Electronic Supplementary information

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1. Pt/Co separation – feasibility study

At first a feasibility study was carried out in order to verify whether a selective separation of Pt from Co could be achieved. Within the feasibility study, each operation was performed only once. Although a very efficient leaching of both metallic elements can be obtained using the H_2O_2/HCl mixture, this operation is however not selective. It was thus further investigated whether both metals could be separated within the following separation steps. However, it was observed that no selective separation can be achieved when the solvent extraction or ion exchange are carried out (Table S1). Both metals are extracted/sorbed simultaneously in the case of both separation techniques tested in this work. When only one separation stage is carried out up to 82% of Pt can be extracted using Cyanex 923 in octanol extraction system, but 60% of Co are also co-extracted. In the case of Lewatit MP 62 ion exchange resin, slightly lower removal efficiency have been observed for separated both elements separated. In order to increase the removal efficiencies a multi-stage separation operation must thus be carried-out.

Table S1: Influence of separation alternation, on the Pt and Co removal efficiency from MEA leachate (T = 25°C; Solvent: 15% Cyanex 923 in octanol, A/O=1, t=5 min; Resin: 20g Lewatit MP62 L^{-1}, 5h).

	Extraction efficiencies	
	Co	**Pt**
Solvent	60%	82%
Resin	37%	72%

Afterwards, regeneration tests with NaOH solutions were performed so as to test the feasibility of Pt/Co separation from the loaded solvent and resin phases recovered after the extraction tests. In the case of solvent back extraction the NaOH concentration range tested varied from 0 to 3 mol L^{-1} and the results are shown in **Figure S1**. Simple water stripping seems to be very efficient to recover Co, however more than 50% of Pt are co-stripped too. When the NaOH concentration is increased in the stripping media the Pt stripping efficiency increases significantly and Co stripping remains still high. However, a very interesting phenomenon appears when the NaOH exceeds 2.8 mol L^{-1}. Beyond this concentration in the stripping media the cobalt ions undergo an immediate and quantitative precipitation (certainly due to cobalt oxide (CoO_4) or hydroxides ($Co(OH)_2$ or $Co(OH)_3$) formation in basic conditions[1]). Thus a selective separation can be achieved by what will be further called Solvent alternative where Co is recovered as a solid after an additional filtration step, while Pt stays in alkaline solution and will further be re-used.

