72nd BHT Colloquium

KK5: Sustainability, recycling and secondary metallurgical processes 2

Recycling of PGMs – an essential step for the sustainable hydrogen-based economy

L. Sandig-Predzymirska, T. V. Barreiros, A. Weigelt, A. Charitos

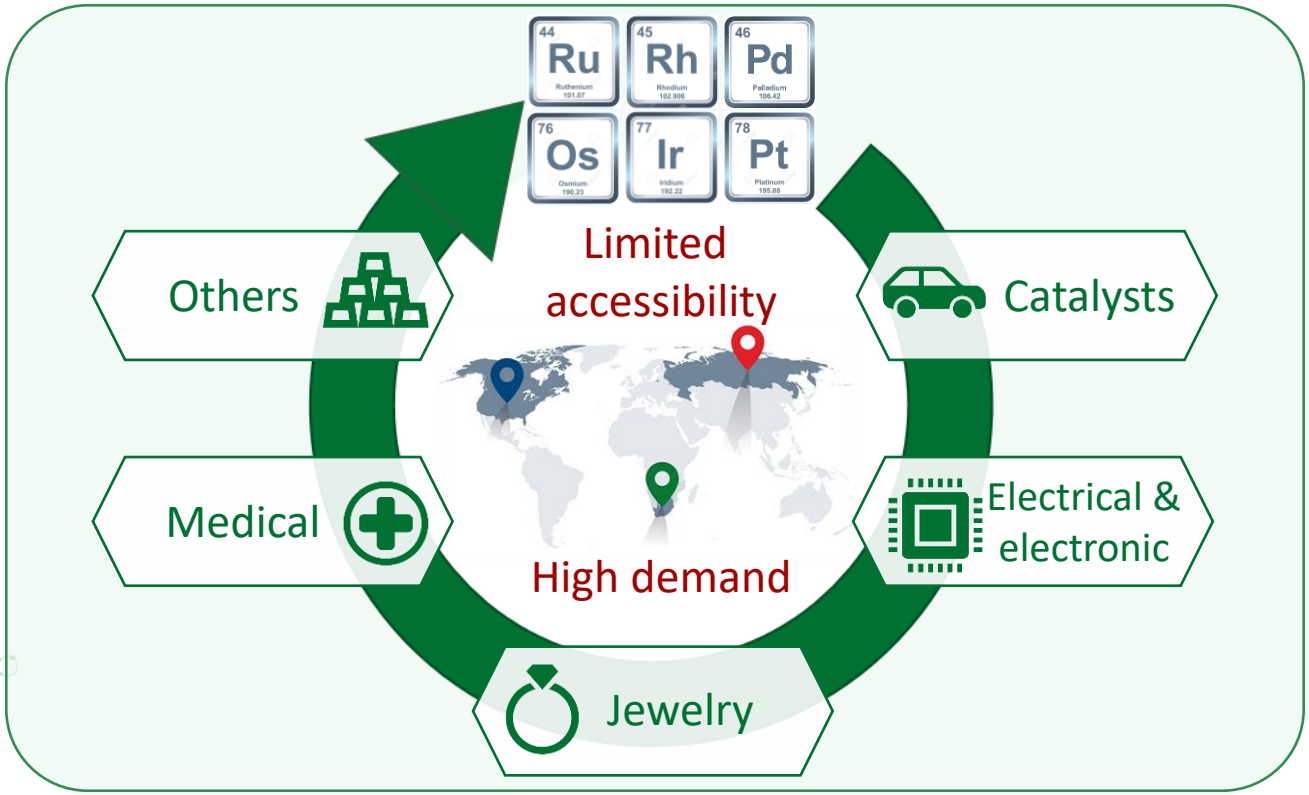
+ RECYCALYSE -

INEMET

June 09-11

DANISH TECHNOLOGICAL INSTITUTE · Sustainable INNOVATIONS · TECHNISCHE UNIVERSITÄT BERGAKADEMIE FREIBERG · VERTECH GROUP · TWI · PRÜFREX · ACCUREC RECYCLING GMBH · Danish Power Systems · HyCentA HYDROGEN CENTER AUSTRIA · Fraunhofer ICT · u b UNIVERSITÄT BERN

