75. BHT – FREIBERGER UNIVERSITÄTSFORUM
FK6 2024: Circular Economy in Freiberg

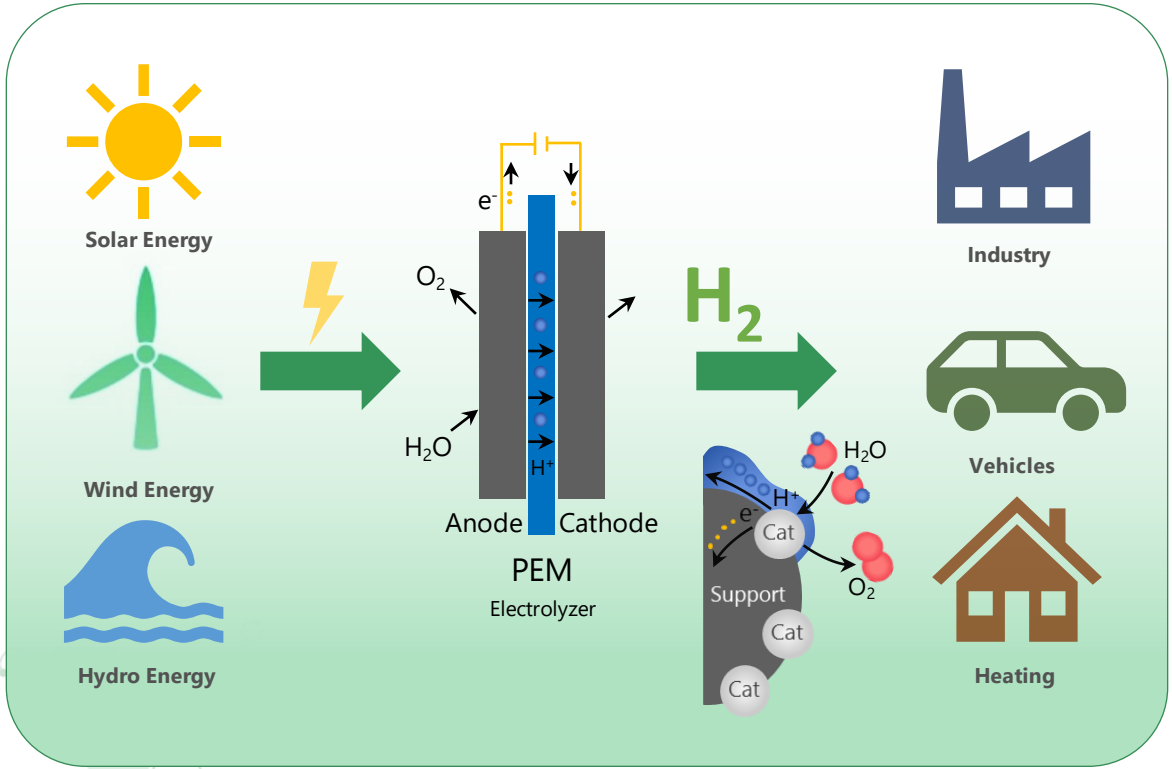
+ RECYCALYSE -

Circularity of Critical Raw Materials in PEM Water Electrolyzers

L. Sandig-Predzymirska, A. Charitos

5th of June 2024

Project goals



OBJECTIVES:

1. Develop and manufacture highly active sustainable **oxygen evolution catalysts for PEM** (Proton Exchange Electrolyzer) that will **reduce or eliminate the use of CRMs** (Critical Raw Materials), thus decreasing CO_2 emissions and reducing cost

2. Establish a **recycling scheme** for proton exchange membrane electrolysers catalysts, electrodes and overall systems, by **implementing the recovered elements in the new developed catalysts**, thus reaching a full circular economy

