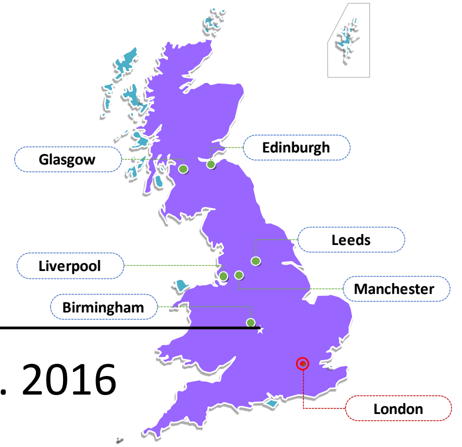
Critical Resource Management for Fuel Cells & Electrolysers

Dr Michelle Lynch, CChem FRSC

Hydrogen Tech Expo, Telford

30th March 2023

Enabled Future



Inc. 2016

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Key Clients

MENNTA ENERGY SOLUTIONS
exacer catalyst support
Gefn
TCG The Catalyst Group Assessment > Knowledge > Impact
GLG
hensel recycling
European Commission
PRIMARY INSIGHT
NexantECA
ECONIC TURNING CO_2 INTO ENDLESS POTENTIAL
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Nickel Institute knowledge for a brighter future
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CCD PARTNERS
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Enabled Future Limited Business Proposition

Optimising Technology Portfolios

Enabled Catalysts

Enabled Circular

Enabled Power

Enabled Metals

Consulting – Training – Multiclient Reporting
Thought Leadership – Industry Tracking

New Membership Programme As Of November 2022

Contents

- Platinum Group Metals Used for Fuel Cells & Electrolysers
- Platinum Substitution with Palladium
- Fuel Cell Recycling
- Take Home Messages

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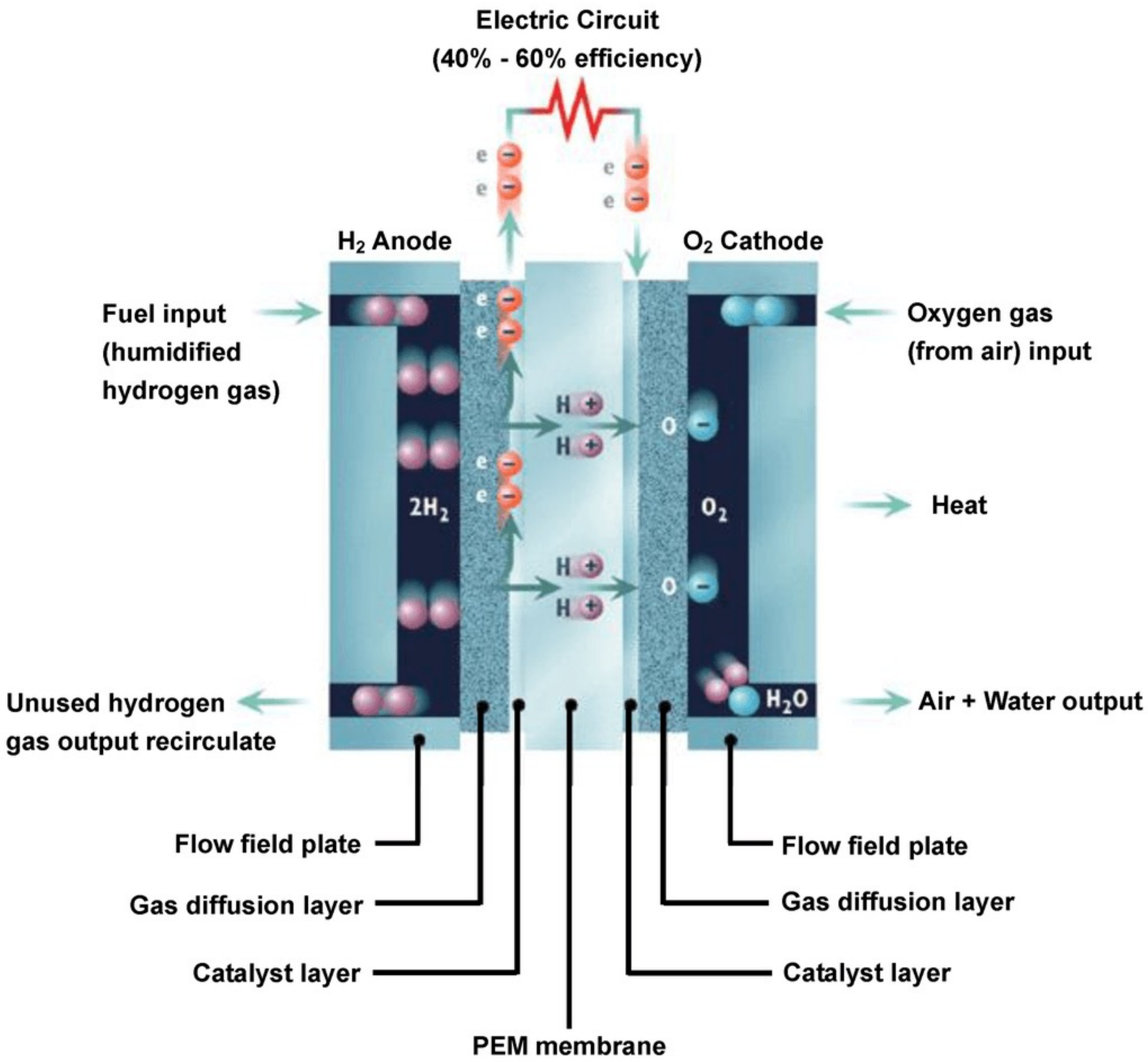
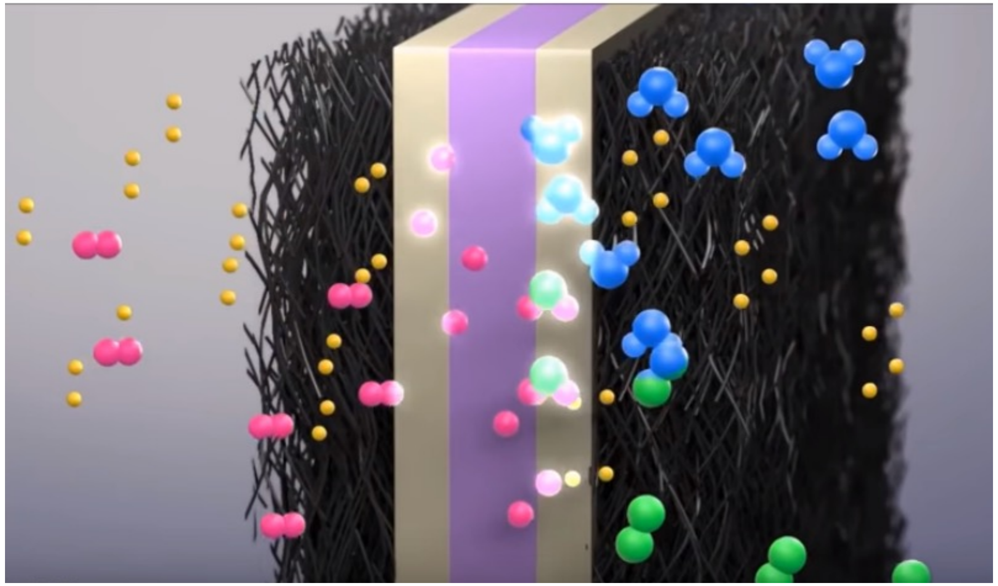
Platinum for PEMFCs



