

Keywords

Platinum dissolution; iodide; iodine, PEMFCs; EQCM

1. Introduction

Fuel cells are electrochemical devices which generate current capable of performing useful work in an external electrical circuit by separating two half cell reactions with an electrolyte. Proton exchange membrane fuel cells (PEMFCs), which oxidize hydrogen to water, are of particular interest due to their characteristically high current density and consequent suitability for application in automotive power. Currently the majority of these devices use platinum nanoparticles as the principal catalyst, and with a typical PEMFC automotive stack consisting of greater than a hundred individual cells estimates state 34% of the total stack cost in 2010 was directly due to platinum content (Papageorgopoulos 2011). Despite efforts to find means of either reducing platinum content or eliminating it entirely using alternative catalysts, platinum content and cost are likely to remain significant issues for the fuel cell industry for the foreseeable future (Wilson and Gottesfeld 1992, Wee et al. 2007, Proietti et al. 2011, Serov et al. 2012). Global demand for platinum group metals (PGMs) is anticipated to continue to increase while supply from refineries is likely to remain stagnant putting additional pressure to effectively use the metal as well as incentivising Pt metal value recovery from end-of-life devices. Within the European Union (EU) this is acutely recognised and platinum groups metals are part of the 14 strategic materials which are considered vital for continued economic development and as such receive special attention through EU grants and schemes. Recycled platinum currently represents approximately 25% of the global platinum supply stream, and total output has increased annually since 2004 (Johnson Matthey 2014). Existing recycling methods are well established and have been shown to be capable of achieving total metal value recovery, but economic and environmental considerations continue to be problematic.

Recovery processes can typically be classified in three different ways: selective chlorination or gas phase volatilization, pyrometallurgical, and hydrometallurgical (Jha et al. 2013). Selective chlorination processes make use of differing vapour pressures of metal chlorides in order to selectively remove

target metals via gas phase adsorption on a sacrificial matrix. Kim et al. demonstrated it was possible to recover over 90% of PGMs with a chlorination process from spent automotive catalytic converters (Kim et al. 2000). While these processes are highly tuneable and are capable of producing high purity metals, gas phase volatilization does require the use CO and Cl₂, both hazardous gases (Kim et al. 2000). The hazards associated with using these gases for any process of appreciable capacity lead to some significant health and environmental risks. In the UK the storage and use of chlorine on site requires special registration and working procedures on the UK Control of Major Accident Hazards (COMAH) legislation which adds significant costs to a project (HS&E 2015).

Pyrometallurgical processes operate at temperatures between 1500 and 1700°C and are used to separate PGM from other metals; however these methods are ill-suited for devices containing significant fluorine content, such as PEMFCs, due to the possible formation of hydrofluoric acid, carbonyl fluoride, and other COF compounds under oxidative conditions (Ario and Soda 1977, Samms et al. 1996, Benson et al. 2000, Conesa and Font 2001). Finally hydrometallurgical processes are the most diverse, but can be generally characterised by leaching Pt in oxidizing solutions. While capable of attaining yields in excess of 95% these processes can be improved upon significantly (Bonucci and Parker 1984, Tyson and Bautista 1987, Bautista et al. 1988, Kim et al. 1994, Angelidis and Skouraki 1996, Woo et al. 2000, Angelidis 2001).

Most hydrometallurgical methods reported require extremely aggressive conditions immersing the spent material in highly acidic and oxidising chloride containing media such as aqua regia (Schreier and Edtmaier 2003, Barakat and Mahmoud 2004, Baghalha et al. 2009, Jimenez de Aberasturi et al. 2011). Barakat and Mahmoud investigated the use of aqua regia to recovery PGMs from spent reforming catalyst, and obtained a 97.5% yield of the metals in high purity forms (Barakat and Mahmoud 2004). Jafarifar et al. and Niemelä et al. investigated PGM dissolution in aqua regia with the addition of a microwave digester. Both groups were able to achieve comparable yields and purities to Barakat and Mahmoud but at significantly reduced time scales and leachate volumes (Jafarifar et al. 2005, Niemelä et al.

2012). Finally Baghalha et al. examined the kinetics of Pt dissolution in aqua regia and determined the rate is limited by the ratio of aqua regia volume to solid content while the process itself is solely a surface chemical reaction (Baghalha et al. 2009). Despite being a highly efficient means of recovering metal value, aqua regia is an extremely corrosive solution with well documented biological and environmental effects making it unattractive for large scale recycling processes. Other groups have investigated means of replacing aqua regia with cyanide extraction (Bruckard et al. 1992, Han and Meng 1994, Han and Meng 1996, Chen and Huang 2006). These groups have shown that it is possible to recover Pt, Pd, and Rh via cyanide extraction, however the proposed system operated at temperatures and pressures exceeding 200°C and 10 bar, making it highly energy intensive (Han and Meng 1996, Chen and Huang 2006).

A less studied, but highly promising alternative to both aqua regia and cyanide extraction is the use of iodine to complex PGMs. Zanjani and Baghalha investigated platinum extraction in acidified 0.12-0.48M iodine-iodide solutions at temperatures between 25-95°C (Zanjani and Baghalha 2009). Their work showed that Pt could be leached from spent materials with sufficient time and iodine oxidant content; however Pt recovery reached a maximum of only 80%, possibly due to limited iodine concentration. Furthermore Zanjani and Baghalha acidified the iodine-iodide solution with HCl, thus reducing the benefit of using a less corrosive solvent. Conversely Dawson and Kelsall investigated the benefits of near neutral iodine-iodide based PGM dissolution, and they were able to show a clear trend stating higher triiodide concentrations increased Pd and Pt dissolution rates (Dawson and Kelsall 2007, Dawson and Kelsall 2013). By immersing a Pt black flag electrode in neutral 4M KI solutions with varying triiodide content, they were able to determine the effective dissolution rate of Pt by measuring the dissolved metal content through UV-Vis Spectroscopy (Dawson and Kelsall 2013). Of the methods previously discussed, this process is viewed as having the

greatest potential because of its mild operating conditions, reduced hazardous chemicals usage, and significantly lower economic investment in the required process plant. Furthermore the platinum iodo complexes generated by this process are reported to be less sensitising than their chloro counterparts reducing the associated risk of processing PGM salts. Despite the numerous benefits there is very little published work in the use of concentrated iodide solutions for Pt recovery, and further investigation was required to validate this process for recovery from commercial devices. The work presented here is comprised of two separate but related studies. The first used electrochemical quartz crystal microbalances (EQCM) in order to monitor *in situ* mass changes of Pt black electrodes. These represent a model platinum based catalyst used in electrochemical devices such as PEMFCs. The second investigated the potential to leach platinum nanoparticles from untested and end-of-life (EOL) PEMFCs. The results published here will be used in the development of a more economical, safe and environmentally benign PGM recovery process.