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

Outlook

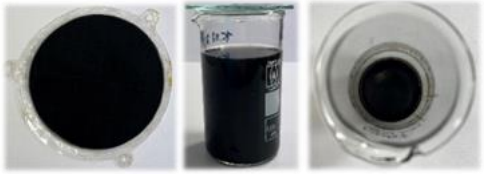
Dismantling

Ti flow plates

MEA

Ti, Fe recycling

in-situ re-activation



Solvent-water mixture

Pre-treatment

Membrane

Solid residue

Na_2O_2

HCl-based solution

Fusion

Leaching

PGM-chloro-complexes

Refining

Volatilization

Ion exchange

Solvent extraction

Precipitation

Ru

Sb

Ir

Pt

Sn

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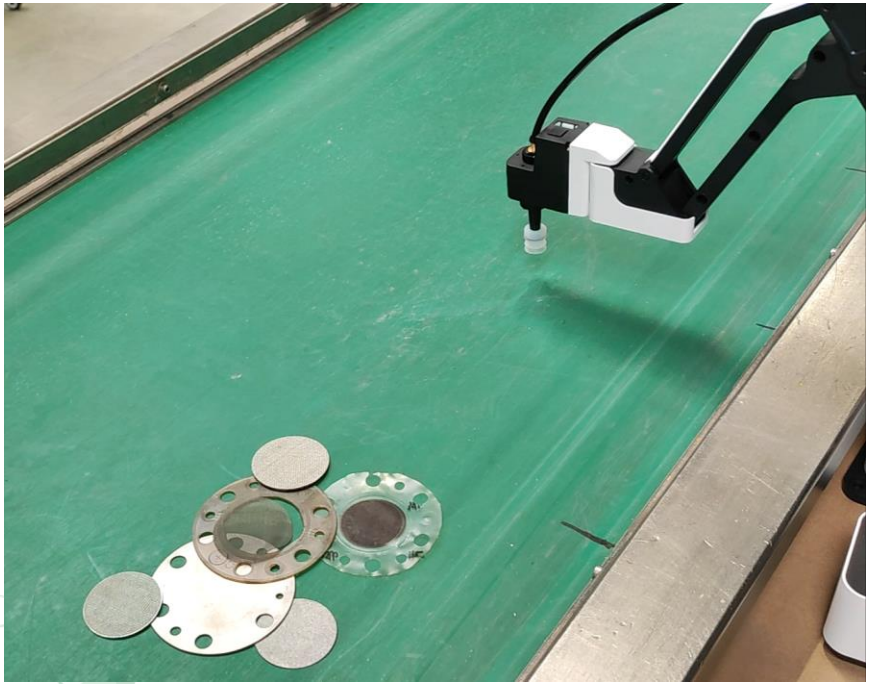
Material sorting

Automated sorting of MEA



Automatic sorting process:

- Capture image in the waste stream
- Detect circle in the image
- Detect color in the image
- Move the robotic arm to pick the detected MEAs (Membrane Electrode Assembly)
- Recycle other parts to recover Ti

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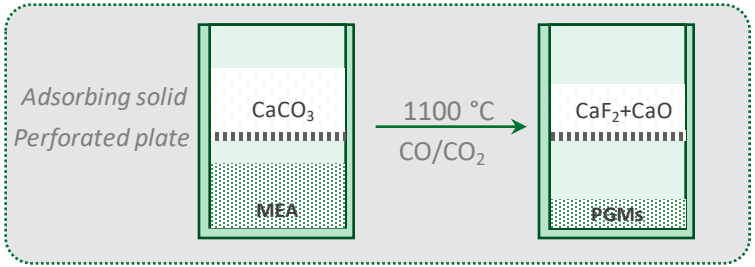
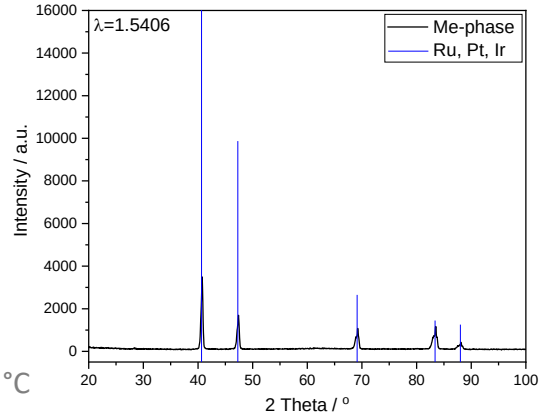
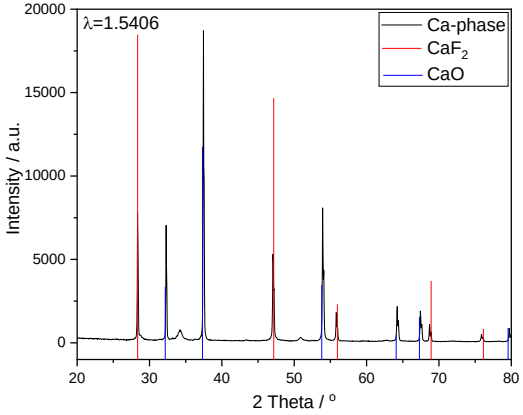
Material recycling - Pyrometallurgy

Pyrometallurgical recovery of CRMs





Metallic bottom-phase



Inorganic top-phase

- → $CaCO_3$ as trapping solid for F-containing gases
- → FactSage® calculation indicated Ru losses above 1100 °C
- → Not all F-containing gasses can be captured by solid, the off-gas cleaning system is required

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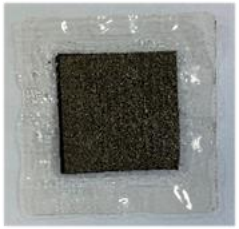
Material samples

Material pre-treatment

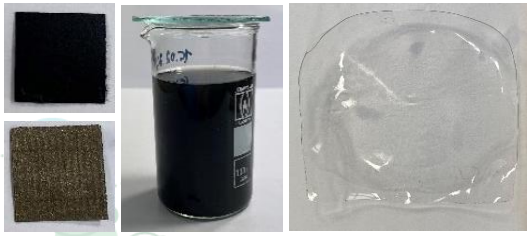
Test MEA

2cm×2cm

- Pt/C
- IrRu/ATO
- Nafion® membrane
- C substrate
- Ti-plated substrate



Pre-treatment
IPA:H_2O / US



MEA

D ~ 9cm

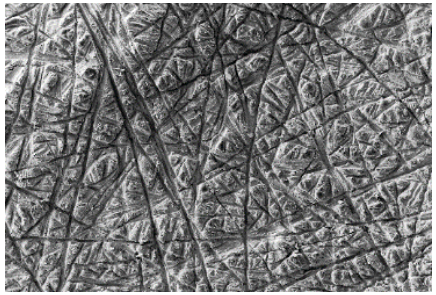
- Pt/C
- IrRu/ATO
- Nafion® membrane
- C substrate

