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Electrodialysis of acid effluents containing metallic divalent salts: recovery of acid with a cation-exchange membrane modified *in situ*

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The recovery of sulfuric acid from effluents containing metallic salts (Mg, Zn, Mn) was achieved by electrodialysis with a Nafion® cation exchange membrane modified *in situ* by electrodeposition of polyethyleneimine on one side of the membrane. The purity of the acid obtained depends on the experimental conditions of this electrodeposition. The total metal leakage through the modified membrane can be lowered to 0.5% with no significant increase in the energy consumption of the process due to a possible increase of the electrical resistance. These results are comparable with, and even better than, those obtained with commercial membranes specially designed for this type of application. The advantage of this modification process is the possibility of regenerating the surface layer directly in the membrane stack.

1. Introduction

Industrial countries are increasingly concerned with environment protection issues. The treatment of spent acids containing divalent metallic salts concerns several industries such as pickling and surface treatment. Among the possible alternatives, membrane technology is progressively replacing traditional techniques such as distillation, evaporation and pyrolysis, allowing acids to be reconcentrated with relatively low membrane areas [1]. Electrodialysis (ED) is an attractive technique for treating waste acids. Purified and reconcentrated acid can be obtained and reused. The advantage of this process is not only the possibility of recycling acid but also the production of lower amounts of salt effluents or sludges. The classical treatment of spent acids consists in neutralization with a base. The principle of ED for this application is schematized in Fig. 1. The spent acid is circulated in the diluate (D) and the purified and reconcentrated acid is obtained in the concentrate (C), if the membranes satisfy the following properties: (i) for anion exchange membranes (AEMs), a very low permeability to protons; (ii) for cation exchange membranes (CEMs), a high permeability to protons but a very high rejection of the divalent metallic ions M^{2+}; and (iii) for both membranes, a low permeability to water in order to limit the acid dilution in the concentrate.

Recently, new AEMs with a reduced proton leakage have been developed [2–4] and are now commercially available. However, a reconcentrated acid with a high level of purity will only be obtained from ED if new CEMs are developed. Experimental research has been devoted to the development and the use of this new type of CEM [5–9]. To obtain CEMs which are preferentially permselective to monovalent cations, two methods can be used: the first consists in manufacturing a suitable homopolar membrane by adjusting the fabrication parameters so that, in contact with a mixed solution of acid and metallic divalent salts, the flux of protons will be much higher than these of metallic ions; the second consists in depositing a thin anion exchange layer on the surface of the CEM, creating positive charges and, therefore, introducing an electrical repulsion barrier which limits the penetration of divalent cations with respect to monovalent ones [6].

Various possibilities concerning the modification of the membrane surface have already been described, such as immersion of the membrane in a surface-active agent solution [10] or in a cationic polyelectrolyte solution [11–13], electrodeposition [14], layer formation on a CEM by acid-amid bonding [15], modification of CEM surface by membrane processes [16–18] or photo-induced polymerization on the surface of the membrane [19].

Among these modification techniques, the simplest consists in immersing the CEM in an aqueous

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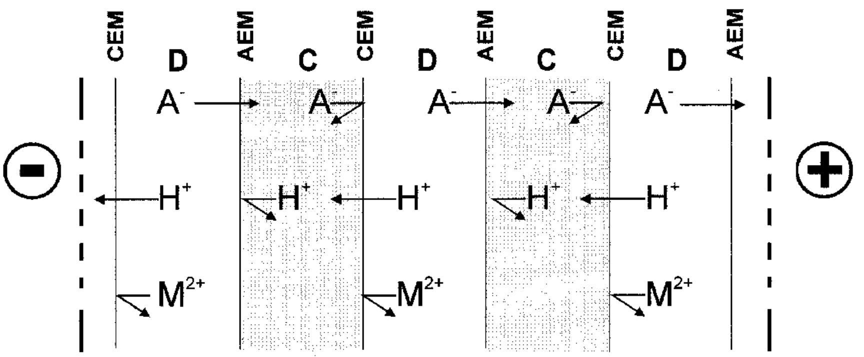