Introduction

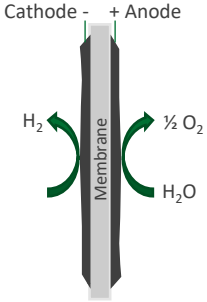


This Project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under Grant Agreement N. 861960

Main objective

Aim: Develop recycling approach for PGM recovery from proton exchange membrane (PEM) electrolysers

PEM electrolyser cell



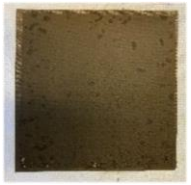
Anode: $H_2O \rightarrow 2H^+ + ½O_2 + 2e^-$

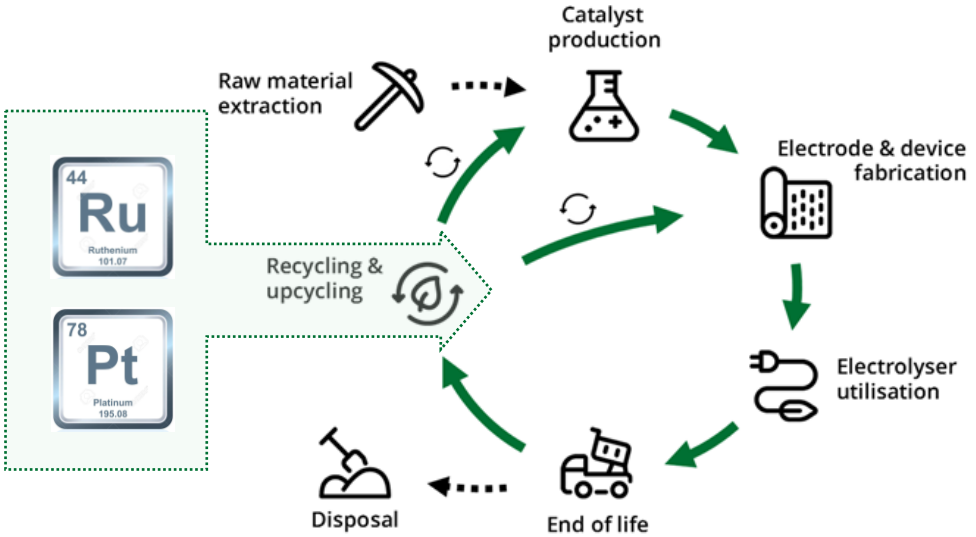
Cathode: $2H^+ + 2e^- \rightarrow H_2$

Overall cell: $H_2O \rightarrow H_2 + ½O_2$

Electrode composition

- Pt (PtRu alloy NPs) 22%
- Ru (PtRu alloy NPs) 11%
- Carbon NPs 11%
- Carbon substrate 41%
- Nafion™ 15%



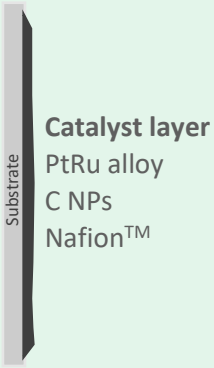


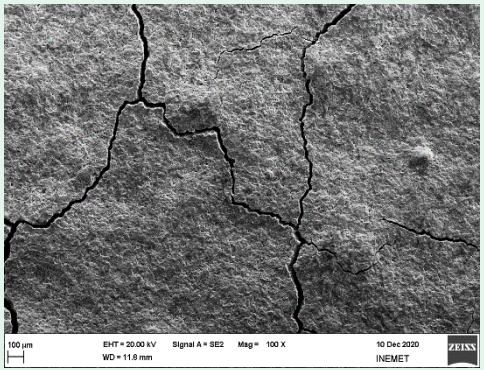
This Project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under Grant Agreement N. 861960

