Equation 1.1 – Half-Cell reaction of a generalised PEMFC

Note that in the overall reaction, electrical energy and wastewater are produced.

Precious metal catalysts within the fuel cell stack are essential for the operation of a cell but do have cost drawbacks. It is estimated that the 34% of the total stack cost can be attributed to the catalytic costs as of 2010 (Papageorgopoulos, 2011).

Fuel cells have many applications within the energy industry. As alluded to, PEMFCs could be applied to the automotive industry but can be applied in the stationary power industry. It is expected that around 50% of the fuel cell application is applied in stationary power with this figure constantly rising – a worldwide increase of 20% in the quantity of units shipped was recorded in 2016 (E4Tech, 2015). There are initiatives such as the Enefarm and Enefield projects that aim to increase the usage of hydrogen based power through use of hydrogen fuel cell stacks. These units are currently expensive, costing around \$20,000 per unit (International Energy Agency, 2015). It is believed that with government aid and increasing quantities of scale the cost could be reduced to as little as \$3500 by 2030 (Ogden et al, 2016). This figure can be reduced further with an increased quantity of precious metal recovery.

Fuel cell membranes are a key component within the fuel cell stack. They allow for the passing of protons from the anode electrode to the cathode electrode. Within the membrane is a catalytic layer that contains precious metals, namely platinum and iridium. These metals are very expensive but very effective for the process. Due to the high cost and low global availability of these metals, efforts are being made to recycle as much of these catalysts as possible. Three main recovery techniques have been created: selective chlorination, pyro-metallurgic processing and hydrometallurgical processing.

Selective chlorination is a process that uses differing vapour pressures from differing metal chlorides in an attempt to selectively remove metals via gas phase absorption. Whilst this has been proven to be successful with yields of up to 90% (Kim et al, 2000) from spent catalytic converters, hazardous gaseous bi-products cause as carbon monoxide and chlorine gas are often produced. Pyro-metallurgical processes have been tested and operate at temperatures between 1500°C and 1700°C. Again, relative success has been found with this process but the high chlorine or fluorine content in the fuel cell membranes creates large quantities of toxic gases. Hydrometallurgical processes are wide in application and have proven to be widely successful. Techniques that include digesting the membrane in highly

acidic solutions, such as aqua regia, have yielded higher metal returns than the previous methods and tend to have lower operation requirements. Disadvantages include the disposal of such acids due to the effects these solutions can have on the environment and biological habitats they contact.

This project aims to apply hydrometallurgical techniques to end of life proton exchange membranes containing platinum and iridium catalysts from electrolysers. By using previously developed techniques and exploring new applications and techniques, the research aims to gain yield rates as high as discovered using less aggressive solvents. This could help reduce overall costs of the process and allow for a more economically and environmentally viable process. By recycling a larger quantity of precious metal catalyst, or reducing the cost of this process, the overall cost of electrolysers can be reduced.

Literature Review

Critical analysis of past research allows for the creation of new, unexplored pathways. This section of the paper seeks to investigate research that has previously been undertaken in an attempt to learn from, and create new data. The literature reviewed below examines different techniques involved in the dissolution of platinum and iridium as metals alone and then metals within a membrane. Work examined also looks at the potential of electroplating iridium.

Dissolution of platinum from catalytic structures is not a well-explored field but work from Syddansk Universitet (2015) explored the use of dissolution in conjunction with precipitation of platinum group metals with change of pH levels. The process also included use of reducing agents and plating of platinum upon carbon-based structures

Platinum wire was used in a three-electrode assembly configuration with a graphite counter electrode and a radiometer standard reference electrode. Hydrochloric acid, 1M, was used as the working electrolyte, with the platinum wire electrode subjected to potential cycles between 0.55V and 1.3V vs. standard hydrogen electrode at a scan rate of 100mVs^{-1} . The dissolution stopped when the total mass lost from the platinum wire was 11mg.

The electrolyte, containing the platinum, was adjusted to a pH of over 10 by addition of 5M sodium hydroxide. The solution was reduced by the addition of ethanol. This resulting solution was added to by high surface area carbon powder ($250\text{m}^2/\text{g}$). This mixture was then refluxed for 2.5 hours in an attempt to create a 20 wt.% of platinum on carbon. Throughout the reflux process, an argon purge was in place to eliminate any oxygen present. Centrifugation at 4500ref for 20 minutes after the solution was cooled to room temperature occurred. The precipitate formed was washed with 18.2 MΩ water and 0.1M silver nitrate until there was no trace of chloride ions. The precipitate dried overnight at 95°C.

The final sample was tested by means of cyclic voltammetry and powder x-ray diffraction whilst UV-Visible absorption was used at several points throughout the tests. These results were collated to investigate the reaction mechanics. It was found that the rate of dissolution of platinum to the electrolyte was constant, the formation of Pt/C was present and the overall platinum loading was found to be 17.8%.

The results of this work are both relevant and useful to this project. The results display that by increasing the pH in a solution allows for re-precipitation of platinum onto a carbon-based structure, which could assist in a recovery step in a process. It also demonstrated that even with weak acids the dissolution of platinum is possible. The rate of dissolution, and the small quantity of platinum being used, are drawbacks to this particular application. The yield for the process is acceptably high however the rate at which the process occurs leaves cause for concern – especially if such a process where to be scaled to an industrial size. The method in which the process occurs also leaves some cause for concern as it takes a relatively long time for the small quantity of metal recovered.

Work by Walter et al (2013) explores the use creating noble metal oxalate complexes from noble metal precursors, similar to those found in PEMFCs. Such work is performed on a large scale due to the ease in which these complexes can be formed. During large-scale operations, safety is paramount due to the large quantities of gas and heat that can be released in a short period. The formation of the metal oxalate complexes is based around the reactions between noble metal precursors and oxalic acid or oxalic acid salts, such as potassium oxalate.

The invention made discusses the techniques used to create noble metal oxalate complexes by addition of "auto-catalysts". It states that by adding small quantities of noble metal oxalates to the reaction mixture of oxalic acid and noble metal precursor, the rate of reaction increases substantially. The increase of rate due to the auto-catalyst is limited however, so only a small amount of auto-catalyst is needed. It is estimated that a stoichiometric ratio of 1.8-2.8:1 of oxalic acid salt to metal precursor is needed, as well as 5×10^{-4} – 7×10^{-3} ratio of auto-catalyst to metal precursor. The addition of the subsequent parts does not need to happen in any particular order but stirring throughout is required to ensure maximum particle interaction.

The results stated that from 10g of platinum in the form of 18.01g $H_2[Pt(OH)_6]$ was converted into 74.49g of platinum oxalate, giving a 99.82% yield relative to platinum. This yield is the highest platinum conversion yield investigated. Whilst the application relates to noble metal precursors, it could be used upon fuel cell membranes. The procedure is relatively simple and has mild operating conditions with excess products being carbon dioxide, water and waste heat. When compared to acid processing techniques the waste products are relatively mild. The application of this process to end-of-life membranes has not been tested and could prove difficult. Issues such as deeply embedded metal and the overall dissolution strength of oxalic acid may cause this technique to be largely ineffective upon membranes and large amounts of noble metals.

Whilst investigating the effects of dissolution on platinum and iridium individually, it is also useful to seek techniques that could separate the two metals should they be in the same solution. Work by Faye and Inman (1963) has been carried out to seek the effectiveness of solvent extraction upon platinum, palladium, rhodium and iridium. By using similar characteristics of palladium and platinum, separation from iridium and rhodium is possible. Following this initial separation, the metals are separated further to create four differing metal salts.

The first step in the procedure was to evaporate the platinum group metals from the sample solution containing their relevant chloro-complexes to incipient dryness in the presence of sodium chloride. The salts were then dissolved in 6M hydrochloric acid, with a further 5ml of aqueous 4% (w./v.) solution of sodium iodide. This allowed for the formation of platinum and palladium complexes to form. This allowed for extraction by the addition of 15% solution of tributyl phosphate in hexane. The aqueous phase was removed and washed with hexane in a separate funnel. This solution is treated later for the separation of rhodium and iridium.

The tributyl phosphate – hexane extracts are stripped of platinum and palladium by the addition of nitric acid. After shaking three separate additions of 10ml nitric acid, the stripping solution is placed in a separator funnel with a dilution of water equal to the stripping solution volume. Further hexane is added at this point to remove as much TBP as possible.

The palladium and platinum solution is treated with sodium chloride and dried. 12M hydrochloric acid is then added and then the solution is dried – with this process, being repeated twice more. A sodium acetate buffer is added, with a dilution of water, and warmed. This is constantly agitated to ensure residue deposits do not form upon the bottom of the beaker. The solution is treated to determine the quantity of palladium in the solution.

An alcoholic 0.5% solution of p-nitrosodimethylaniline and 95% ethyl alcohol is added to the initial solution and diluted with water to form a 50ml solution. The absorbance is measured at 525nm by means of UV spectroscopy and compared to the palladium standards previously created. The resulting solution is transferred to a separator funnel after the addition of further p-nitrosodimethylaniline and ethyl alcohol. The palladium-p-nitrosodimethylaniline complexes are

extracted by the addition of chloroform. The addition of chloroform is stopped when the aqueous mixture changes from yellow to colourless. Filtration of the phase with the addition of concentrated sulphuric acid and concentrated perchloric acid should then occur. Evaporation of the solution and removal of sulphur trioxide fumes should then occur with a subsequent cooling to room temperature. The sample is boiled with 12M hydrochloric acid to create platinum chloro-complexes – which can be measured by spectrophotometrically.

The iridium and rhodium fraction a separated in a similar fashion. The solution is evaporated to near dryness and treated with a small quantity of concentrated nitric acid – to destroy the iodides. The conversion of rhodium and iridium to their respective chloro-complexes is achieved by the addition of 12M hydrochloric acid. The residue salts that are created are then transferred to a separator funnel and washed with 6M hydrochloric acid where TBP and hexane are added. The lower aqueous phase it then transferred to a clean funnel where the extraction step is repeated and then washed with further hexane. This solution is left for determination of rhodium content by the use of stannous bromide method use by Berman and Ironside (1956). The two TBP samples were stripped of iridium by the addition of hydrobromic acid.

Evaporation of the stripping solution in the presence of sodium chloride was then necessary for the recovery of iridium. The subsequent residue was treated with 7ml of concentrated hydrobromic acid, covered and boiled until a 2-3ml solution was remaining. The solution was transferred to a 25ml volumetric flask by means of washing by 3ml of concentrated hydrobromic acid and 7ml of 25% (w./v.) phosphoric acid. After 10 minutes in a boiling water bath, stannous chloride reagent was added, as recommended in literature by Berman and McBryde (1956). The flask was removed and diluted to 25ml by water after exactly 2 minutes and then examined by UV-Visible Spectroscopy at 402nm. This was compared to the absorbance of the standard previously created.

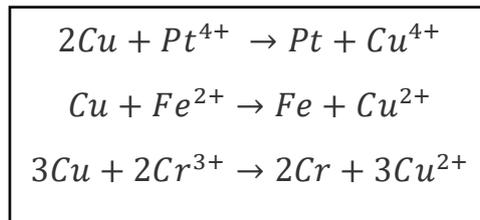
The literature analysed is very useful for several techniques explored in this paper. The separation of platinum and iridium from a heterogeneous solution is important; given final dissolution, mixtures from membranes may contain both. The techniques explored here show that small quantities of precious metals can be separated through this method. Quantities of metals used in the work were not in excess of 50ug and created in a batch system. This could prove difficult to integrate into a larger, continuous operation. The procedure listed above is also difficult to replicate on a large scale given the intricate nature of the experiment and the evaporation of strong acids – hence creating safety issues related to gaseous fumes. The overall extraction of iridium from the starting solution was 97.1% on average. Given this, the exploration of solvent extraction of these platinum group metals could be useful. The effectiveness of hydrobromic acid on the dissolution of platinum and iridium is not well documented and thus explored in this paper.

Acid processing of proton exchange membranes have been tested in several different ways. Attempts have been made to fully separate the membrane from the precious metal catalyst through the dissolution of the metal catalyst. The use of strong oxidants to achieve this is common with Debe et al. (2006) using both sulphuric acid and hydrogen peroxide in differing experiments.

Xu et al. (2009) explores further the separation of fuel cell assemblies via the use of sulphuric acid as an oxidising agent. They believe the key to recycling fuel cell assemblies is the effective and efficient separation of the membrane and catalyst layer, with further separation then needed upon the subsequent precious metal and acid resin layer that forms. By immersing a catalyst coated membrane in 0.5M H₂SO₄ for two hours, drying the membrane in an oven at 80°C under vacuum and then crushing the resulting pieces into 0.5cm² samples were created for testing. By further

treatment over 72 hours with concentrated sulphuric acid at 150°C under constant stirring a transparent solution with a black sediment resting at the bottom of the reaction vessel was created.

By use of atomic absorption spectroscopy, 7.33mg/l of platinum was found in the resulting solution; however, it was acknowledged that this was only a small amount of the platinum that was oxidised. Also present in the spectrum, 16ppm Fe²⁺ and 1ppm Cr³⁺ however, these elements were expected to have been present from the end plates. The copper powder introduced to reduce platinum was found to be reducing agent with the iron and chromium in the solution. The redox reactions are as follows:



Equation 2.1 – Redox Reactions of Copper, Platinum, Chromium and Iron in the End Plates

The total quantity of recycled platinum recorded was 231.7mg, which was a 94.2% recovery rate. This indicates that the process is effective yet simple in its design and replication.

The piece demonstrated that acid processing is an effective treatment of MEAs. The overall design of the experiment is sound and can be used as part of a framework for the research that is demonstrated in this paper. The results are a useful indicator of an industrial standard of recovery rate but shows the drawbacks of using certain acids. The gaseous emissions from this experiment, such as SO₂, are elements that should be removed from the process to enable a sustainable, low emission process. Whilst there are many positives to take from this research it should be noted that the use of Fe²⁺, Cr³⁺ and copper powder create issues when recycling the nafion membrane due to the additional treatment required to remove the metal before further nafion treatment can commence.

Exploring different membrane processing techniques is important to see the scope of research that has been completed. By analysing research done by Dawson and Patel in relation to potassium iodide leaching of end of life PEMFCs, further routes for exploratory research were open.

The work done by Dawson and Patel (2015) investigates the leaching of membranes by differing concentrations of potassium iodide to determine the quantity of platinum deposited upon electrochemical quartz crystal microbalances. By creating 4M KI solutions in 18.2 MΩ DI water, a base of iodine content was created. Further iodine content was added by varying the quantity of 1 N iodide solution added. These differing solutions were heated to 90°C in a flat bottom reactor where a 30-minute nitrogen purge was undertaken in order to remove the oxygen content and thus minimise the risk of premature oxidation of iodine. The EQCM was placed within the vessel in order to measure mass change for a total of 20 minutes. The open circuit potential of the electrodes was measured for the duration of the dissolution process.

Untested and end-of-life fuel cell membranes were cut into 2cm x 0.5cm strips prior to leaching. These strips were placed into the flat bottom reactor at differing conditions. All tests began with 4M KI created by addition to 18.2 MΩ DI water with the afore mentioned iodide solution being added to the reactor to create 5mM, 10mM, 15mM and 20mM concentrations of iodine solutions. After

running for 120 minutes, with samples taken at regular intervals, the experiment ceased. All of the samples taken were treated with ascorbic acid to reduce excess iodine in the sample before being analysed via a UV visible spectrometer to analyse the total quantity of dissolved platinum content. The leached materials were then washed and dried before being analysed with X-ray photoelectron spectroscopy and digested in aqua regia.

The results from this work displayed a trend that shows an increase in platinum dissolution with an increase in iodine content. Due to minor experimental errors within the operation, the trend is not clear but still apparent. There is a clear difference in dissolution between the sample with no additional iodine added (0mM) and those with additional iodine. After 5mM content, the increase in rate is only incremental. Suggested in the literature, from further ICP tests in conjunction with the UV-Vis spectrometry readings that at 5mM of iodine, a yield of 93% of the total platinum occurs.