2. Material and methods

2.1 Electrode Preparation

Platinum black electrodes were produced using 1-inch platinum quartz monitor crystals (Inficon 149240-1) as the substrate using a method adapted from literature (Feltham and Spiro 1971, Feltham and Spiro 1972, Ilic et al. 2000). The crystals used in this study were manufactured for use at 90°C, and have a resonant frequency of 5MHz. The crystals were placed in an EQCM holder (Inficon CHT-100), and functioned as the working electrode in a 3-electrode system. Prior to an experiment the crystals were exposed to air and the electrolyte solution heated to 90°C, each for 30 minutes, to monitor nascent frequency and resistance fluctuations. This was done as a calibration process in order to ensure accurate and reliable measurements could be obtained. The platinum black working electrode and platinum wire

counter electrode were placed in a 0.072M Chloroplatinic acid solution and a saturated calomel reference electrode (SCE) was placed in 1M H₂SO₄ solution with an agar salt bridge connecting both electrolytes. The working electrode was held at 0 V vs standard hydrogen electrode (SHE) for 60 seconds resulting in a visually even Pt black deposit, and the mass of the electrodes were between 100 and 275µg. Figure 1 shows a representative SEM micrograph of the electrode surface.

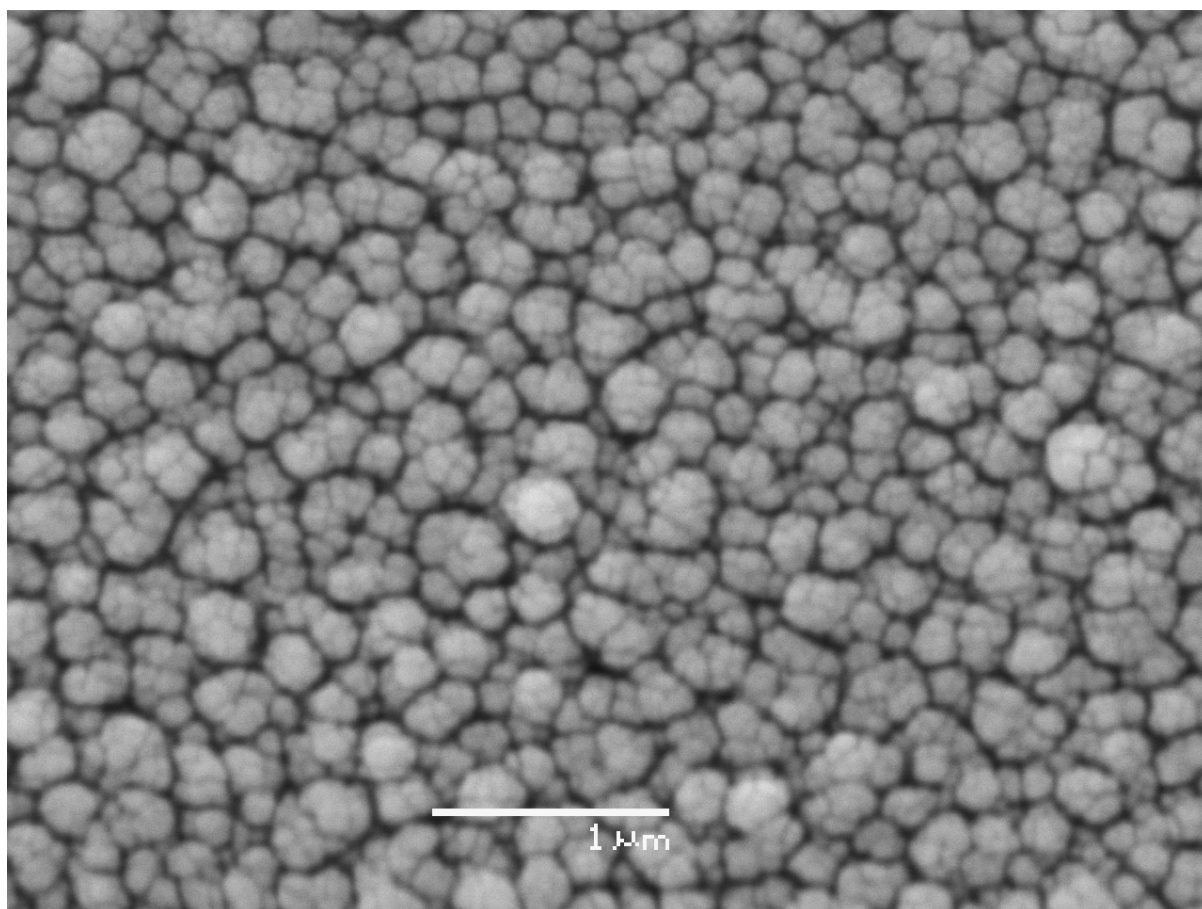


Figure 1. SEM micrograph of Pt black electrode (50,000 times magnification, 15 kV, JEOL 5600 SEM). Image courtesy of Dr. Nigel Fullwood (n.fullwood@lancaster.ac.uk).

Hydrogen adsorption was used to determine the active surface of the platinum black electrode, and the method described here is adapted from the referred text (Kinoshita et al. 1973). The working electrode was placed in deoxygenated 0.5M H₂SO₄ solution and 5 cyclic voltammetric sweeps between 0 and 1.5V (SHE) at 0.1 V s⁻¹ were performed. The charge

passed between 0 and 0.4 V (SHE) was calculated and divided by $210\mu\text{C}$, the charge necessary to form a 1cm^2 monolayer of hydrogen, in order to determine the surface area. (Conway et al. 1973) The surface areas of the Pt black electrodes were found to be between 44.5 and 77cm^2 .