Fig. 1. Principle of the electrodialysis applied to the recovery of strong acids from acid-metal salt mixed solutions: (AEM) anion-exchange membrane; (CEM) modified cation-exchange membrane; (C) concentrate compartment; (D) diluate compartment.

polyelectrolyte solution bearing positive fixed charges in order to create an anion-exchange layer on the surface of the CEM. For a process which functions for a long-time, the deposited film must remain on the surface of the membrane, or an *in situ* electrodeposition must be achieved in order to regenerate the electric barrier to the metallic divalent cation transfer.

The aim of this work is to enhance the selectivity of a commercial CEM towards protons with respect to divalent metallic cations by electrodeposition of positively charged polyelectrolyte on the surface of the CEM through an *in situ* method. The polyelectrolyte chosen is polyethyleneimine (PEI) whose generic group $-(CH_2-CH_2-NH)_n-$ can be protonated to $-(CH_2-CH_2-NH_2^+)_n-$ in acid solution, giving a positively charged surface film which is sufficiently stable for our experiments [20]. The CEM studied in the Nafion® 117 membrane, known for its excellent proton conducting behaviour [21, 22]. This kind of modification has already been achieved on the laboratory scale. The originality of this work consists in achieving the *in situ* electrodeposition of PEI on the surface of the membrane in a preindustrial pilot working under the process conditions. The modified membrane was then used to obtain purified concentrated sulfuric acid from acid solutions containing $MgSO_4$, $ZnSO_4$ and $MnSO_4$.

2. Experimental details

2.1. *Electrodialysis stack*

The ED stack is a commercial ED unit (model CS-0) from the Asahi Glass Co. Apart from a factor of scale, this pilot system is similar to the industrial model. It includes a modular cell with filter-press type circulation having an apparent effective area of $172\,\mathrm{cm}^2$ per membrane. The distance between two membranes is 0.75 mm. This ED cell is composed of a compartment stack of n-pairs (n up to 10), a platinized titanium anode and a stainless steel cathode in the 6-configuration depicted in Fig. 2. Four hydraulic circuits feed the cell: the diluate (D), the concentrate (C), the anolyte (EA) and the catholyte (EC). The anolyte and the catholyte compartments (H_2SO_4 $10\,\mathrm{g\,dm^{-3}}$) are mixed in a single tank to minimize pH variations. Acid recovery experiments were performed using the Solvay ARA anion-exchange membrane (AEM), which is nowadays one of the AEM presenting the lowest proton leakage in H_2SO_4 solutions [4], and a commercial CEM: Nafion® 117 produced by Du Pont de Nemours. This CEM is known to have a much reduced sulfate ion leakage in sulfuric acid media (the transport number of sulfate is lower than 0.5% in $4\,\mathrm{M}$ H_2SO_4 solutions) [23]. The characteristics of the two membranes used are collected in Table 1. They were stored in distilled water before use, and equilibrated with a $1\,\mathrm{M}$ H_2SO_4 solution for at least 12 h before each experiment. The circulation rate in each compartment was $5\,\mathrm{cm\,s^{-1}}$ corresponding to a flow of $80\,\mathrm{dm^3\,h^{-1}}$ for the dilute and the concentrate, and $200\,\mathrm{dm^3\,h^{-1}}$ for the electrode compartments.