From the literature, it is possible to see the effectiveness of iodine leaching upon end of life and untested membranes. This technique appears to have more benefits than the previously analysed piece. This is due to the less aggressive solvents used and thus less toxic gases released. This is an important factor to consider given the possible industrial scaling of such a product. The increase of iodine content is also an important consideration to account for in this piece. It indicates that platinum dissolution from the membrane has dependant factors that are manipulatable to increase the yield of the platinum recovery. Factors that affect the rate of the dissolution have not been addressed but could be explored in the research being undertaken by changing alternative factors such as pH and temperature. Overall, the paper is a strong basis to work upon given the positive results obtained at moderate operating temperatures and without the use of acids that create harmful side products – meaning the application of this work is repeatable at a lower cost relative to current methods.

Platinum is a more abundant metal than iridium. This has created an increase importance upon iridium recovery from spent industrial areas. The electro-deposition upon titanium and stainless steel (A304) yielded promising results in iridium recovery. Lopez et al (2015) stated that hydrometallurgical and pyro-metallurgic techniques used for iridium recovery but were limited in recovery rate and needed large quantity of solvents. By moving towards electrodeposition techniques, the yield and speed of recovery increases.

The experiment created by Lopez et al. used a conventional electrochemical cell of three electrodes. Stainless steel (A304) and titanium were used as working electrodes with graphite being used as a counter electrode. An electrolytic solution was created using 14.8Ω water and a 1000ppm iridium standard solution dissolved in 1M hydrochloric acid. Concentrations containing 3ppm, 6ppm and 12.5ppm were created.

The behaviour of the electrodeposition was measured by use of voltammograms at differing iridium concentrations. The results displayed that there was significant iridium deposit the stainless steel. Upon the titanium electrode, there was a decrease in electrode charge compared to the solution without iridium. The drop is associated with the absorbed hydrogen substitution upon the chloro-iridium complex ($[\text{IrCl}_6]^{3-}$) altering the kinetic and thermodynamic characteristics of the electrode. Conversely, there is a significant increase in electrode charge upon stainless steel. This indicates a lack of hydrogen substitution due to the soluble iron complex species forming readily compared to the absorbed chloride ions. This allows for increase iridium deposit upon the electrode surface. There is a limit charge upon the higher concentrations of 6ppm and 12.5ppm however, that indicates that electro-transference is the driver of the process.

Analysis by energy dispersive spectroscopy x-ray indicated the iridium deposits upon each of the electrodes. Stainless steel and titanium yielded 5.09% and 0.61% respectively. From the results, it appears that stainless steel is the better electrode to carry out iridium deposition at low concentrations due to the low absorption of chloride ions on the steel surface.

The information gathered from these results is helpful in initiating a recovery step once precious metal is stripped from the membrane. Electrodeposition may allow a fast way to separate iridium from any other contaminants in solution. Issues with the viability of this process given the highly acidic conditions used in stripping precious metals from the membrane. This may affect the durability of the steel and the effectiveness of plating given the higher concentration of halide ions present. Higher concentrations of iridium in solution are also present which may cause further problems given the charge limit present for stainless steel at 12.5ppm.

Methodology

Route Selection

After a full review of the literature, a plan was created to research areas of membrane dissolution that had not previously been explored. By using framework and results in previous work, a route was selected to maximise the quantity of pathways that could be covered most effectively.

An initial experiment was designed to understand the initial dissolution of platinum black and iridium at room temperature (25°C). Five different solvents were used; potassium iodide, potassium oxalate, potassium bromide, hydrobromic acid and water.

Pure water was used as a control to determine the base amount of dissolution, if any, was possible. Potassium iodide was used in the form previously stated in work by Dawson et al. (2013). Whilst results concerning platinum were not expected to differ, there is little literature to suggest the effect of potassium iodide upon iridium. Similarly, there is literature to suggest dissolution of iridium by means of hydrobromic acid but little literature of the effects of hydrobromic acid upon platinum alone. Potassium bromide was chosen to see the effects of pH upon the dissolution when relating the results to hydrobromic acid. Given the work previously referenced on the formation of noble metal oxalates, potassium oxalate was chosen to see the effects on larger quantities of precious metals.

Running experiments at both room temperature (25°C) and near boiling point (90°C), at a range of pH, iodide and bromide concentrations, a large matrix of results can be created. Analysis of these results can lead to the optimum results to test the membranes to find the effectiveness of selective conditions upon dissolution.

Room Temperature Testing

Each solvent was created in a 25ml quantity and placed into a plastic vial along with 0.25g of platinum black (CEMIG Lot 18-16089-05) and Iridium-Ruthenium black (90%-10%) (CAS no. 277318-98-6). The first vials contained 18MΩ pure water and the precious metal only. Following this, 18MΩ of pure water was used to create a 4M solution of potassium iodide (>99.5% purity, analytical reagent, Alfa Aesar). 4M potassium bromide (>99% purity, laboratory reagent, Sigma-aldrich) and 2M potassium oxalate (>99% purity, Alfa Aesar) were created using this technique. 8.90M Hydrobromic acid (48% by solution in water, Acros Organics) was used and added directly to the metal samples. Iodine solution was added to the 4M potassium iodide solution to increase iodide content

These samples were then left at room temperature under a fume cupboard. The samples were then agitated by hand every 24 hours. After 10 days, 20 days, 30 days and 100 days, samples were taken. In the case of potassium iodide solvent, L-Ascorbic acid (Reagent grade, crystalline, Sigma-Aldrich) was added until the sample changed from red to yellow/colourless. By adding ascorbic acid complexes are all reduced to a 2+ state, hence creating a uniform solution of metal ions. This allows for an accurate reading of metal dissolution. Products created by the addition of ascorbic acid are not visible on the spectroscopy range and hence do not affect the final readings. Samples were filtered by use of filter paper (>20μm, Fisher Brand) and then placed within a UV-Visible spectrometer (Sigma-Aldrich). The measurements were compared to standards creating from iridium (1000μg/l in 10% HCl – Sigma Aldrich) and platinum atomic absorption standards (1000μg/l in 10% HCl – Sigma Aldrich) mixed with the relevant solvent and then diluted to create an array of different absorbance levels.

Testing at 90°C

The solvents were prepared in the same method explained in the room temperature methodology section with 50ml of solvent rather than 25ml being only change with solvents. 0.15g of platinum black was used for experiments based upon platinum dissolution and 0.15g of iridium was used for iridium dissolution experiments. The solvents were placed in a flat-bottomed reactor vessel and heated to 90°C. The vessel was sealed once the temperature of the liquid was 90°C the precious metal was added to the reactor. The solution was agitated by use of vibrational stirring at 1000rpm. The configuration included a condenser to ensure evaporation of the solvent was kept to a minimum. Samples were taken every hour and allowed to cool before filtration. An aliquot of the filtrate was taken and measured in the UV-Visible Spectrometer. The readings from these samples were then compared to the standards previously created.

It should be noted that the same process of adding L-ascorbic acid to the potassium iodide solvent was also conducted for each sample taken.

Bromide and Iodide Testing

Following the results of the 90°C experiments, a variation of pH and bromide or iodide content were created to find the most effective conditions for dissolution of iridium and platinum from the conditions tested. For use with platinum black, the molarity of potassium iodide varied between 2M KI, 3M KI and 4M KI. The concentration for hydroiodic acid was varied between 8.90M, 5.93M and

2.9M. The conditions for dissolution of platinum black are listed in the table 3.1 and the conditions for iridium dissolution are listed in table 3.2. Samples containing iodine also had 1-2ml of iodine solution added to increase iodide content.

Sample Number	Weight of Platinum Black (g)	Quantity of 2M KI (ml)	Quantity of 3M KI (ml)	Quantity of 4M KI (ml)	Quantity of 2.97M HI (ml)	Quantity of 5.93M HI (ml)	Quantity of 8.90M HI (ml)
1	0.15	50	0	0	0	0	0
2	0.15	0	50	0	0	0	0
3	0.15	0	0	50	0	0	0
4	0.15	0	0	0	50	0	0
5	0.15	0	0	0	0	50	0
6	0.15	0	0	0	0	0	50
7	0.15	25	0	0	25	0	0
8	0.15	25	0	0	0	25	0
9	0.15	25	0	0	0	0	25
10	0.15	0	25	0	25	0	0
11	0.15	0	25	0	0	25	0
12	0.15	0	25	0	0	0	25
13	0.15	0	0	25	25	0	0
14	0.15	0	0	25	0	25	0
15	0.15	0	0	25	0	0	25

Table 3.1 – Dissolution conditions for 0.15g of Platinum under differing concentrations of Potassium Iodide and Hydroiodic Acid

Sample Number	Weight of Iridium (g)	Quantity of 2M KBr (ml)	Quantity of 3M KBr (ml)	Quantity of 4M KBr (ml)	Quantity of 2.97M HBr (ml)	Quantity of 5.93M HBr (ml)	Quantity of 8.90M HBr (ml)
1	0.15	50	0	0	0	0	0
2	0.15	0	50	0	0	0	0
3	0.15	0	0	50	0	0	0
4	0.15	0	0	0	50	0	0
5	0.15	0	0	0	0	50	0
6	0.15	0	0	0	0	0	50
7	0.15	25	0	0	25	0	0
8	0.15	25	0	0	0	25	0
9	0.15	25	0	0	0	0	25
10	0.15	0	25	0	25	0	0
11	0.15	0	25	0	0	25	0
12	0.15	0	25	0	0	0	25
13	0.15	0	0	25	25	0	0
14	0.15	0	0	25	0	25	0
15	0.15	0	0	25	0	0	25

Table 3.2 – Dissolution conditions for 0.15g of Iridium under differing concentrations of Potassium Bromide and Hydrobromic Acid

Samples were taken every 30 minutes for 6 hours. Each sample was filtered. An aliquot of the filtrate was taken and placed under UV-Visible Spectroscopy and measured against a standard previously created. As before, samples containing potassium iodide and iodide solution were treated with L-ascorbic acid before the filtration step.

Membrane Leaching

Using the optimum solution composition found by iodide and bromide testing, three differing types of membranes were tested. 125 μ m PFSA PEM platinum black (both anode and cathode), 125 μ m PFSA PEM 50m²/g IrO₂ (anode catalyst) with 40% Pt/C (cathode catalyst) and 125 μ m PFSA PEM 100m²/g IrO₂ (anode catalyst) with 40% Pt/C (cathode catalyst) were used. The membranes were cut into 1cm x 1cm squares and weighed to ensure the same quantity of precious metal was used as in previous experiments. The membranes were placed into a flat-bottomed reactor vessel with 50ml of pre-heated 90°C solvent. Samples were taken every 30 minutes for a six-hour period. These samples were allowed to cool before they were filtered. An aliquot of the filtrate was then taken for analysis by UV-Visible spectroscopy. These results were compared to standards previously created. Samples containing potassium iodide and iodide solution were treated with L-ascorbic acid before the filtration step to ensure there was not an excess of iodide ions in the solution.

Results

Room Temperature Results

The results from UV-visible spectroscopy were analysed against standards of known quantities of iridium and platinum. An estimated quantity of platinum and iridium from the intensity of the peaks can be determined. This can be extrapolated over time to create an estimated dissolution over time. An extinction point of 10 $\mu\text{g/l}$ was chosen when creating the standards. Any results without a numerical value indicate that the reading taken was below this extinction point. A 10 μg extinction point was chosen due to the nature of recovery needed. If dissolution is less than 10 μg , application to a larger scale would become difficult and expensive.

Table 4.1 displays the estimated dissolution of 0.25g platinum over time at room temperature (25°C). This displays the dissolution in the solvents listed; 18.2M Ω ultra-pure water, 2M potassium oxalate, 4M potassium iodide, 4M potassium bromide and 8.90M hydrobromic acid.

Time (days)	Solvent (25ml)				
	Water (estimated dissolution of Pt) (μg)	Potassium Oxalate (estimated Dissolution of Pt) (μg)	Potassium Iodide (estimated Dissolution of Pt) (μg)	Potassium Bromide (estimated Dissolution of Pt) (μg)	Hydrobromic Acid (estimated Dissolution of Pt) (μg)
10	11.028	11.026	218.612	300.33	872.4
20	15.651	13.625	384.729	325.88	1448.1
30	19.325	15.240	402.734	344.57	2384.3
100	29.450	25.130	526.01	369.12	2690.3

Table 4.1 – Estimated Dissolution of 0.25g of Platinum in Different Solvents at 25°C

The results show that hydrobromic acid caused the most dissolution over time when compared to the other solvents. Water and potassium oxalate, whilst dissolving some platinum, were largely ineffective compared to other results. Potassium iodide proved to dissolve at a similar rate to potassium bromide over the first 30 days. After the 30-day period the quantity of dissolution in potassium iodide rose at a faster rate than potassium bromide. The effect of pH upon the dissolution of platinum in bromide can be seen between potassium bromide and hydrobromic acid. An increase in level of pH can be seen to increase the rate of dissolution greatly. A graphical display of these results are shown in figure 4.1.

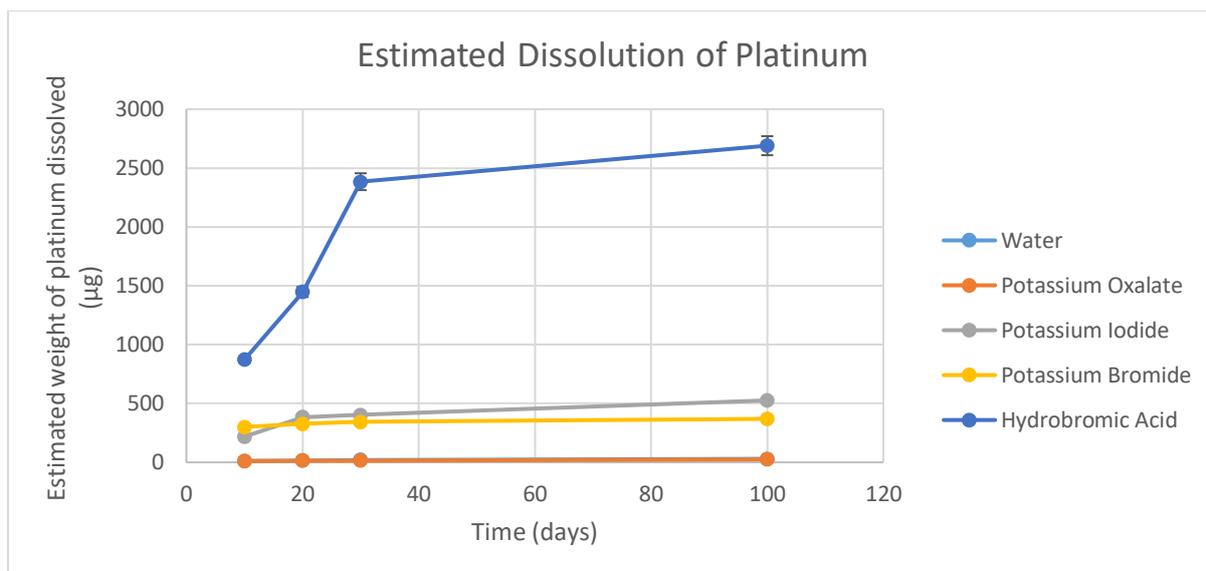


Figure 4.1 – Estimated Dissolution of 0.25g of Platinum in Different Solvents at 25°C

From figure 4.1 a dissolution limit can be seen to be approached by many of the solvents. Over the 100-day period, the rate of dissolution begins to slow after 30 days until it begins to become level. This indicates a saturation limit.

Results for iridium were found by using the same method. The results of the dissolution of 0.25g of iridium over 100 days in different solvents is shown in table 4.2. The solvents displayed in the table are the same solvents seen in table 4.1; 18.2MΩ ultra-pure water, 2M potassium oxalate, 4M potassium iodide, 4M potassium bromide and 8.90M hydrobromic acid. From table 4.2, the most effective solvent for iridium dissolution is 8.90M hydrobromic acid. After 100 days, the sample reaches a maximum estimated dissolution that is approximately twice as high as the nearest alternative. Potassium oxalate does not have any numerical values in the table as readings from all samples taken fell below the extinction point of 10µg.