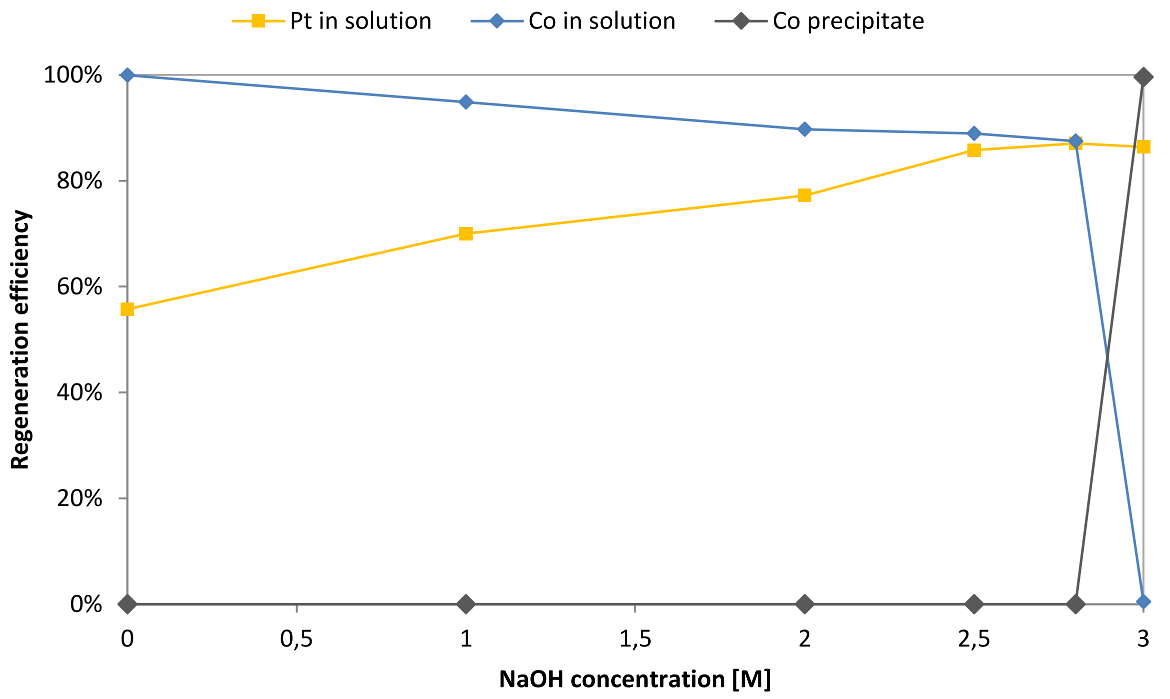

Figure S1: Influence of NaOH concentration, on Pt-Co back-extraction efficiency from 15%vol Cyanex 923/Octanol organic phase (T = 25 °C, $C_{\mathrm{Lix}}^{\mathrm{Pt}}$ = 2 g L^{-1}, $C_{\mathrm{Lix}}^{\mathrm{Co}}$ = 0.2 g L^{-1} O/A = 1; $t_{\mathrm{stripping}}$ = 5min, t_{settling} = 30 min).

In the case of ion exchange resin desorption, the influence of NaOH concentration was only studied within the 0 – 1 mol L^{-1} range and the results are displayed in Figure S2. Interestingly, a simple water flushing of the saturated resin can be sufficient to desorb a significant quantity of Co without desorbing Pt desorption. The Pt can then be selectively desorbed by alkaline rinsing. The NaOH concentration increase leads to an important Pt desorption efficiency increase from 1 to 81 % on the range 0.1 – 0.25 mol L^{-1} and has no significant influence on Pt desorption for higher NaOH concentrations. More than 99% of the cobalt can be desorbed from the loaded resin with aqueous solutions containing NaOH concentrations on the range 0 – 0.1 mol L^{-1}. However, using higher NaOH concentrations in the regeneration solution leads to cobalt precipitation in the form of cobalt oxides or hydroxides, as observed in the solvent tests. In this case the Pt/Co separation can be performed in two successive steps:

- cobalt desorption from the resin by water flushing,
- platinum recovery in solution using a 0.25 - 1 mol L^{-1} NaOH solution.

The experimental results have shown that the Pt/Co separation can be performed after the platinum extraction step. The metal separation is simpler with the resin as no precipitation is involved in this case, Co is recovered as aqueous solution which can be re-used in other applications, while Pt is kept in the alkaline solution which will be re-used for Pt/C re-synthesis.