Pre-treatment
IPA:H_2O / US / 40 °C

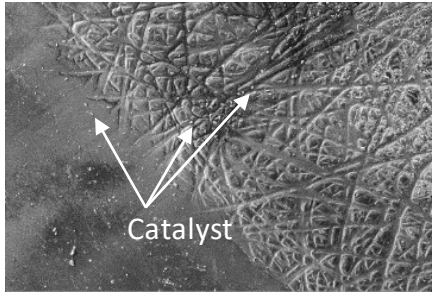
Solid residue

Pt	10.89±0.79%
Ir	6.44±0.19%
Ru	1.50±0.15%
Sb	0.94±0.08%
Sn	14.85.0±0.24%

SEM-images (x100)



MEA anode side - untreated



MEA anode side – IPA+H_2O

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Material recycling - Hydrometallurgy

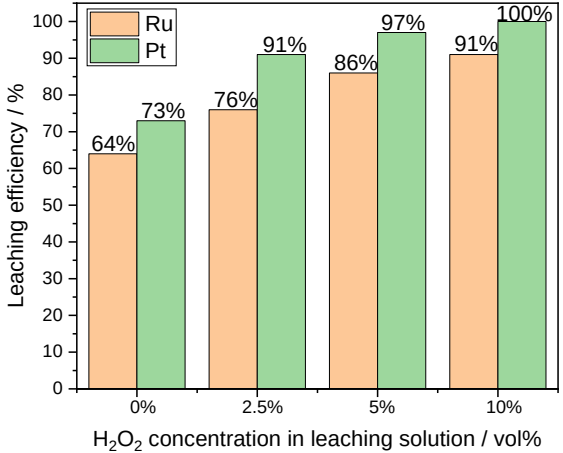
Leaching

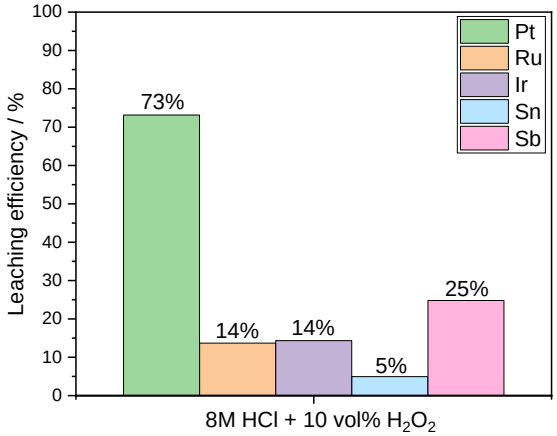
- Pt (PtRu alloy NPs) 37.5%
- Ru (PtRu alloy NPs) 18.8%
- Carbon NPs 18.8%
- Nafion® 24.9%

HCl-based solution → **Leaching** → PGM-chloro-complexes

Optimized parameters:

- HCl conc. – 8 M
- H_2O_2 conc. – 10 vol%
- Additive – $AlCl_3$
- Temperature – 75 °C
- S/L ratio – 4 g/L
- Stirring rate – 500 rpm





- Easy leaching of PtRu/C catalyst in HCl-based solution
- High resistance of IrRu/ATO catalyst in acidic media
- An additional step (fusion) is required to improve the dissolution of IrRu/ATO

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L. Sandig-Predzymirska, T. V. Barreiros, A. Thiere, A. Weigelt, D. Vogt, M. Stelter, A. Charitos: Recycling strategy for the extraction of PGMs from spent PEM electrodes, Proceedings of EMC 2021, GDMB Verlag GmbH, ISBN: 978-3-940276-96-4, pp. 103-114

