Life Cycle Analysis of the use of Platinum as a Catalyst for Proton Exchange Membrane Fuel Cells.

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1 Introduction

As the world tackles the issue of climate change, many countries are pursuing the switch from a fossil fuel driven economy, to a renewable energy driven economy with the goal of vastly reducing CO2 emissions. However, renewable energy that is cheap and efficient enough to replace fossil fuels has so far proven elusive and is still some distance away in the future. As a result, there has been great effort in developing technologies that instead reduce the impact of burning fossil fuels. Carbon Capture & Storage (CCS) technologies play a major role in reducing the net CO2 emissions released when burning hydrocarbons and allow us to bridge the gap between fossil fuels and renewable energy. Although CCS technologies show great promise in solving many of the issues related to burning fossil fuels for large scale power generation, a large proportion of CO2 emissions come from transportation vehicles which cannot be easily captured with CCS technology. The US Environmental Protection Agency estimates that passenger vehicles emit an average of 4.6tCO_2/yr (EPA, (2018)). Data from Statistica shows that as of 2015, approximately 1.25 billion vehicles were in use worldwide (Wagner.I, (2018)) which is a projected 7BtCO_2/yr of uncapturable CO_2.

The most attractive solution to reducing vehicle GHGEs is to use an alternative mode of power that relies on 'clean' energy, rather than fossil fuels, to completely eliminate GHGEs. Battery powered electric vehicles (BPEVs) are one solution, but BPEVs have many problems, the most prominent issues being their range and recharge time. These issues, as well as economics, have been a large obstacle to the commercial success of BPEVs. A promising alternative to BPEVs is to power vehicles with proton exchange membrane fuel cells (PEMFCs) which are fuelled with hydrogen. Not only do PEMFCs eliminate GHGEs completely, but their performance, refuelling, and range are comparable to internal combustion engine vehicles (ICEVs); and while it is true that hydrogen is not a primary source of energy, meaning the fuel has to be generated using primary sources of energy such as fossil fuels, the benefit is that hydrogen fuel allows GHGEs to be localised at large fuel generating facilities where CCS technologies can be used.

Hydrogen powered electric vehicles (HPEVs) are not without their flaws though. The most popular material used to ionise the hydrogen and oxygen is platinum because of its stability, activity, and selectivity. In fact, platinum is currently considered irreplaceable as it is the only element that can withstand degradation in the harsh environments at the anode and cathode. However, platinum is a rare an expensive metal that has the potential to negate the environmental and economic benefits of PEMFCs (platinum makes up 91% of the cost and 90% of the environmental impact of the membrane electrode assembly (MEA) (Duclos.L.*et.al*, (2020))) and is proving to be a major obstacle in the commercialisation of PEMFCs. Therefore, it is vital that life cycle assessments of platinum are performed in order to understand where the environmental and economic hotspots are so that they can be improved. It is also crucially important to understand the potential social impacts of any new technology.

2 Platinum as an Electro-catalyst

Platinum is an irreplaceable material for use in PEMFCs as a catalyst due to its almost ideal electrochemical properties. Platinum adsorbs hydrogen and is able to break the H-H bond, yet the H-Pt bond is not too strong so that the hydrogen atoms cannot be liberated of their electrons. This allows for very high fuel cell efficiency (Doris.S, (2014)). Unfortunately, platinum is an incredibly expensive material and is a severe environmental burden due to the shear amount of ore needed to extract it (Pt concentration in ore typically 3-5Ptg/t (Thethwayo.B.P, (2018))). Therefore, since there is currently no substitute for platinum, there is an urgency to find ways to reduce its usage during manufacturing of PEMFCs and also to recover it from spent fuel cells.

3 LCA Scope

The aim is to identify only the major environmental hotspots in the life cycle of platinum as a catalyst in a PEMFC. Environmental markers are quantified where possible, (likely) waste is identified, and social and environmental impacts are investigated. The goal is to build a reasonably accurate, but not precise, understanding of the life cycle. As such, since the energy inputs for manufacturing and (the leading candidate for) recycling are thought to be negligible in comparison with extracting new platinum (SRENSEN.B, (-)), they are omitted; only the (likely) wastes have been identified for recycling.

4 Platinum Extraction & Refining

Platinum is part of a group of noble metals referred to as platinum-group metals (PGM). The six platinum-group metals are often found together due to their similar material properties and are only found in mineable quantities in a handful of places around the world. Most platinum is found in South Africa. In fact, the South African reserves account for approximately 88% of the global platinum group metals (PGMs) and approximately 80% of all new platinum (Platinum.A.A, (-)). The majority of platinum is found in arsenide minerals $PtAs_2$ (Sperrylite) and $PtAs_2S_2$ (Unnamed). Some is also found in sulphides (Pt,Pd,Ni)S (Cooperite) where Ni and Pd may, or may not, be present.

