Silver recovery from oxygen depolarized cathodes in methane sulfonic acid

Jil Schosseler, Anna Trentmann, Prof. Dr. Ing. Dr. h.c. Bernd Friedrich

RWTH Aachen University, IME – Process Metallurgy and Metal Recycling
Intzestraße 3
52056 Aachen, Germany

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Abstract

The demand for chlorine for the industrial sector is mainly covered by energy cost-intensive electrolysis [1]. To reduce energy consumption while sodium chloride electrolysis, new cathodes for the membrane process were developed in the last decades [2]. In the future the industrial use of this so called oxygen depolarized cathodes (ODC) will gain importance and a recycling process for the used cathodes must be considered. The cathodes consist of around 70 % silver, 25 % nickel and 5 % polytetrafluoroethylene (PTFE) [2]. Within a project funded by the German Federal Ministry of Education and Research (BMBF) various recycling approaches are developed. A possibility consists of a combination of serval processing steps, leaching and silver powder electrolysis in order to follow a zero-waste concept. Here in particular, the leaching step with methane sulfonic acid will be investigated. For this purpose a first parameter study is done to identify the influence of temperature, hydrogen peroxide as oxidizing agent and time. The aim is the generation of a suitable electrolyte for a silver electrolysis with one leaching step.

Introduction

Chlorine is one of the basic chemicals due to its versatile use. It is applied in the polymer, pharmaceutical, colour and crop protection industry. To meet the demand for chlorine, almost 95 % of chlorine is currently produced by sodium chloride electrolysis with amalgam, diaphragm or membrane processes [1]. In order to make chlorine production more sustainable, the processes have been refined to reduce energy consumption and thus CO_2 emissions during electrolysis. Over the past decades a new cathode for the newest process, the membrane process, was developed [1, 2]. So called oxygen depolarized cathodes (ODC) can reduce energy consumption up to 30 % compared to standard membrane process and up to 50 % to amalgam and diaphragm technology [1]. Recently Bayer AG has managed to bring the new cathodes to industrial size. It is apparent that in future consumed cathodes will have be recycled to make the process more sustainable. Here a zero-waste concept should be sought.

The oxygen depolarized cathodes have a nickel grid as a matrix. Catalytically active silver particles are located on PTFE (polytetrafluoroethylene), which maintains as a binder and for hydrophobising. [1] With a silver content of approx. 70 %, recycling of ODC is particularly interesting. One problem for a recycling process is PTFE. Since the polymer forms toxic gases during thermal decomposition [2], a pyrometallurgical treatment is only possible with a complex exhaust gas treatment. In addition a zero-waste approach would not be possible as PTFE will completely pyrolized. For a hydrometallurgical concept, several possibilities are worth considering.

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Hydrometallurgy based process

First possibility is to extract silver and nickel simultaneously with concentrated nitric acid and separated silver as silver chloride. After purification a reduction step will lead to silver particles, which can be reused as catalyst for ODCs. Nickel can be precipitated as nickel sulphate. This step allows a regeneration of nitric acid. After leaching, PTFE can be fed into a recently new developed recycling process. This process possibility is investigated by a project partner and will not be part of this work.

A second concept is based on the silver powder recovery via electrolysis. The leaching step must here generate a suitable electrolyte. The requirements for the electrolyte are amongst others good conductivity, metal salts solubility, stability and possible recirculation [3], pH value of 5 – 6 and low nickel concentration. To fulfil the pH range without strong neutralisation, the leaching must be performed at low acid concentrations. The presence of nickel while electrolysis has influence on the morphology of silver particles and consequently on the future catalytic activity [4]. One possible electrolyte system is methane sulfonic acid, which has gained importance in recent years in the field of electrolysis [3]. Methane sulfonic acid (MSA) is characterized by its good properties such as high solubility of its salts, high redox and chemical stability, low vapor pressure (no corrosive gas phase) and non-toxicity [5]. The strong acid (pKs = -1.9 [6]) has at high concentrations no oxidizing properties and is not as corrosive as comparable inorganic acids [5]. As leaching medium for silver MSA is not suitable because the acid will not dissolve the noble metal. The addition of an oxidizing agent is necessary. To fulfill the requirements of a clean electrolyte, hydrogen peroxide is a possible choice due to its decomposition in oxygen and water (Eq. 1) [7]. The addition does not result in a contamination of the electrolyte.