Material recycling - Hydrometallurgy

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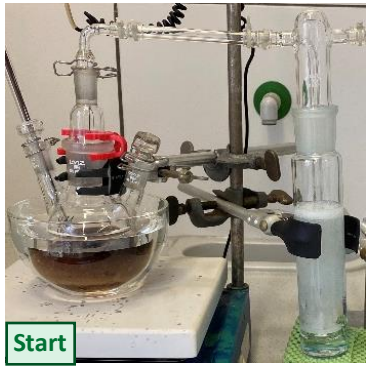
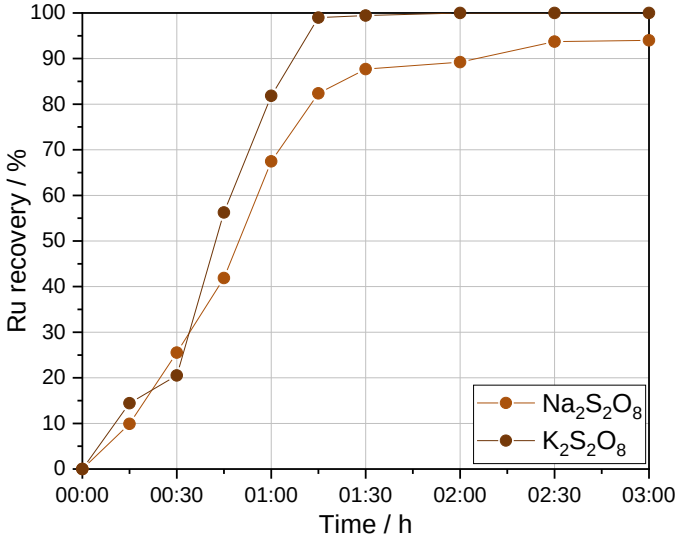
Ru volatilization





*Feed material: IrRu/ATO, T = 60 °C

- Soft oxidation conditions (from 55 °C) by using persulfate salt
- High Ru recovery (up to 100 %) from the catalyst solution
- Sulfonic and carboxylic acids work very well for RuO_4 capture → method patented

L. Sandig-Predzymirska, T.V. Barreiros, A. Thiere, A. Weigelt, M. Stelter, A. Charitos: "Verfahren zur Rückgewinnung von Ruthenium aus einem Ruthenium-haltigen Material" DE102022111440

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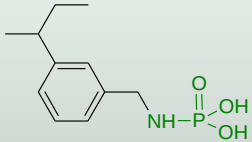
Material recycling - Hydrometallurgy

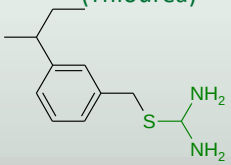
+ RECYCALYSE -

Ion exchange

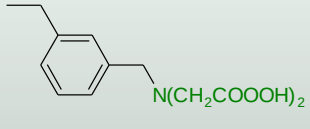
Lewatit MP TP260
(Amino methyl phosphonic acid)



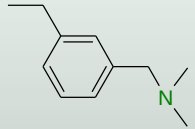
Lewatit MP TP214
(Thiourea)



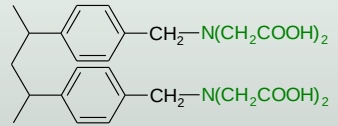
Lewatit TP207
(Iminodiacetic acid)

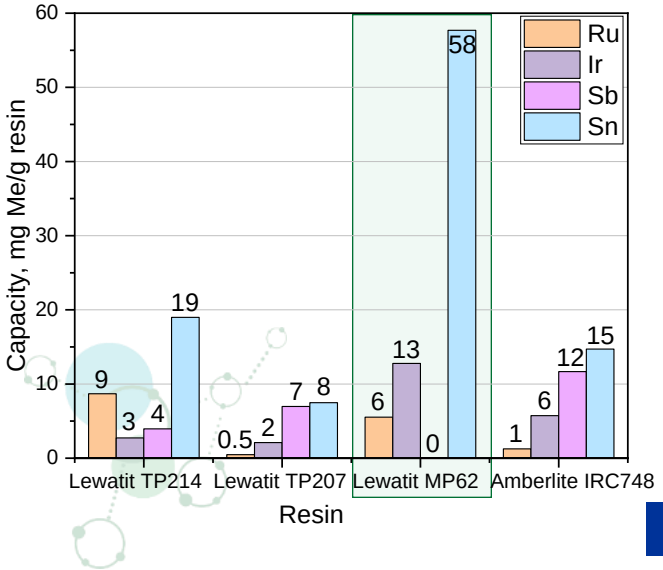


Lewatit MP62
(Tertiary amine)

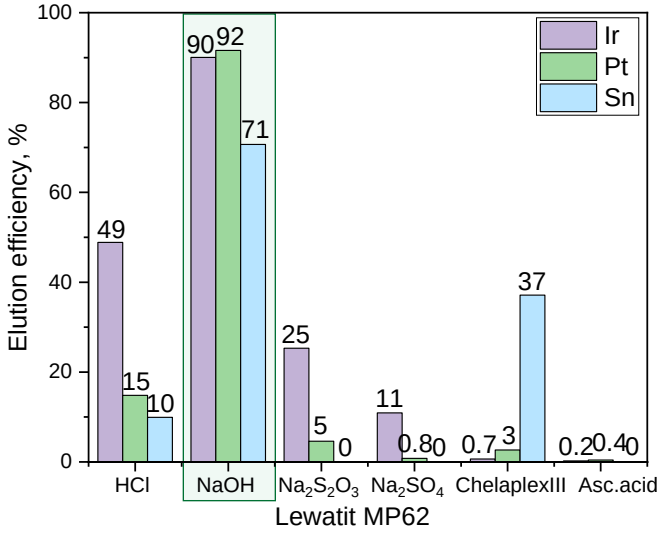


Amberlite IRC748
(Iminodiacetic acid)





- Sb separation from other metals is possible with Lewatit MP62
- Search for selective eluents was performed