Time (days)	Solvent (25ml)				
	Water (estimated Dissolution of Ir) (µg)	Potassium Oxalate (estimated Dissolution of Ir) (µg)	Potassium Iodide (estimated Dissolution of Ir) (µg)	Potassium Bromide (estimated Dissolution of Ir) (µg)	Hydrobromic Acid (estimated Dissolution of Ir) (µg)
10	18.863	-	834.73	250.64	982.84
20	25.876	-	1137.73	293.76	1498.3
30	31.127	-	1587.3	387.34	2454.12
100	56.931	-	2240.9	581.55	4001.4

Table 4.2 – Estimated Dissolution of 0.25g of Iridium in Different Solvents at 25°C

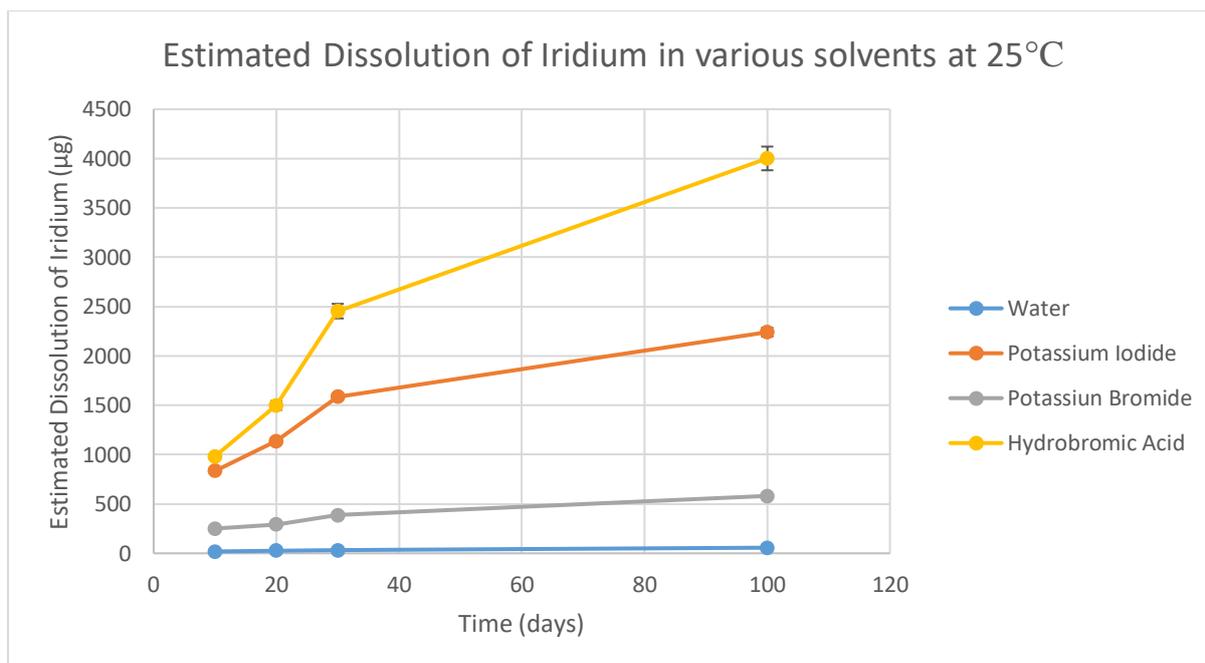


Figure 4.2 – Estimated Dissolution of 0.25g of Iridium in Different Solvents at 25°C

Figure 4.2 displays similar trends to figure 4.1. After initial increases in dissolution over the first 30-day period, the total rate of dissolution found in each sample decreases. This could be down to the solubility limit of the solvent being reached.

When comparing the results of iridium to platinum there are several trends. Both precious metals have the highest dissolution in hydrobromic acid, potassium iodide and then potassium bromide. This firstly indicates that pH could have a positive effect upon increasing the amount of dissolution. Other indications suggest that using different halides could increase overall dissolution. Whilst both metals showed similar dissolution trends with these solvents, iridium dissolved markedly better than platinum in all cases. The only area that platinum dissolution was better was in the case of potassium oxalate.

Experiment Findings at 90°C

The results from UV-visible spectroscopy were analysed against standards of known quantities of iridium and platinum. An estimated quantity of platinum and iridium from the intensity of the peaks can be determined. An extinction point of 5µg was chosen, below which readings were not taken. This was due to the high dissolution needed when applying the solvent to a membrane.

Table 4.2 displays the estimated dissolution of 0.15g of platinum in the solvents tested at 90°C. The solvents tested were 18.2MΩ ultra-pure water, 2M potassium oxalate, 4M potassium iodide, 4M potassium bromide and 8.90M hydrobromic acid. There are no recorded dissolution weights for water. This is due to all samples falling below the extinction point. Similar to the room temperature results, the highest amount of dissolution occurred in hydrobromic acid. Potassium iodide was also effective at dissolving platinum. Potassium bromide was not as effective as initial room temperature results suggested – indicating that temperature has an adverse effect in this case.

Time (hours)	Solvent (25ml)				
	Water (estimated Dissolution of Pt) (µg)	Potassium Oxalate (estimated dissolution of Pt) (µg)	Potassium Iodide (estimated dissolution of Pt) (µg)	Potassium Bromide (estimated dissolution of Pt) (µg)	Hydrobromic Acid (estimated dissolution of Pt) (µg)
1	-	5.221	545.06	91.448	1767.76
2	-	6.987	428.87	77.781	1314.22
3	-	5.878	360.77	-	1771.49
4	-	5.211	389.86	-	3049.54
5	-	5.515	569.60	-	3128.34
6	-	5.318	789.49	-	3216.84

Table 4.3 – Estimated Dissolution of 0.15g of Platinum in Different Solvents at 90°C

Figure 4.3 displays the dissolution of each sample over time. There is a large difference in overall dissolution of platinum in hydrobromic acid than the other solvents. For all solvents, a similar pattern is apparent – the total dissolution is fast to begin with and then slows as time goes on. This is clear by the decreasing gradient of the curves over time. This could be due to the saturation point of solvent.

When compared to the room temperature results, potassium oxalate is much less effective at 90°C. This could be due to decomposition of the platinum-oxalate complexes at higher temperatures – thus preventing effective dissolution of platinum. Potassium bromide also dissolves higher quantities of platinum at room temperature over the selected time than at 90°C. At 90°C it does not appear that a larger amount of dissolution would occur as potassium bromide is already reaching the solubility limit after six-hours. Potassium iodide and hydrobromic acid dissolve larger quantities of platinum at 90°C. This can in future work due to the shorter period of time over which a larger dissolution occurs.

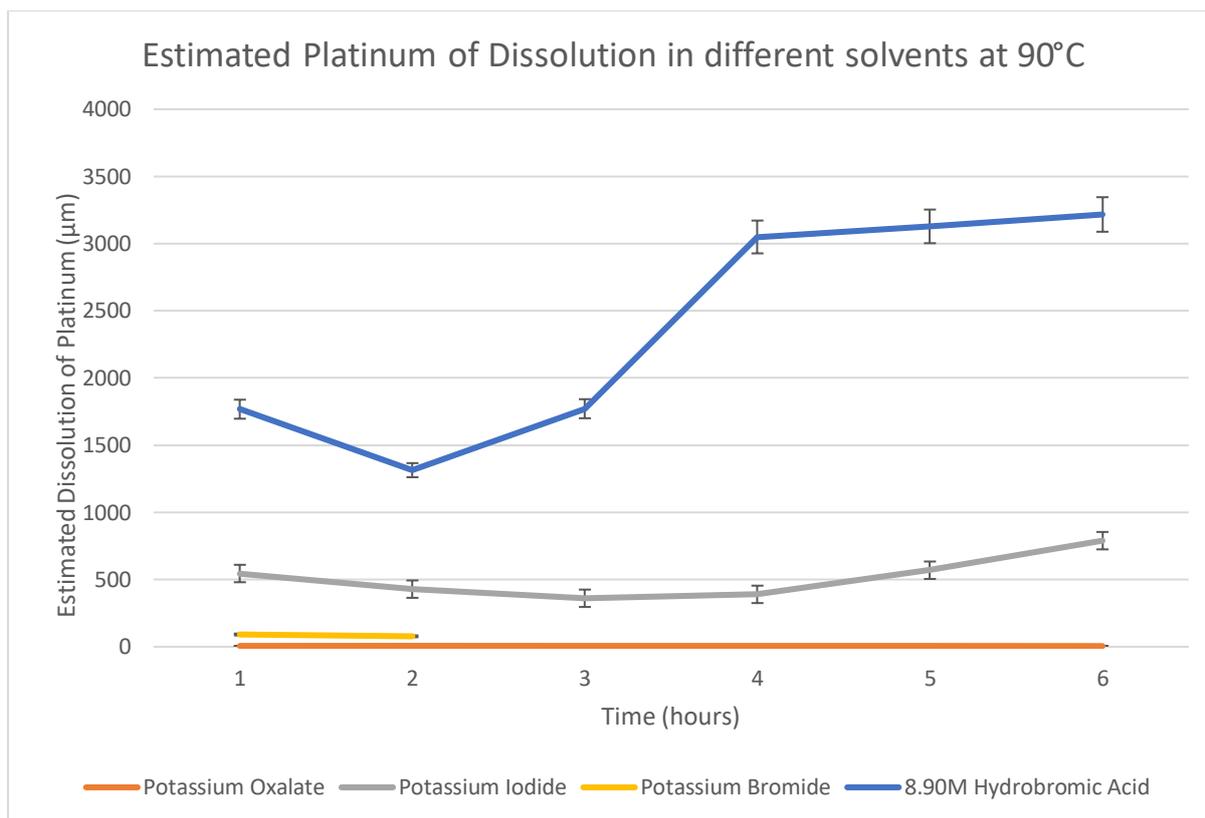


Figure 4.3 – Estimated Dissolution of 0.15g of Platinum in Different Solvents at 90°C

The results in table 4.4 for the dissolution of 0.15g of iridium were found in the same way. The same solvents listed previously were used. As with platinum, all of the samples tested with water as a leaching agent fell below the extinction point and thus there are no numerical readings are listed in the table. Potassium iodide was the best solvent for dissolution in this case. Hydrobromic acid performed better than potassium bromide – showing that at increased temperatures, increased pH still improves the rate of dissolution. Potassium oxalate was significantly better at dissolving iridium than platinum. The gradual decline of the iridium found suggests that the iridium oxalate complexes decompose at 90°C over time.

Time (hours)	Solvent (25ml)				
	Water (estimated dissolution of Ir) (µg)	Potassium Oxalate (estimated dissolution of Ir) (µg)	Potassium Iodide (estimated dissolution of Ir) (µg)	Potassium Bromide (estimated dissolution of Ir) (µg)	Hydrobromic Acid (estimated dissolution of Ir) (µg)
1	-	69.419	2220.9	182.22	1014.0
2	-	83.717	7303.7	237.64	1387.7
3	-	49.079	7370.0	358.14	643.88
4	-	43.676	12113.7	256.87	961.79
5	--	56.488	15924.1	526.84	1206.0
6	-	34.81	28864.9	729.64	1412.5

Table 4.4 – Estimated Dissolution of 0.15g of Iridium in Different Solvents at 90°C

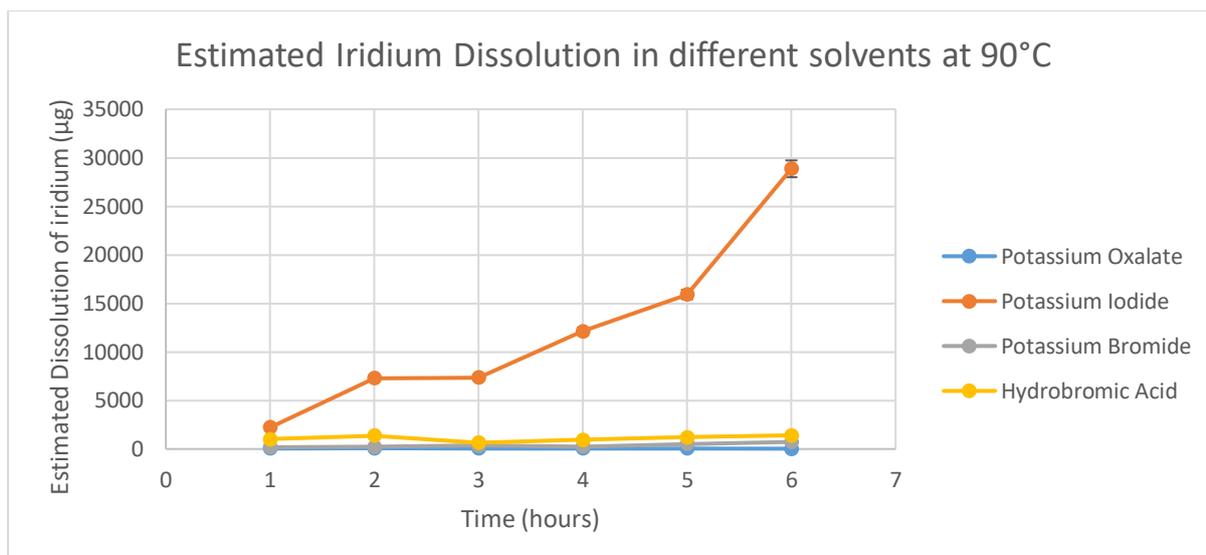


Figure 4.4 – Estimated Dissolution of 0.15g of Iridium in Different Solvents at 90°C

The results displayed in table 4.4 are plotted graphically in figure 4.4. Potassium oxalate, potassium bromide and hydrobromic acid display similar behaviours. Over the recorded period an initial rate of dissolution increases, after which the rate slows and becomes level. This indicates the saturation point of each solvent has been reached. Potassium iodide continues to rise over the six-hour period. This indicates that over a longer period, an increased level of dissolution of iridium could be reached. Whilst potassium iodide was more successful at dissolving iridium it should be noted that the dissolution found in hydrobromic acid was also sizable and hence should be explored further.

In the case of iridium dissolution, initial room temperature results were not as effective as indicating results at 90°C. Water dissolved more iridium than at 90°C whilst potassium oxalate was a better solvent at the higher temperature. Similar to platinum, iridium dissolution was worse at 90°C than at room temperature whilst potassium iodide showed a large improvement in its ability to dissolve precious metal. Hydrobromic acid was not as effective as the results from room temperature displayed. This could be due to the much larger dissolution recording time at room temperature.