$$H_2O_2 \rightarrow \frac{1}{2} O_2 + H_2O \qquad (1)$$

The silver dissolution in MSA with hydrogen peroxide will undergo following reaction [3]:

$$2\ Ag + H_2O_2 + 2\ MeSO_3H \rightarrow 2\ Ag^+ + 2\ MeSO_3^- + 2\ H_2O \qquad (2)$$

However, the use of hydrogen peroxide is associated with some problems. The oxidizing agent has a thermal instability and the presence of metallic particles and acid will lead to a catalytic decomposition [7, 8]. Thus the leaching parameter must be chosen carefully.

As stated above, the silver electrolysis needs low nickel concentrations to produce suitable powder for new ODCs. Nickel is less noble than silver and will dissolve in diluted acid easier. It can be assumed that during leaching it will barely be possible to achieve a high silver selectivity. A processing step of ODCs with a nickel removing step is necessary. Here a combination of cryogenic milling, screening and magnetic separation has proven to be successful.

Fig. 1 shows the proposed recycling process for used ODCs with processing, MSA leaching and electrolysis for silver powder recovery.

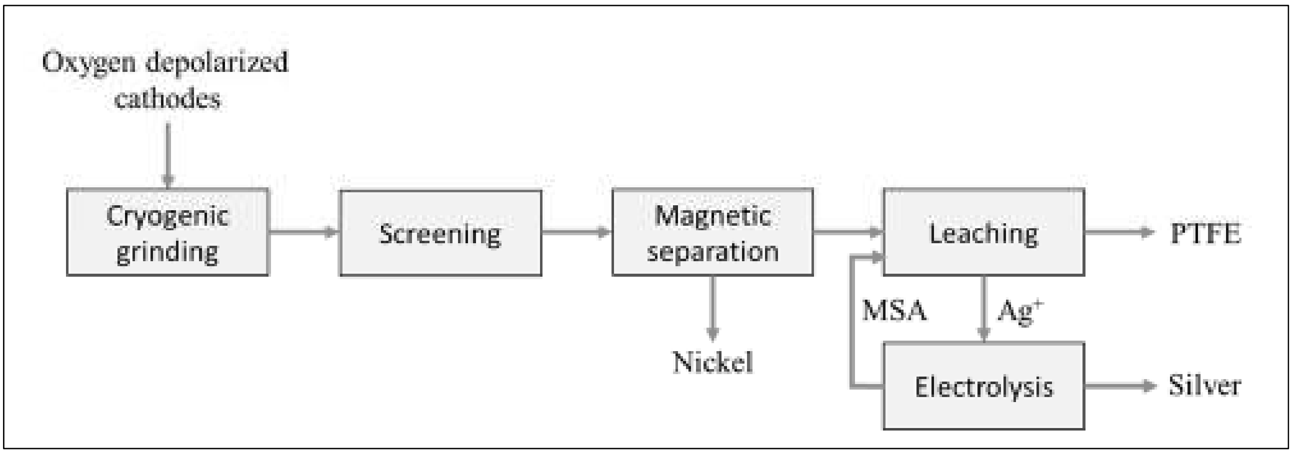

Figure 1: Flow sheet of the proposed recycling process.

Material

Before processing the oxygen depolarized cathodes, the material composition is around 70 % silver, 25 % nickel and 5 % PTFE. The comminution of ODCs has the following purposes:

- Easier handling,
- To generate better acid to solid contact,
- To release nickel for the magnetic separation,
- To expose enclosed silver in PTFE.

Cryogenic grinding was done in a cutting mill. The low temperature of liquid nitrogen leads to embrittlement of PTFE and nickel and facilitates the crushing. To improve nickel separation, three screening and magnetic separation steps were alternately performed. The nonmagnetic fractions, which contain silver and PTFE, were mixed together and homogenized. The analysis shows, that processing can reduce nickel content to 0.3 wt-% (Tab. 1). The ICP-OES analysis of the nonmagnetic fraction was conducted after a microwave digestion in concentrated nitric acid. The amount of PTFE was determined by back weighting afterwards as the polymer is insoluble.