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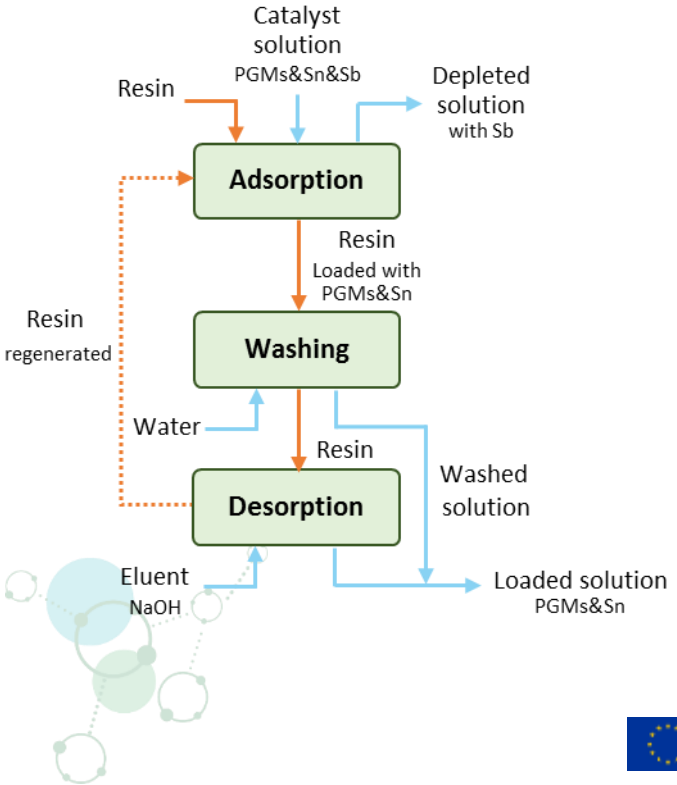
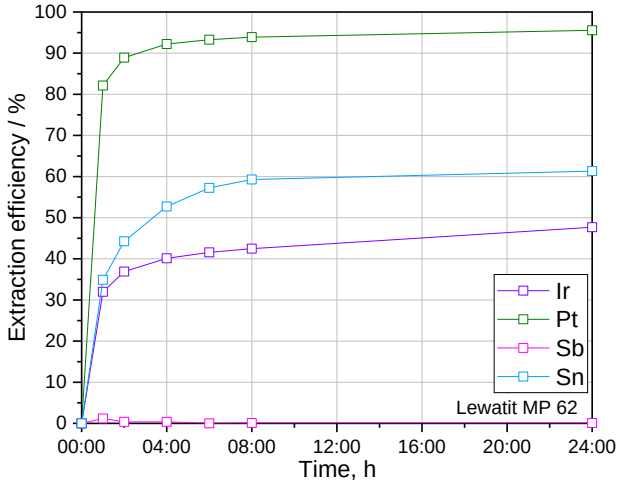
Material recycling - Hydrometallurgy

Ion exchange

Ion exchange scheme





- Lewatit MP62 adsorption step: Pt (96%) was removed and some Sn&Ir (61% and 48%), no Sb was adsorbed
- Washing step: 3h with water (~20-25% Sn, <0.5% PGMs)
- NaOH removed all metal ions – at 0.1M (100% Ir, 95% Pt, and 77% Sn)

→ As the result above 95% (washing+elution steps) of metals was recovered

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Material recycling - Hydrometallurgy

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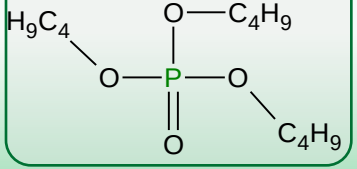
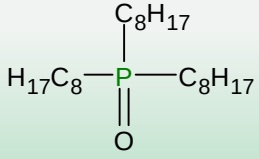
Solvent extraction

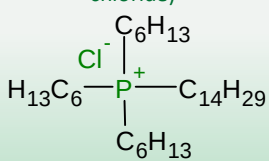
TBP
(Tributylphosphate)



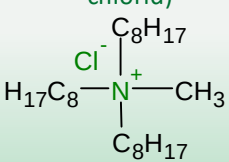
Cyanex 923
(Trialkylphosphine oxides)

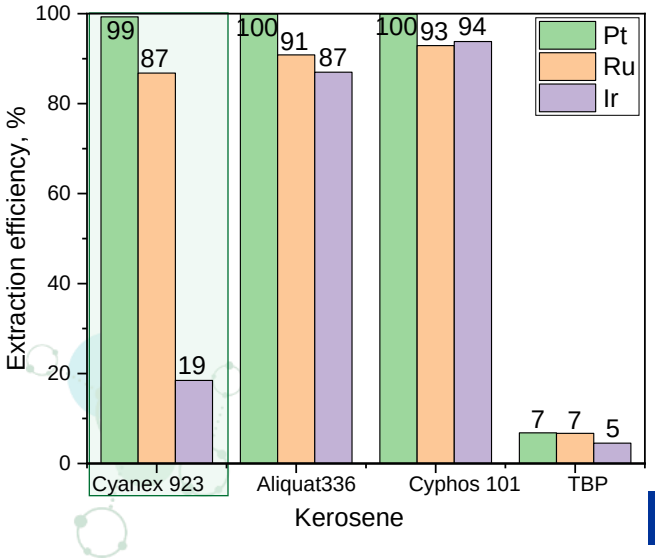


Cyphos IL 101
(Trihexyl(tetradecyl)phosphonium chloride)