2.2 Platinum Black Dissolution

Potassium iodide (ReagentPlus[®]) was supplied by Sigma-Aldrich, and was used to produce 0.15dm^3 of 4M KI solutions in $18.2\text{M}\Omega$ quality DI water. For some experiments iodine was added to the reaction vessel solution by using a 1 N iodine solution (Sigma-Aldrich 319007-100ML) to produce 5, 10, and 15 mM solutions. Experiments conducted without additional iodine will be labelled as 0 mM throughout this work however it should be noted adventitious iodine was present under these conditions due to the oxidation of iodide by atmospheric oxygen dissolving in the solutions during preparation. The 4M KI solution was heated to 90°C in a flat-bottomed reactor vessel and sparged with nitrogen for 30 minutes in order to remove dissolved oxygen content. The reactor was only open to atmosphere during experiments via a water cooled condenser attached to the vessel. This minimized evaporative losses whilst elevated temperatures were maintained without the complexity and safety concerns of pressurisation. The EQCM was then placed in the reactor vessel where mass changes were monitored for 20 minutes. Additionally the open circuit potentials of these electrodes were monitored constantly during the dissolution process in the varying iodine concentrations.

To understand further the kinetics of the Pt dissolution at applied potentials the dissolution rate of Pt black at varying potentials in 4M KI with 0mM iodine was also investigated. The platinum black electrode and platinum wire counter electrodes were placed in the reaction vessel, and the reference electrode was connected via an agar salt bridge while placed in a

separate, ambient temperature 4 M KI solution. Using a computer controlled potentiostat (Compactstat, Ivium Technologies, Netherlands) cyclic voltammetry was performed between 0 and 1.23 V (SHE) at 20 mV s^{-1} for a total of 5 sweeps.

2.3 PEMFC Leach

PEMFCs were provided by a fuel cell manufacturer as both untested and EOL samples. These materials were cut into strips measuring approximately 0.5 cm by 2 cm prior to leaching in order to allow them to fit in the reaction vessels used but would also be representative of possible comminution processes which could be applied in practice. The untested materials consisted of a catalyst coated membrane (CCM) while the EOL material was comprised of the CCM compressed between two gas diffusion layers which could not be cleanly delaminated. Due to the difference in materials 0.1 g of untested material were used per experiment while 0.3 g of EOL material were leached per experiment. 0.2 dm^3 of 4 M KI solution were prepared per experiment using $18 \text{ M}\Omega$ quality DI water and sparged with N_2 for 30 minutes prior to leaching. Iodine was also added to the reactor volume to produce 5, 10, 15, and 20 mM concentrations. The solution was heated to 90°C and continuously stirred during the leach process. The reactor was closed and a water circulating condenser was attached to the vessel in order to minimize evaporative losses. The experiment ran for 120 minutes, with 1 cm^3 samples of the solution being taken after predetermined intervals. These samples were then treated with ascorbic acid to reduce excess iodine before being analysed using a UV-Visible spectrometer (Evolution 220, Thermo Scientific, UK) to determine dissolved Pt content (Balcerzak and Kaczmarczyk 2001, Balcerzak and Pergol 2003). The leached materials were filtered from the solution, then washed and dried before being analysed with X-ray photoelectron spectroscopy (XPS) and digested in aqua regia.

2.3.1 Aqua Regia Digestion

A final digestion phase in extremely aggressive conditions was used to determine any residual Pt left on the iodide leached materials. As stated previously aqua regia digestion is a well-documented and established method for PGM recovery, and was viewed as the most reliable method for accurately determining residual platinum content in the PEMFC materials. Aqua regia was prepared prior to each digestion by combining 37 wt% HCl and 65 wt% HNO₃ (obtained from Sigma-Aldrich) in a 3:1 ratio to produce 0.080 dm³ of acid. The acid was placed in a flat-bottom reactor vessel and heated to 105 ± 2°C whilst stirred continuously. PEMFC material was added to the reactor and allowed to digest for 2 hours after which the acid was decanted and stored. A sample was then diluted with 18 MΩ quality DI water to approximately 2.2 wt% aqua regia and analysed for Pt content via ICP-OES (Thermo Fisher Scientific iCAP Duo 6300). Dilution was required to be compatible for use with the instrument set up.

2.3.2 XPS Analysis

XPS measurements were conducted at the NEXUS facility located at Newcastle University, and were performed using a Thermo Scientific K-Alpha XPS. The instrument produced X-rays with an energy of 1486.6 eV with an equipped microfocused monochromatic Al-Kα source. The membrane layer for each sample was analysed in three distinct spots, measuring 400 μm by 800 μm. Survey scans were taken in order to determine elemental composition and were carried out with pass energies of 200 eV and dwell times of 10 ms. Charge neutralisation was used throughout the analysis; however spectra were calibrated using the binding energy of graphitic carbon, 284.45 eV, in order to negate the possibility of charge build-up (Wertheim et al. 1980, Smith and Black 1984).

3. Results and Discussion

3.1 Platinum Black Dissolution

Figure 2 shows the E-pH diagram for the platinum-iodine system, and shows the available window for platinum dissolution and triiodide formation (Bard et al. 1985). From previous work it has been established that two possible complexes can be formed through the following oxidation reactions:

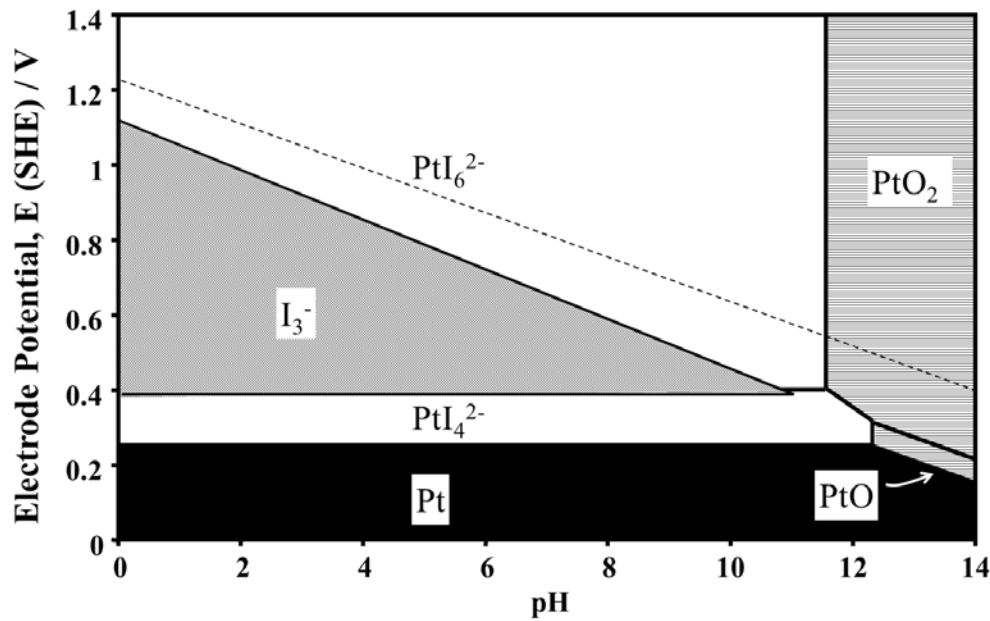
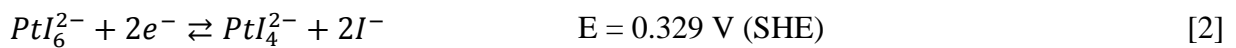
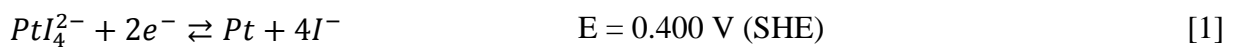


Figure 2. E-pH diagram for Pt-Iodo complexes which shows the potential and pH window of PtI_4^{2-} and PtI_6^{2-} formation (Bard et al. 1985). Complete oxidation of platinum to PtI_6^{2-} was the desired product for the dissolution process, however iodine concentration in solution must be sufficient to inhibit the formation PtI_4 , an insoluble precipitate



The complete oxidation of Pt metal to Pt^{IV} is the most likely in the conditions used for this study, and can be visibly observed by the distinctive purple of the $PtI_6^{2-}_{(aq)}$ complex formed during the experiments. High iodide concentrations are used to suppress the dissolution potential and to help prevent the formation of any products with limited solubility such as PtI_4 (Dawson and Kelsall 2013).

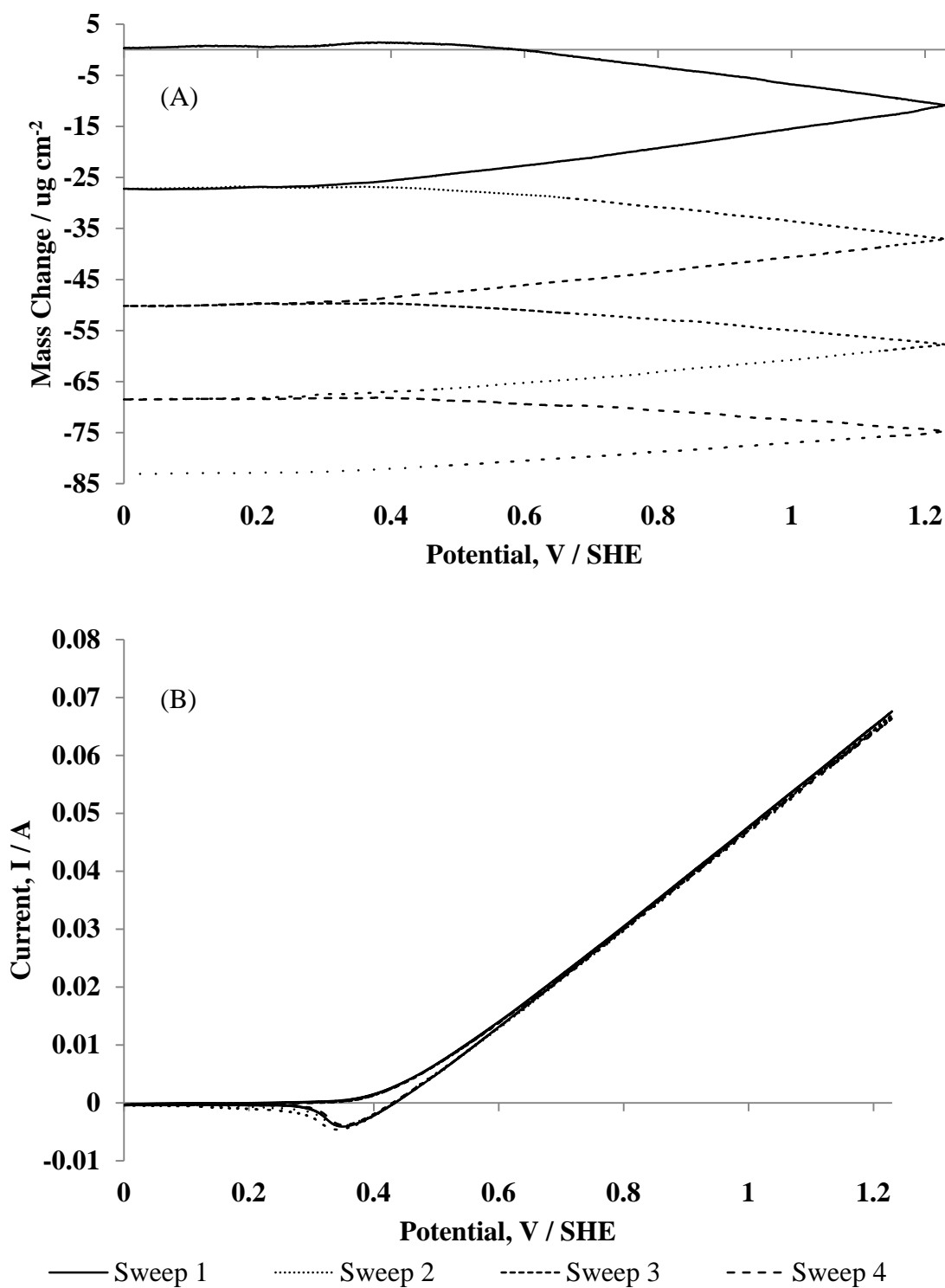


Figure 3. The recorded mass changes of a platinum black electrode in 90°C 4 M KI solution with adventitious iodine (A) during a cyclic voltammetric sweep (B) conducted at 20 mV s^{-1} . The electrode experiences a steady-state mass loss irrespective of electrode potential, suggesting the dissolution process is determined by a rate limiting process, such as film formation or surface oxidation.