Source: http://www.fuelcellstore.com/blog-section/fuel-cell-characterization



Source: https://www.youtube.com/watch?v=GtsWhLtNc5E

2nd Generation Toyota Mirai

128 kW PEMFC stack

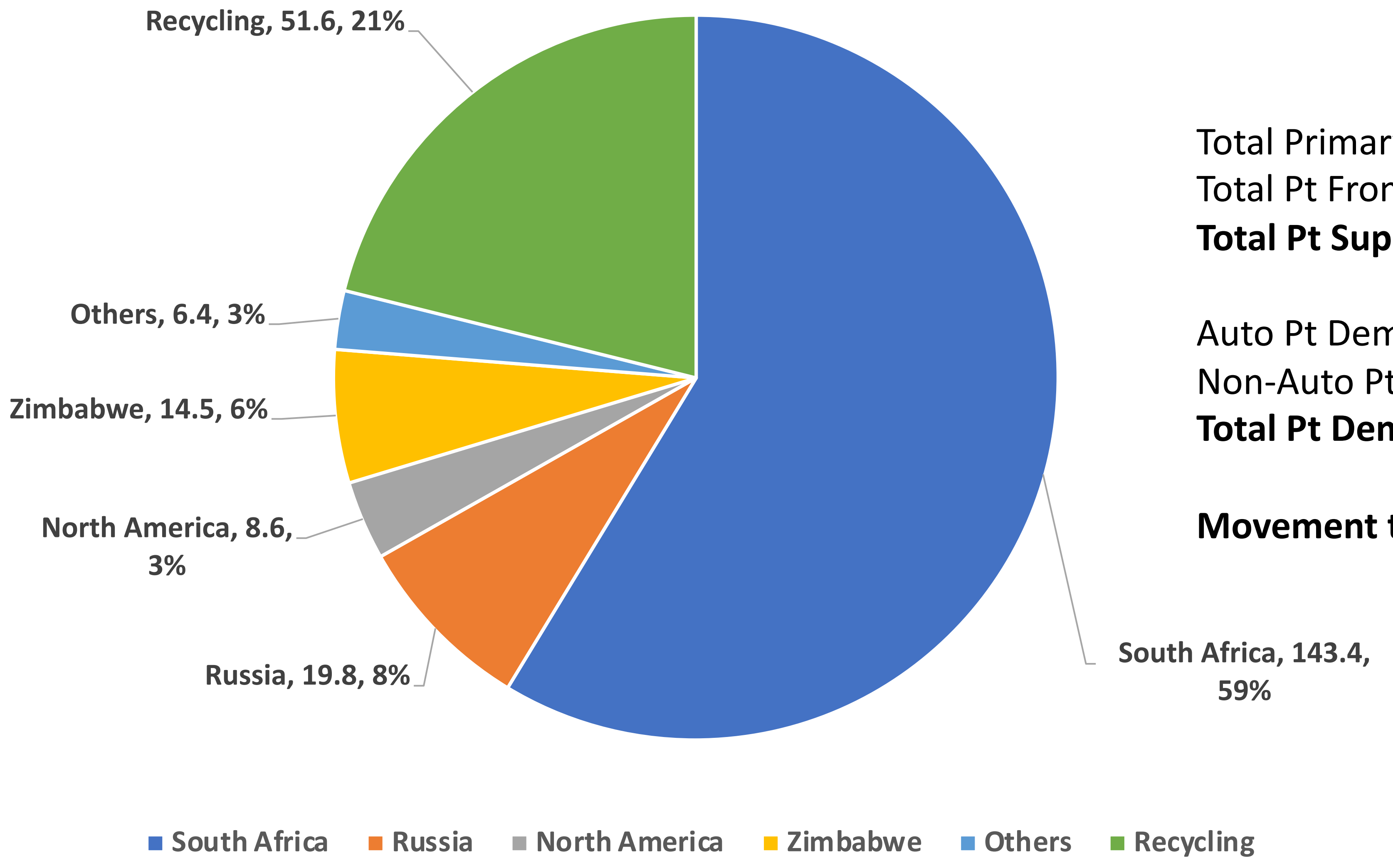
330 Cells connected in series

Weight - 52 kg

PtCo alloy FC catalyst – Pt/car ~15 g (Source: WPIC)

Titanium 3D fine-mesh flow field cathode

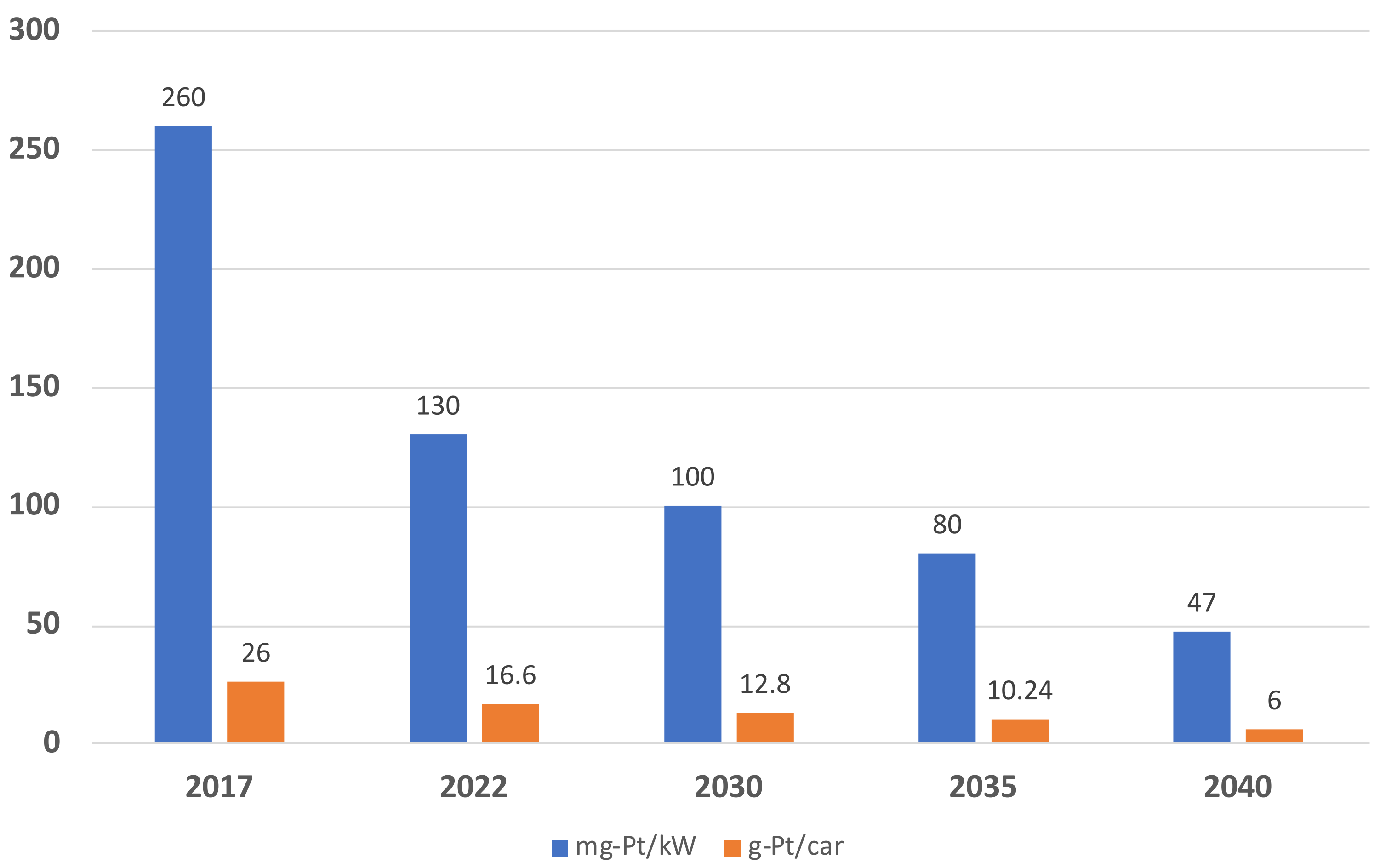
Platinum Supply/Demand 2021



Total Primary Pt Supply	= 192.7	tons
Total Pt From Recycling	= 51.6	tons
Total Pt Supply	**= 244.3**	**tons**
Auto Pt Demand	= 73.1	tons
Non-Auto Pt Demand	= 136.9	tons
Total Pt Demand	**= 210.0**	**tons**
Movement to Stocks	**= 34.3**	**tons**

Source: Adapted from Data from Johnson Matthey Platinum Book, May 2022

Thrifting Expectations for Platinum in PEMFC



- Pt levels for PEMFC are still too high for wide scale deployment
- If all current Pt Auto Demand was used for PEMFC – less than 5 million cars could be produced in total.
- However, Pt is also needed for PEMEL, and heavy duty applications so this figure is an overestimate
- It's possible to produce more Pt – but this makes the supply criticality higher
- Fuel cells in transport are however very suited to heavy duty applications – trucks, buses, rail etc as well as energy storage.