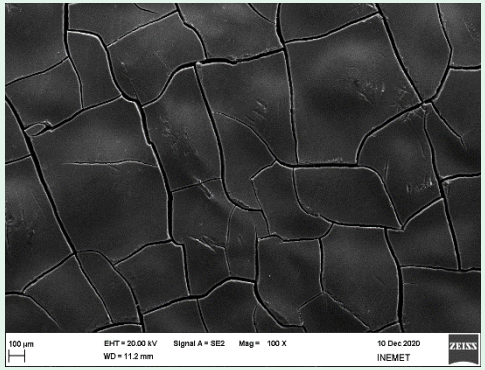
Pre-treatment procedure

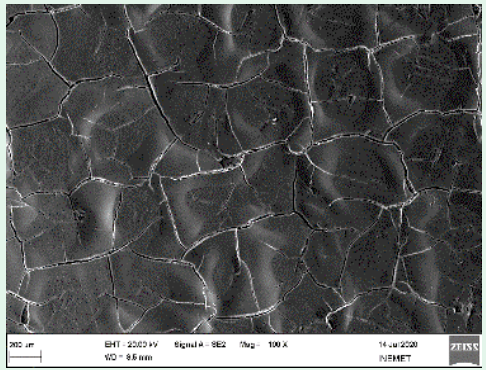
+ RECYCALYSE -

Treatment of PtRu-based electrode with the alkyl alcohol

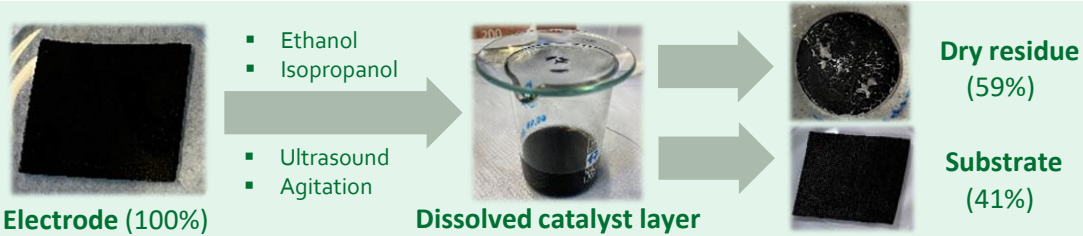








SEM images (× 100): **PtRu-based electrode material** | **C-substrate (new)** | **C-substrate after treatment**



This Project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under Grant Agreement N. 861960

Leaching step

Hydrometallurgical approach

- $HCl + HNO_3$ — **88% Ru; 97% Pt**
- $HCl + H_2O_2$ — **91% Ru; 100% Pt**

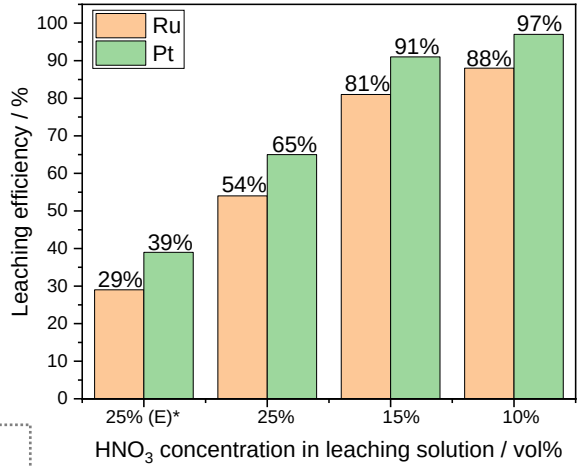
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O \quad E^0 = 0.96V$

$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad E^0 = 1.77V$

Leaching efficiency:

