

Recovery of platinum group metal value via potassium iodide leaching



Anant Patel, Richard Dawson *

Engineering Department, Faculty of Science and Technology, Lancaster University, Lancaster, LA1 4YW, United Kingdom

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ABSTRACT

Platinum recovery from secondary sources such as end-of-life polymer electrolyte fuel cells (PEMFCs) via electro-winning and chemical dissolution in deoxygenated 4 M potassium iodide with varying added iodine content was investigated. Previous research in this field has shown that complete platinum recovery from model systems is possible, but further study was necessary to determine the process viability with Pt containing devices. The work presented here investigated the leach rate of platinum black deposited on an electrochemical quartz crystal microbalance (EQCM) as well as the effective recovery of Pt from untested and end-of-life polymer electrolyte membrane fuel cells. Platinum black dissolution rates were found to be dependent on added iodine content, with higher concentrations accelerating the reaction. Platinum recovery from leached materials, as determined by aqua regia digestion, was found to be 98.7% and 96.7% for untested and end-of-life PEMFCs, respectively. Results indicate that higher iodine concentrations continuously improved recovery efficiency, but increasing iodine concentration above 5 mM resulted in comparatively minor improvements.

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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 cell estimates which state that 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 (Proietti et al., 2011; Serov et al., 2012; Wee et al., 2007; Wilson and Gottesfeld, 1992). Global demand for platinum group metals (PGMs) is anticipated to continue to increase whilst supply from refineries is likely to remain stagnant putting additional pressure to effectively use the metal as well as incentivising Pt metal values 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 (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 that it was possible to recover over 90% of PGMs with a chlorination process from spent automotive catalytic converters (Kim et al., 2000). Whilst 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; Benson et al., 2000; Conesa and Font, 2001; Samms et al., 1996). Finally hydrometallurgical processes are

* Corresponding author at: D11 Engineering Building, Lancaster University, Bailrigg, Lancaster LA1 4YW, United Kingdom.

E-mail address: R.Dawson@lancaster.ac.uk (R. Dawson).

the most diverse, but can be generally characterised by leaching Pt in oxidising solutions. Whilst capable of attaining yields in excess of 95% these processes can be improved upon significantly (Angelidis, 2001; Angelidis and Skouraki, 1996; Bautista et al., 1988; Bonucci and Parker, 1984; Kim et al., 1994; Tyson and Bautista, 1987; Woo et al., 2000).

Most hydrometallurgical methods reported require extremely aggressive conditions immersing the spent material in highly acidic and oxidising chloride containing media such as aqua regia (Baghalha et al., 2009; Barakat and Mahmoud, 2004; Jimenez de Aberasturi et al., 2011; Schreier and Edtmaier, 2003). 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 that the rate is limited by the ratio of aqua regia volume to solid content whilst 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; Chen and Huang, 2006; Han and Meng, 1994, 1996). 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 (Chen and Huang, 2006; Han and Meng, 1996).

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 0.12–0.48 M iodine–iodide solutions at temperatures between 25 and 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 that higher triiodide concentrations increased Pd and Pt dissolution rates (Dawson and Kelsall, 2007, 2013). By immersing a Pt black flag electrode in neutral 4 M 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 microbalance (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, 1972; Ilic et al., 2000). The crystals used in this study were manufactured for use at 90 °C, and have a resonant frequency of 5 MHz. 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 min, 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 0.072 M Chloroplatinic acid solution and a saturated calomel reference electrode (SCE) was placed in 1 M 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 s resulting in a visually even Pt black deposit, and the mass of the electrodes was between 100 and 275 µg. Fig. 1 shows a representative SEM micrograph of the electrode surface.

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 0.5 M H₂SO₄ solution and 5 cyclic voltammetric sweeps between 0 and 1.5 V (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 µC, the charge necessary to form a 1 cm² 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 77 cm².

2.2. Platinum black dissolution

Potassium iodide (ReagentPlus®) was supplied by Sigma-Aldrich, and was used to produce 0.15 dm³ of 4 M KI solutions in 18.2 MΩ quality DI water. For some experiments iodine was added to the reaction vessel solution by using a 1 N iodine solution (Sigma-Aldrich 319007–100 mL) 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.

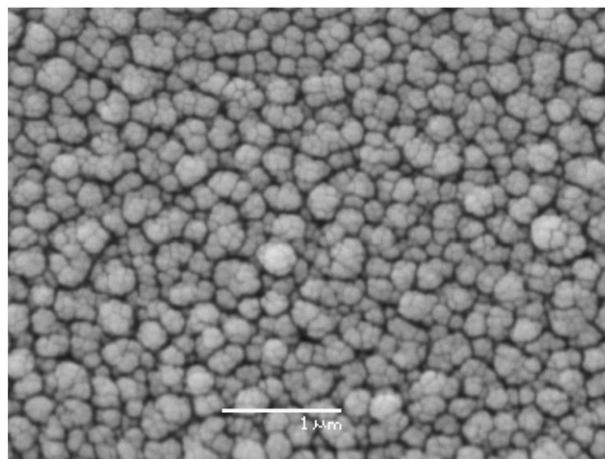


Fig. 1. SEM micrograph of Pt black electrode (50,000 times magnification, 15 kV, JEOL 5600 SEM). Image courtesy of Dr. Nigel Fullwood (n.fullwood@lancaster.ac.uk).

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