

Comparison of anionic membranes used to concentrate nitric acid to beyond the azeotropic mixture

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Abstract

The electrolysis of concentrated nitric acid solutions was carried out in an electrochemical cell with parallel plates (FM01-LC ICI). An anionic membrane that permits the migration of nitrate ions under the influence of an electrical field separated the anodic and cathodic compartments. The current efficiency for the transported nitrate ions was evaluated for several membranes, at a constant current. All the membranes allowed the transport of nitrate ions at different current efficiencies, following the increase in acid concentration in the anodic compartment. This electroseparation membrane process concentrated nitric acid from 25% up to 90% in successive stages. A special case to be noted was when the acid concentration was near the azeotropic value. In this case, the acid concentration in the anodic compartment rose above the azeotropic value of 68.5%, thus breaking the azeotrope mixture. It is expected that, for some niche applications, this process could be competitive with extractive distillation. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Nitric acid is one of the main industrial reagents; its annual production reached 8×10^6 tonnes at the end of the 1970's, ranking its production in the USA within the top 10 main reagents [1]. The size of the total world market production of nitric acid has currently reached 55–60 million tonnes. Ammonium nitrate, which is the major end-use for nitric acid, accounts for 80% or more of the world nitric acid markets [2], and it has been roughly estimated that fertilizer accounts for

more than 85% of the world ammonium nitrate market. Thus, nitric acid consumption is greatly impacted by the state of the agricultural market. Other important end-use markets are the manufacturing of explosives and the manufacturing of intermediates for the production of fibres, plastics, elastomers and for organic synthesis.

The nitric acid industry is mature and has not grown appreciably in recent years. Indeed, in Western Europe, the industry has been declining because of concern about nitrate levels in groundwater, which have been affected by the level of fertilizer use [3]. The conventional production of the acid is by the catalytic oxidation of ammonia, giving a solution of 50–70% [4]. However, nitric acid at 100% is more efficient, particularly for the nitration of organic compounds. High acid concentrations can be achieved by extrac-

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tive distillation by means of a dehydrating agent such as sulfuric acid or magnesium nitrate in order to break the azeotropic mixture; however, the process involves further separations.

On the other hand, due to the economic and environmental benefit that the recovery of used acids represents, acid recovery processes have been increasing in recent years. The recovery of nitric, hydrochloric and sulfuric acids from chemical processes such as organic synthesis, the cleaning and dissolution of metals, among others, can be carried out by distillation, or alternatively, by a process using a membrane. In the latter process, the increase in concentration of nitric acid is performed by electrodialysis (ED), or by electro-electrodialysis (EED). ED is a process in which several anionic and cationic membranes alternate in an electrochemical cell in separate compartments. In the EED process, a cationic or anionic membrane is placed with each pair of electrodes within the cell. The EED process using an anionic membrane, which selectively transports nitrate ions to the anolyte [5–9], results in an increase in the concentration of nitric acid. In a recent study of simulated waste nitric acid solutions, the highest concentration of nitric acid reached by EED using an anionic perfluorinated membrane was 10 M [10].

Ideally, during ED, it is desirable that the electrolysis of water, i.e. the evolution of hydrogen and oxygen, takes place in the cathode and the anode, respectively, but in the EED of nitric acid, nitrate ions can be reduced to nitrite and further to ammonia. Simultaneously, protons can be reduced to hydrogen gas. Several authors have studied the reduction of nitrate ions in alkaline [11–16] and acidic media [17–19]. However, these studies used low nitrate concentrations (<1 M). Harrar et al. carried out one of the few studies using high nitrate concentrations; they used a divided cell to produce N_2O_5 , with anolyte solutions of N_2O_4 in approximately 99% nitric acid, and with catholyte solutions of the acid alone. The cathodic reaction was the production of N_2O_4 , which in theory, after separation from water, could be recirculated and used as the anolyte feedstock [20,21].

The principal aim of this paper was to study the breaking of the nitric acid azeotrope using an electromembrane process, and to analyze parameters such as membrane duration, cathodes, and the influence of the cathodic reaction during the EED process. Our ex-

perimental evidence suggests that the main cathodic reaction is the formation of NO_2 in equilibrium with N_2O_4 and the further reduction of NO_2 to the NO_2^- ion.