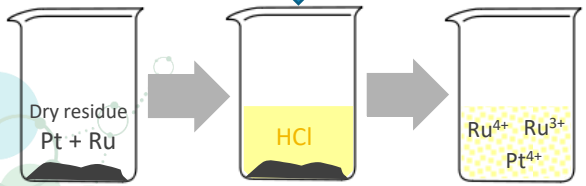
$$\frac{c(PGM\ in\ sol.) * V(sol.)}{m(sample) * w(PGM\ content)} * 100\%$$

Leaching conditions: 12M HCl, 75 °C, 3h



*E - Electrode

Oxidation agent



$Pt^{4+} + 4e^- \rightarrow Pt \quad E^0 = 1.15V$

$[PtCl_6]^{2-} + 4e^- \rightarrow Pt + 6Cl^- \quad E^0 = 0.74V$

$[RuCl_6]^{2-} + e^- \rightarrow [RuCl_6]^{3-} \quad E^0 = 0.83V$

This Project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under Grant Agreement N. 861960

Leaching step

HCl-based leaching system

- H_2O_2 content (1-5%, 7.5%, 10%, 20%)
- HCl concentration (2M, 3M, 4M, 8M, 12M)
- Additives ($NaCl$, $CuCl_2$, $AlCl_3$)

This Project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under Grant Agreement N. 861960

Leaching step

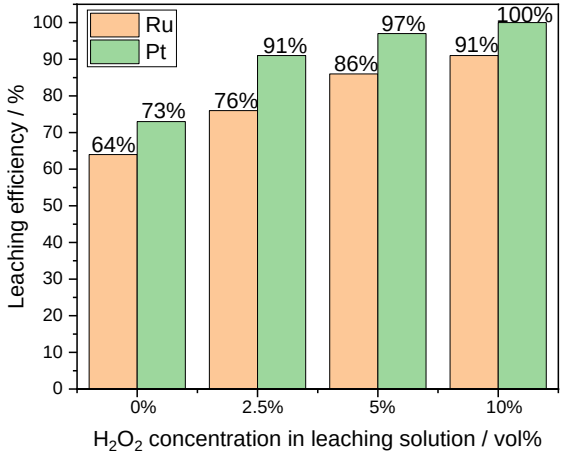
HCl-based leaching system

H_2O_2 content
(1-5%, 7.5%, **10%**, 20%)

HCl concentration
(2M, 3M, 4M, 8M, 12M)

Additives
($NaCl$, $CuCl_2$, $AlCl_3$)

Leaching conditions: 12M HCl, 75 °C, 3h



This Project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under Grant Agreement N. 861960

Leaching step

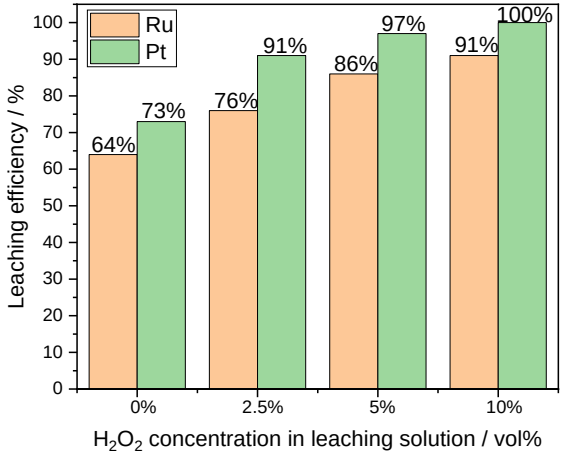
HCl-based leaching system

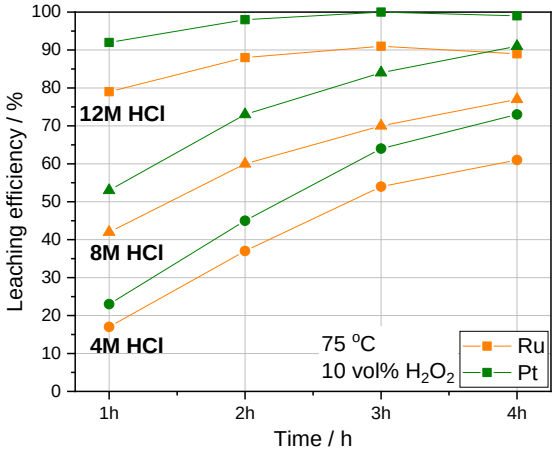
H_2O_2 content
(1-5%, 7.5%, **10%**, 20%)