2.2. *Modification protocols*

Polyethyleneimine used (PEI) has a molecular weight

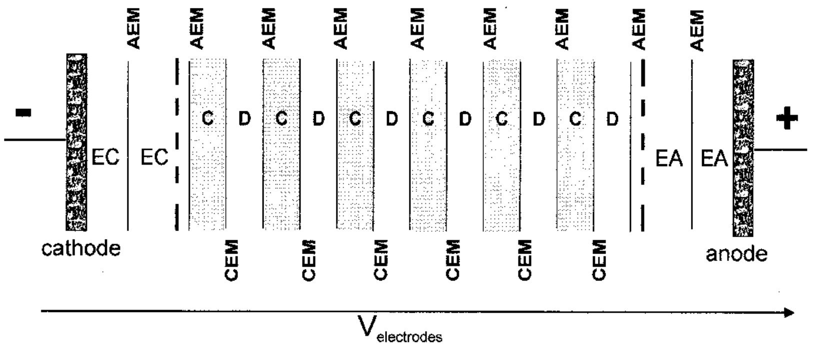

Fig. 2. The Asahi Glass CS-0 electrodialysis cell. Compartments: (D) diluate; (C) concentrate; (EC; EA) electrodes. Membranes: (AEM) anion-exchange; (CEM) cation-exchange. V is the voltate applied between the two electrodes.

Table 1. Basic physicochemical characteristics of the ion-exchange membranes used

Membrane	*Manufacturer*	*Main component*	*WC*/%	*R*/Ω cm^2	*EC*/meq g^{-1}	$t_{Na^+ \text{ or } Cl^-}$	*Thickness*/μm
Nafion® 117 (CEM)	Du Pont de Nemours	Fluorinated copolymer	22	1.1*	0.9	0.99‡	210
ARA (AEM)	Solvay	Fluorinated polymer	9.0	1.3†	0.6	0.94§	160

* Electrical resistance measured in a 10 g dm^{-3} NaCl solution.
† Electrical resistance measured in a 0.1M HCl solution.
‡ Sodium transport number calculated from the measurements of membrane potential 0.1M NaCl/1 M NaCl.
§ Chloride transport number calculated from the measurements of membrane potential 0.1M HCl/1 M HCl.
The Nafion® 117 membrane bears sulfonic ion exchange groups.
The ARA membrane bears vinylpyridium ion exchange groups.

in the range (6–10) × 10^5 (Fluka Chemika). When dilute PEI solutions in H_2SO_4 are submitted to an electric field, protons and positively charged PEI can migrate through the cation-exchange membrane towards the cathode. Of course, the greater mobility of protons favours its crossing. To deposit charged PEI on the membrane surface and not more deeply in the membrane, experimental conditions for current density and concentrations have to be determined.

Two types of protocols were carried out with the diluate and concentrate compartments filled with H_2SO_4 only. These can be distinguished by the value of the applied current with respect to the limiting current (concentration polarization). This last value was estimated from the I/V responses of the cell.

2.2.1. Protocol 1. The electrodeposition conditions of PEI were chosen so as to be far from the situation where concentration polarization is prevailing. The value of the current density used for this electrodeposition of PEI has therefore to be low to get a sufficiently long electrodeposition time before the establishment of concentration polarization. 200 ppm of PEI were added to the dilute (50 g dm^{-3} H_2SO_4). For low H_2SO_4 concentrations, the increase in sulfate ion content modifies the production of the PEI leading to a cloudy solution. The modification attempts by electrodeposition are codified as follows: *m*01 for the first, *m*02 for the second and so on. After the CEM modification, the solutions were removed and the compartments were rinsed with distilled water before introducing the acid–metallic salt mixed solutions to be treated.

2.2.2. Protocol 2. PEI electrodeposition was carried out with significance to concentration polarization. To enhance penetration of PEI into the CEM, the H_2SO_4 concentration was reduced to more rapidly reach conditions of concentration polarization and so increase the fraction of current carried by the charged PEI [24]. The contribution of protons to the current transport is lowered while the transport number of PEI becomes significant. Conditions for a more favourable penetration of PEI into the membrane are therefore established. The initial H_2SO_4 concentration of the diluate was 35 g dm^{-3} instead of 50 g dm^{-3}, while that in the concentrate was maintained at 50 g dm^{-3}. Moreover, the initial PEI concentration in the diluate was increased (1000 ppm instead of 200 ppm). Under these new experimental conditions, the duration of the modification was 2 h 30 instead of 4 h, because of the drastic decrease in the diluate electric conductivity and the establishment of a polarization concentration regime after a relatively short time. After the CEM modification, the solutions were removed and the solutions to be treated were introduced without rinsing the compartments, in contrast with protocol 1.