Whilst some of the dissolution rates for both platinum and iridium were below that of the room temperature samples, the decision to continue to work at 90°C was taken due to the unfeasibility of waiting up to 100 days for samples to partially dissolve. Further measures can be taken such as recycling the flow of the solvent or adding larger quantities of solvent to increase the overall dissolution of the precious metal. This is more feasible when scaling up to an industrial setting rather than allowing dissolution to occur over a much larger period of time for similar yields. -

Bromide and Iodide Tuning Results

Analysis of the results at 90°C indicated that potassium bromide was largely ineffective as dissolving platinum. Iridium dissolution by potassium bromide was possible and hence would allow for the separation of iridium from a membrane containing both platinum and iridium. Given this, a matrix was designed to test the dissolution of platinum at different operating conditions varying the molarity of potassium iodide used and the overall pH of the solution by varying the concentration of hydrobromic acid used. The testing conditions can be seen in table 4.5

Sample Number	Weight of Iridium (g)	Quantity of 2M KBr (ml)	Quantity of 3M KBr (ml)	Quantity of 4M KBr (ml)	Quantity of 2.97M HBr (ml)	Quantity of 5.93M HBr (ml)	Quantity of 8.9M HBr (ml)
1	0.15	50	0	0	0	0	0
2	0.15	0	50	0	0	0	0
3	0.15	0	0	50	0	0	0
4	0.15	0	0	0	50	0	0
5	0.15	0	0	0	0	50	0
6	0.15	0	0	0	0	0	50
7	0.15	25	0	0	25	0	0
8	0.15	25	0	0	0	25	0
9	0.15	25	0	0	0	0	25
10	0.15	0	25	0	25	0	0
11	0.15	0	25	0	0	25	0
12	0.15	0	25	0	0	0	25
13	0.15	0	0	25	25	0	0
14	0.15	0	0	25	0	25	0
15	0.15	0	0	25	0	0	25

Table 4.5 – Dissolution conditions for 0.15g of Iridium under differing concentrations of Potassium Bromide and Hydrobromic Acid

The results of altering the concentration of potassium bromide alone are displayed in table 4.6. The results show that over time for both 3M potassium bromide and 4M potassium bromide the concentration of iridium in the solutions increase. This is not the same in 2M potassium iodide. In this case, the quantity of iridium found in each sample taken is similar, between 90µg and 100 µg, for the first four hours. After this time, the quantity of iridium found decreases sustainably. This could be due to local variation in the samples taken. It should be assumed that saturation point for iridium dissolution in 2M KBr is approximately 100 µg/l due to the results found over the first four samples. The results displayed in table 4.6 are displayed graphically in figure 4.5.

Time	Estimated Dissolution of Platinum (µg)		
	2M KBr	3M KBr	4M KBr
1	94.549	44.019	182.22
2	97.036	157.68	237.64
3	92.885	229.34	358.14
4	91.499	274.73	256.87
5	43.032	593.55	526.84
6	30.384	502.35	729.64

Table 4.6 – Estimated Dissolution of 0.15g of Iridium in Different Concentrations of Potassium Bromide at 90°C

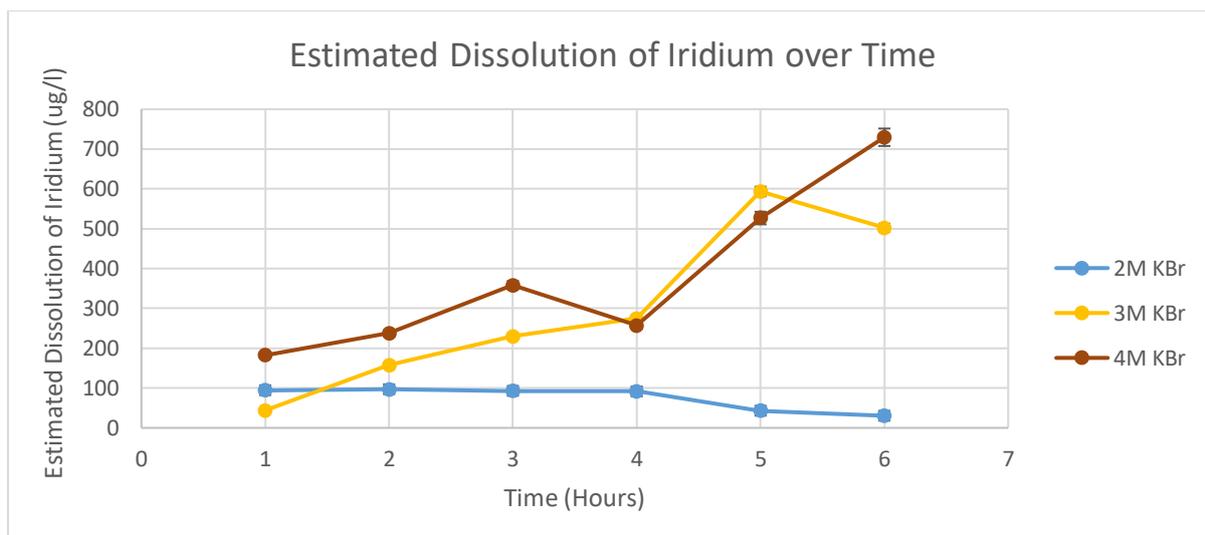


Figure 4.5 – Estimated Dissolution of 0.15g of Iridium in Different Concentrations of Potassium Bromide at 90°C

From figure 4.5, it is clear to see the saturation limit of 2M potassium bromide has been reached. Variations in results between 3M and 4M potassium iodide are displayed on the graph. 4M potassium bromide starts with a faster rate of dissolution but appears to slow after three-hours. 3M potassium bromide consistently rises in the quantity of iridium dissolves for the first five hours but then slows thereafter. After six hours, 4M potassium bromide has dissolved a larger quantity of iridium than 3M potassium bromide. The variations between 3 and 5 hours could be considered to be sample variation given the other data suggests that 4M potassium bromide dissolves iridium with greater ease than its 3M counterpart.

Conditions varying the pH were then tested. This was achieved by diluting hydrobromic acid to form three different concentrations – 2.97M, 5.93M and 8.90M. The results of these tests are in table 4.7. After 1 hour, solvents containing 2.97M and 5.93M hydrobromic acid appeared to reach the solubility limit. Between 1 hour and 6 hours, the estimated weight of iridium in solution did not change substantially. The dissolution of iridium appears to be twice as successful in 5.93M hydrobromic acid than in 2.97M hydrobromic acid hence indicating a linear relationship between the two. The results at 8.90M hydrobromic acid by solution varied over the recorded period. There was a substantial decrease in iridium found after 3 hours but the overall dissolution of platinum increased substantially over the next 3 hours.

Time (hours)	Estimated Dissolution of Platinum (µg)		
	2.97M HBr	5.93M HBr	8.90M HBr
1	648.09	1438.8	1014.0
2	671.92	1395.18	1387.7
3	710.63	1443.01	643.88
4	709.67	1361.82	961.79
5	398.99	1455.81	1206.2
6	685.25	1321.21	1438.8

Table 4.7 – Estimated Dissolution of 0.15g of Iridium in Different Concentrations of Hydrobromic Acid at 90°C

Figure 4.6 plots the data from table 4.7 graphically. As previously stated, the saturation point of all solvents is reached after 1-2 hours. Figure 4.6 also displays the negligible effect of increasing acidity

in the solvent after 5.93M hydrobromic acid by solution. This indicates that pH does have an effect on the total dissolution of iridium but there is a limit.

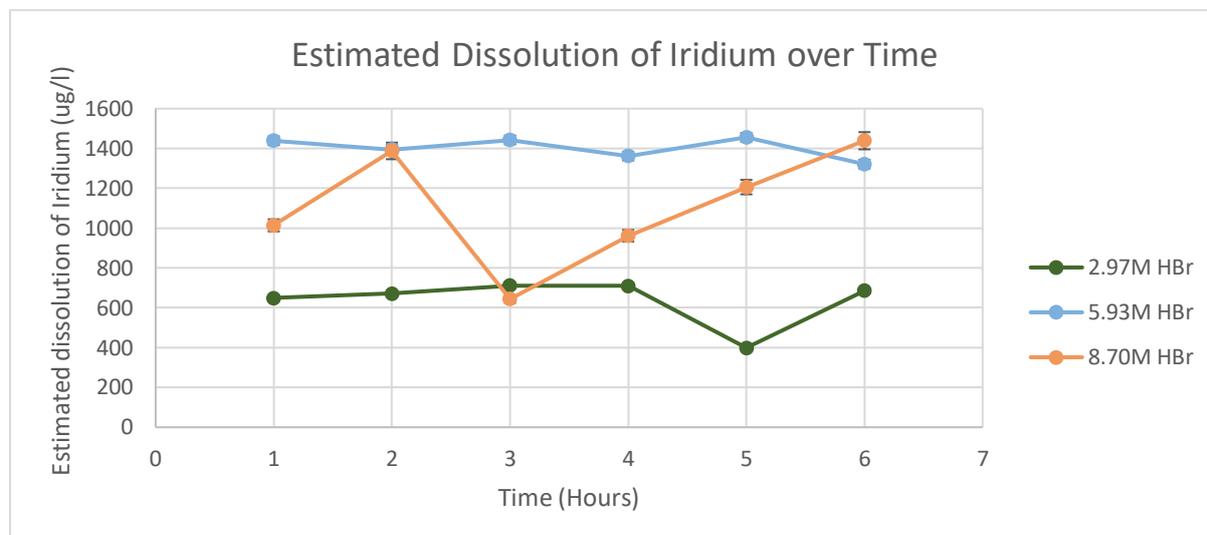


Figure 4.6 – Estimated Dissolution of 0.15g of Iridium in Different Concentrations of Hydrobromic Acid at 90°C

Tests with mixtures of differing concentrations of potassium bromide and hydrobromic acid were completed. Results of solutions with added concentrations of hydrobromic acid were compared to results of potassium bromide alone. Table 4.8 displays the effects of adding differing concentrations of hydrobromic acid to 2M potassium bromide.

Time	2M KBr	2M KBr + 2.97M HBr	2M KBr + 5.93M HBr	2M KBr + 9.80M HBr
1	94.549	520.75	783.44	2099.608
2	97.036	793.79	896.25	2349.5
3	92.885	997.78	983.25	2151.8
4	91.499	486.53	1112.6	2027.11
5	43.032	981.86	852.64	2344.74
6	30.384	143.96	1305.8	2074.73

Table 4.8 – Estimated Dissolution of 0.15g of Iridium in 2M Potassium Bromide with different Concentrations of Hydrobromic Acid at 90°C

The results of table 4.8 are displayed in figure 4.7. The data shows as the concentration of hydrobromic acid increases, the overall dissolution increases. Unlike the results displayed in table 4.7, as the concentration of hydrobromic acid increases over 5.93M, the estimated weight of iridium continues to increase. The results still show a tendency of the solvents to reach their saturation limit after 1-2 hours. 2M potassium bromide with concentrations of 2.97M and 5.93M of hydrobromic acid act in a similar fashion. After initial dissolution both solvents fluctuate up and down in iridium absorbance but do so with an overall upward trend.

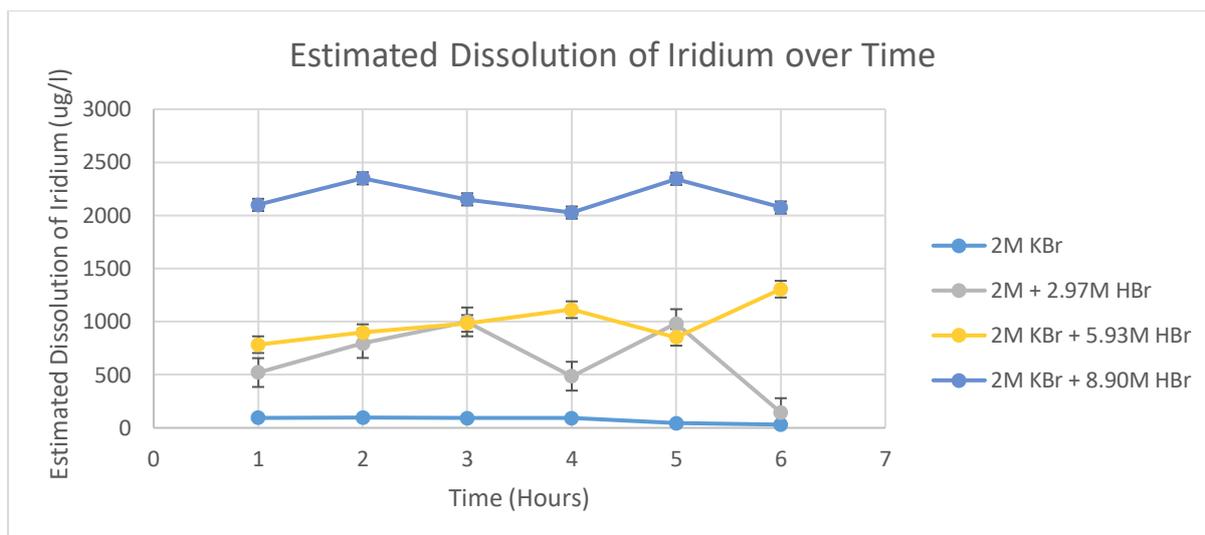


Figure 4.7 – Estimated Dissolution of 0.15g of Iridium in 2M Potassium Bromide with different Concentrations of Hydrobromic Acid at 90°C

Results of 0.15g of iridium with 3M potassium bromide with 2.97M, 5.93M and 8.9M hydrobromic acid testing are presented in table 4.9. The results are similar to those found in table 4.8 but have lower values – indicating that the use of 3M potassium bromide may not be as effective as 2M potassium bromide.

Time	Estimated Dissolution of Platinum (µg)			
	3M KBr	3M KBr + 2.97M HBr	3M KBr + 5.93M HBr	3M KBr + 8.90M HBr
1	44.019	770.79	823.39	845.26
2	157.68	942.39	782.32	925.78
3	229.34	620.76	1047.43	1094.3
4	274.73	667.57	786.15	1317.9
5	593.55	492.89	758.26	843.74
6	502.35	642.41	636.46	1261.89

Table 4.9 – Estimated Dissolution of 0.15g of Iridium in 3M Potassium Bromide with different Concentrations of Hydrobromic Acid at 90°C

The results of table 4.9 are plotted in figure 4.8. Addition of any molarity of hydrobromic acid appears to create a much higher initial dissolution rate. After this time, 2.97 and 5.93M hydrobromic acid appear to fluctuate in overall dissolution of iridium with a downward trend becoming apparent. By the end of the six-hour period, estimated dissolution of 3M potassium bromide is near that of potassium bromide with 2.97M and 5.93M additions. The 8.9M hydrobromic acid sample tends to increase in iridium dissolution over time. By the end of the recorded period, the estimated dissolution of iridium is nearly twice that of potassium bromide with 5.97M hydrobromic acid. This shows that with 3M potassium bromide, increasing pH causes an increased amount of overall dissolution.

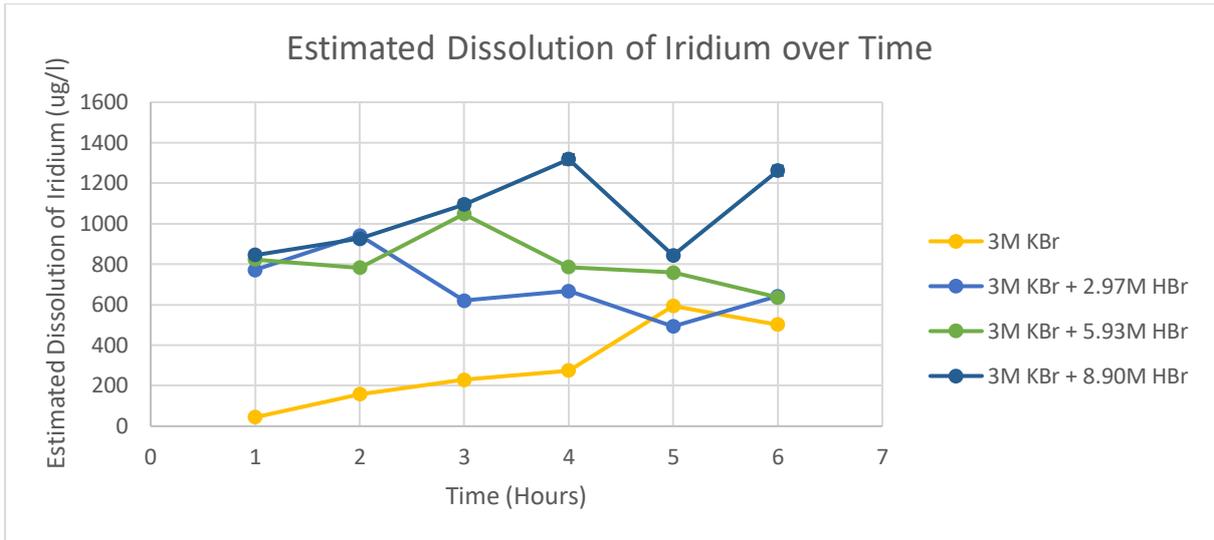


Figure 4.8 – Estimated Dissolution of 0.15g of Iridium in 3M Potassium Bromide with different Concentrations of Hydrobromic Acid at 90°C

Table 4.10 displays the results of adding different concentrations of hydrobromic acid to 4M potassium bromide over time. When compared to the previous results displayed with 2M and 3M potassium bromide the dissolution of iridium is higher.