Table 1: Chemical composition of nonmagnetic fraction.

Material	Ag	Ni	PTFE
wt.-%	91	0.3	5.4

Design of experiment

There is barely literature for silver leaching with methane sulfonic acid. Furthermore, the combination of silver particles on and in PTFE with low nickel content is unique. Thus, no experience can be used for experimental design and a wide range of parameters must be investigated. To reduce the amount of trials, the concept of design of experiments (DOE) is useful. First of all, the parameters to be examined must be determined.

As methane sulfonic acid will not directly take part in the dissolution reaction of silver, acid concentration will not be investigated. The acid concentration must be high enough, that no saturation concentration of silver methane sulfonate will be reached and the cations will be remain in solution at any time. To give a first idea of the behaviour of the system the main interesting parameters seem to be the amount of hydrogen peroxide, temperature and time. The instability of H_2O_2 will have an influence on the reaction, so that not only the concentration will be investigated but also the influence on a second addition of the oxidizing agent. Parameters as solid to liquid ratio and stirring speed can be investigated later on in detail. For the screening tests a fractorial design is chosen with four factors and two level each (Tab. 2).

Table 2: Used levels of the factors.

factor		lower level (–)	upper level (+)
Temperature	[°C]	35	50
H_2O_2 /Ag ratio	[-]	1.5	3
Time	[h]	4	8
second addition of H_2O_2	[-]	none	1

Thinking about the chosen parameters with two levels will lead to 16 experiments. With DOE a reduction to eight trials is possible without losing too much information. An overview of chosen DOE is shown in Tab. 3.

Table 3: Factorial design of $2^{(4-1)}$ plan.

	temperature	H_2O_2/Ag ratio	time	second addition of H_2O_2
1	–	–	–	–
2	–	–	+	+
3	–	+	–	+
4	–	+	+	–
5	+	–	–	+
6	+	–	+	–
7	+	+	–	–
8	+	+	+	+

The chosen 2^3 fractorial plan has a resolution of IV, which means that the interactions of the main factors will not be clearly assigned, but will give first understanding of the main effects.

Experimental work

Before each experiment, the acid was prepared freshly to minimize the acid-induce decomposition of hydrogen peroxide. For this 33.5 mL (0.47 mol) of 70 wt.-% methane sulfonic acid was diluted with a certain amount of hydrogen peroxide to 0.750 L, which corresponds to a 1.5 stoichiometry of acid to silver content in solid material. The needed amount of hydrogen peroxide was calculated for a 1 : 1.5 and 1 : 3 Ag:H_2O_2 stoichiometry, that equals to 20.7 mL and 41.5 mL of 35 wt.-% H_2O_2. To reduce inhomogeneity, the Ag / PTFE was mixed before every trail and 37.500 g were weight out (s/l = 50 g/L). In a magnetic stirred beaker (300 rpm) the diluted acid was heated up while the beaker was covered with a watch glass to minimize evaporation losses. After reaching reaction temperature, the Ag / PTFE was added and the reaction time started. If a second addition of hydrogen peroxide was intended, the same volume of H_2O_2 was added at half of the reaction time. At the end of the experiment, the residue was filtered, washed and dried. The volume of filtrate was determined and a liquid sample of 5 mL was taken for ICP-OES analysis. The metal yield calculation takes the loss through evaporation and second addition of oxidizing agent in account.

Results and discussion

By adding the Ag / PTFE fraction into the diluted MSA / H_2O_2 mixture, a gas formation was observed for all experiments. The only explanation is the catalytic decomposition of hydrogen peroxide, which takes place on the metal surface. The decomposition results in a temperature increase of approximately 5 °C. With a starting H_2O_2/Ag ratio of 3, the suspension clears up faster.

Before and after leaching microscopic images were taken (Fig. 2). A visual removal of silver can be observed comparing (a) with (b). On the image after leaching, the white PTFE particles are identifiable, only few remains of silver can be seen. Image (c) shows remaining nickel threats after leaching.