4.1 Typical Platinum Extraction Process

A paper produced by (Thethwayo.B.M, (2018)) contains detailed information of the typical platinum extraction and refining process in South Africa and the composition of the material inputs and outputs at each step; a summary is given here.

1. **Ore Comminution.** Extracted PGM ores are ground and milled into fine particles.
2. **Floatation Separation.** Fines are submerged in an aqueous solution. Air bubbles attach to hydrophobic PGM-rich fines and float to the surface. The PGM concentrate froth is skimmed off.
3. **Smelting.** The concentrate is smelted in an electric smelter where the silicates and sulphides are separated. The PGM sulphide matte is tapped from the smelter.
4. **Converter.** The converter converts iron sulphide into iron oxide and sulphur into sulphur dioxide and removes them from the matte.
5. **Base Metal Refinery.** The converter matte is leached of base metals such as copper and nickel.
6. **Precious Metal refinery.** The PGMs are separated into individual elements using solvent and precipitation methods.

4.2 Waste Materials

Tailings. According to (Mohamed.S.*et.al*, (-)), 'PGM tailings typically contain four major elements (11% Al_2O_3; 12% MgO; 22% Fe_2O_3; 34% Cr_2O_3), with lesser amounts of SiO_2 (18%) and CaO (2%)'. These tailings are produced at the floatation, smelting, and converting steps.

Gangue Minerals. Chromite spinel $FeCr_2O_2$; Pryoxenes (Mg, Fe)SiO_3-Ca(Mg,Fe)SiO_6; Olvine $(Mg, Fe)_2SiO_4$; Plagioclase/feldspar $NaAlSi_3O_8$-$CaAl_2Si_2O_8$; Quartz SiO_2; Haematite FeO_3. Gangue minerals are removed at the smelting stage (Thethwayo.B.M, (2018)).

Reagents/ Solvents. Xanthate and dithophosphate collectors are typical reagents for flotation separation. Nitric and hydrochloric acid, along with ammonium chloride and used to refine the PGMs from the base metal refinery to recover the pure platinum (Bell.T, (2019)).

4.3 Environmental Effects of Waste

Tailings. These make up the bulk of the mining waste. Tailings are disposed of in two ways: tailings piles and tailing ponds. Both methods have the potential to generate acid water which pollutes the surrounding environment.

- **Tailing piles.** These are large deposits of dry, loose rock and dust comparable in size to a hill. They are unstable and prone to landslides, however, they are preferred because they eliminate many of the problems associated with tailing ponds. One major concern with dry stacking is dust. Tailing dust is often toxic and can be transported into nearby communities by the wind and can lead to serious health issues over time.
- **Tailing ponds.** These are large reservoirs of slurry typically held back by a dam. The advantage of a tailings pond is it does not suffer from dust pollution and it is cheaper then dry stacking. However, the water in the slurry has the potential to leach toxic substances from the pond into the environment and possibly contaminate the local water table. There have also been many tailing dam failures where millions of tons of slurry have been suddenly released and caused environmental devastation to the surrounding area, also flattening nearby communities in some cases.

  Large quantities of fresh water is often used to create the slurry ponds. In regions where freshwater is scarce, such as South Africa, high water consumption can have a large impact on the surrounding communities.

Reagents/ Solvents. Ammonium chloride, and Xanthate & dithiophosphate collectors are toxic to aquatic life if released into water sources. Nitric acid is extremely corrosive but degrades quickly and does not build up in the environment (PHE, (2017)). Hydrochloric acid does affect the environment and can acidify soils which may change the local ecology (HA, (2020)).

4.4 Other Impacts of Platinum Extraction

An article from Bloomberg (Burkhardt.P, (2015)) highlights some of the socio-economic issues surrounding the platinum mining industry. There has been long civil unrest between mining unions and platinum mining companies in South Africa, often breaking out into strikes and violence. The unions demand higher wages for the workers, but the mining companies say it is not possible due to a combination of rising electricity costs, suppressed platinum market prices, lower demand due to increased platinum recycling, and higher grade ore reserves being depleted. Falling platinum prices over the last decades have forced many mine closures and large redundancies in a country which already struggles with high unemployment. These issues make it difficult to predict the long term availability and price of new platinum. It is also difficult to predict whether the commercialisation of HPEVs would positively or negatively affect Africa, but it is thought that Africa would experience a net benefit due to increased demand.