The experimental conditions of the membrane modification according to the two previous protocols are reported in Table 2.

2.3. *Separation tests protons–metallic divalent cations*

Separation tests (4 h, 50 mA cm^{-2}) were performed in batch mode with 2 dm^3 of solution in each tank. The compositions of the solution to be treated (the diluate) were close to that encountered in zinc hydrometallurgy: 10 g dm^{-3} of Zn^{2+}, 10 g dm^{-3} of Mg^{2+}, 5 g dm^{-3} of Mn^{2+} (in the sulfate forms) in H_2SO_4 solutions of 200 g dm^{-3}. At the beginning of the experiments the dilute stream was a mixed solution of sulfuric acid and metallic sulfate salts. The concentrate and the electrode solutions were H_2SO_4 (5 g dm^{-3} for the concentrate and 10 g dm^{-3} for the electrode-compartments). All streams were sampled seven times during the ED for chemical analysis (20 mL samples). Variations in the compartment volumes, temperature and voltage cell were recorded between samplings. Direct titration by sodium hydroxide allowed analysis of the acidity while metal

Table 2. Experimental conditions of the two modification protocols

Protocol 1	*200 ppm of PEI in* H_2SO_4 *50 g dm*$^{-3}$|*Nafion*®|H_2SO_4 *50 g dm*$^{-3}$	
Code	*Duration*/h	*Current density*/mA cm^{-2}
*m*01	4	15
*m*02	1	50
*m*03	16	3
Protocol 2:	*1000 ppm of PEI in* H_2SO_4 *35 g dm*$^{-3}$|*Nafion*®| H_2SO_4 *50 g dm*$^{-3}$	
*m*04 to *m*06	2.5	50

*m*07 modification consists only in an introduction of 200 ppm of PEI in the dilute solution to be treated (acid + divalent mentallic cations); the Nafion® membrane is used non-modified.

analyses were performed either by complexometric titration with EDTA for the diluate containing the largest metal contents, or by plasma atomic emission spectrometry for concentrate in which the metal content was theoretically lower. It was established that the possible presence of PEI in the concentrate and diluate did not modify the analytical results.

The following final experimental parameters were then derived: (i) mass of the species transferred (concentration × volume product), (ii) yield of acid recovery (ratio of the acid transferred toward the concentrate over the acid present initially in the diluate), (iii) fraction of metal passing through the membrane, or metal leakage (ratio of metal at time t over metal at initial time), (iv) flux of water towards the concentrate ($\mathrm{mol\,F^{-1}}$) and (v) specific energy consumption (kWh per kg of purified acid obtained). Furthermore, a mass balance was carried out on the acid and metallic species. It agreed within 3%, which can be considered as satisfactory taking into account the experimental errors.

3. Results and discussion

In studying the influence of the modification of the Nafion® membrane on the metal leakage, we refer to the non-modified Nafion® membrane. For $[\mathrm{Zn^{2+}}] = [\mathrm{Mg^{2+}}] = 10\,\mathrm{g\,dm^{-3}}$, $[\mathrm{Mn^{2+}}] = 5\,\mathrm{g\,dm^{-3}}$ in solutions of $200\,\mathrm{g\,dm^{-3}}$ H_2SO_4, the metal leakage is 34% for each metal species. For the test nomenclature, *nafref* concerns the results with the non-modified Nafion® membrane, *m*01*t*01 and *m*01*t*02 the results of the first and the second tests after the first modification, *m*02*t*01 and *m*02*t*02 those of the first and the second tests after the second modification, and so on.