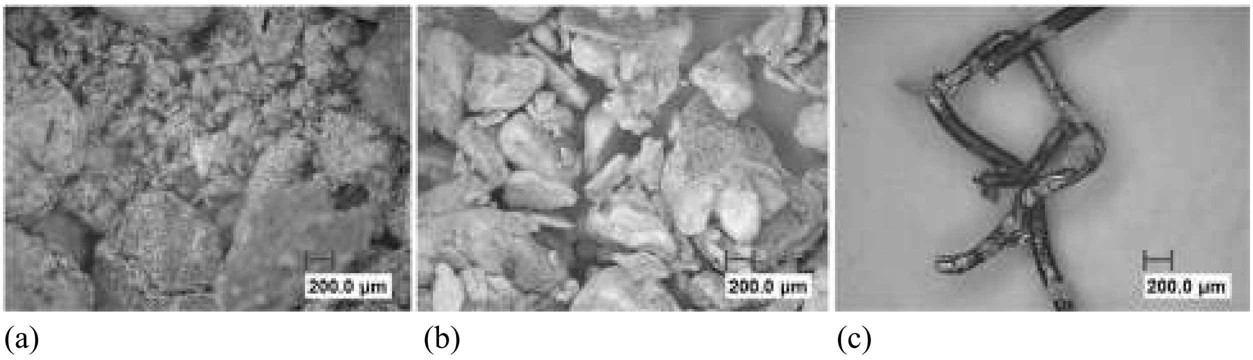

Figure 2: Microscopic images under 100 x magnification. (a) Processed Ag / PTFE before leaching, (b) leaching residue, (c) nickel threads after leaching.

The first run of the DOE with the calculated yield is shown in Tab. 4.

Table 4: Results of the first run of DOE.

	T [°C]	H_2O_2/Ag	t [h]	Second addition	Ag yield [%]	Ni yield [%]
1	35	1.5	4	0	48.0	26.3
2	35	1.5	8	1	95.8	27.2
3	35	3	4	1	92.9	20.1
4	35	3	8	0	95.8	26.6
5	50	1.5	4	1	60.0	30.1
6	50	1.5	8	0	21.6	32.3
7	50	3	4	0	80.9	33.3
8	50	3	8	1	92.9	40.8

The highest silver yield with 94.7 % can be achieved with 35 °C, 1.5 H_2O_2/Ag ratio, 8 h and a second addition or with 35 °C, 3 H_2O_2/Ag ratio, 8 h and no second addition. Comparing the temperature influence, silver yield is in average 19 % lower at 50 °C as for 35 °C. High hydrogen peroxide concentration seems to have a positive influence on silver extraction. Nickel dissolution shows the opposite behavior. The highest nickel concentration can be reached with the higher temperature and the hydrogen peroxide concentration decreases the nickel yield. The fact that at no time a higher extraction of 40.8 % is remarkable, because H_2O_2 should dissolve the ignoble metal. Under magnification, the nickel surface is not silvery bright as expected before leaching (Fig. 3 (c)). The gray green surface indicate an oxidized form of nickel like nickel oxide or hydroxide. While chlorine electrolysis, the cathodes have contact to sodium hydroxide and oxygen. Under this condition an oxidation of the nickel grid is possible and leads to layer, which cannot be oxidized any further through hydrogen peroxide. Thus nickel has a certain passivation layer over the acid medium as methane sulfonic acid does not attack metal oxides.