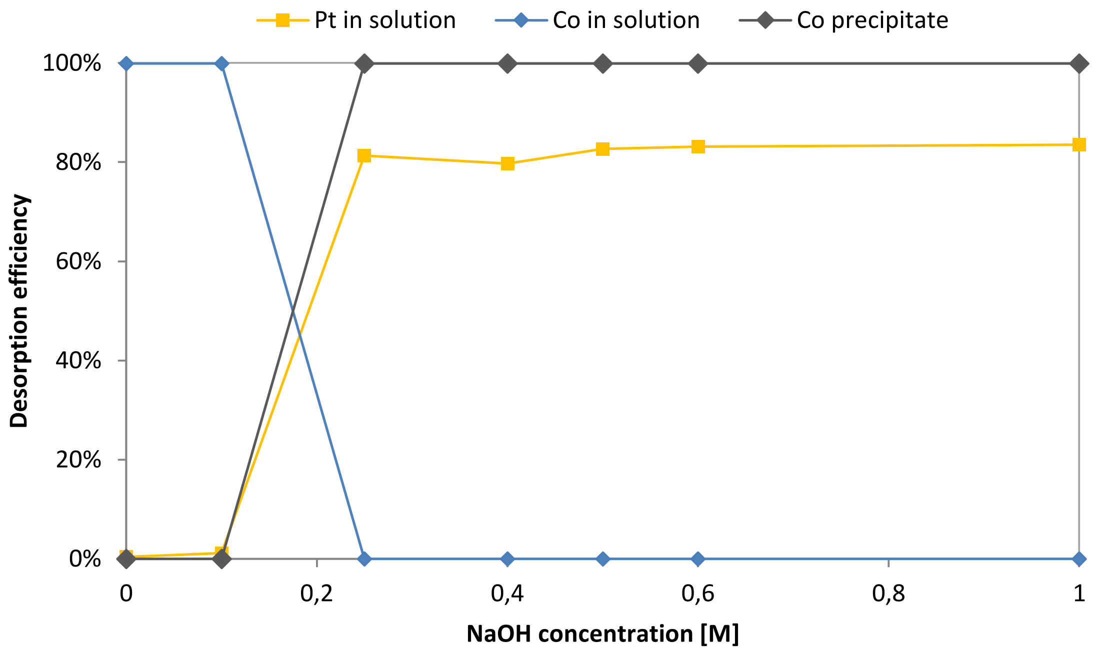

Figure S2: Influence of NaOH concentration, on Pt-Co separation from saturated Lewatit MP62 resin (T = 25 °C, $C_{\mathrm{Lix}}^{\mathrm{Pt}}$ = 2 g L^{-1}, $C_{\mathrm{Lix}}^{\mathrm{Co}}$ = 0.2 g L^{-1}, $\%_{\mathrm{Resine}}$ = 20 g L^{-1}, t = 30 minutes).

2. Separation Pt/Co – optimization study

Table S2: Overview of optimized process parameters for selective Pt/Co separation from used MEAs of a PEMFC.

Stage	**Temperature**	**Products**	**Parameter**	**Value**
Recycling part				
Leaching	25 °C	H_2O_2/HCl solution	Oxidant concentration	3 vol.%
			Pt/leaching solution	2 g L^{-1}
Resin separation	25 °C	Lewatit-MP-62	R/A ratio	20 g L^{-1}
			Stages number	3
Co desorption		Water	/	/
		Lewatit-MP-62	R/A ratio	20 g L^{-1}
			Stage number	1
Pt desorption		NaOH solution	Concentration	1 mol L^{-1}
		Lewatit-MP-62	R/A ratio	20 g L^{-1}
			Stages number	3
Liquid-liquid extraction	25 °C	Cyanex 923/Octanol	Extractant concentration	15 vol.%
			O/A ratio	1
			Stages number	3
Pt and Co stripping		NaOH solution	Concentration	3 mol L^{-1}
			O/A ratio	1
			Stages number	3

3. Pt/C synthesis

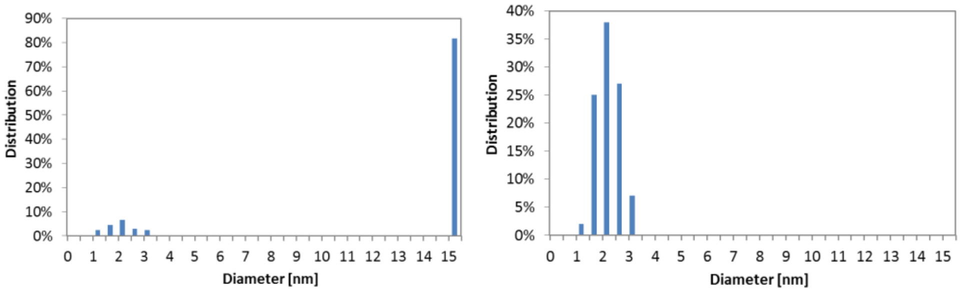

Figure S3 Pt particle size distribution of Pt/C synthetized from (right) solvent regeneration and (left) resin desorption solution with polyol process.

4. Life cycle assessment

Table S3: Recycling processes energy and mass balance including wastes treatment (amounts per kg of Pt at process inlet).

	Process inlets		
	Products/ ***energy***	**Alternative**	
		Solvent	**Resin**
	Nafion® (kg)	0.7	0.7
	20% PtM/C(kg)	5	5
	HCl without water (kg)	208	208
	H_2O_2 without water (kg)	5	5
	Deionised water (kg)	5300	5000
	Cyanex® 923 (kg)	156	/
	Pentanol (kg)	827	/
	Anionic resin (kg)	/	60
	NaOH without water (kg)	595	180
	NH_4Cl (kg)	124	/
	Electricity low voltage {RER} (MJ)	800	1700
	Process outlets		
	Wastes or products/ ***treatment process***	**Alternative**	
		Solvent	**Resin**
Solid wastes	Pt (kg)	0.24	0.28