Source: CME Group; Toyota Mirai Specifications

Patent Spotlights for Pt Metal Thrifting/Substitution (I)

HYBRID CATALYST SUITABLE FOR USE IN PROTON EXCHANGE MEMBRANE FUEL CELL (Google)
Applicants: UNIV NEW YORK STATE RES FOUND [US] / GINER INC [US] / WO 2022272126 A2

This patent application describes work to develop a novel MEA catalyst with a hybrid formulation. **The support is a Mn-doped zeolitic imidazolate frameworks (ZIFs)** made via an aqueous method on to which nanoparticles of Pt are deposited using impregnation of hexachloroplatinic acid and a cobalt salt, sonicating in an ice-bath, freeze drying and calcining under a forming gas, leaching in perchloric acid, vacuum-drying and heating in argon to give a cubic L12Pt3CO alloy with a 20-40 wt% Pt loading on a MnN4-C catalyst termed the "**Pt Co@HS Mn-N-C hybrid catalyst**". The carbon used can be a **porous graphitic carbon (PGC).**

The catalyst achieved ORR mass activity (MA) of 0.58 A/mgPt and retention of 83.7 % of the initial value after 30,000 accelerated stress test (AST) voltage cycles in an MEA **with low cathode loading of 0.1 mgPt /cm2.***

Also, a power density of 1132 mW cm-2 at 0.67 V. 40 wt% Pt catalysts with PGC supports performed better than those with carbons from TKK and were close to DOE targets for heavy-duty vehicles for 150,000 cycles (25,000 hrs).

The work described is important because the catalyst meets or exceeds US DOE technical targets in the testing performed at a low catalyst loading. Results were promising from Heavy Duty Vehicles (HDV's) which is a sector that can benefit from fuel cell powertrains.

*With a 10 m2 active area – 0.1 mg/cm^2 corresponds to 10 g per fuel cell stack.

Patent Spotlights for Pt Metal Thrifting/Substitution (II)

ELECTRODE CATALYST SLURRY, METHOD FOR PRODUCING THE SAME, CATALYST COATED MEMBRANE, AND FUEL CELL; Current Owner: FAW GROUP; CN113921831B

This patent describes work that aims to provide a **more uniform coating of catalyst on the ionomer membrane in a PEMFC with higher catalyst utilization**. Using a method that involves self-assembly of the catalyst particles and freeze drying.

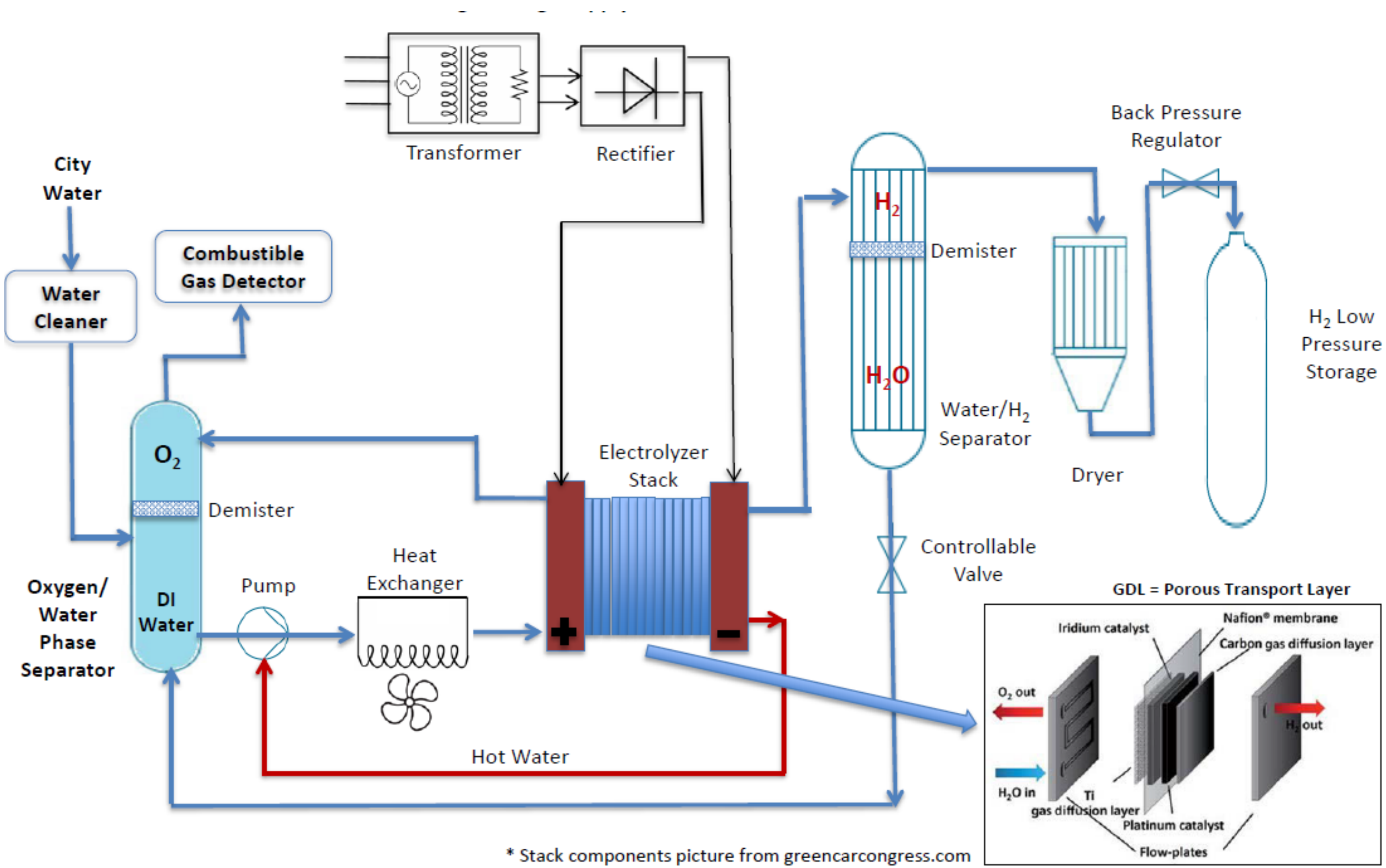
Preparing electrode catalyst slurry: weighing 1g of **Pt-Co on carbon alloy catalyst**, wetting with 0.1g of deionized water, then dropwise adding 5wt% of Nafion solution, Nafion:Catalyst = 2.8:1. 234g of isopropanol is added dropwise added into the ionomer-coated catalyst, the mixture is stirred and mixed uniformly by ice bath and ultrasound, and shearing and dispersion are carried out to prepare electrode catalyst slurry.

The prepared electrode catalyst slurry is sprayed on two sides of a proton exchange membrane at 50 °C by an ultrasonic spraying machine. **The cathode spraying mass is 0.2mg/cm2 The anode spraying mass is 0.03mg/cm 2 (ii**) a Drying under vacuum adsorption condition at 50 deg.C for 2min to obtain CCM.

Carbon paper is put on two sides of the prepared CCM, and hot pressing is carried out for 30s at the temperature of 60 °C/0.1MPa, to form gas diffusion layers and obtain the membrane electrode assembly.

The work described is important because the catalyst layer is more robust and has a lower catalyst loading and higher scarce resource efficiency.