The cyclic voltammogram and associated mass losses for a platinum black electrode in 4 M KI and adventitious iodine heated to 90°C are shown in Figure 3. Figure 3A shows the

electrode gained mass initially during the anodic sweep before reaching 0.4 V (SHE) at which time the deposit began to steadily lose mass. The initial increase in mass is assumed to be due to iodine adsorption as has been established in literature (Schardt et al. 1989, Shu and Bruckenstein 1991). The mass loss observed continues during the cathodic sweep before reaching 0.4 V (SHE), at which point the electrode mass remains constant. This pattern is repeated during the remainder of the experiment but with each subsequent scan removing less material; the reduced dissolution rate is most likely to be due the diminished surface area of the platinum black electrode. The voltammogram in Figure 3B shows a clear oxidation process occurring from 0.4 to 1.23 V (SHE), achieving a maximum of 64.75 mA, and is a combination of the dominant iodide oxidation reaction and platinum dissolution. From Figure 3A it can be assumed that the dissolution reaction achieves a near steady-state rate of mass loss at potentials above 0.5 V (SHE), indicating that Faraday's Law of Electrolysis can be used to determine the current the dissolution process would produce. Knowing the sweep rate was 20 mV s^{-1} and assuming the dissolution reaction is the oxidation of Pt to Pt^{II} , approximately 0.342 mA of the observed current can be attributed to the mass loss during the first cycle. This steady state mass loss with increasing potential suggests that the dissolution rate limit is highly dependent on a diffusion limited process such as the build up a thin film of oxidised Pt product or adsorbed iodine which restricts the Pt dissolution rate. This suggests that increasing the redox potential of any leach solution, for example by the addition of more oxidant, in a commercial leaching process above a certain level will have little positive effect on the dissolution rate and consequent process time.

Table 1.Characteristics of Pt Black Electrodes

[I ₂] (mM)	Mass Removed (μg)	Surface Area (cm^2)	Number of spheres	Radius (nm)	Molar Flux ($\text{mol m}^{-2} \text{ s}^{-1}$)

0	70.9	77.0	3.01×10^{14}	1.37	-3.41×10^{-8}
5	158.2	59.2	3.37×10^{13}	3.73	-6.13×10^{-8}
10	175.0	50.0	1.66×10^{13}	4.89	-7.77×10^{-8}
15	278.8	59.1	1.09×10^{13}	6.59	-2.83×10^{-7}

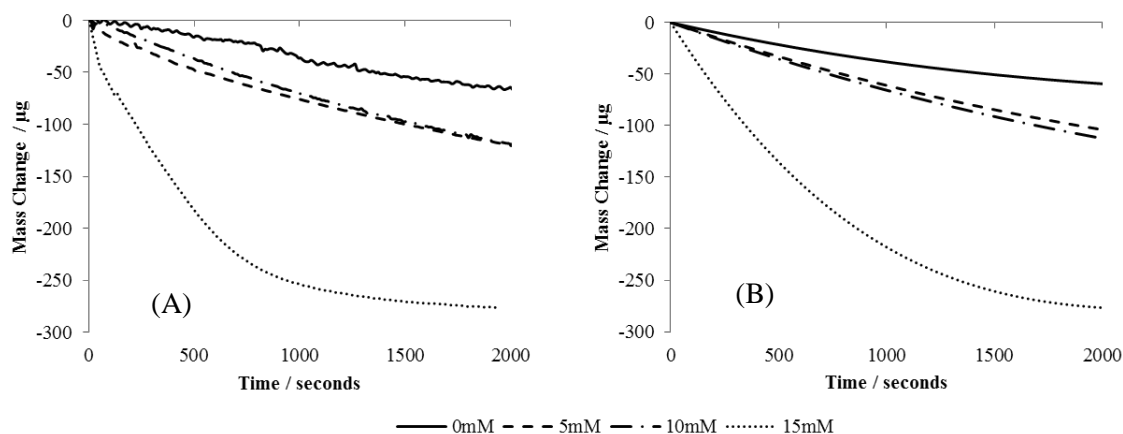


Figure 4. Measured losses of Pt black electrodes (A) and calculated mass losses (B) in varying iodine concentration. Despite iodine concentration having a noticeable effect on observed mass losses, it is believed accessible surface area is the limiting factor for the dissolution process.

As stated previously the effect of iodine concentration on Pt dissolution was also investigated. The initial surface areas of the platinum black electrodes as well as the total mass removed during each experiment is shown in Table 1. Additionally Figure 4a shows the recorded mass losses during the course of the experiment; however the data shown has been truncated to 2000s for clarity as some of the conditions required significantly longer time frames to reach completion. The figure shows a trend indicating increasing iodine concentration accelerates the dissolution process, but the level of the effect is less apparent due to surface area inconsistencies between electrodes. This complication is most obvious when comparing the results between 5 and 10mM which show approximately the same dissolution rate ($-110 \mu\text{g} / 2000\text{s}$) but with significantly different surface areas. In addition, though the 0mM experiment had the slowest rate, losing $70.39 \mu\text{g}$ over the selected time frame, the electrode had the highest surface area (77cm^2) which may have increased the

apparent dissolution rate. Furthermore during these experiments the open circuit potential was monitored and was found to sit between 0.40 and 0.42 V (SHE) for all conditions. This result is in good agreement with those obtained from cyclic voltammetry and with previously established literature values, and supports the conclusion that oxidant concentration has limited impact on the dissolution rate.