1.1. Membrane current efficiency

For a membrane process, the current efficiency is the amount of charge transported through the membrane by a specific contra ion (NO_3^-), per total charge, passed through the membrane. The integral current efficiency (ICE) is an average value of the current efficiency over a period of time. The mathematical definition is

$$\eta_{ICE} = \frac{Nz\mathcal{J}}{\int_0^t i dt}$$

However, in practice, it is calculated as

$$\eta_{ICE} = \frac{N(t) - N(0)}{F(t)}$$

This is valid for systems that are geometric and hydrodynamically similar due to their historical dependence (N increases with time). Where N , z , F and \mathcal{J} are the number of moles, the charge, the number of Faradays and the Faraday's constant, respectively; $N(t)$ and $N(0)$ are the number of moles at the times t and 0, respectively.

The differential current efficiency (DCE), on the other hand, is calculated on a differential element of time. It represents the value of the current efficiency over a very small period of time rather than that of an average over a considerable period of time.

The mathematical definition is

$$\eta_{DCE} = \frac{dN}{dt} \frac{z\mathcal{J}}{i}$$

In an experimental situation, however

$$\eta_{DCE} = \frac{N(t+1) - N(t)}{F(t+1) - F(t)}$$

It is important to note that η_{DCE} is highly sensitive to small experimental errors and fluctuations.

For an anion exchange membrane (AEM), the charge transported by protons from one molecule of water to another within the membrane limits the current efficiency. Thus, acids tend to diffuse at higher

rates than other ions, particularly when the water content of the membrane is high.

2. Experimental

The electrochemical cell used was a filter press type with parallel plates (ICI FMO-1 LC), operated in batch with Calomel electrodes as a reference. Fig. 1 shows an outline of this cell with two compartments divided by an anionic membrane. The flow system was arranged as shown in Fig. 2. Flow within the cell was kept at approximately 66 cm s^{-1} . Each electrode had a turbulence promoter made of poly(tetrafluoroethylene) (PTFE). The cathode electrodes used were a stainless steel 304-L, a stainless steel 316 and a 'Hastelloy' alloy. Niobium platinized in the form of a grill 'Lantern Blade' was used as an anode. The complete description of this cell, its characteristics and local variations of transport have been outlined in detail in the literature [22–24]. A standard dc power supply was used to apply constant current. The anionic membranes used were all commercially available: AW and ARA from

Solvay, France, Raipore 5035 and Raipore 6030 from Pall, UK, and ACS and AFN7 from Tokuyama, Japan. The AW, ARA, ACS and AFN7 membranes have been used in several ED studies and their characteristics such as ionic exchange capacity, water content, transport number and nature of ionic sites can be found in the literature [25–29]. The Raipore membranes 5035 and 6030 are for the separation of acids with low proton leakage. The membrane 6030 was specially manufactured for the experimental production of N_2O_5 with a thickness of 6–7 mil; in comparison, the rest of the membranes have a thickness within the range of 2–4 mil. The ionic exchange sites of such Raipore membranes were quarternized benzylamine graft on a fluorinated polymer film [30]. In the experiment with a three-compartment cell, a cationic Raipore 4010 membrane protected the cathode. On the other hand, tubing, valves, and heads of the centrifuge bombs were manufactured from PTFE. The $\text{NO}_2/\text{N}_2\text{O}_4$ gas mixture, which formed in the catholyte compartment during the EED experiments, was diluted with nitrogen. This mixture was passed through a gas scrubber containing sodium hydroxide, in order to neutralize the