Time	Estimated Dissolution of Platinum (µg)			
	4M	4M + 2.97M HBr	4M + 5.93M HBr	4M + 8.90M HBr
1	182.22	724.61	998.84	0
2	237.64	737.43	831.43	304.74
3	358.14	431.67	1038.0	683.93
4	256.87	509.24	1104.6	1396.8
5	526.84	271.18	1127.77	2801.1
6	729.64	566.52	804.07	2809.5

Table 4.10 – Estimated Dissolution of 0.15g of Iridium in 4M Potassium Bromide with different Concentrations of Hydrobromic Acid at 90°C

Figure 4.9 is a graphical display of the results shown in table 4.10. The results indicate that the addition of hydrobromic acid increases the amount of dissolution that occurs – as with the 2M and 3M potassium bromide results. The quantity of iridium dissolved in the samples is higher than the previous data sets. From figure 4.9 it is apparent that 4M potassium bromide only, as well as with the additions of 2.97M and 5.97M hydrobromic acid, that the limit of dissolution was reached after 1-2 hours. The sample containing 8.9M hydrobromic acid did not reach a solubility limit until 5 hours, indicating a slower yet more successful dissolution of iridium.

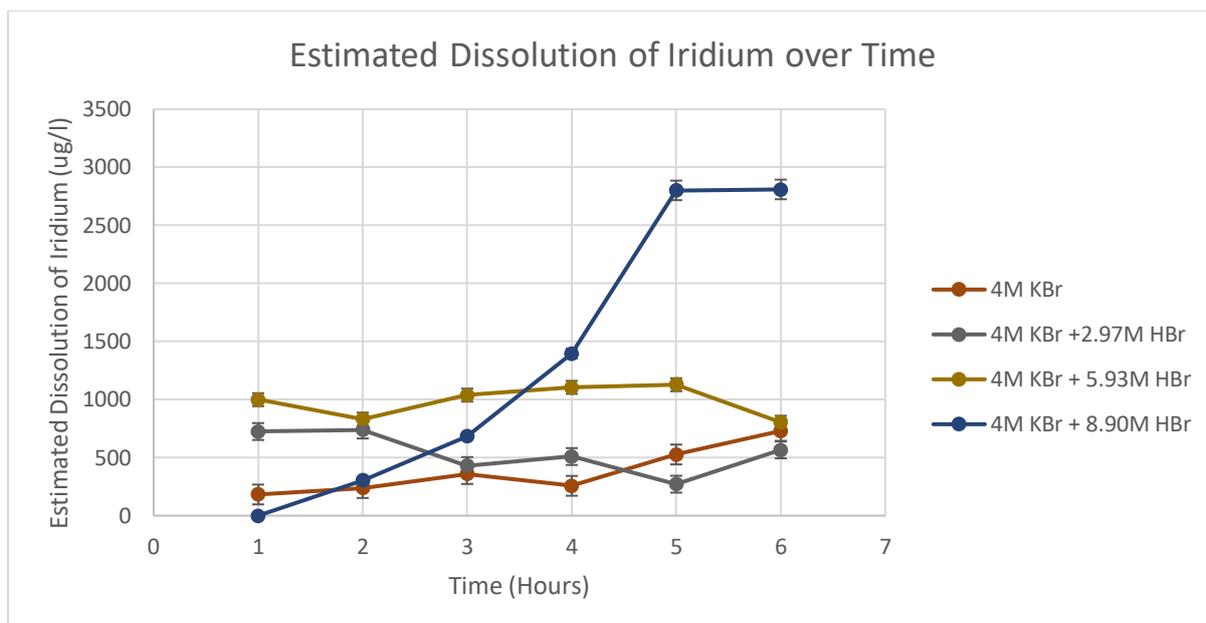


Figure 4.9 – Estimated Dissolution of 0.15g of Iridium in 4M Potassium Bromide with different Concentrations of Hydrobromic Acid at 90°C

An alternative method to leaching platinum without the use of hydrobromic acid was tested. An alternative was needed after the successful leaching of iridium from 4M potassium bromide and 8.9M hydrobromic acid. By finding an alternative leaching solution for platinum, selective dissolution of precious metals from fuel cell membranes may be possible.

Variation of pH upon platinum leaching was tested by use of potassium iodide and hydroiodic acid. By varying the molarity of the hydroiodic acid at differing potassium iodide concentrations a matrix of results can be created to find the optimal conditions for platinum dissolution under these conditions. The variation in solvents can be seen in table 4.11.

Sample Number	Weight of Platinum (g)	Quantity of 2M KI (ml)	Quantity of 3M KI (ml)	Quantity of 4M KI (ml)	Quantity of 2.97M HI (ml)	Quantity of 5.93M HI (ml)	Quantity of 8.9M HI (ml)
1	0.15	50	0	0	0	0	0
2	0.15	0	50	0	0	0	0
3	0.15	0	0	50	0	0	0
4	0.15	0	0	0	50	0	0
5	0.15	0	0	0	0	50	0
6	0.15	0	0	0	0	0	50
7	0.15	25	0	0	25	0	0
8	0.15	25	0	0	0	25	0
9	0.15	25	0	0	0	0	25
10	0.15	0	25	0	25	0	0
11	0.15	0	25	0	0	25	0
12	0.15	0	25	0	0	0	25
13	0.15	0	0	25	25	0	0
14	0.15	0	0	25	0	25	0
15	0.15	0	0	25	0	0	25

Table 4.11 – Dissolution conditions for 0.15g of Platinum under differing concentrations of Potassium Iodide and Hydroiodic Acid

The results for 0.15g of platinum black in differing concentrations of potassium iodide is seen in table 4.12. The cells marked with a dash indicate the sample taken fell below the 5 μ g extinction point and were not recorded. The empty cells relating to 4M potassium iodide samples were due to frequency of samples taken previously. 2M and 3M potassium iodide samples were taken every 30 minutes whereas previous samples were taken every hour. Samples were taken every 30 minutes to better examine the behaviour of each solvent in relation to the rate of dissolution.

Time	Estimated Dissolution of Platinum (μ g)		
	2M KI	3M KI	4M KI
0.5	-	-	
1	-	30.653	314.704
1.5	41.566	59.485	
2	57.280	87.026	202.30
2.5	43.946	111.69	
3	88.343	150.08	134.20
3.5	122.37	175.30	
4	142.38	225.34	163.29
4.5	128.87	257.27	--
5	113.09	262.57	297.72
5.5	112.47	285.95	-
6	146.78	337.78	386.37

Table 4.12 – Estimated Dissolution of 0.15g of Platinum in Different Concentrations of Potassium Iodide at 90°C

The results in table 4.12 are displayed in figure 4.10. By increasing the concentration of potassium iodide, the overall quantity of dissolution of platinum increases. Both 2M and 3M potassium iodide increase in the quantity of dissolution over time at a near uniform rate. This suggests that the

solubility limit of the solvents are yet to be reached. Similarly, the quantity of dissolution over time increases after 3 hours substantially. The drop in platinum available in the solvent between 1 in 3 hours could be attributed to localised variations. Whilst a further increase in potassium iodide could further increase the quantity of dissolution, it has be found by Patel and Dawson (2015) that the increase is only incremental after this point and hence could become a resource strain.

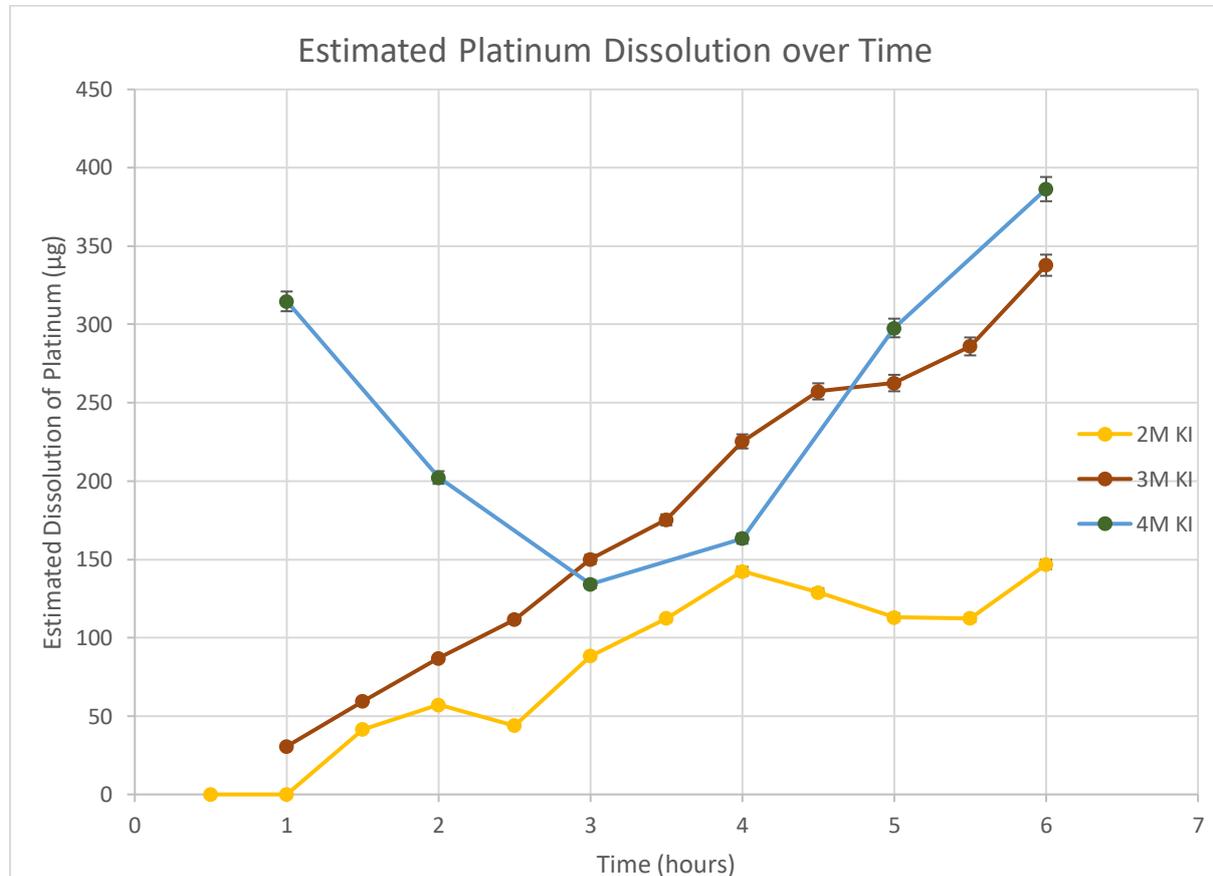


Figure 4.10 – Estimated Dissolution of 0.15g of Platinum in Different Concentrations of Potassium Iodide at 90°C

The effect of increasing pH upon the leaching of platinum was then tested. By use of 2.97M, 5.93M and 8.9M hydroiodic acid, 0.15g of platinum was heated to 90°C. The samples were taken every 30 minutes with the results displayed in table 4.13.

Time	Estimated Dissolution of Platinum (μg)		
	2.97M HI	5.93M HI	8.90M HI
0.5	70.265	84.081	83.303
1	83.654	97.881	61.191
1.5	71.258	95.018	44.480
2	59.632	90.447	41.699
2.5	32.898	56.109	27.408
3	40.854	47.251	71.434
3.5	55.47	42.150	40.533
4	74.325	153.96	93.128
4.5	62.485	17.118	99.695
5	80.265	11.417	113.54
5.5	91.265	18.731	104.76
6	55.348	17.696	118.29

Table 4.13 – Estimated Dissolution of 0.15g of Platinum in Different Concentrations of Hydroiodic Acid at 90°C

The results from table 4.13 are plotted in figure 4.11. The results do not display a clear trend. Most results fluctuate between 40 μg and 100 μg of estimate dissolution over the six-hour period. After 4.5 hours, the samples containing 5.93M Hydroiodic acid can be seen to fall to 20 μg of absorbance and stay at that level. This is in contrast to 2.97M and 8.9M samples that show a general trend upwards. From this information it is not apparent the effect that changing pH will have upon the dissolution of platinum.

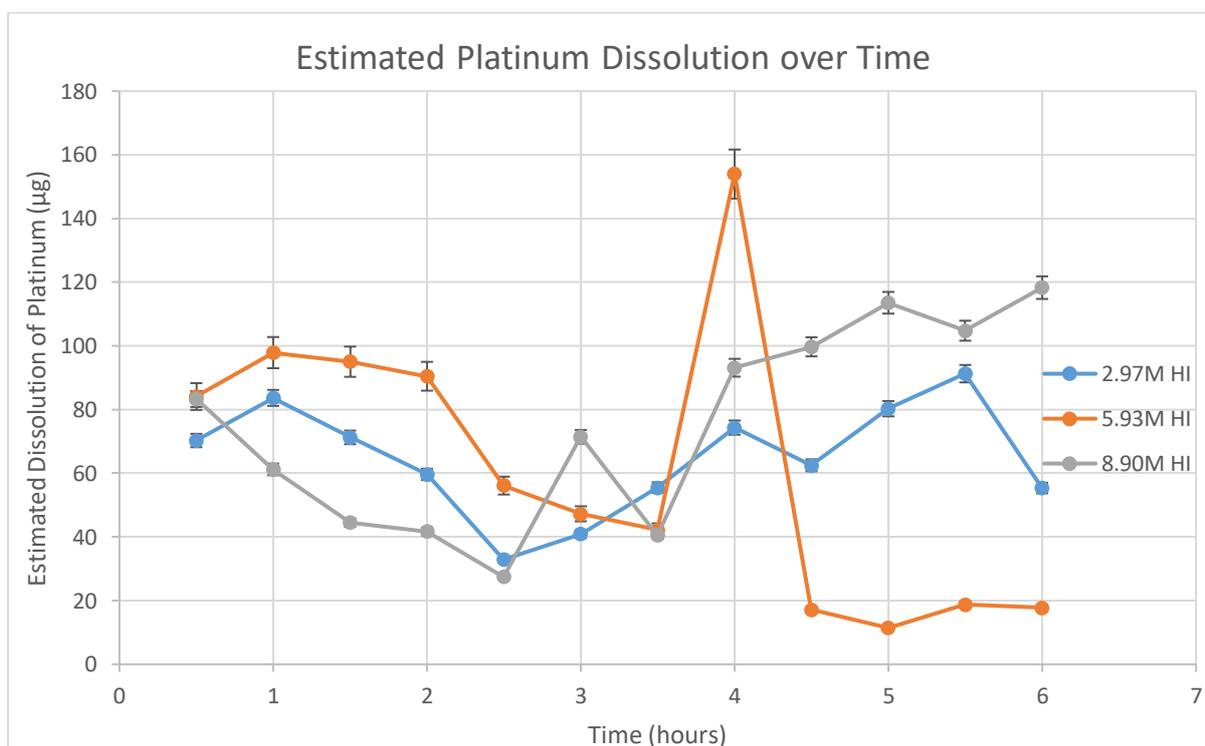


Figure 4.11 – Estimated Dissolution of 0.15g of Platinum in Different Concentrations of Hydroiodic Acid at 90°C

Solutions containing known concentrations of both hydroiodic acid and potassium iodide were created and added to 0.15g of platinum and heated to 90°C. Table 4.14 displays the results of samples taken with 2M potassium iodide and varied concentrations of hydroiodic acid.