Platinum & Iridium for PEMELs



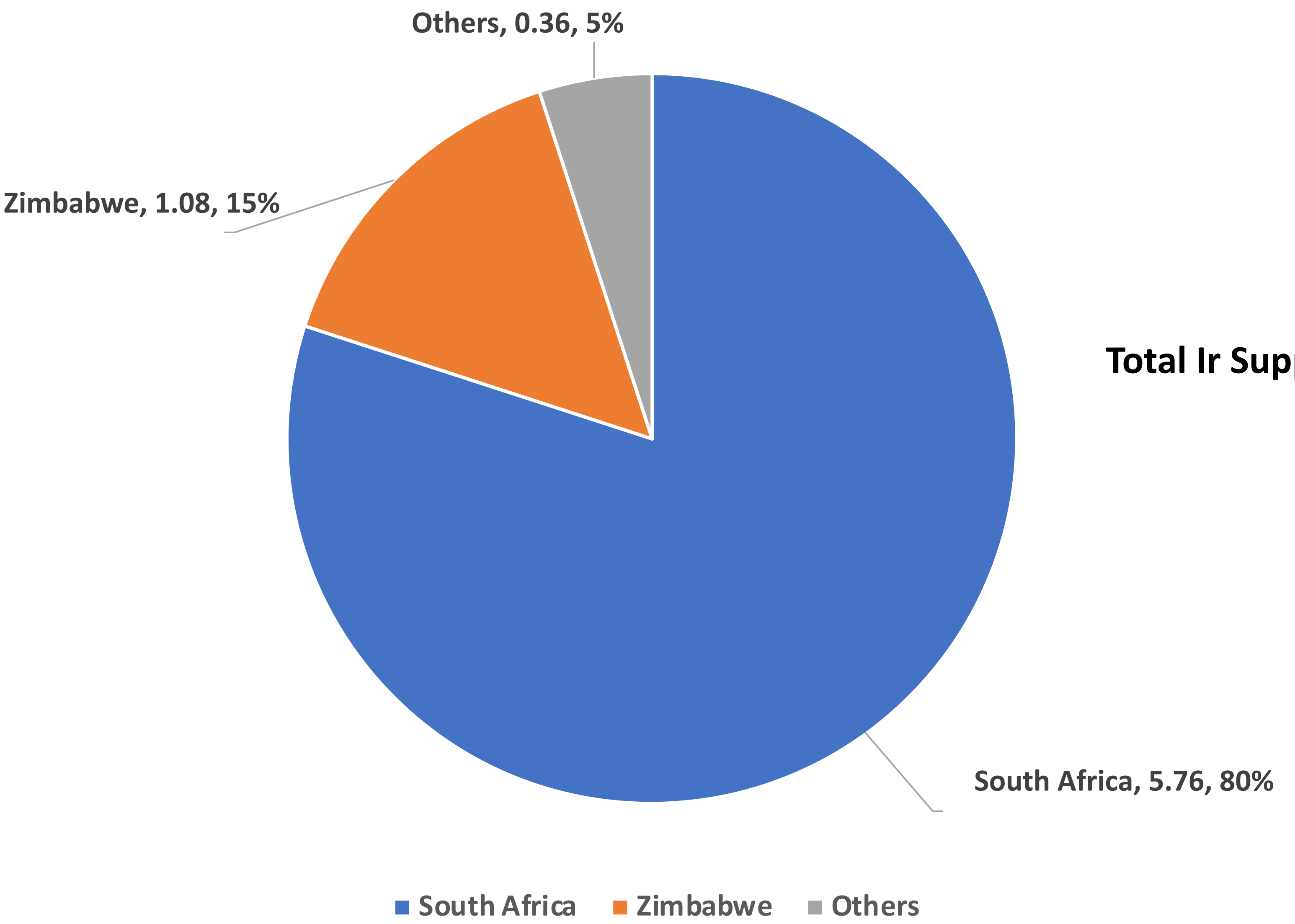
* Stack components picture from greencarcongress.com

In a 3-layer PEMEL cell, different catalysts are coated on each side of the CCM – platinum on the cathode and iridium for the anode.

These can be supplied as 5-layer cells, with the CCM already placed between gas diffusion layers (GDL) acting as current collectors or as a 7-layer cell with two more layers which seal the cell.

Each electrolyser contains several hundred cells in a stack and the stack sits at the heart of the overall hydrogen production plant

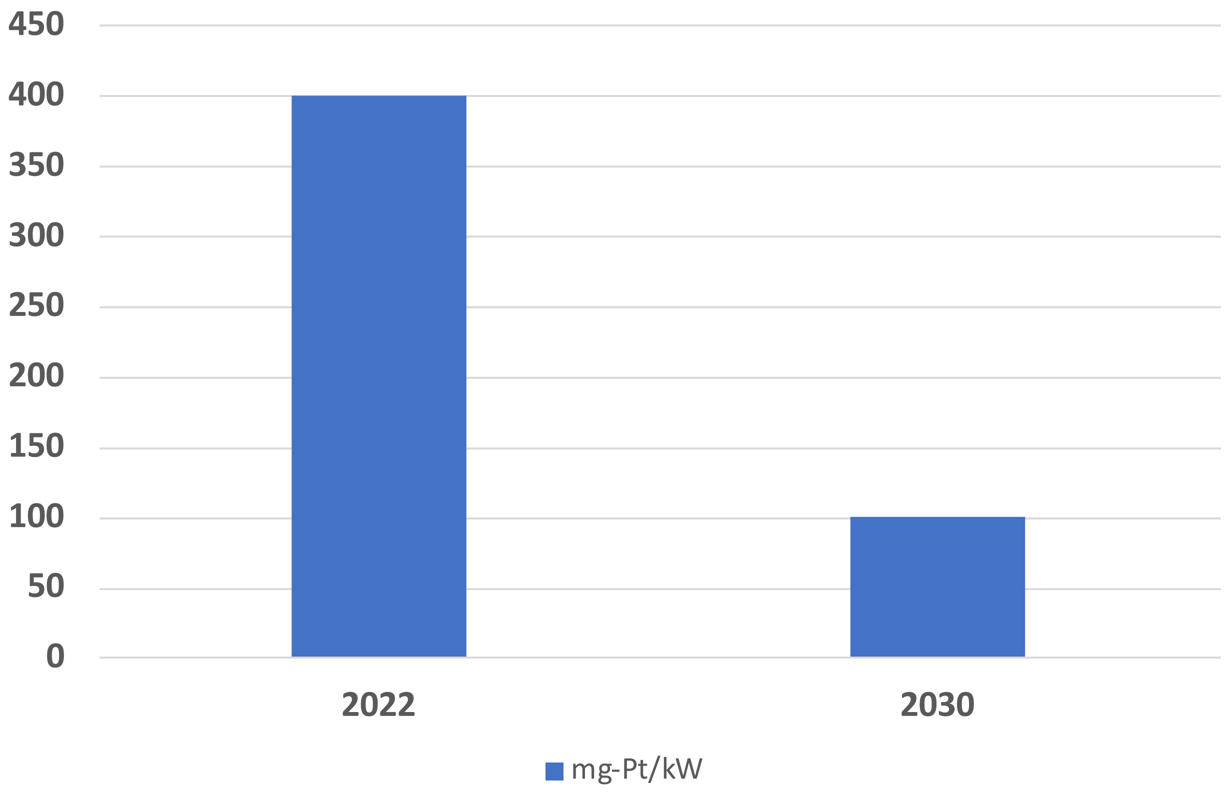
Iridium Supply 2021



Total Ir Supply = 7.2 tons

Source: Based on Gross Demand Data from Johnson Matthey Platinum Book, May 2022 and Heraeus Precious Metal Forecast Report 2022