In order to separate the relative effects of both electrode surface area and iodine concentration it was necessary to calculate a molar flux, v_0 , and thus provide a more rigorous conclusion regarding Pt black dissolution. The electrodes were then approximated as a collection of identical spheres shrinking at the rate prescribed by v_0 . To find the molar flux second-order polynomials were fit to the 4 curves to generate relationships correlating recorded mass loss with time. These equations were then differentiated and solved at $t = 0s$, and the resulting value divided by the initial surface area and molar mass of platinum to give a unique molar flux coefficient. To determine the number and radius of the spheres necessary of the model, Equations 3 and 4, equations for the surface area and mass of identical spheres, where A is the measured electrode surface area and M is the electrode mass, were solved simultaneously for r , radius, and n , number of spheres.

$$A = 4\pi r^2 n \quad [3]$$

$$M = (4/3)\pi r^3 n \rho \quad [4]$$

Using these values it is possible to calculate the dissolution of Pt from the electrode over time, the results of which can be seen in Figure 4b. Due to the simplicity of the approximation of the model it should be noted that it has been assumed that the reaction rate remains constant and that there are no switches between kinetic and transport control regimes during the dissolution process. Comparing the predicted results to those obtained experimentally shows good agreement, however the approximation typically underestimates

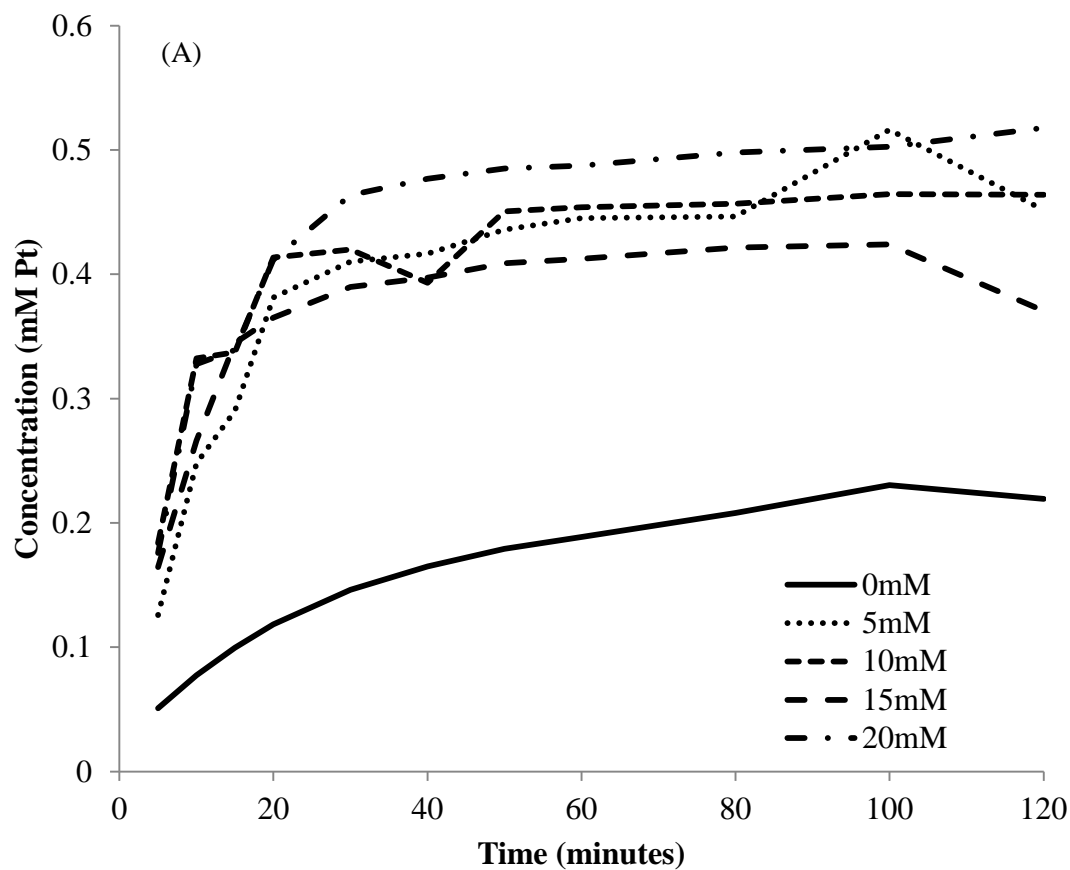
the actual dissolution rate. Additionally, though the method used predicts Pt to exist as nanoparticles, Figure 1 clearly shows the surface is composed of aggregates on the sub-micrometre scale. In practice some pore diffusion limitation might be expected but the closeness of the fit from the simple model suggests that increasing complexity by accounting for this is not necessary to adequately describe the dissolution rates.

Finally, it remains that despite accounting for surface area, the tabulated molar flux grows drastically from 10mM to 15mM and there is little explanation for why this discontinuity, if real, exists. It is possible that the dissolution rate observed is being affected by a switch between a kinetic and transport control process further compounded by the difference in the initial surface area of the electrode but this seems unlikely given the cyclic voltammetry results. Further investigation is required before a more definitive conclusion can be made.

3.2 PEMFC Dissolution

Figure 5 plots the dissolved platinum content as measured by UV-Vis spectrometer against time for both untested and cycled PEMFC materials. Fluctuations in the results are likely due to minor experimental error in this study, rather than changes in Pt concentration. For both sets of materials a clear trend between iodide concentration and dissolution rate is apparent with 0 mM samples containing significantly lower Pt content than all other conditions. Furthermore experiments with additional iodine content all showed very similar behaviour with increasing concentrations leading to more rapid dissolution; however increasing iodine concentration above 5 mM only led to incremental changes. This is consistent with the EQCM results shown in Figure 3A. For the untested materials the leaching process was able to achieve near total dissolution after approximately 20 minutes. Additionally the final dissolved Pt concentration was similar for each experiment with added iodine, indicating the dissolution process for 0 mM may have been oxidant limited. Furthermore because the

materials were leached without being subjected to destructive testing protocol it is probable the platinum was present in an idealized form, sub 5 nm nanoparticles decorating the electrode surface, which would contribute favourably to the observed dissolution rates.