Time	Estimated Dissolution of Platinum (µg)			
	2M KI	2M KI + 2.97M HI	2M KI + 5.93M HI	2M + 8.90M HI
0.5	-	-	-	-
1	-	13.163	18.377	36.254
1.5	41.566	-	12.700	27.555
2	57.280	6.329	14.867	24.666
2.5	43.946	8.011	13.793	23.477
3	88.343	-	10.127	23.795
3.5	122.37	13.479	16.148	27.978
4	142.38	6.629	18.802	29.667
4.5	128.87	10.121	22.314	30.255
5	113.09	9.283	17.851	28.272
5.5	112.47	-	21.512	33.394
6	146.78	-	43.671	43.671

Table 4.14 – Estimated Dissolution of 0.15g of Platinum in 2M Potassium Iodide with different Concentrations of Hydroiodic Acid at 90°C

The results from the samples taken show that 2M potassium iodide is more effective at leaching platinum than any iteration containing hydroiodic acid. Samples taken from the leaching solution containing 2.93M Hydroiodic acid regularly fell below the 5µg extinction point – further displaying the poor leaching qualities of such a solution. The overall dissolution of platinum from the leaching solutions containing hydroiodic acid remains near constant, as displayed in figure 4.12 – thus indicating the solubility limit has been reached. These solutions do show a trend, indicating a lower pH causes increased dissolution of platinum when used in conjunction with 2M potassium iodide – this is marginal however.

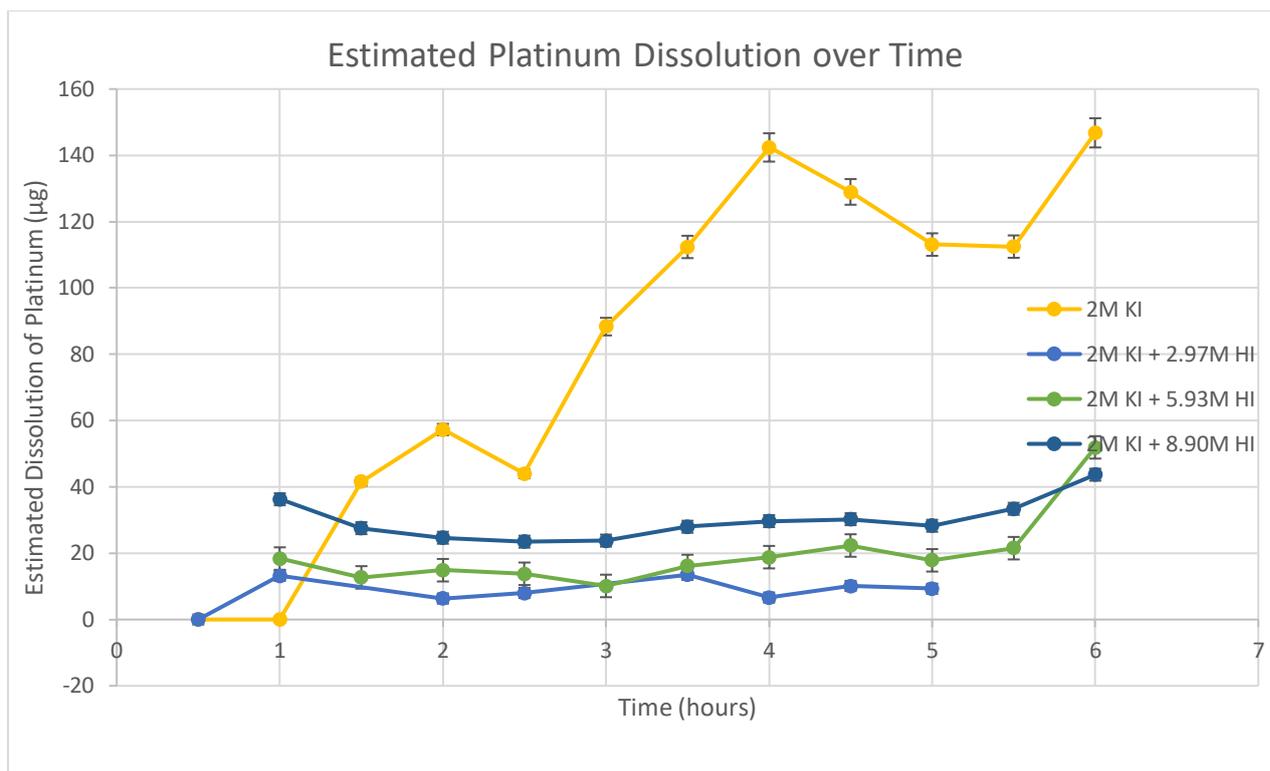


Figure 4.12 – Estimated Dissolution of 0.15g of Platinum in 2M Potassium Iodide with different Concentrations of Hydroiodic Acid at 90°C

The concentration of potassium iodide was then increased to 3M. The procedure of creating solutions with varying in hydroiodic acid content remained the same. The results of these experiments are recorded in table 4.15.

Time	Estimated Dissolution of Platinum (µg)			
	3M KI	3M KI + 2.97M HI	3M KI + 5.93M HI	3M KI + 8.90M HI
0.5	-	62.925		13.28055
1	30.653	32.241	-	10.020
1.5	59.485	10.850	19.369	8.419
2	87.026	11.174	10.826	9.538
2.5	111.69	11.192	12.707	8.559
3	150.08	6.133	10.852	5.753
3.5	175.30	11.753	11.528	6.632
4	225.34	11.442	9.648	5.872
4.5	257.27	10.019	17.456	7.684
5	262.58	14.255	16.613	7.624
5.5	285.95	16.819	14.651	7.580
6	337.78	23.221	20.016	7.550

Table 4.15 – Estimated Dissolution of 0.15g of Platinum in 3M Potassium Iodide with different Concentrations of Hydroiodic Acid at 90°C

Analysis of the results indicates that the addition of hydroiodic acid is hindering the dissolution of platinum rather than assisting it. 3M potassium iodide is at least 10 times more effective at dissolving platinum at any given point than any of the variations containing hydroiodic acid. At higher acidities it appears that the amount of dissolution falls. This can be seen figure 4.13. 2.97M and 5.93M hydroiodic acid containing leach solutions have very similar readings but the average

dissolution of 2.97M solution is higher. The leach solution containing 8.90M hydroiodic acid has the lowest dissolution quantity of all of the solutions listed in table 4.15. All of the solutions in figure 4.13 appear to have reached the limit of platinum leaching.

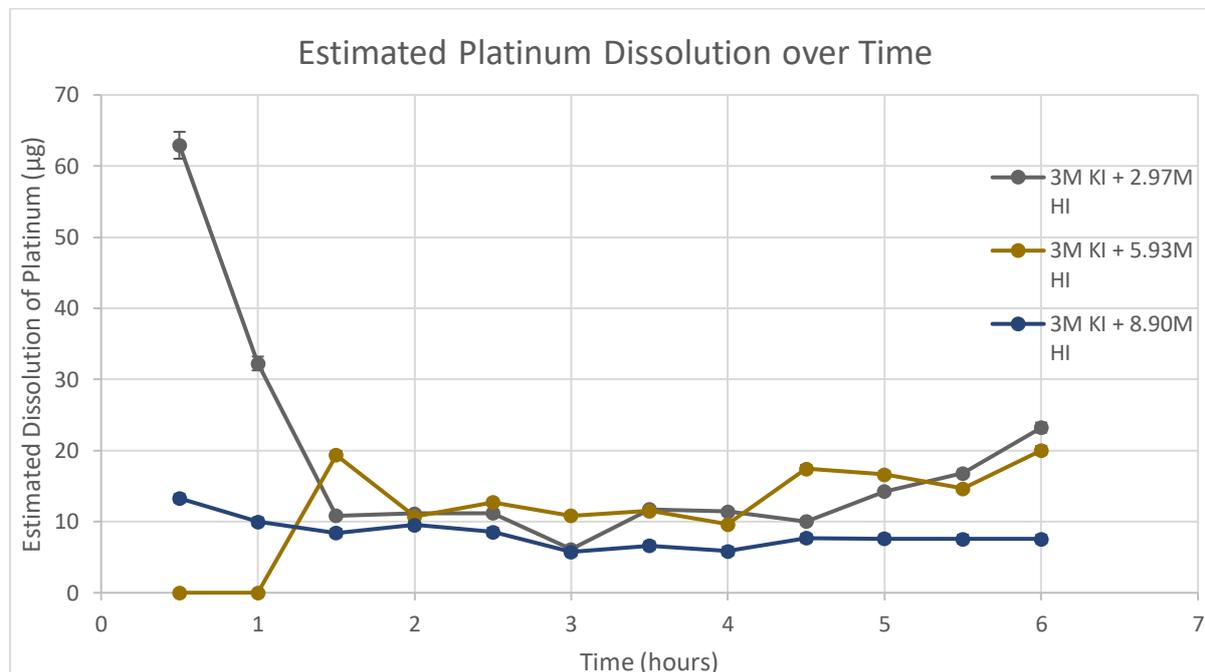


Figure 4.13 – Estimated Dissolution of 0.15g of Platinum in 3M Potassium Iodide with different concentrations of Hydroiodic Acid at 90°C

The effect of adding hydroiodic acid to 4M potassium iodide was tested. The results are displayed in table 4.16. As before, blank cells indicate no measurement was taken at that time and dashed inputs indicate the sample fell below the 5µg extinction point.

Time	Estimated Dissolution of Platinum (µg)			
	4M KI	4M KI + 2.97M HI	4M KI + 5.93M HI	4M + 8.90M HI
0.5		-	-	-
1	314.704	-	8.767	9.310
1.5		5.387	6.167	7.187
2	202.30	9.952	10.354	6.222
2.5		9.129	7.037	8.337
3	134.20	8.969	9.928	8.456
3.5		12.971	9.765	6.688
4	163.29	12.906	9.524	-
4.5		9.149	10.112	7.930
5	297.72	9.725	6.253	8.543
5.5		14.645	4.020	9.526
6	386.37	15.101	5.578	11.736

Table 4.16 – Estimated Dissolution of 0.15g of Platinum in 4M Potassium Iodide with different Concentrations of Hydroiodic Acid at 90°C

Potassium iodide alone was a better leach solution than any variation containing hydroiodic acid. The decrease in pH, in case of 4M potassium iodide, proved to be a hindrance. Figure 4.14 displays the results of the addition of different concentrations of hydroiodic acid to a 4M potassium iodide solution in the presence of 0.15g of platinum. Even at such low levels of dissolution, it appears that

increased concentrations of hydroiodic acid cause the amount of platinum leaching to fall. This mirrors the results that were presented in table 4.15.

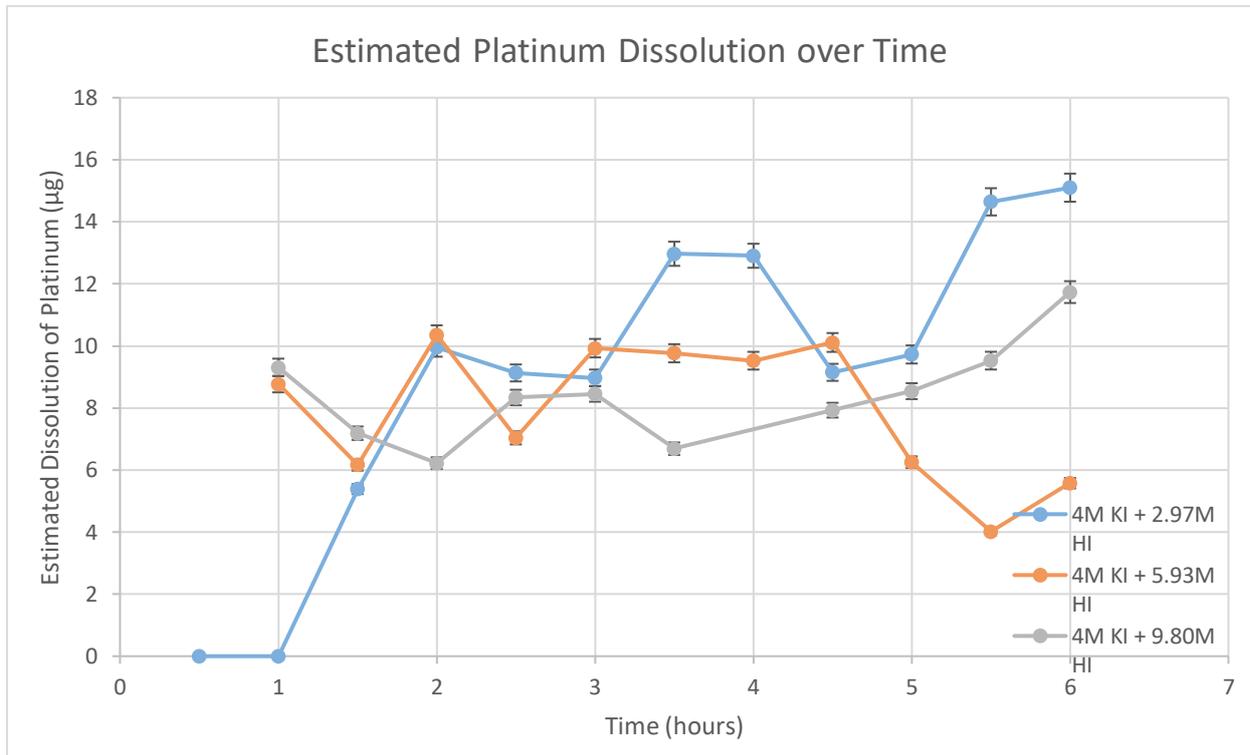


Figure 4.14 – Estimated Dissolution of 0.15g of Platinum in 4M Potassium Iodide with different concentrations of Hydroiodic Acid at 90°C

The addition of hydroiodic acid to leaching solutions is ineffective at increasing the overall dissolution of platinum. Due to this an a leaching solution containing 4M potassium iodide with a iodine solution will be used upon membranes to maximise dissolution

Membrane Leaching Results

Using the results from the bromide and iodide tuning work, 4M potassium iodide and a 4M potassium bromide with 8.9M hydrobromic acid leaching solutions were used on membranes. 125µm PFSA PEM platinum black (both anode and cathode), 125µm PFSA PEM 50m²/g IrO₂ (anode catalyst) with 40% Pt/C (cathode catalyst) and 125µm PFSA PEM 100m²/g IrO₂ (anode catalyst) with 40% Pt/C (cathode catalyst) membranes were used. After cutting the membranes into 1cm x 1cm strips, they were placed in the relevant solvent at 90°C. Samples were taken every 30 minutes. These samples were filtered and then placed into a UV-Visible spectrometer. The results from these samples were compared against pre-made standards containing known quantities of precious metal.

Table 4.17 displays the estimated quantity of platinum found in solution when stripped from a 125µm PFSA PEM platinum black membrane.

Time (hours)	Solvent Used	
	4M KI	4M KBr + 8.90M Hydrobromic acid
	Estimated Dissolution of Pt (µg)	
0.5	55.378	51.588
1	78.145	334.32
1.5	153.87	532.50
2	178.13	616.78
2.5	223.95	738.74
3	221.58	648.27
3.5	266.45	634.37
4	285.18	555.43
4.5	372.33	394.67
5	340.58	321.20
5.5	362.77	299.98
6	335.11	318.597

Table 4.17 – Estimated Dissolution of Platinum from Pt/C – Pt/C Membrane in different solvents

Over a six-hour period, the rate of dissolution by both solvents is different. The 4M potassium bromide and 8.90M hydrobromic acid solution begins with a fast rate of dissolution but slows considerably after the 3-hour point. Conversely, the potassium iodide leach begins slowly but after 6-hours has a sample that contains more platinum than the bromide solution. This could indicate that if the leaching time was to be prolonged the overall quantity found in the iodide samples could be higher than that found in the bromide samples. A graphic display of the results can be found in figure 4.15.