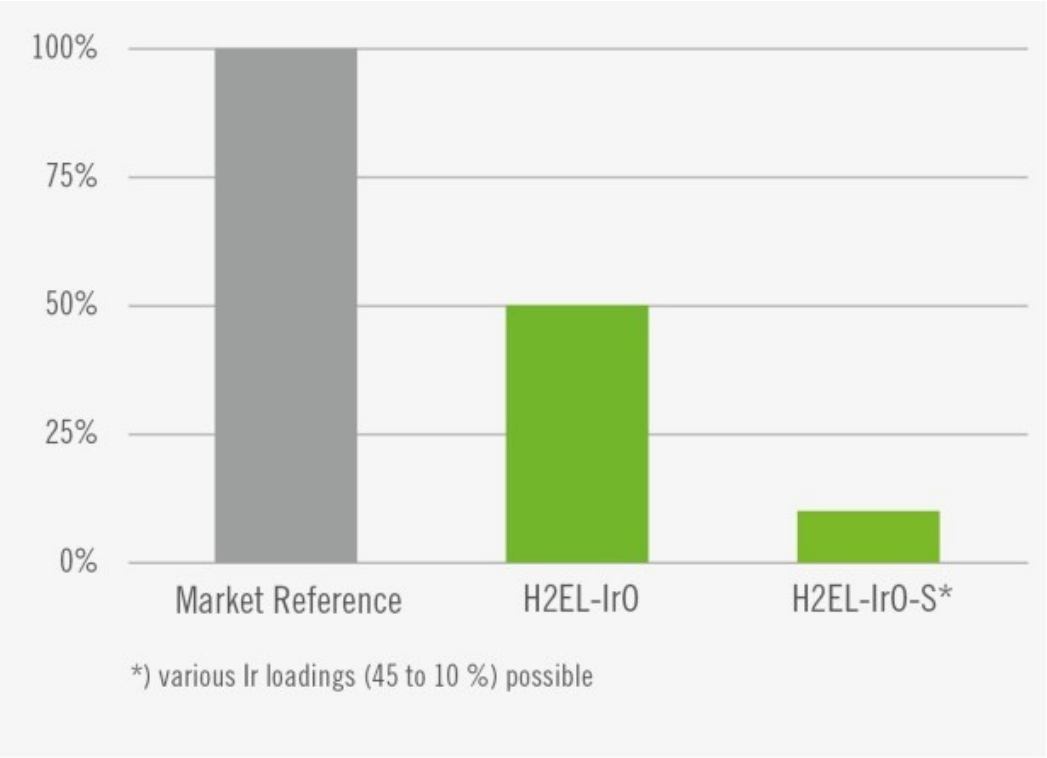
Thrifting Expectations for Iridium in PEMEL



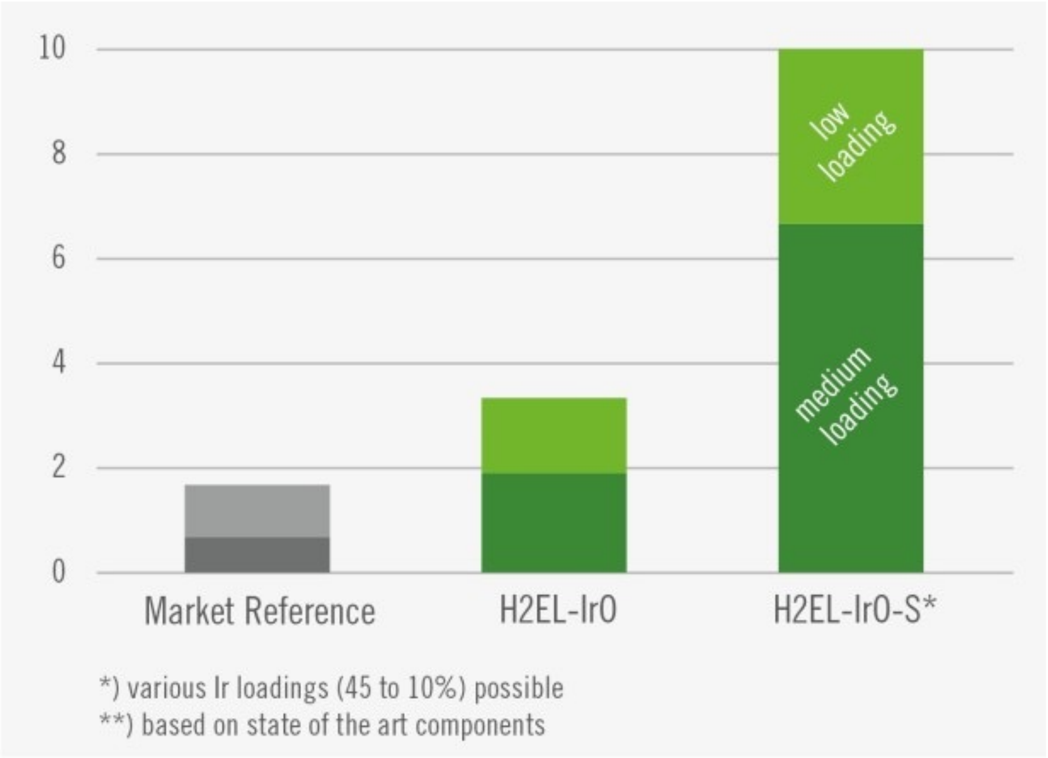
Source: Recycling and thrifting: the answer to the iridium question in electrolyser growth | Johnson Matthey

- Ir is a very “thin metal” with a fraction of the supply of Pt (<3%).
- It has a range of growing applications e.g., in copper foil production for electronics including for LIB; PEMEL electrode catalysts; ballast water treatment as well as traditional uses in chemicals, iridium crucibles production and premium spark plugs.
- Water electrolyser demand is expected to be the only growth area for Ir in 2023 (source: SFA Oxford)
- Over the period critical to scale PEMEL, there is no “relief factor” for Ir coming back from ICE automotive applications which adds to its criticality.
- Thrifting of Ir is a major priority for PEMEL electrocatalysts in order to meet the green hydrogen production targets.

Heraeus Water Electrolysis Catalysts With Lower Ir Loadings



Iridium savings in PEM electrolyzer anode catalyst



PEM electrolyzer capacity (in GW) when using 1 t of Iridium

- H2EL-IrO-S is a supported IrOx material with only 30% of the Ir content. It has a mass activity @1.45 Vcell (iR-free) [A/g] of 570 compared with 86 for unsupported IrOx (H2EL-IrO).
- A next generation material Ir/Ru 30/70 wt% mixed oxide also achieves 400 A/g.

Source: [PEM Electrolysis: Iridium Catalysts for Electrodes Heraeus]

Patent Spotlights for Ir Metal Thrifting/Substitution (I)

Low-iridium electrolyzed water catalyst as well as preparation method and application thereof
Applicants: UNIV OF SCIENCE & TECHNOLOGY OF CHINA/ CN115369422A

This patent application describes **work to prepare a low-iridium catalyst for water electrolysis**. **A silicon oxide composite nanomaterial with an amorphous iridium oxide coating layer** is used as a catalyst for acidic water electrolysis**. Because the IrOx is used as an outer layer coating, the coverage of active sites of the catalyst is effectively reduced, and the IrOx layer can be further converted into crystalline IrOx by subsequent high-temperature calcination**.

The electrocatalyst is prepared by mixing ethyl orthosilicate, ammonia water and ethanol to prepare a nanospherical SiO2 material (D=50-100 nm). Then adding 20 mg of the SiO2 to 10ml DI water, uniformly dispersing by ultrasonic wave, uniformly stirring and mixing with chloroiridic acid and precursor alkaline mixed solution (comprising surfactant), and controlling the mass ratio of Ir:SiO2, carrying out hydrothermal reaction at 2,180 ℃ for 24h; then washing, centrifuging and drying the obtained product to obtain IrOx /SiO2 (Ir:SiO2 =1:2) Testing showed higher catalyst activity than conventional materials.

This work is important because it helps to alleviate the main bottleneck for PEMEL scale-up – Ir consumption, lowers the PEMEL catalyst cost and achieves higher OER catalytic activity and stability.