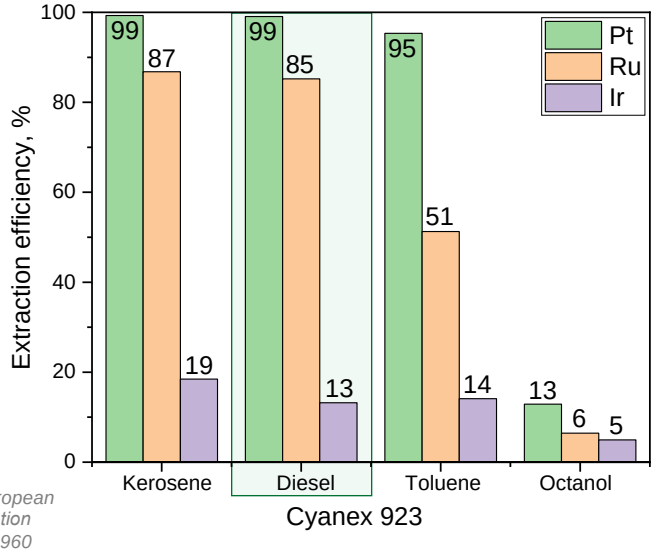
Aliquat 336
(Methyltrioctylammonium chlorid)





Diluent	Dielectric constant
Kerosene	1.8
Diesel	2.1
Toluene	2.38
Octanol	10.3

- Pt/Ir separation is possible with Cyanex 923 in Diesel



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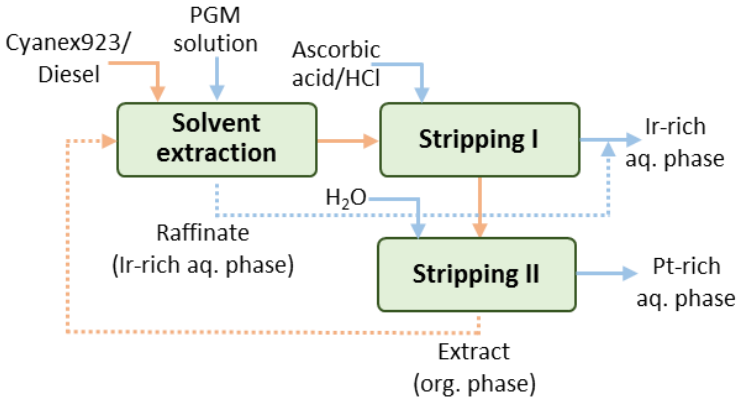
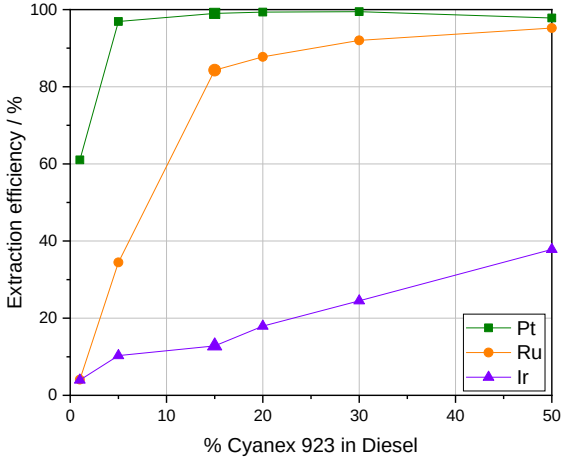
Material recycling - Hydrometallurgy

Solvent extraction





Stripping agents

1. Organic compounds:
ascorbic acid, oxalic acid, thiourea

2. Sodium salts:
$NaNO_3$, NaCl, Na_2SO_4, Na_2CO_3, NaOH

3. Mineral acids:
HNO_3, H_2SO_4, HCl

Optimized extraction parameters:

- Cyanex 923 conc. – 1 - 50 vol%
- Diluent – Diesel, Toluene, Benzene, Octanol
- HCl conc. – 2 - 10 M
- Aq.:Org. – 3:1 - 1:10
- Mixing time – 5 - 120 min
- Stirring rate – 200 - 700 rpm
- PGM conc. – 50 - 1000 mg/L
- Temperature – 25 - 50 °C

➢ At optimized parameters:
Pt = 99.2 ± 0.3%
Ir= 8.0 ± 1.3%

Number of cycles	1	2	3	4
Extraction efficiency of Cyanex 923 Pt (%)	99.24	99.22	99.35	99.07