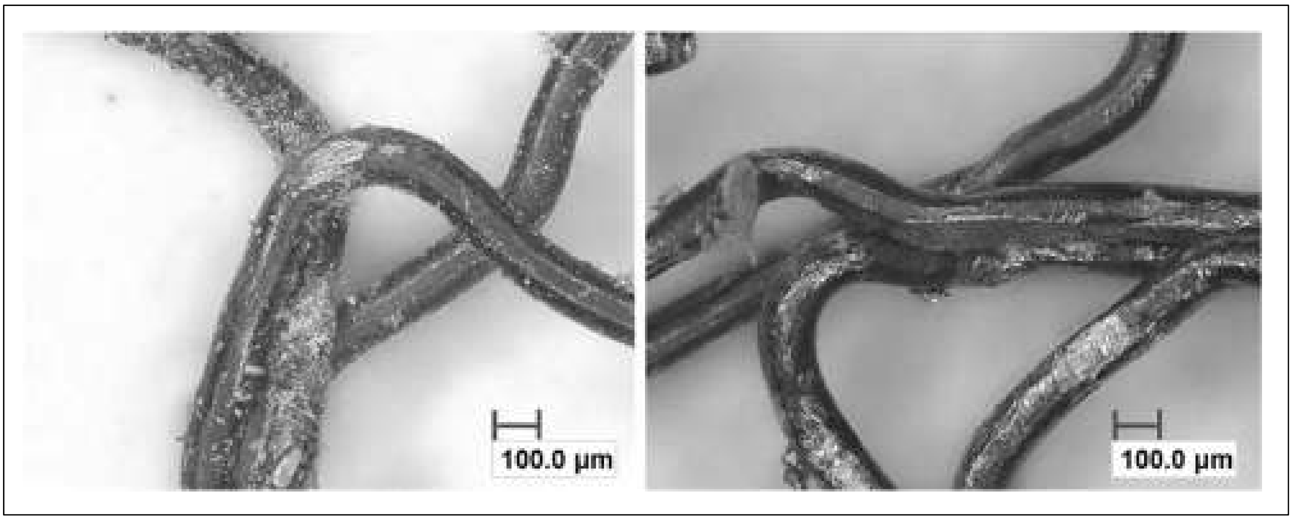

Figure 3: Microscopic images under100 x magnification.
(a) Nickel threats before leaching, (b) nickel threats after leaching with MSA / H_2O_2.

By using *Minitab17* software the received results in Tab. 4 were evaluated and a model for each of the two metals was generated. By successive eliminations of interactions and factors with the lowest significance, the model was improved up to a point until R^2 decreased again. To prove the assumptions made by the model, a residue analyses was conducted. If necessary the model was adjusted.

The obtained main effect plots for silver dissolution in MSA is shown in Fig. 4. The model has a R^2 of 98.5 %. For the best results the main effect *time* was removed and only the interactions of *temperature * H_2O_2/Ag ratio* and *H_2O_2/Ag ratio * second addition* remain in the model. As the chosen 2^3 fractorial plan has only a resolution of IV, the interactions plots are not shown. In the main effect plots of silver, the factor *H_2O_2/Ag ratio* shows the highest significance, as the slope of the means of silver yield is the steepest. A factor has an influence on the investigated system, if the slope is steep. With a nearly horizontal orientation, the factor has hardly any influence. A positive effect on the yield has also the lower temperature and a second addition of hydrogen peroxide. A doubling of reaction time seems to have low influence.

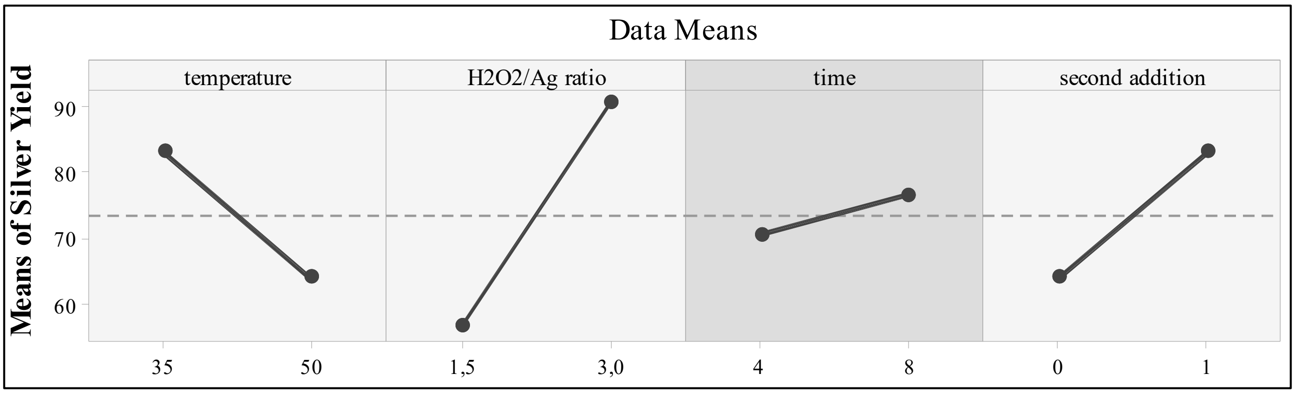

Figure 4: Main effect plots for silver generated with Minitab. Dark gray marked factor was removed out of the model.