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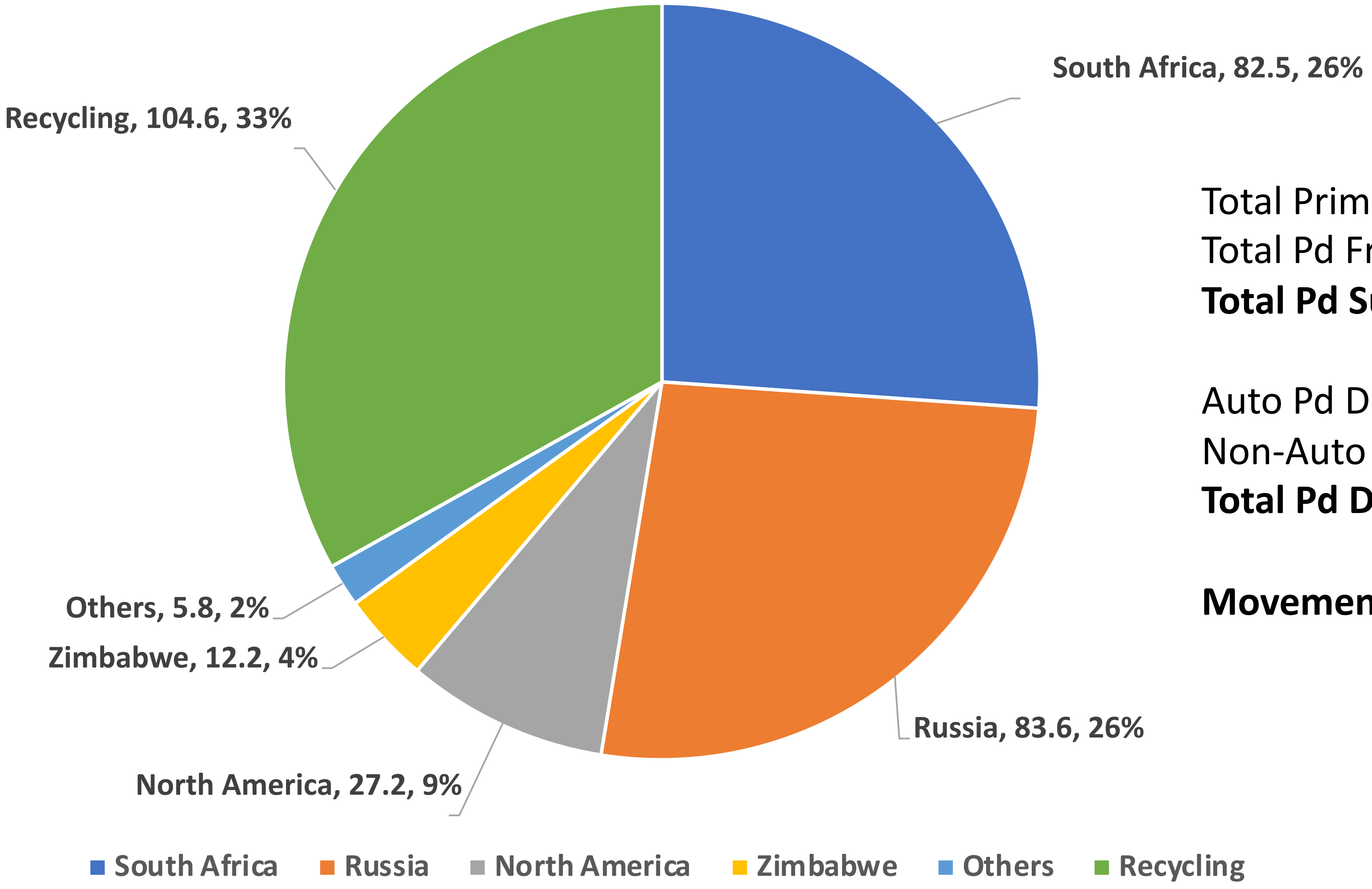
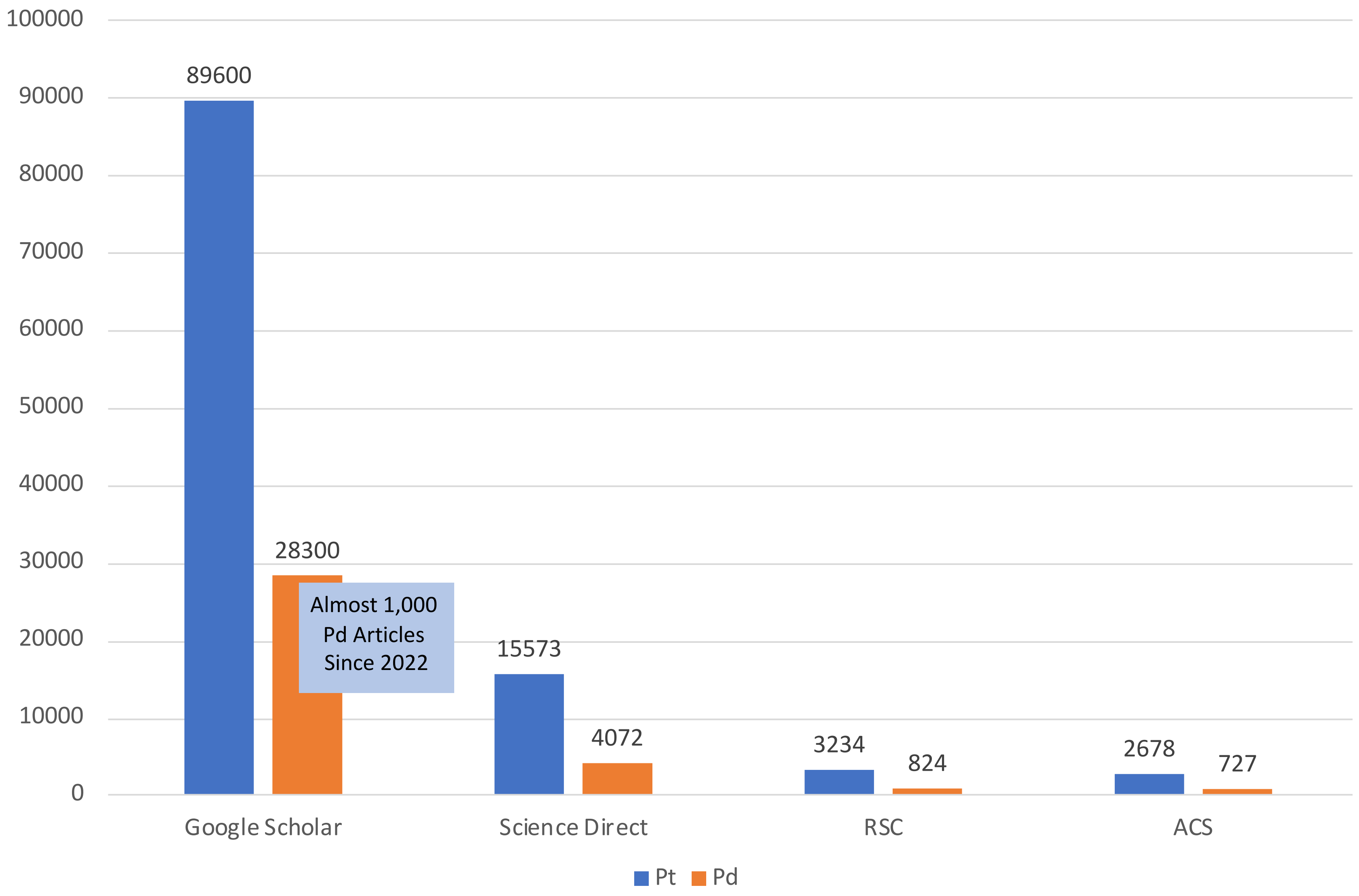
Palladium Supply 2021



Total Primary Pd Supply	= 211.3	tons
Total Pd From Recycling	= 104.6	tons
Total Pd Supply	**= 315.9**	**tons**
Auto Pd Demand	= 259.4	tons
Non-Auto Pd Demand	= 54.7	tons
Total Pd Demand	**= 314.1**	**tons**
Movement to Stocks	**= 1.8**	**tons**

Source: Data from Johnson Matthey Platinum Book, May 2022

Literature Publications Platinum Vs Palladium



Search: Metal + polymer electrolyte membrane + fuel cell*

Recent progress in palladium-nonmetal nanostructure development for fuel cell applications

Developing highly efficient and durable electrocatalysts plays a central role in realizing a broad range of fuel cell application**. Palladium (Pd)-nonmetal nanostructures**, as a special class of **Pd-based alloys**, have exhibited diversified advantages for fuel cell reactions. In this minireview, the most recent progress in the synthesis of Pd-nonmetal nanostructures and their applications in fuel cells are reviewed. First, the merits and advantages of Pd-nonmetal nanostructures are clarified. Next, strategies for enhancing the performance of Pd-nonmetal nanostructures are summarized by demonstrating the most typical examples. **It is expected that this review will generate more research interest in the development of more advanced Pd-nonmetal nanocatalysts**