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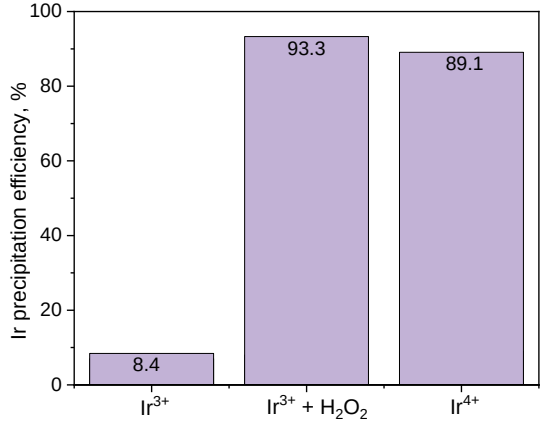
U. Otgonbayar, L. Sandig-Prezdymirska, A. Thiere, A. Charitos, Solvent extraction of Pt, Ru, and Ir using Cyanex 923 in chloride media to develop a recycling route for spent polymer electrolyte membrane (PEM) electrolyzers, Hydrometallurgy, 2024, 226, 106303, https://doi.org/10.1016/j.hydromet.2024.106303

Precursors synthesis

Oxidation and precipitation

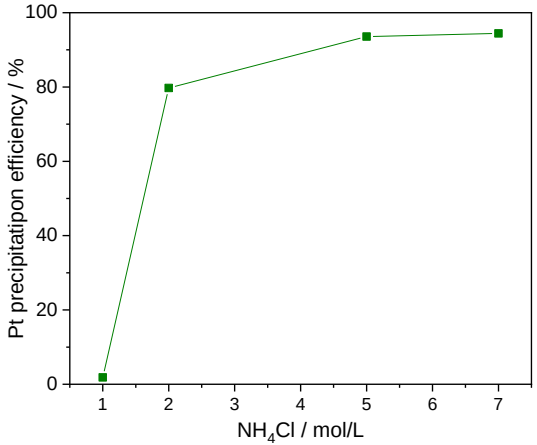


$IrCl_3 + 1/2H_2O_2 + HCl \rightarrow IrCl_4 + H_2O$

- Ir^{3+} oxidation to Ir^{4+} takes place with H_2O_2
- Ir^{4+} precipitates at HCl conc. > 1M

→ At optimized conditions up to 97.6% of Ir was precipitated

$H_2MeCl_6 + 2NH_4Cl \rightarrow (NH_4)_2MeCl_6 + 2HCl$



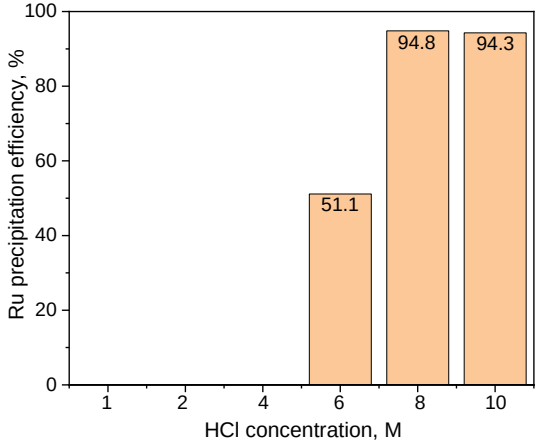
- No co-precipitation of Sn and Sb

→ Up to 94.4% Pt was precipitated with 5M NH_4Cl

- Ru recovery from trapping solution:
  - Oxidize Ru^{3+} to Ru^{4+}

$6H_3RuCl_6 + NaClO_3 \rightarrow 6H_2RuCl_6 + NaCl + 3H_2O$

  - Precipitate Ru^{4+} at HCl conc. > 4M



→ At optimized conditions up to 94.8% of Ru was precipitated

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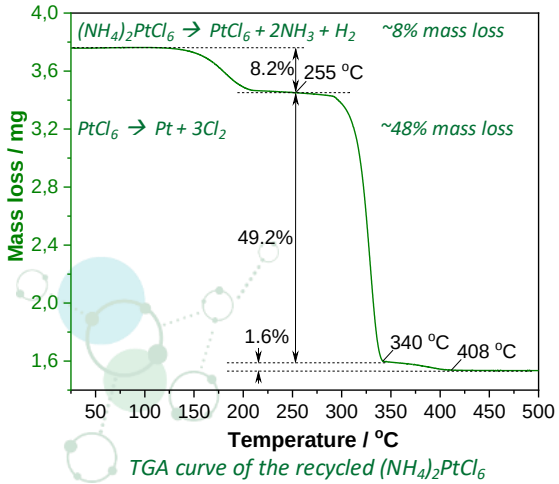
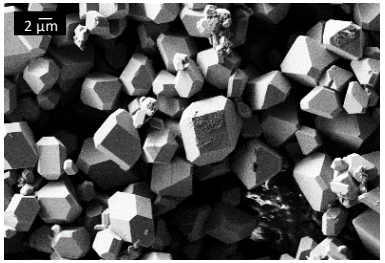
Precursors analysis