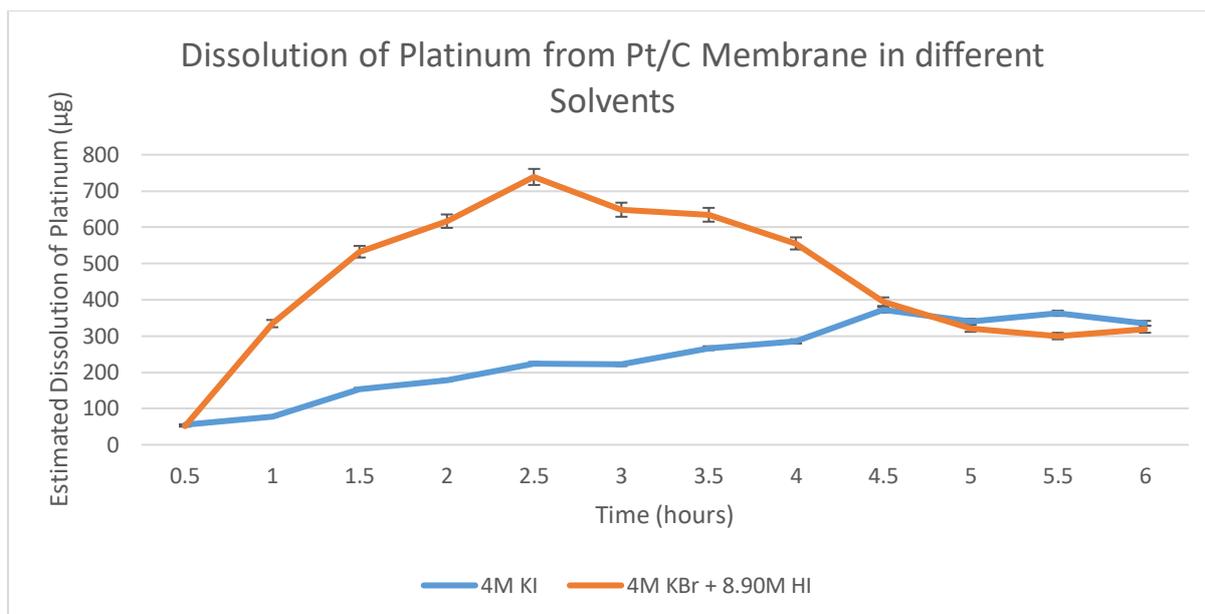


Figure 4.15 – Estimated Dissolution of Platinum from Pt/C – Pt/C Membrane in different solvents

Platinum leaching from a 125um PFSA PEM 50m²/g IrO₂ (anode catalyst) with 40% Pt/C (cathode catalyst) was then recorded. The same iodide and bromide leaching solutions were used. The results are listed in table 4.18.

Time (hours)	Solvent Used	
	4M KI	4M KBr + 9.80M Hydrobromic acid
Estimated Dissolution of Pt (µg)		
0.5	15.617	20.949
1	19.348	38.663
1.5	28.838	71.436
2	28.700	69.269
2.5	50.840	110.98
3	31.927	96.931
3.5	54.961	98.642
4	56.673	89.367
4.5	79.713	91.744
5	77.088	91.234
5.5	81.200	109.91
6	81.979	254.65

Table 4.18 – Estimated Dissolution of Platinum from 50m²/g IrO₂– 40% Pt/C Membrane in different solvents

Platinum dissolutions from the 50m²/g IrO₂ - 40% Pt/C membrane under both solvents appears very similar. Both follow a similar increase in overall dissolution over time with both appearing to reach solubility limit after 4.5 hours as seen in figure 4.16.

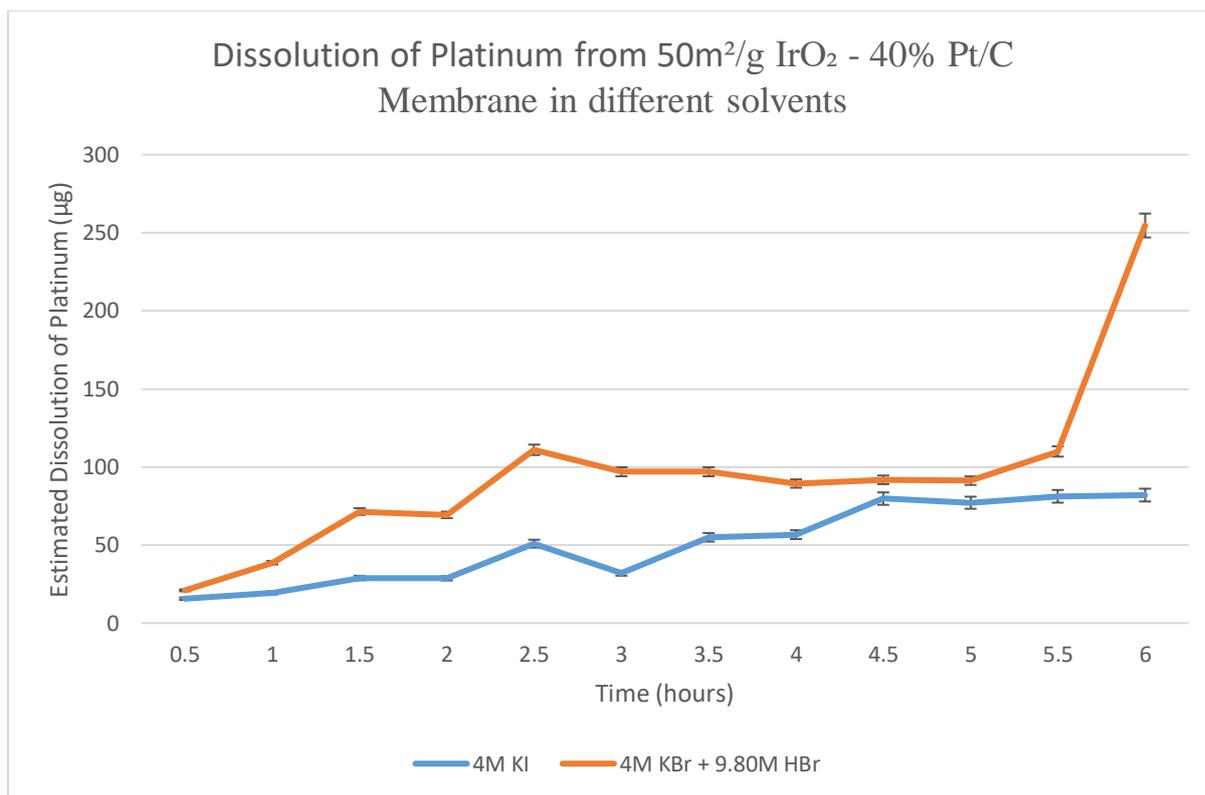


Figure 4.16 – Estimated Dissolution of Platinum from 50m²/g IrO₂– 40% Pt/C Membrane in different solvents

Platinum leaching from the final membrane, 125um PFSA PEM 100m²/g IrO₂ - 40% Pt/C, was recorded. The same iodide and bromide leaching solutions were used. The results are listed in table 4.19.

Time (hours)	Solvent Used	
	4M KI	4M KBr + 9.80M Hydrobromic acid
	Estimated Dissolution of Pt (µg)	
0.5	15.981	88.824
1	19.304	439.32
1.5	23.720	217.40
2	24.519	645.96
2.5	26.119	321.84
3	26.540	903.01
3.5	36.881	361.45
4	40.132	577.704
4.5	41.730	596.36
5	46.902	651.73
5.5	70.531	682.43
6	74.321	697.97

Table 4.19 – Estimated Dissolution of Platinum from 100m²/g IrO₂– 40% Pt/C Membrane in different solvents

The data presented in table 4.19 shows bromide leaching of platinum to be highly successful when compared to iodide leaching. The iodide leach solution steadily increases in platinum content over the period measured but only dissolves a small quantity when compared to the bromide leaching solution. The samples taken during the bromide leaching fluctuated greatly in their values until 4.5 hours – after which the quantity of platinum dissolved slowly reached a plateau. This could be down to localised variations within the leaching solution. After 4.5 hours the estimated amount of platinum found in each sample was approximately 675µg.

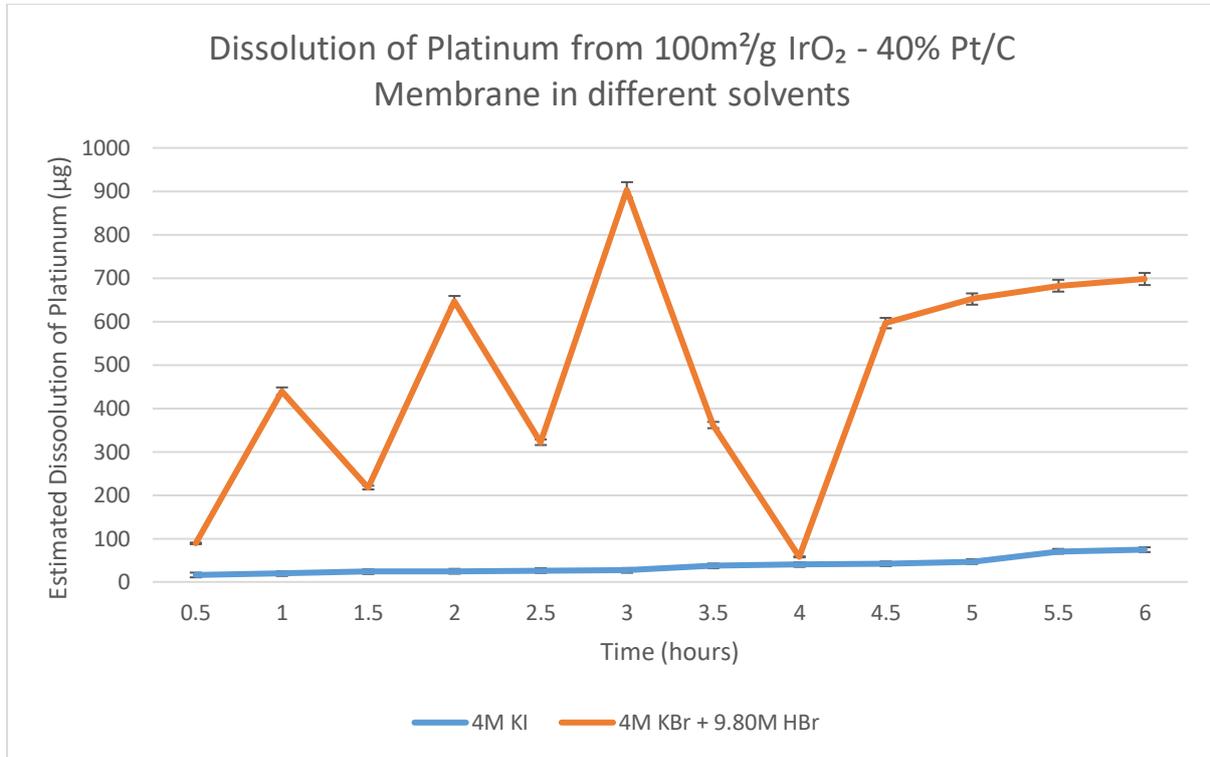


Figure 4.17 – Estimated Dissolution of Platinum from 100m²/g IrO₂– 40% Pt/C Membrane in different solvents

When testing for the quantity of platinum in the 50m²/g IrO₂– 40% Pt/C and 100m²/g IrO₂– 40% Pt/C membranes, iridium dissolution was measured simultaneously. As with platinum, that mass of iridium being used was as close to 0.15g as possible – in order to give comparable results to the previous work. The results of the iridium dissolution over time from the 50m²/g IrO₂– 40% Pt/C membrane can be seen in table 4.20

Time (hours)	Solvent Used	
	4M KI	4M KBr + 8.90M Hydrobromic acid
	Estimated Dissolution of Pt (μg)	
0.5	60.865	210.24
1	89.478	483.57
1.5	330.306	1273.66
2	323.29	1250.9
2.5	490.039	1991.5
3	401.17	1721.0
3.5	628.09	1794.7
4	663.36	1533.5
4.5	896.92	1098.95
5	796.48	1126.85
5.5	900.03	1943.7
6	924.64	363.78

Table 4.20 – Estimated Dissolution of Iridium from 50m²/g IrO₂– 40% Pt/C Membrane in different solvents

Both leaching solutions proved to be very effective at dissolving large quantities of iridium. The potassium iodide solution started with a small amount of dissolution but slowly rose in the quantities of iridium per sample over time. After 6 hours, the rate of increase of dissolution had not slowed sustainably indicating that higher amounts of iridium could be dissolved over a longer period. After 2.5 hours, the bromide leaching solution appeared to reach its solubility limit as seen in figure 4.18. Quantities of iridium found after this time mainly fluctuated between 1500 μg and 2000 μg . Given this, the bromide solution appears to be a better leaching solution over a 6 hour period, however over a longer period, potassium iodide could prove to be better.

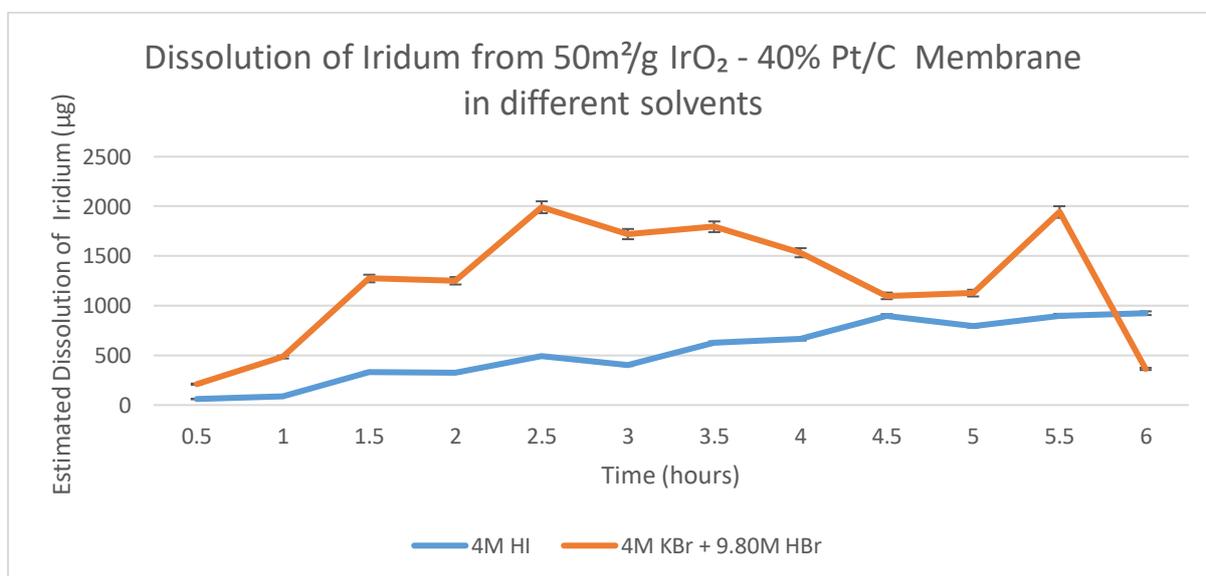


Figure 4.18 – Estimated Dissolution of Iridium from 50m²/g IrO₂– 40% Pt/C Membrane in different solvents

The dissolution of iridium from the 100m²/g IrO₂- 40% Pt/C membrane was then tested. As before, mass of iridium being used was as close to 0.15g as possible – in order to give comparable results to the previous work. This allows for comparison between IrO₂ membranes to see the effect, if any, of specific surface area. The results from the 100m²/g IrO₂- 40% Pt/C membrane in regards to iridium dissolution are shown in table 4.21.

Time (hours)	Solvent Used	
	4M KI	4M KBr + 9.80M Hydrobromic acid
	Estimated Dissolution of Pt (µg)	
0.5	314.19	342.64
1	381.08	1163.41
1.5	442.57	657.46
2	450.96	1413.3
2.5	477.77	933.0
3	489.18	1912.2
3.5	739.15	298.47
4	812.3	528.83
4.5	834.21	1439.4
5	902.67	1521.6
5.5	1360.0	1578.4
6	1410.9	1638.2

Table 4.21 – Estimated Dissolution of Iridium from 100m²/g IrO₂- 40% Pt/C Membrane in different solvents

Similar to the 50m²/g IrO₂- 40% Pt/C membrane results, both leaching solutions contained a large amount of iridium. The iodide leach slowly rose in the quantity of iridium found per sample over time whereas the bromide leaching solution tended to fluctuate at larger values before setting at a lower dissolution quantity after 4.5 hours (as seen in figure 4.19). The solubility limits for both solvents appear to have been reached after 5-6 hours as the increase in iridium found per sample continues to diminish.