4.5 Platinum Extraction Data.

The top 4 platinum mining companies account for about 67% of the new platinum. The data in Table 1 is taken from two sustainability reports from two of the largest platinum mining companies, Anglo-American Platinum (Platinum.A.A, (2019b)), and Lonmin (Lonmin, (2018)). Anglo-American Platinum accounts for around 40% of new platinum (2.4 million ounces) and Lonmin account for around 10% (¿ 650,000 ounces) (Bell.T, (2019b)). Both companies are operating primarily in South Africa, so the information in their sustainability reports are thought to be representative of the industry.

N.B. Where direct estimates per Pt.oz are not available, annual quantities are normalised by annual production/sales of platinum..

Environmental Markers			
	Ang.American	Lonmin	Average
Energy Usage (Gj)	3.84	4.86	4.35
Water Consumption (m^3)	4.81	6.23	5.52
GHGEs (tCO_2.)	0.825	2.36	1.60
Waste (Per Pt.oz)			
Non-Mineral (Kg)	1.5	154	-
General (Kg)	-	12	-
Total Hazardous (Kg)	1	101	-
Hazardous $CaSO_3$ (Kg)	-	67	-
Precious Metal Effluent (Kg)	-	31	-
Oils/Chemicals (Kg)	-	1.9	-

Table 1: Environmental Markers for Platinum Extraction. **N.B** Waste numbers may not be comparable, and are assumed non-comparable, due to possible differences in waste classification.

5 End-of-Life Platinum Recovery.

Since platinum extraction is such an economic and environmental burden, even a relatively inefficient platinum recovery process can provide large reductions in the overall impacts. However, platinum recovery from PEMFCs is still largely academic, according to (Duclos.L*et.al*, (2016)), which contains an extensive literature review on platinum recovery catalysts used in automotive vehicles, mentions that 'regarding the Pt recycling from spent PEM fuel cells very few studies are currently available'. The paper also introduces the concept of a novel MEA recycling process that proposes a room temperature hydro-metallurgical process to recover over 75% of the platinum from the MEA in the form of an ammonium salt $(NH_4)_2PtCl_6$.

The process is further developed in a later paper written by the group (Duclos.L*et.al*, (2020)). This paper finds that an ionic exchange resin method to recover the platinum is the most environmentally friendly option and concludes that 'the feasibility of closed loop Pt/C catalyst recycling has successfully been proven'.

5.1 Ionic Exchange Method

The information in (Duclos.L*et.al*, (2016)) is used to outline the process.

1. **Leaching.** The Pt/C or MEA are leached using HCL and an oxidant; either H_2O_2 or HNO_3. The solution is then filtered to remove the carbon powder, leaving the $PtCl_6^{2-}$ in the leachates.
2. **Resin Sorption & Desorption.** The platinum is then recovered from the leachates using resin ion exchange; the resin absorbs the $PtCl_6^{2-}$. The Platinum-rich resin is then stripped with a $NaOH$ solution.
3. **Platinum Precipitation.** Ammonium chloride is used to treat the remaining solution and precipitate the platinum in $(NaH_4)_2PtCl_6$ form.

5.1.1 Likely Wastes and Other Impacts

Since the process is done at ambient temperature, the main environmental impact is likely to be from the hazardous chemical sewage. The hazardous chemical sewage is assumed to be the leachates (after leaching) and used resin stripping agent (after precipitation).

6 Analysis Limitations

The report is limited in its scope and only aims to provide a very rough picture of the most important aspects of the platinum life cycle. It is believed that the main issues of using platinum as a catalyst have been addressed adequately to build a reasonably accurate evaluation of its life cycle. The decision to omit the analysis of the platinum catalyst manufacturing was because it is assumed the energy inputs are small and would not change the main message of the analysis. Also omitted were the energy inputs for the recycling process, for the same reason.

While types of waste could be identified, it was difficult to quantify them with any amount of certainty, and so specific wastes were only highlighted. Further research is needed to better understand the true environmental impacts of the hazardous wastes created.

7 Analysis Findings

The extraction and purification of new platinum is believed to be, by far, the biggest contributor to the economic and environmental impact of using the material as an electro-catalyst in PEMFCs. Recycling can help to reduce the negative impacts of platinum extraction greatly. The promise of a low energy closed loop recycling process to recover the majority of platinum from spent fuel cells allows for 75%+ of the platinum to be recovered. Essentially, this allows the need for extracting new platinum to be cut by 75%, and thus, the energy usage, GHG emissions, and other environmental impacts tied to the extraction of platinum are reduced by approximately this amount too. Further reductions and improvements in platinum usage efficiency can be found by alloying; platinum alloys for ultra-low platinum loading catalysts aims to also reduce the amount of platinum needed for PEMFCs (Chong.L.*et.al*, (2018)).

While platinum is currently a large burden of a PEMFC's life cycle, future research into improvements, in both manufacture of catalysts and Pt recovery from MEAs, do have the potential to make HPEVs economically competitive and environmentally superior to conventional ICEVs.

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