The big impact of hydrogen peroxide is plausible as the dissolution of silver takes only place with the oxidizing agent. Due to the observed decomposition of H_2O_2 a second addition is helpful, because at some time all H_2O_2 is consumed and the remaining silver has no reaction partner left. But it has to be considered that if there is too high amount of H_2O_2, only the catalytic decomposition takes place. Adjusting the required amount is important to avoid wastage.

Main effect plots for nickel are shown in Fig. 5. The model considers the main factors *temperature*, *H_2O_2/Ag ratio* and *time*, and the interactions *temperature * H_2O_2/Ag ratio* and *H_2O_2/Ag ratio*time*. With this combination a R^2 of 99.7 % is reached. The factor temperature shows a big significance and nickel dissolution is higher at higher temperature. Also a longer reaction time favors nickel extraction. Hydrogen peroxide in contrast has no significant influence. As stated above, it can be assumed that oxides on the surface act as passivation layer.

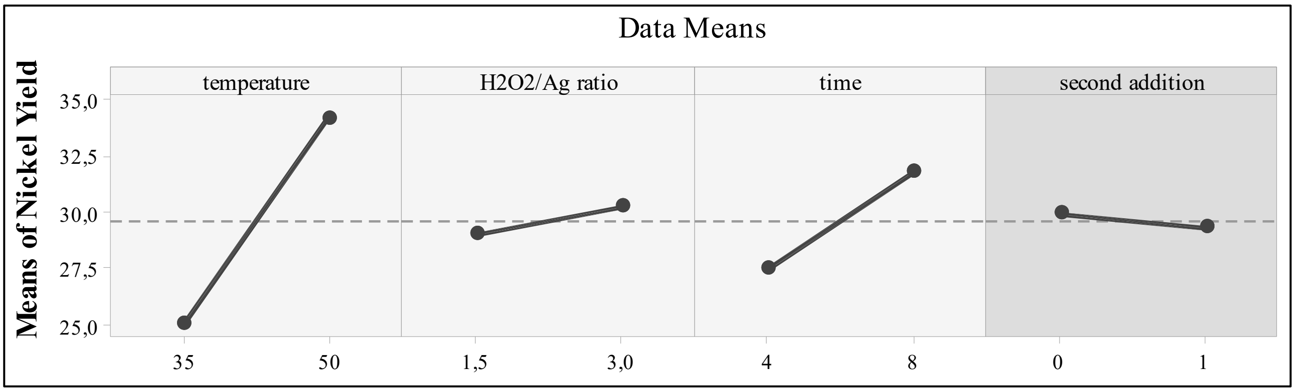

Figure 5: Main effect plots for nickel generated with Minitab. Dark gray marked factor was removed out of the model.

Regarding the different behavior of silver and nickel while leaching with MSA / H_2O_2, it is possible to reach a high silver to nickel selectivity which has a positive effect on the quality of the gained electrolyte. The highest selectivity S(Ag : Ni) = 4.6 can be reached with a H_2O_2/Ag ratio of 3, a second addition, at 35°C after 4 h.

Conclusion and Outlook

A methane sulfonic acid-based electrolyte system is suitable for silver winning electrolysis due its properties. The most important properties are good metal salts solubility, environmental performance, non-formation of corrosive vapours and stability.

The first leaching trials with a methane sulfonic acid-based system show the potential of dissolving silver from processed ODCs. The combination of the pre-processing, to reduce nickel content, and the leaching step allow the generation of an electrolyte for silver electrolysis to produce powder for new ODCs. The parameter study points a highly influence of hydrogen peroxide addition on silver dissolution. Best silver yields result at high concentrations and with a second addition of the oxidizing agent. Nickel dissolution shows opposite behaviour. Here a high temperature and low H_2O_2 concentration favour the nickel yield. A formed oxide layer while chlorine electrolysis passivate the nickel threats surface. To prove results retry attempts must be performed.

As silver yield of 95.8 % is reached, a further optimization of leaching parameters will probably lead to even better silver extraction. For this purpose extend studies on the H_2O_2 addition should be performed, where the needed amount should be determined in order to prevent unnecessary decomposition of H_2O_2. Further a continuous addition should be investigated.

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