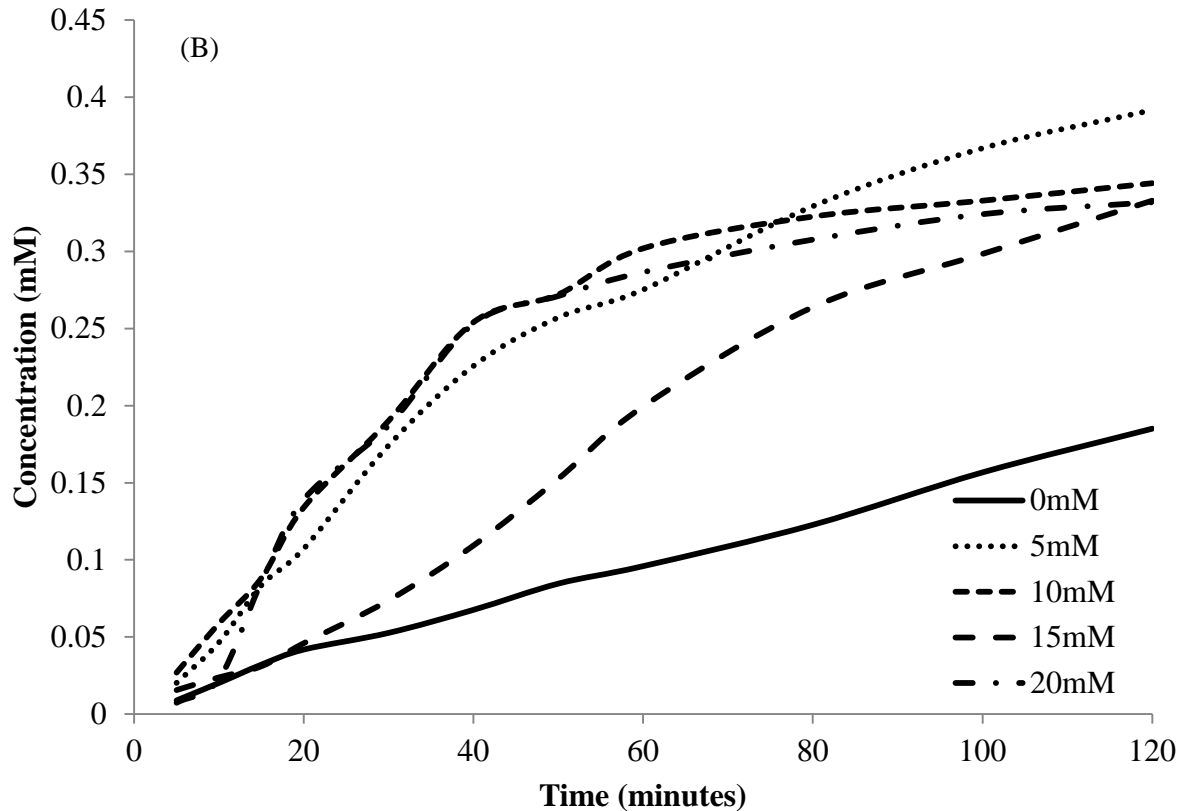


Figure 5. (A) Dissolved platinum concentration in 4M KI from untested PEMFC material which clearly shows trend indicating additional iodine is required to achieve near total metal value recovery. (B) Dissolved platinum concentration in 4M KI from cycled PEMFC materials which shows a similar trend to the untested materials but on a significantly longer timescale to achieve similar concentrations.

While the cycled materials exhibit the same trends as the untested samples, dissolved Pt content rises at a much slower rate for the cycled samples, achieving near complete dissolution after 60 minutes. This delay is most likely due to physical changes caused by the testing protocol used, and suggests that future investigation should be targeted toward improving leach rate rather than yield. The exact source of the difference is unclear though nanoparticle sintering, oxidation of the carbon support leading to restricted pore diameters, and subsurface particles are believed to be the most likely cause. In addition while increasing reactor iodine concentration led to more effective Pt dissolution, the cycled material leached with 15 mM iodine shows markedly inferior results to the 10 and 20 mM experiments, most likely caused by localized variations in the PEMFC tested.

3.2.1 ICP results

Table 2 lists the residual platinum content from the leached materials as determined by aqua regia digestion. The residual content is calculated by dividing measured platinum concentration the total mass of material digested. By comparing calculated values of the leached materials to the control samples, it can be shown that the leaching process removed 42.7-98.7% of Pt from the untested samples and 67.2-96.7% of Pt from the cycled samples during the 120 minute leaching process. These results are in good agreement with those obtained from UV-Vis spectroscopy, and indicate increasing iodine concentration in solution improves Pt leaching in 4M KI; however the data suggests a threshold iodine concentration is required to achieve near total recovery and more concentrated solutions only provide incremental benefit. For the samples used in this work a concentration of 5 mM iodine was sufficient to remove approximately 93% of the platinum present in the untested samples, but that value could differ for other materials.

Table 2. Platinum Concentration in Solution as Determined by ICP

Iodine Concentration (mM)	Mass (g)	Reactor Concentration (PPM)	PPM (Platinum) / g (Material)	Residual
Standard	0.106	150.2	1417.0	--
0	0.101	82	811.9	57.3%
5	0.091	8.6	94.5	6.7%
10	0.078	5	64.1	4.5%
15	0.083	6.4	77.1	5.4%
20	0.079	1.4	17.7	1.3%
Standard	0.096	32.8	341.7	--
0	0.419	47	112.2	32.8%
5	0.372	10.4	28.0	8.2%
10	0.362	10	27.6	8.1%
15	0.344	20.8	60.5	17.7%
20	0.372	4.2	11.3	3.3%

3.2.2 XPS results

XPS analysis of the samples show that the materials go through significant chemical changes during both cycling and leaching protocols. Survey scans for the control samples can be seen in Figure 6, and the atomic weight percentages of 4 elements, carbon, oxygen, fluorine, and platinum, are listed for each sample in Table 3. Comparing the two control samples it is clear the cycling protocol used to test the cells has caused a significant reduction in the fluorine content, suggesting breakdown of the ion-exchange membrane, as well as removing platinum from the surface. These two changes are believed to be the principal causes for the reduced Pt leach kinetics. Additionally because both sets of experiments achieved comparable dissolved platinum concentrations it has been assumed the total platinum flushed from the system because of the testing protocol was minimal. Instead it is thought platinum instead migrated toward the membrane or gas diffusion layers, outside of the 10 nm sampling depth. This hypothesis is supported by the presence of detectable platinum on the cycled 0 mM sample, suggesting the solution provided a sufficiently large chemical gradient to bring platinum within the XPS sampling depth, but insufficient to fully dissolve the metal. The KI leaching process also alters the elemental composition of the samples, most notably by increasing oxygen content for all leached samples, though it is probable this change occurred during the washing process to remove excess salt from the samples rather than during the leaching process itself. The C-F ratio changes for each leached sample, but the trends are reversed for the untested and cycled samples with fluorine content decreasing for the untested samples, and carbon decreasing for the cycled materials. Overall the leached samples have similar elemental compositions showing the recovery process causes significant chemical alterations to the target materials.