3.1. *Separation tests after the first protocol of modification*

The separation tests relative to the first modification protocol are codified from *m*01 to *m*03. Between two separation tests (i.e., *m*01*t*01 and *m*01*t*02), the diluate and concentrate were only renewed after the compartments had been rinsed by circulation of distilled water. From the value of 34% for the non-modified Nafion® membrane, the mean value of the metal leakage decreased to 18% for the modified one (200 ppm of PEI, $15\,\mathrm{mA\,cm^{-2}}$ for 4 h), as new modifications were undertaken as shown in Table 3. Moreover, the evolution of the water transport through the CEM followed the same sequence, showing that PEI is progressively sorbed more deeply in the membrane, thus acting like a cross-linking agent for the negative sulfonic sites of the membrane. No significant difference in selectivity was detected between $\mathrm{Zn^{2+}}$ and $\mathrm{Mn^{2+}}$, while $\mathrm{Mg^{2+}}$ seemed to be retained to a slightly greater extent in the diluate. Moreover, the modification of the Nafion® membrane had no influence on both acid recovery and energy consumption, as reported in Table 4.

The metal leakage remains important and these first results clearly show that this type of *in situ* modification has to be improved to envisage further industrial application.

3.2. *Separation tests after the second modification protocol*

The separation tests relative to this second modification protocol are codified from *m*04 to *m*06. The general idea of the *in situ* modification by electrodeposition of PEI from H_2SO_4 solutions is conserved. However, the experimental conditions for the electrodeposition were modified in order to enhance the penetration of PEI into the membrane. With this new modification protocol, the results of the metal/acid separation were excellent, as shown in Table 5. Though acid recovery was not modified (Table 4), the metal leakage was drastically reduced to 0.3% instead of an average of 20% for the first protocol (Table 3), and 34% for the nonmodified Nafion® membrane (*nafref*). Moreover, this remarkable increase in separation was not accompanied by a significant increase in specific energy consumption due to a possible increase in the CEM electric resistance, as reported in Table 4. In fact, the variation of the electric resistance of the modified CEM should be negligible compared to the total applied voltage, which is interesting for further industrial application. The water transport, initially equal to $2.9\,\mathrm{mol\,F^{-1}}$ for the non-modified Nafion® and to $2.0\,\mathrm{mol\,F^{-1}}$ for the membrane modified, according protocol 1 (Table 3), was now $0.9\,\mathrm{mol\,F^{-1}}$, as shown in Table 5. The decrease in water transport is one of the necessary

Table 3. Membrane performances after the first protocol of modification: Metal leakage and water transport. Nafref: as-received Nafion® membrane; m01t01: results of the first separation test achieved on the CEM after the first modification
Diluate: $\mathrm{Zn^{2+}} = \mathrm{Mg^{2+}}$: $10\,\mathrm{g\,dm^{-3}}$; $\mathrm{Mn^{2+}}$; $5\,\mathrm{g\,dm^{-3}}$; H_2SO_4: $200\,\mathrm{g\,dm^{-3}}$
Concentrate: H_2SO_4: $5\,\mathrm{g\,dm^{-3}}$

	Nafref	*m01t01*	*m01t02*	*m02t01*	*m02t02*	*m03t01*
Metal leakage						
$t_{\mathrm{Mg^{2+}}}$	36.3	30.8	24.6	22.2	19.2	16.0
$t_{\mathrm{Zn^{2+}}}$	33.8	32.2	26.8	25.6	22.4	19.8
$t_{\mathrm{Mn^{2+}}}$	34.8	30.7	25.4	24.5	21.4	23.6
Water transport						
$\mathrm{mol\,H_2O\,F^{-1}}$	2.92	2.55	2.19	2.01	2.01	2.01

Table 4. Influence of the modification of the Nafion® membrane on both the acid recovery and the specific energy consumption(kWh kg^{-1} of purified acid)
Diluate: $Zn^{2+} = Mg^{2+}$: 10 g dm^{-3}; Mn^{2+}: 5 g dm^{-3}; H_2SO_4: 200 g dm^{-3}
Concentrate: H_2SO_4: 5 g dm^{-3}
4 h duration separation tests, 50 mA cm^{-2} (8.5 A)
Nafion® membrane modified according to the first protocol