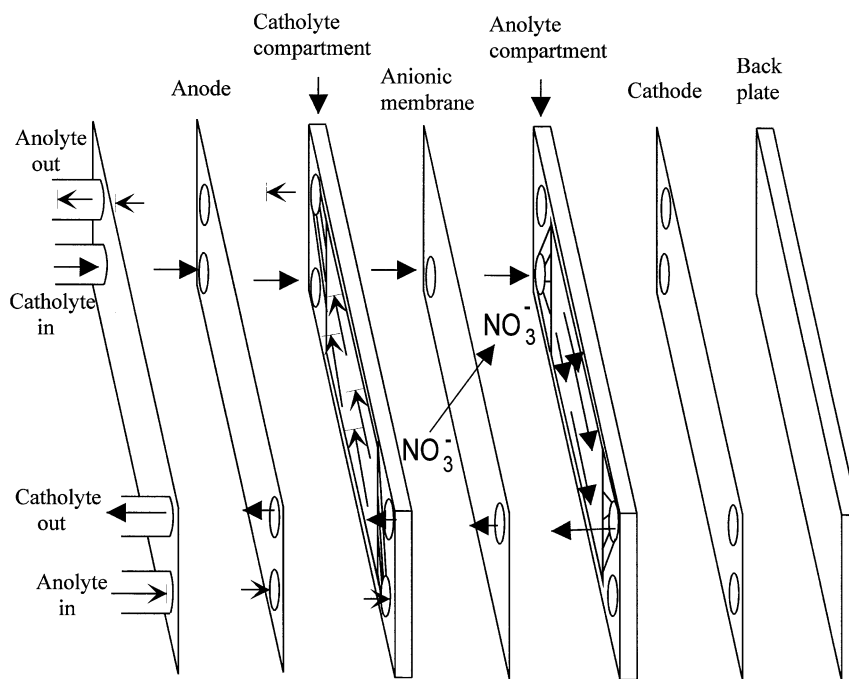


Fig. 1. Schematic diagram of a two-compartment cell for EED experiments.

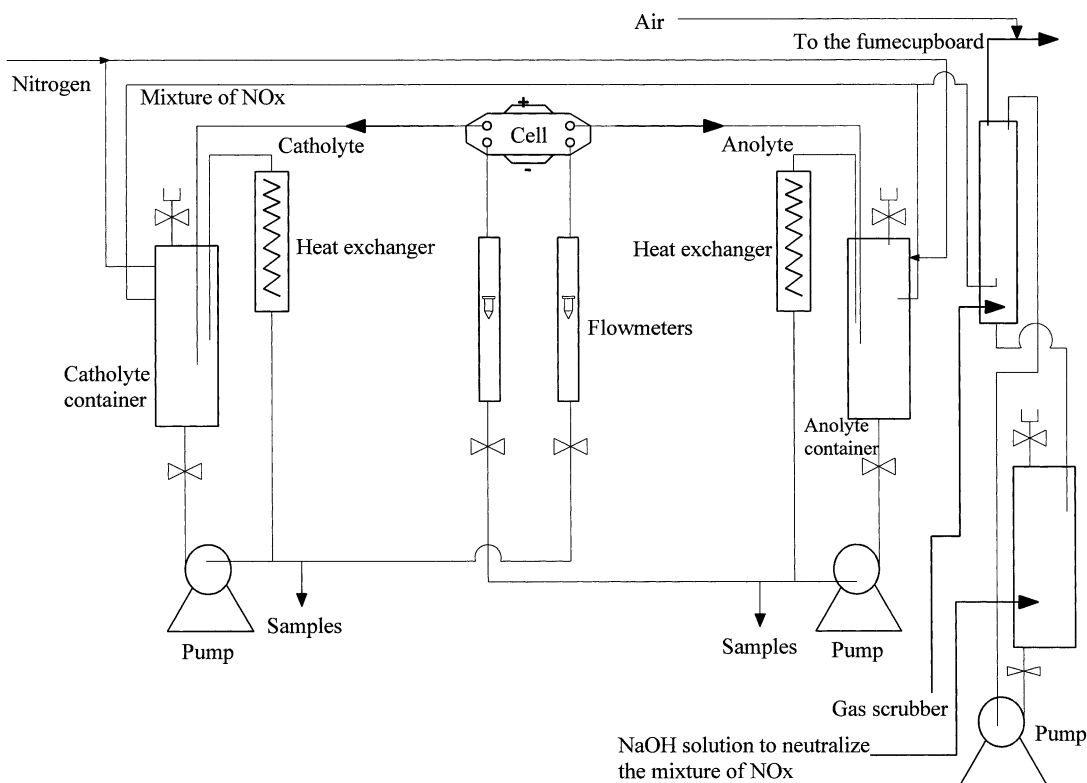


Fig. 2. Outline of the experimental rig.