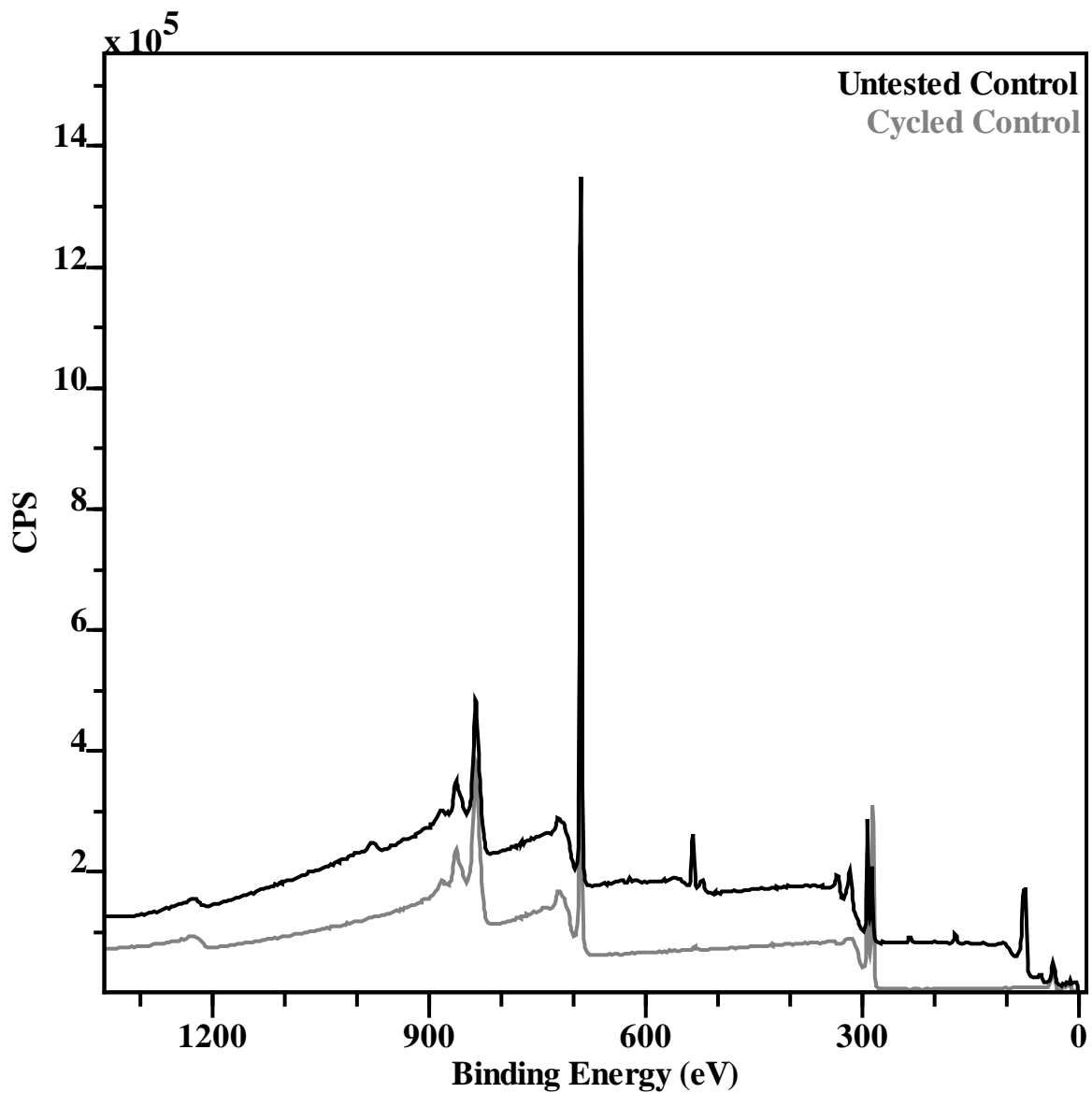


Figure 6. Survey spectra for the untested (black) and cycled (grey) PEMFC control materials. Several chemical changes have occurred during the cycling protocol, most notably the absence of a Pt 4f peak in the cycled material, indicating the metal was undetectable within the instruments sampling depth.

Table 3. Atomic Weight Percentages for Detected Elements

Sample	C%	F%	O%	Pt%
MEA Control	44.6	48.6	4.8	2.0
MEA 0mM	62.9	27.0	9.1	1.0
MEA 5mM	53.8	38.9	7.3	0.0
MEA 10mM	52.5	39.5	8.0	0.0
MEA 15mM	55.9	35.0	9.0	0.1
MEA 20mM	58.6	33.1	8.3	0.0
AST Control	59.8	39.9	0.4	0.0
AST 0mM	56.5	33.5	9.5	0.5
AST 5mM	57.7	35.0	7.2	0.0
AST 10mM	50.4	39.9	9.6	0.1
AST 15mM	48.3	45.9	5.8	0.0
AST 20mM	54.0	39.8	6.1	0.0

4. Conclusions

Platinum recovery from target substrates was shown to be feasible using 4M KI solutions heated to 90°C. By monitoring the mass loss of Pt black through EQCM measurements a clear affect between iodine concentration and dissolution rate was observed. This can be accounted for by transport limitations in the cases of very low oxidant concentration and limitation due to film build up at higher concentrations. Additionally the dissolution process was shown to occur spontaneously with the rate being determined by the electrode's chemically accessible surface area. Through cyclic voltammetric scans and application of Faraday's law of electrolysis it was shown that the principal reaction which would occur during electrowinning procedures is the formation of iodine / triiodide, not platinum dissolution, making direct electrochemical methods ineffective. A practical application of the process through recovery of platinum from PEMFCs showed excellent potential; for both untested and EOL materials more than 95% of the platinum content was removed after 120 minutes. As with the platinum black electrodes, increasing iodine concentration improved recovery rates and yields; however, the necessary iodine concentration is likely sample

dependent with concentrations above this value providing only minor improvements to dissolution kinetics.

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Data Access Management

Due to confidentiality agreements with research collaborators, supporting data can only be made available to bona fide researchers subject to a non-disclosure agreement. Details of the data and how to request access are available at Lancaster University research portal:

<http://dx.doi.org/10.17635/lancaster/researchdata/19>.

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