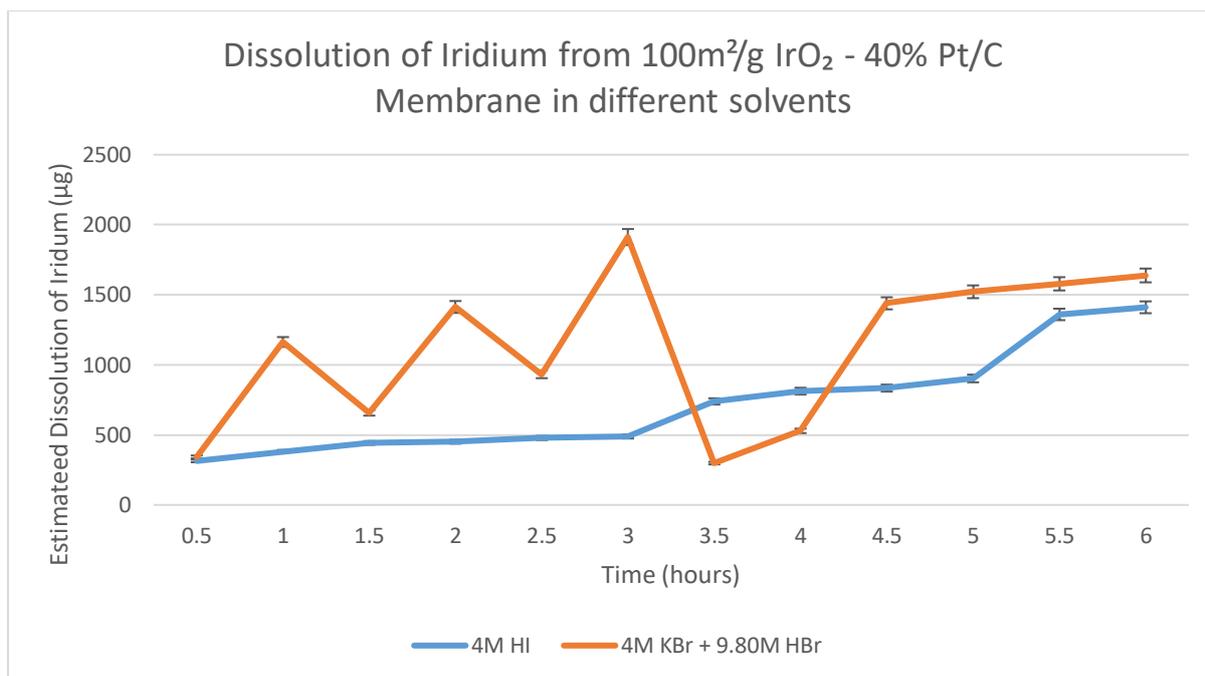


Figure 4.19 – Estimated Dissolution of Iridium from 100m²/g IrO₂– 40% Pt/C Membrane in different solvents

Analysing the effect of particular stripping solutions upon each metal and on different membranes gives useful results. When analysing the data presented figure 4.20, it is apparent that 4M potassium iodide is better at dissolving iridium from a membrane than platinum. This is the case for both 50m²/g IrO₂ – 40% Pt/C and for 100m²/g IrO₂ – 40% Pt/C. The difference in relative dissolution between platinum and iridium is larger upon the 100m²/g IrO₂ – 40% Pt/C membrane than the 50m²/g IrO₂ – 40% Pt/C membrane. This indicates that the specific surface area of the membrane has an effect on both iridium dissolution.

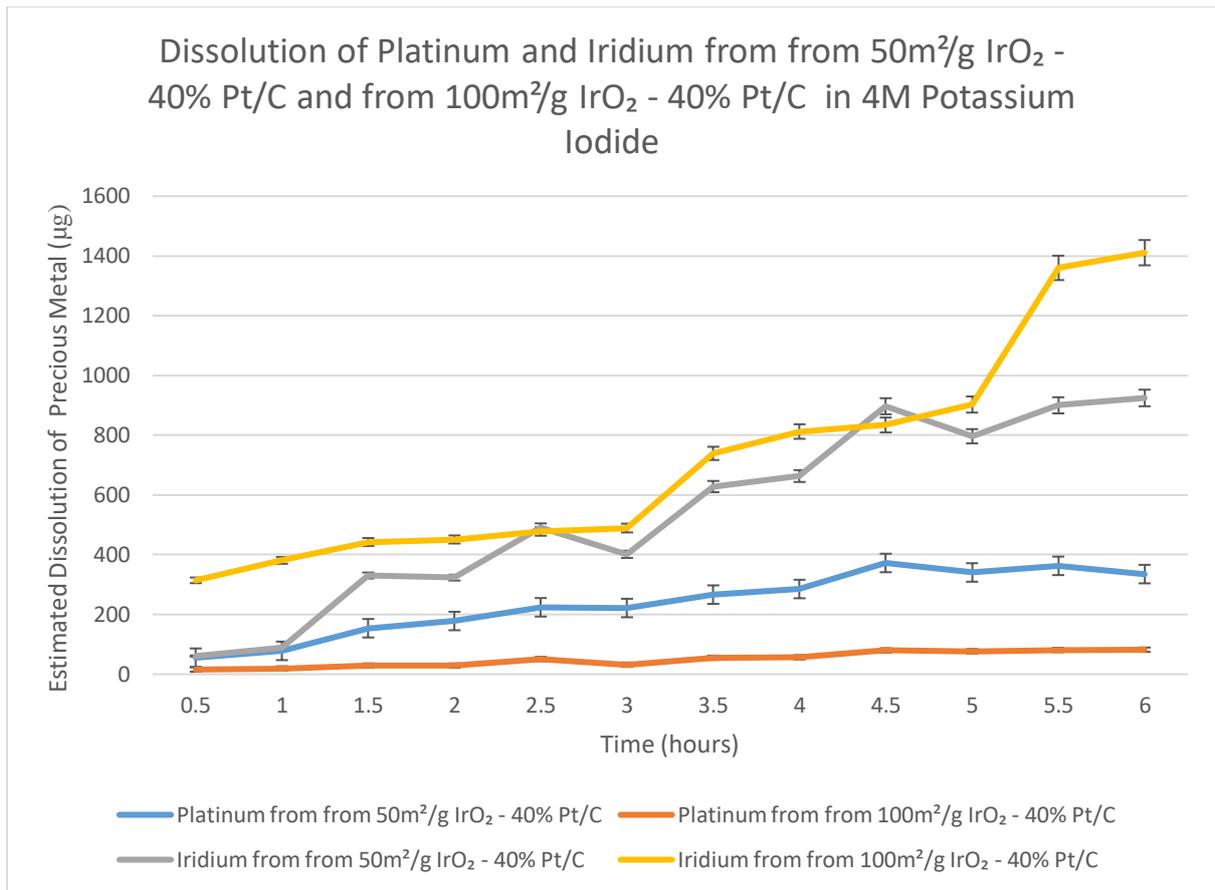


Figure 4.20 – Estimated Dissolution of Platinum and Iridium from 50m²/g IrO₂ – 40% Pt/C and 100m²/g IrO₂– 40% Pt/C Membrane in 4M Potassium Iodide

The effect of the 4M potassium bromide and 8.90M hydrobromic acid leaching upon both iridium-based membranes was examined. The effects upon the quantity of both iridium and platinum were examined and can be seen graphically in figure 4.21. Similar patterns are seen with the bromide leaching solution as were seen with the iodide leaching solution. Iridium is found in higher quantities than platinum in both cases but the disparity between the quantities found is less. The dissolution of iridium from both of the membranes is similar throughout the recorded period but in the case of the 100m²/g IrO₂ – 40% Pt/C membrane, the dissolution appears to settle after 4.5 hours at around 1500µg. The results indicate the bromide leaching solution could dissolve platinum with greater ease than the iodine solution but lacks selectivity. By creating a process that incorporates both leaching solvents, all of the metal could be removed at a high selectivity. By first leaching the membrane with an iodine solution, a large quantity of iridium could be removed with a small pollution of platinum. After a satisfactory amount of iridium has been recovered, a second leaching process, involving the bromide solution, could be used to remove the remaining iridium and the bulk of the platinum at a faster rate than the iodide leaching solution could.

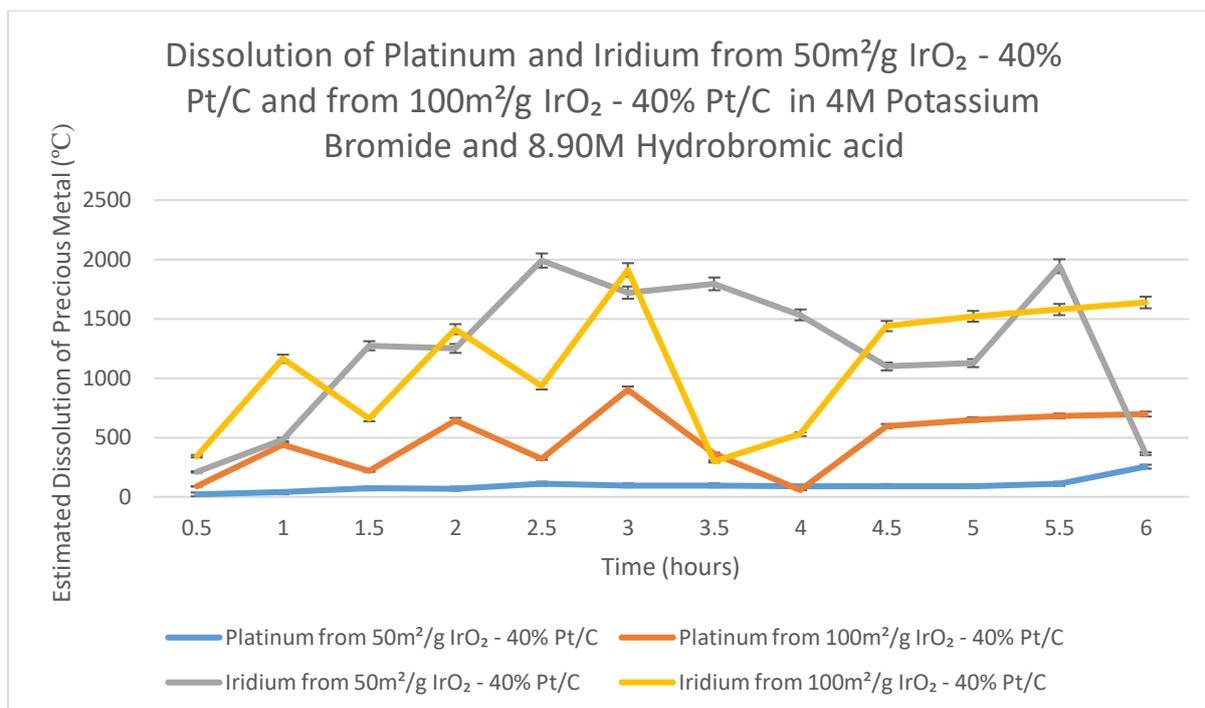


Figure 4.21 – Estimated Dissolution of Platinum and Iridium from 50m²/g IrO₂ – 40% Pt/C and 100m²/g IrO₂– 40% Pt/C Membrane in 4M Potassium Bromide and 8.90M Hydrobromic acid

The overall dissolution of iridium and platinum is less than that found when compared to the results that used powered precious metal alone. Multiple factors need to be taken into consideration. The surface area of the powdered metal, and hence the overall surface area of available metal, is much lower higher than that of the membrane. This causes higher dissolution as there are more particle interactions between the solvents and the precious metal. Degradation of the membrane can also cause issues related to overall dissolution of the metal catalysts. Membrane degradation can cause the metals to recede deeper into the membrane surface, thus making dissolution of the metal harder. This decreases the overall surface area of metal available to be targeted by leaching solutions and thus decreasing the overall efficiency of the process. The solubility limit of the solvents is also currently hindering the maximum absorbance possible of the solvents.

Conclusions

The results from the dissolution processes have been promising. Indications suggest that partially selective separation of precious metals can be possible at 90°C with the use of potassium iodide. The effectiveness of iridium dissolution from 50m²/g IrO₂ – 40% Pt/C and 100m²/g IrO₂ – 40% Pt/C membranes by potassium iodide was not as high as results gaining from pure iridium-ruthenium powder. This was also the case for platinum within the membrane and the platinum black powder. This allows for the separation of iridium and platinum from the membrane as iridium dissolution in excess of 3 times as much in the 50m²/g IrO₂ – 40% Pt/C membrane and up to 15 times in the 100m²/g IrO₂ – 40% Pt/C membrane. Use of a leaching solution containing equal quantities of 4M potassium bromide and 8.90M hydrobromic acid the leaching of platinum from the tested membranes was high. The rate of dissolution of iridium under these conditions is also high and thus cannot separate the precious metals from the membrane directly, but could be used to strip the membrane of the catalytic metals for later separation.

Overall recovery percentage of the metal per sample was not high but this was found to be due to the solubility limit of the leaching agents used. This could be overcome in future work by creating a flow of leaching solution to ensure dissolution of precious metal is not limited by the solution. This could create a much higher total recovery rate of precious metal.

Temperature appears to effect the rate of dissolution. Comparisons between results found at 25°C and 90°C show, in general, that increased temperature allows for a high quantity of dissolution in a much shorter time. The results also show that potassium bromide dissolves higher quantities of platinum at moderate temperatures than at 90°C. Further investigation of the results indicated that potassium oxalate was not a suitable leaching agent for either platinum or iridium.

Dissolution of iridium in bromide based leaching agents is influenced by acidity. The higher the acidity content of the solution, the larger quantity of iridium dissolved. This was seen across all tests of iridium under bromide-based solvents. Conversely, platinum dissolution was reduced when acidity was increased in iodide solutions.

The recovery of precious metals from end of life PEMFCs is viable with the use of halide-based leaching solutions. This can be completed with relative ease and with high success. Limiting factors include the quantity of leaching solution needed or the necessity to strip the solution of precious metal before recycling the leaching stream. Partially selective leaching is possible due to a 4M potassium iodide leach at 90°C selecting higher quantities of iridium than platinum. Membrane degradation and metal deformation may cause issues in recovery of 100% of the metal but very high rates of recovery through this process can be expected.

Further Work

Whilst not covered in the scope of this research, there are further recovery steps that can be taken to recover precious metals from PEMFC membranes. The scope of this work has aimed to separate platinum and iridium into solution, awaiting further separation into precious metal precursors.

The process of dissolution of the precious metals can be extended from the work outlined in this research. By creating a system that cycles leaching solvents past the membranes in multiple cycles can help offset the issues created by the solvents approaching their saturation limit. By creating a cycle that allows 4M potassium iodide to strip membranes of iridium for period of 5-6 hours before refreshing the feed of potassium iodide a continuous cycle of iridium stripping can occur. By neutralising this feed and converting the iridium to its chloro-complex, a deposition onto stainless steel (A304) could be possible as stated by Lopez et al. (2015).

After a satisfactory quantity of iridium has been leached from the system, a feed of 4M potassium bromide and 9.80M hydrobromic acid could be introduced. This would increase the rate of leaching of platinum and allow any remaining iridium to be aggressively leached. This feed could leach the membrane for a set period as stated before (i.e. 5 hours) and then removed. This would allow for another fresh feed of bromide leaching solution to continue to dissolve the precious metal in the membrane. By neutralising this feed, platinum and iridium can be separated. This would involve creating platinum-iodide complexes as outline in work by Faye et al (1963). This could create total separation of the precious metals from PEMFC membranes.

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