HCl concentration
(2M, 3M, 4M, **8M**, 12M)

Additives
($NaCl$, $CuCl_2$, $AlCl_3$)

Leaching conditions: 12M HCl, 75 °C, 3h





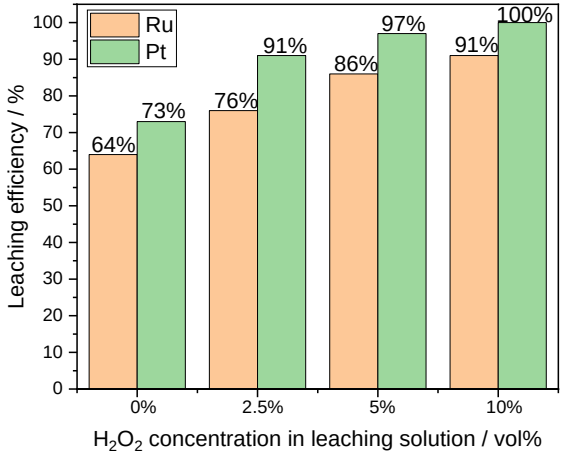
This Project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under Grant Agreement N. 861960

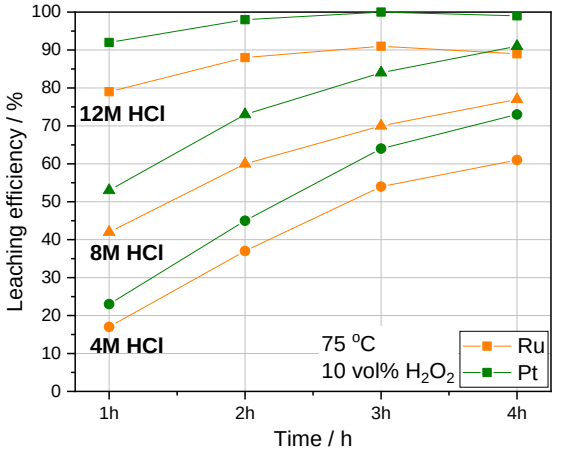
Leaching step

HCl-based leaching system

- H_2O_2 content (1-5%, 7.5%, **10%**, 20%)
- HCl concentration (2M, 3M, 4M, **8M**, 12M)
- Additives (NaCl, $CuCl_2$, **$AlCl_3$**)