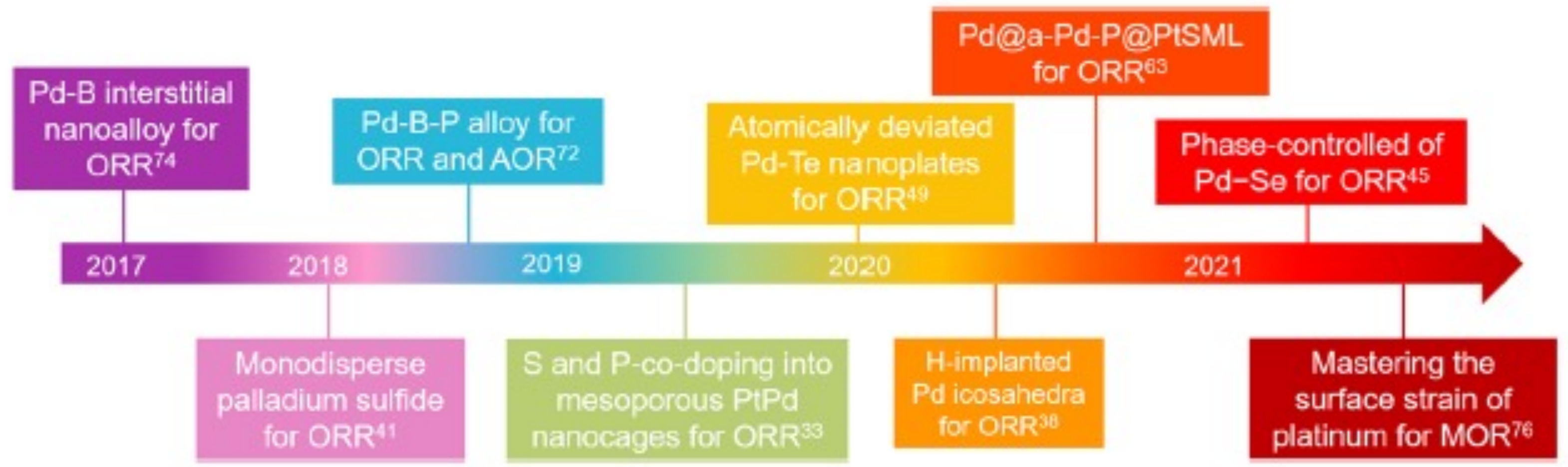
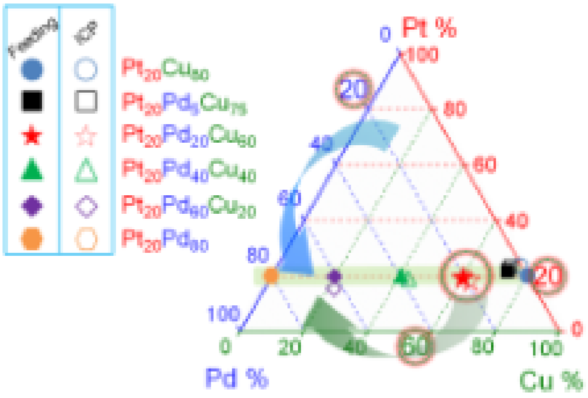


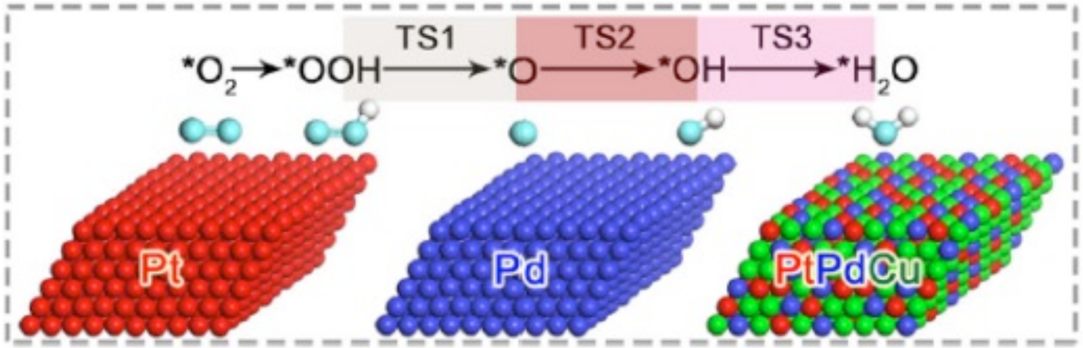
Fig. 2 Development schedule. Timeline for the development of Pd-nonmetal nanostructures.

Wang et al. NPG Asia Materials (2022) 14:78
https://doi.org/10.1038/s41427-022-00423-2

Alloying–realloying enabled high durability for Pt–Pd-3d-transition metal nanoparticle fuel cell catalysts

Alloying noble metals with non-noble metals enables high activity while reducing the cost of electrocatalysts in fuel cells. However, under fuel cell operating conditions, state-of-the-art oxygen reduction reaction alloy catalysts either feature high atomic percentages of noble metals (>70%) with limited durability or show poor durability when lower percentages of noble metals (<50%) are used. **Here, we demonstrate a highly-durable alloy catalyst derived by alloying PtPd (<50%) with 3d-transition metals (Cu, Ni or Co) in ternary compositions**. The origin of the high durability is probed by in-situ/operando high-energy synchrotron X-ray diffraction coupled with pair distribution function analysis of atomic phase structures and strains, revealing an important role of realloying in the compressively-strained single-phase alloy state despite the occurrence of dealloying. **The implication of the finding, a striking departure from previous perceptions of phase-segregated noble metal skin or complete dealloying of non-noble metals, is the fulfilling of the promise of alloy catalysts for mass commercialization of fuel cells**.





NATURE COMMUNICATIONS | (2021) 12:859 | https://doi.org/10.1038/s41467-021-21017-6 | www.nature.com/naturecommunications

Hierarchical palladium catalyst for highly active and stable water oxidation in acidic media

Acidic water electrolysis is of great importance for boosting the development of renewable energy. However, it severely suffers from the trade-off between high activity and long lifespan for oxygen evolution catalysts on the anode side. This is because the sluggish kinetics of oxygen evolution reaction necessitates the application of a high overpotential to achieve considerable current, which inevitably drives the catalysts far away from their thermodynamic equilibrium states.

Here we demonstrate a new oxygen evolution model catalyst-hierarchical palladium (Pd) whose performance even surpasses the benchmark Ir- and Ru-based materials. The Pd catalyst displays an ultralow overpotential (196 mV), excellent durability and mitigated degradation (66 μV h^{-1}) at 10 mA cm^{-2} in 1 M $HClO_4$. Tensile strain on Pd (111) facets weakens the binding of oxygen species on electrochemical etching-derived hierarchical Pd and thereby leads to two orders of magnitudes of enhancement of mass activity in comparison to the parent Pd bulk materials. **Furthermore, the Pd catalyst displays the bifunctional catalytic properties for both oxygen and hydrogen evolutions and can deliver a current density of 2 A cm^{-2} at a low cell voltage of 1.771 V when fabricated into polymer electrolyte membrane electrolyser**

National Science Review; 10: nwac108, 2023
https://doi.org/10.1093/nsr/nwac108

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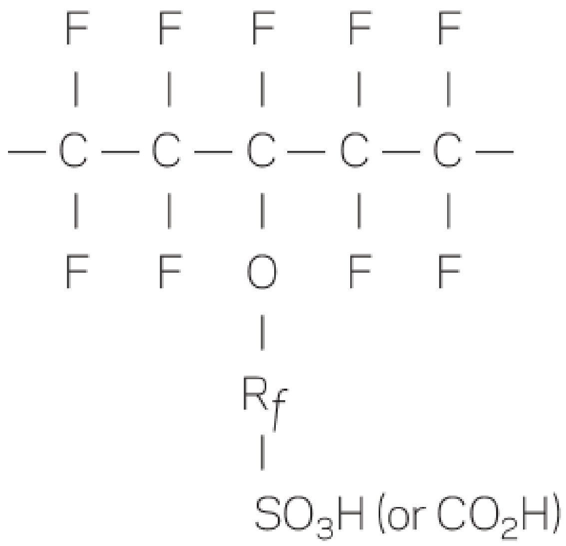
Nafion™ PFSA Polymer Composition