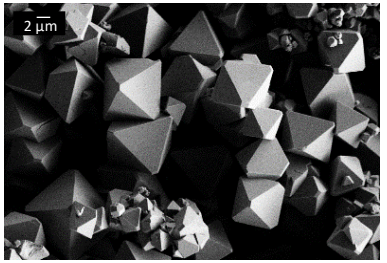
TGA curve of the recycled $(NH_4)_2PtCl_6$

SEM-images (x5.000)



$(NH_4)_2PtCl_6$

$(NH_4)_2RuCl_6$



$(NH_4)_2IrCl_6$

Material	Efficiency, %	Metal content, %			
		Calculated	Commercial		Recycled
			Given by the producer	Analysed by ICP-OES	Analysed by ICP-OES
$(NH_4)_2PtCl_6$	94%	43.9	43.4	47.9	42.3
$(NH_4)_2RuCl_6$	95%	28.9	28.4	30.9	30.6
$(NH_4)_2IrCl_6$	96%	43.6	43.0	45.9	45.8

- The slightly higher deviation for Pt salt (ICP-OES) → NH_4Cl residues (2-8% (XRD) T_{dec}=340°C)
  → Pt salt can not be as easily washed after filtration as Ru or Ir salts with ethanol

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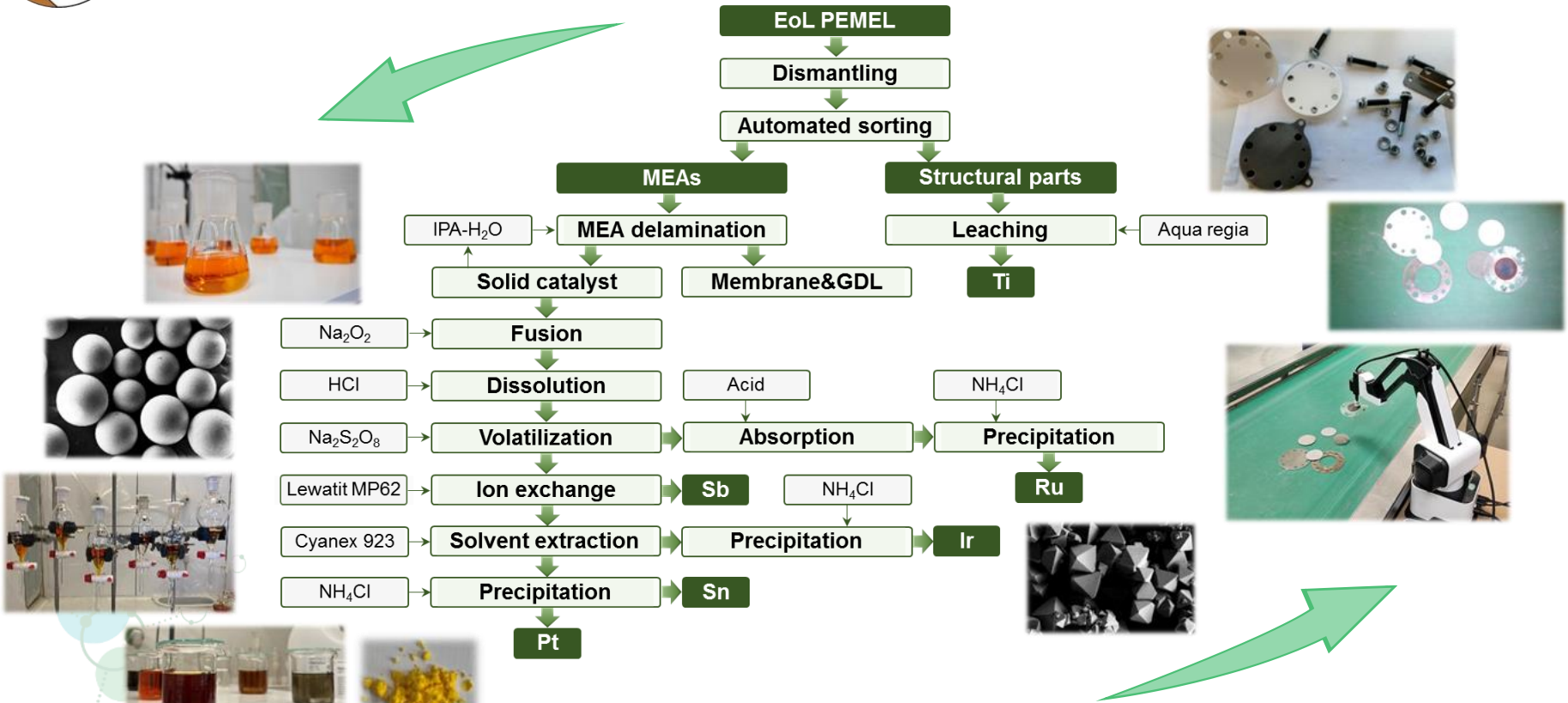
Recycling scheme



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J. Melke et al. Recycalyse – New Sustainable and Recyclable Catalytic Materials for Proton Exchange Membrane Electrolysers, Chem. Ing. Tech. 2024, 96, No. 1–2, 1–18, https://doi.org/10.1002/cite.202300143

Thanks a lot for your attention!

Questions?

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