Leaching conditions: 12M HCl, 75 °C, 3h



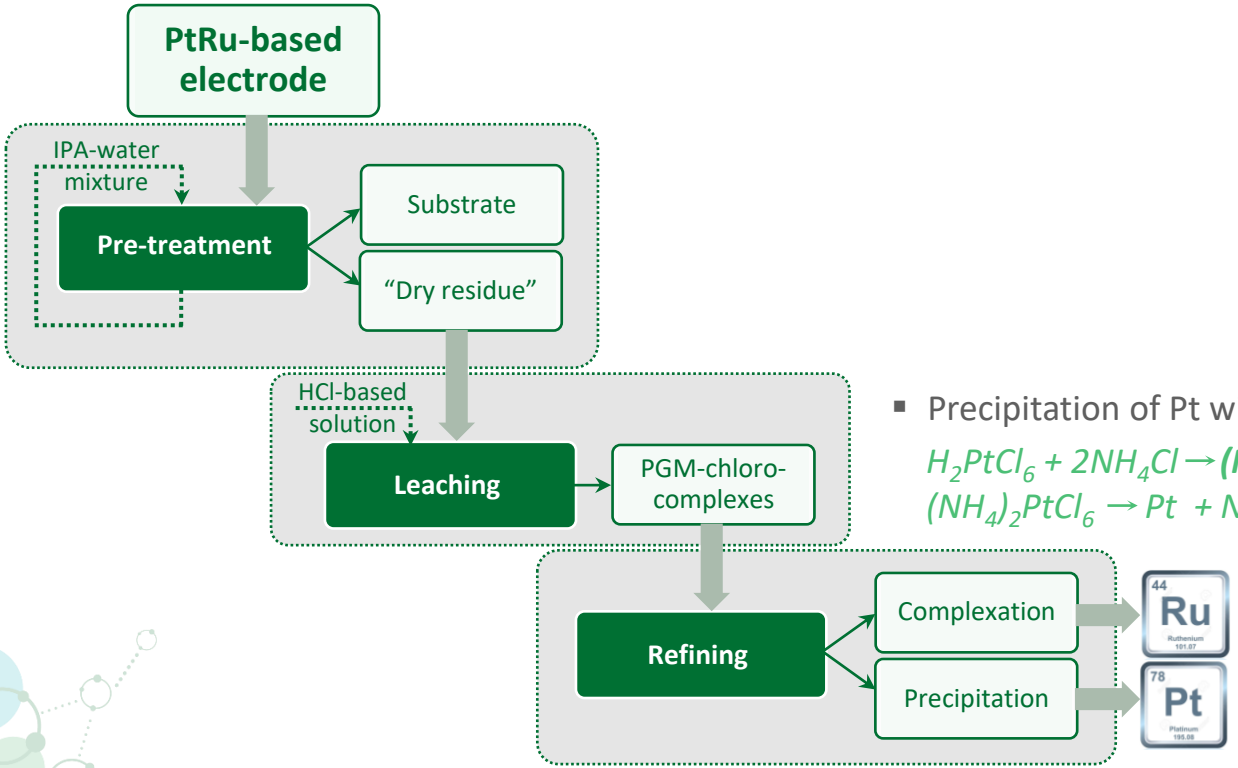


$AlCl_3$	$CuCl_2$	NaCl	Total Cl^-	Ru, %	Pt, %
0.5M	-	-	5.2M	**72**	**81**
-	0.75M	-	5.2M	**56**	**67**
-	-	1.5M	5.2M	**73**	**82**
-	1.5M	-	6.7M	**79**	**90**
1.5M	-	-	8.1M	**84**	**96**

Leaching conditions: 4M HCl, 75 °C, 5 vol% H_2O_2

This Project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under Grant Agreement N. 861960

Recycling strategy



- Precipitation of Pt with ammonium chloride

$$H_2PtCl_6 + 2NH_4Cl \rightarrow \mathbf{(NH_4)_2PtCl_6} + 2HCl$$

$$(NH_4)_2PtCl_6 \rightarrow Pt + NH_4Cl + Cl_2$$

This Project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under Grant Agreement N. 861960

Summary

- Effective **separation of the catalytic layer** by treating the electrode with isopropanol-water mixture.
- The **influence of reagents concentration** to optimize the leaching system was investigated.
- The **use of chlorides** lowers the required HCl concentration and the acidity of the leaching solution.
- **Selective precipitation of Pt** with the efficiency above 90 %.
- **Recycling scheme for PGM recovery** from spent electrodes has been proposed.

This Project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under Grant Agreement N. 861960

Outlook

- Test multimetallic catalysts (e.g. Pt/Ru/Ir).
- Further investigation of the PGM separation from the leach solution.
- Reuse of obtained PGM complexes to manufacture the electrocatalyst.

Thank you for your attention!
Questions?

This Project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under Grant Agreement N. 861960

Speaker: Lesia Sandig-Predzymirska
TU Bergakademie Freiberg
Institute for Nonferrous Metallurgy and Purest Materials
Leipziger St. 34, Freiberg 09599
Tel.: +49373139-2027
E-Mail: Lesia.Sandig-Predzymirska@inemet.tu-freiberg.de