NO_x gases. The remaining gases, including the oxygen produced in the anolyte, were diluted to a ratio of 1:5 with air and sent through the fume cupboard.

During electrolysis, samples from the catholyte and the anolyte were taken at regular intervals. The determination of the total acid was carried out by standard volumetric analysis [31]. An in-line density meter measured the density of the acid. The concentration of the NO_2^- ion was determined by the addition of 0.1 N ammonium, and an excess of ceric sulfate solution, followed by the reverse titration with 0.1 N sodium thiosulphate [31]. The nitric acid was of a technical grade and the other reagents were of an analytic grade.

3. Results and discussion

3.1. Electrodes

Three cathode electrodes were tested, a stainless steel 316, a stainless steel 304-L and a Hastelloy alloy.

The current efficiencies ICE and DCE were slightly larger with stainless steel electrodes than with the Hastelloy electrode. However, the stainless steel 316 electrode lost 0.55% of its weight after 700 min at 300 mA cm^{-2} . With a stainless steel 304-L, there was no change in weight under the same conditions. Similarly, the anode electrode made of platinized niobium kept a constant weight.

3.2. Electrochemical reactions

Concentrated nitric acid has not been studied extensively with regard to electromembrane processes. Most literature relates to nitrate recovery, generally describing low concentration feed streams as applicable to the water industry. The recommended level of nitrates in drinking water is $<25 \text{ mg l}^{-1}$ ($\sim 0.004 \text{ M}$). Since electromembrane processes are suitable for depleting ions from concentrated solutions, leaving behind a very dilute solution of ions, this has prompted

nitrate recovery via electromembrane processes in recent years [8,32,33]. Nitrates can form nitrites, nitriles and nitrosamines, and various mechanisms have been proposed for the nitrate reduction pathway, which increases in complexity with the presence of metal ions in the system. Despite the fact that this mechanism has not been fully understood yet, overall two key reduction products, which are nitrite and ammonium, have been highlighted at low concentrations (<1.2 M). At higher concentrations (>2 M), the cathodic reactions depend mainly upon the predominant species in the solution. At concentrations below 10 M (~50%), the evolution of hydrogen gas is the main reaction, since the acid is completely dissociated. As the concentration increases, the degree of ionization is lower. The predominant form of nitric acid at 68.5% (azeotropic mixture) is the hydrated and dehydrated NO_2OH species. Under these conditions, the evolution of hydrogen gas does not take place at an appreciable rate, but the main reaction is the reduction of the dehydrated nitric acid and the nitrate ions. On the other hand, it is assumed that the only anodic reaction is the oxidation of water [19].

The aforementioned literature research shows that the reduction of nitrate leads to NO_2 nitrite molecule and its reduction forms NO_2^- nitrite ions. Further reduction of these ions results in ammonia. At high concentrations, we found that the first reduction product, that is, NO_2 , was in equilibrium with N_2O_4 . However, this mixture was not analyzed during the electrolysis of the azeotropic mixture. Instead, the concentration of NO_2^- nitrite ions, both in the catholyte and in the anolyte, was determined. Fig. 3 shows the change in concentration of the NO_2^- ion versus catholyte concentration during the EED of nitric acid. It can be seen that the concentration of nitrite ions increased during electrolysis. The current efficiency, assuming the cathodic reaction $\text{NO}_3^- + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{NO}_2^- + \text{H}_2\text{O}$ instead of the one-electron reaction $\text{NO}_3^- + 2\text{H}^+ + \text{e}^- \rightarrow 1/2\text{N}_2\text{O}_{4(\text{g})} + \text{H}_2\text{O}$, was 0.80 during the first 2 h and then it dropped. Since the NO_2 molecule was the reactant for the NO_2^- , the equilibrium conditions of the reaction $2\text{NO}_2 = \text{N}_2\text{O}_4$ affected the concentration of the nitrite ions in the solution. The depletion of nitrite ions after 2 h was attributed to a shift to the right in the above