	Nafref	*m01t01*	*m01t02*	*m02t01*	*m02t02*	*m03t01*
Acid recovery/%	65.9	66.2	58.4	67.2	60.0	59.5
Specific energy consumption/kWh kg^{-1}	1.20	1.14	1.01	1.07	1.01	1.05

Nafion® membrane modified according to the second protocol

	m04t01	*m04t02*	*m04t03*	*m05t01*	*m06t01*	*m07t01*
Acid recovery/%	59.5	63.4	65.6*	66.1†	65.2	61.6
Specific energy consumption/kWh kg^{-1}	1.05	1.29	1.01*	1.07†	1.10	1.08

* *m*04*t*03: after the modified membrane used in the *m*04*t*02 separation test has been stored during three months in distilled water.
† *m*05*t*01: after an additional modification of the membrane used in the *m*04*t*01 separation test.

Table 5. Membrane performances after the second protocol of modification: Metal leakage and water transport.
Nafref: as-received Nafion® membrane; m04t01: results of the first separation test achieved on the CEM after the fourth modification. m07t01: results after a simple addition of PEI (200 ppm) into the diluate with the as-received Nafion® membrane as CEM.
Diluate: $Zn^{2+} = Mg^{2+}$: 10 g dm^{-3}; Mn^{2+}: 5 g dm^{-3}; H_2SO_4: 200 g dm^{-3}
Concentrate H_2SO_4: 5 g dm^{-3}

	Nafref	*m04t01*	*m04t02*	*m04t03*	*m05t01*	*m06t01*	*m07t01*
Metal leakage							
$t_{Mg^{2+}}$	36.3	0.52	0.41	0.24	0.22	0.55	34.3
$t_{Zn^{2+}}$	33.8	0.69	0.57	0.36	0.27	0.81	33.7
$t_{Mn^{2+}}$	34.8	0.79	0.52	0.40	0.32	0.78	32.7
Water transport							
mol H_2O F^{-1}	2.92	0.91	0.91	0.72	0.72	0.36	2.01

criteria to obtain concentrated acid. These excellent separation results have been confirmed with a new set of as-received Nafion® membranes. These results are very encouraging because, in similar experimental conditions, they are better than those obtained for a commercial modified CEM (4% for the CMS membrane from Tokuyama Soda Co. [25]). From an experimental point of view, the electrodeposition of PEI on the CEM surface must be achieved with low acid concentration in the diluate and relatively high PEI concentration. In these conditions, PEI enters the membrane material, contributes to lowering the water transport and remains more bound to the membrane. With this couple of membranes (ARA as AEM and modified Nafion® as CEM), the water transport from diluate to the concentrate is due to the electroosmotic flux through the CEM. Meanwhile, the modification step carried out *in situ* before separation tests is fundamental. Separation tests carried out directly from non-modified Nafion® membranes (*m*07*t*01) with only an addition of PEI in the diluate provided no enhancement in the selectivity proton/divalent cation with respect to the nonmodified membrane.

4. Conclusion

The increase in selectivity of a Nafion® membrane towards protons with respect to divalent metallic cations was achieved by an *in situ* electrodeposition method. The surface of the membrane was directly modified in the electrodialysis stack used for the separation process. Separation tests of 4 h duration allow the reduction of the metal leakage from 34% for the as-received Nafion® membrane to less than 1%. This process requires a first modification step in which the experimental conditions become rapidly that of an increase of the protonated PEI transport number to enhance the penetration of the polyelectrolyte more deeply into the membrane. In the case of a decrease in selectivity, the advantage of this process lays in the possibility of renewing the modification *in situ*, by regenerating the surface PEI film without having to remove the membrane from the stack. However, to envisage an industrial application of this process, much longer duration separation tests will have to be undertaken.

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