	Carbon black (kg)	5	5
	Hazardous waste, for incineration {GLO} (kg)	5.3	5.3
	Nafion® (kg)	0.7	0.7
	Nafion incinerator (kg)	0.7	0.7
	Anionic resin (kg)	/	60
	Spent anion exchange resin from potable water production {GLO} (kg)	/	120
Aqueous wastes	HCl (kg)	283	268
	Hydrochloric acid neutralization (kg)	284	269
	Water (kg)	5500	5000
	H_2O_2 (kg)	4	4
	NaOH (kg)	595	180
	NH_4Cl (kg)	124	/
	Wastewater, average {CH} treatment of capacity 4.7E10l/year (m^3)	5.5	5.0
Organic wastes	Cyanex® 923 (kg)	156	/
	Pentanol (kg)	827	/
	Spent solvent mixture {GLO] (kg)	983	/
Products	$PtCl_6^{2-}$ in solution without water (kg of Pt)	0.83	0.77

Table S4: Pt/C synthesis process energy and mass balance including wastes treatment (amounts per kg of Pt at process inlet).

	Process inlets	
	Products/*energy*	**Polyol process**
	Deionised water (kg)	750
	Ethylene glycol (kg)	2200
	Ar (kg)	340
	H_2SO_4	9
	Carbon black (kg)	4
	Electricity low voltage {RER} (MJ)	120000
	Process outlets	
	Wastes/*treatment process*	**Polyols process**
Gaseous emissions	Argon (kg)	9
Aqueous wastes	Water (kg)	1000
	Wastewater, average {CH} treatment of capacity 4.7E10l/year (m3)	1
Organic wastes	Ethylene glycol (kg)	2200
	Spent solvent mixture {GLO] (kg)	2200

The fluoropolymer H^+ sites can be converted in alkali metal group cation form so as to avoid the electrolyte degradation during the dissolution step. The required equivalent of sodium hydroxide amount for acid site neutralisation was estimated considering a 1 meq g^{-1} membrane capacity[2] and the following reaction (R representing the fluoropolymer skeleton) :

$$RSO_3H + NaOH \rightarrow RSO_3Na + H_2O \qquad \textbf{Reaction [1]}$$

The solvent consumption of the dissolution process was calculated considering a 5% Nafion® concentration in the obtained organic solution (corresponding to fluoropolymer concentration in commercial solutions). The process energy utilization was estimated from laboratory reflux system power.

An evaporation process followed by a solvent condensation step was selected so as to model solvent/Nafion® separation. The energy consumption was estimated by adding the sensible and latent heats necessary for solvent evaporation from 25 °C. The solvent condensation with water through a heat exchanger was chosen. The water consumption was determined performing a heat balance considering a maximal water temperature increase of 10 °C. The water pumping impact was modelled with the module: *"Tap water {Europe without Switzerland}| tap water production, underground water without treatment"*. The EcoInvent incineration module: *"Spent solvent mixture {GLO]"*, was used so has to consider the solvent elimination.

Table S5: Membrane dissolution step energy and mass balance including wastes treatment (amounts per membrane surface at process inlet in m^{-2}).

	Process inlets	
	Products/*energy*	**DMSO dissolution process**
	Deionised water (kg)	5
	Dimethylsulfoxide (kg)	7.5
	NaOH without water (kg)	0.01
	Electricity low voltage {RER} (MJ)	40
	Process outlets	
	Wastes/*treatment process*	**DMSO dissolution process**
Aqueous wastes	Water (kg)	5.0
Organic wastes	Dimethylsulfoxide (kg)	7.5
	Spent solvent mixture {GLO] (kg)	7.5
	Electricity low voltage {RER} (MJ)	7
Nafion®/solvent separation	*Tap water production, underground water without treatment (kg)*	170

References

1 M. Pourbaix, J. Van Muylder and N. De Zoubov, *Electrochemical equilibriums atlas at 25°C (in French)*, Gauthier-Villars et Cie, 1963.

2 Chemours Product bulletin P-12, https://www.chemours.com/Nafion/en_US/assets/downloads/dfc101.pdf, (accessed 10 February 2019).