Nafion™ PFSA Thermal Degradation Products

Compound	Evolution Temperature, °C (°F)	Mg/g Sample
SO_2	280 (536)	15
CO_2	300 (572)	30
HF	400 (752)	*
CO	400 (752)	3
R_fCOF	400 (752)	10**
COF_2	400 (752)	3
COS	400 (752)	Trace
R_fOH	400 (752)	Trace

*Significant level, but could not calculate because HF reacts with and absorbs on cell walls.
**Mixture of products

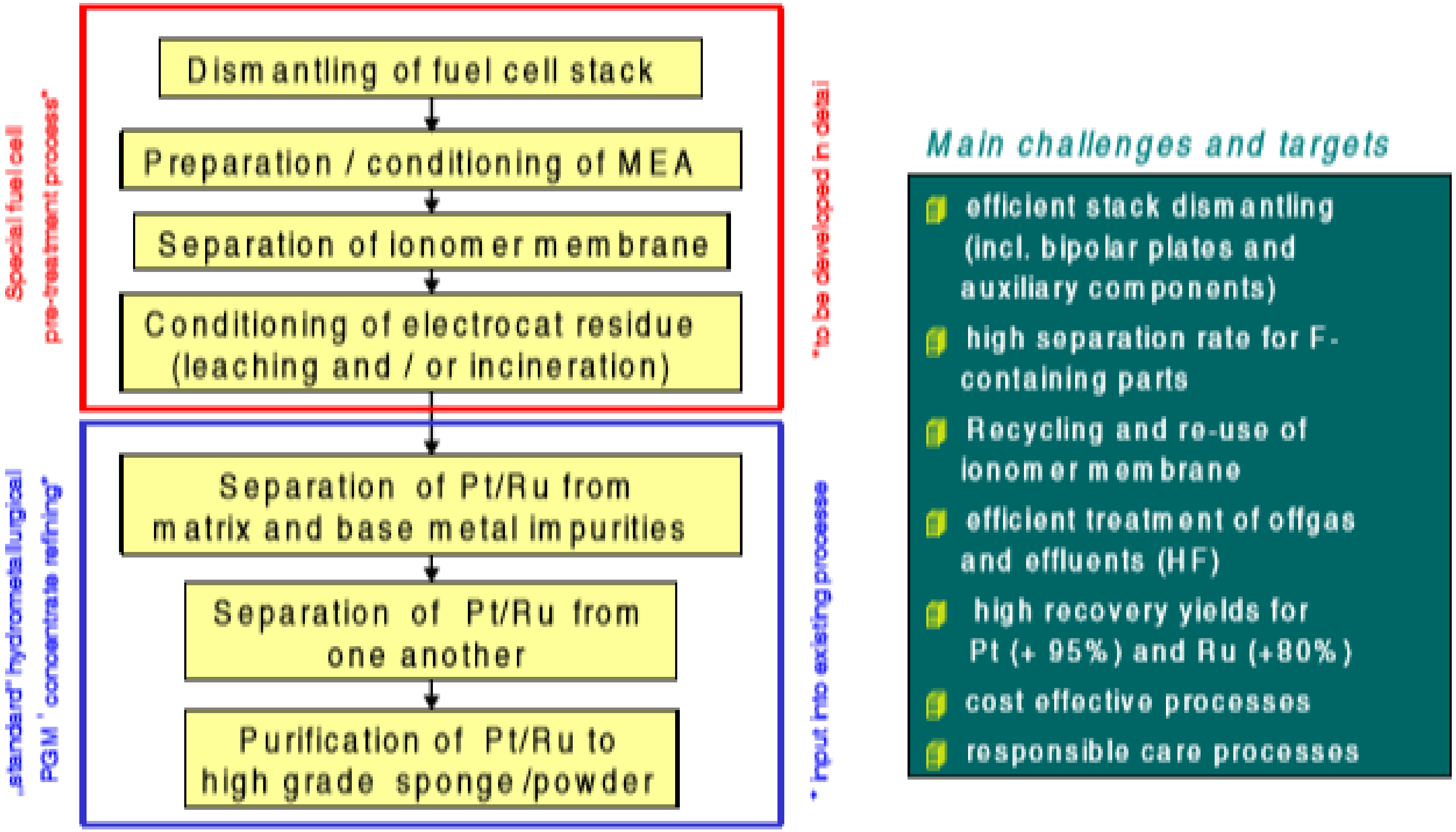
Source: Chemours, Nafion Safe Handling in Use, Technical Bulletin T-01

- Nafion™ perfluorosulphonated membrane (PFSA) and similar materials from other suppliers containing sulfonic acid end groups or from copolymers containing both sulfonic acid and carboxylic acid groups.
- Thermal degradation products of PFSA include several fluorinated and other acidic species which would badly corrode equipment during incineration and require scrubbing. Fumes can cause “polymer fume fever” which is a temporary flu-like condition which comes on 24-48 hrs of exposure. HF is extremely harmful to human health and all exposure must be avoided.

Patent Summary for Fuel Cell Recycling

Current Owner	Patent Families	Technology Approach
BASF SE	5	Wet chemistries – solvent extraction, acid treatments
A2A SPA	5	Swelling, leaching in acid/ionic liquids, electrolysis
WUHAN UNIV OF TECHNOLOGY	4	Electrolytic methods, SOFC recycling
HEE SUNG METAL LTD	4	Wet chemistries – solvent extraction, acid treatments
TOSHIBA CORP	4	Redox/electrochemical methods, acid leaching, PAFC recycling
TOYOTA GROUP	4	Swelling, leaching, use of magnetic fields
ROBERT BOSCH	3	Treatment in aqueous electrolyte in oxidation and reduction stages
TANAKA	3	PAFC Pt/C electrodes recovered by burning, HCl/H_2O_2 treatment
UMICORE	3	Grinding, addition of a Ca passivator, incineration
HERAEUS	1	Lining of an incineration furnace with a refractory
SUMITOMO	1	Leaching methods
JOHNSON MATTHEY	1	Solvent extraction methods

Umicore's Fuel Cell Recycling Process – Grinding and Passivating Approach



Source: Umicore Hageleuken et al, Recycling of Precious Metals from Fuel Cell Components Conference, Paper, 2004
https://www.researchgate.net/publication/292148122

Umicore to build large-scale fuel cell catalyst plant in China to cater for accelerated hydrogen clean mobility growth

"Umicore will invest in building a large-scale fuel cell catalyst plant in Changshu in China to capture the fast-emerging growth in fuel cell technology.

The plant will enable the accelerated transformation to hydrogen-based clean mobility, serving demand through to 2030. The greenfield facility is planned and prepared to be carbon neutral from the start and will contribute to reducing scope 3 emissions in the value chain.

Located in the northwest of Shanghai, the facility is expected to become operational by the end of 2024 and will be scalable to align with the growth of our customers.

It will reinforce Umicore's leading technology and market position in Proton Exchange Membrane (PEM) fuel cell catalysts and complement Umicore's current pioneering production and R&D facilities in Germany and in Korea."

https://www.umicore.com/en/newsroom/umicore-to-build-large-scale-fuel-cell-catalyst-plant-in-china-to-cater-for-accelerated-hydrogen-clean-mobility-growth

Key Takeaways

- PGM criticality needs to be judged not just on supply issues, but also how much is needed for non-automotive applications – because this supply is largely closed off except for thrifting.
- Ir criticality is v. high because of its growing needs in industrial applications. New applications will more than offset thrifting in those non-automotive applications
- The level of thrifting required for PEM electrolysers to meet their scale-up targets is aggressive and needs to be achieved quickly
- Pd has much lower criticality – a large % comes back in open-loop recycling which reduces the dependence on the regions where primary supply is based
- Introduction of palladium and other less critical metals into fuel cells and electrolysers would be a very good solution to criticality however it needs to be taken seriously across the supply chain
- Recycling technology for fuel cells is a big positive driver for managing critical resources and Umicore has successfully scaled its process

Thank you for listening!

Catch us at Battery Tech Expo, Silverstone on 20th April 2023
Stand M12
https://www.batterytechexpo.co.uk/

Catch us at the Vehicle Electrification Expo/Advanced Material Show at the Birmingham NEC, 28th & 29th June, 2023
Visit the Vehicle Electrification Expo 2023 (ve-expo.com)

The Advanced Materials Show I NEC, Birmingham, 28th & 29th June 2023