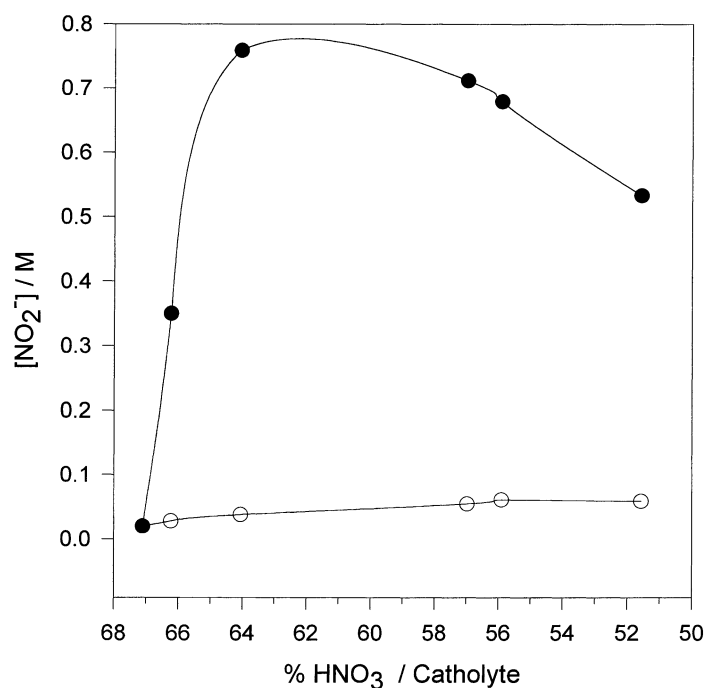


Fig. 3. Evolution of NO_2^- ion for both catholyte ● and anolyte ○ with the change in nitric acid concentration in the catholyte compartment. The electrolysis was carried out using an AW membrane at a current density of 300 mA cm^{-2} in a two-compartment cell.

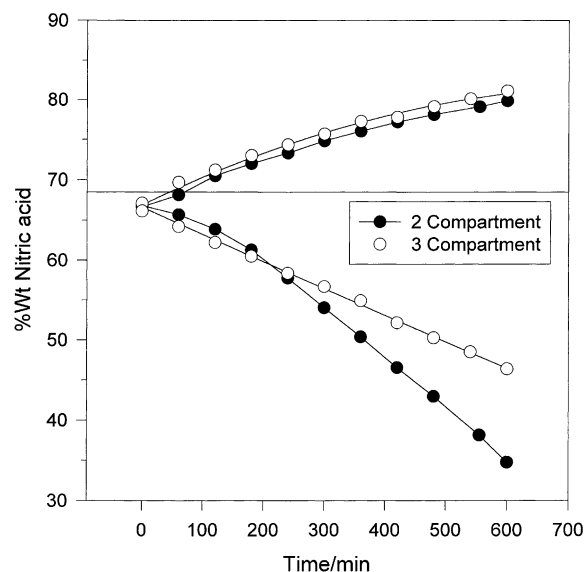


Fig. 4. Change in the acid concentration with time in both anolyte and catholyte during an electrolysis in a two- and a three-compartment cell. In the two-compartment cell, the membrane used was an AW, whereas in the three-compartment cell, the membranes were: anionic AW, cationic Raipore 4010. In both experiments, the current density was at 300 mA cm^{-2} .

reaction due to the increase in temperature from 20 to 30°C during EED, leading from the cathodic reduction of nitrate to the formation of N_2O_4 as a main product. Fig. 4 gives an example of the change in the concentration of nitric acid in the catholyte and in the anolyte.

It was observed that hydrogen evolution started only when the catholyte concentration dropped below 45–50%, thus suggesting that nitrate reduction to $\text{NO}_2 = \text{N}_2\text{O}_4$ was the main cathodic reaction at a concentration above 50% nitric acid. Harrar et al. did not observe hydrogen evolution at 99% nitric acid; however, they did produce N_2O_4 at the cathode [20,21].

The changes in color in the catholyte during the EED of the acid were interesting. During the first hour at concentrations between 55 and 67%, the color of the solution changed from transparent to dark brown in equilibrium with red gases. This was due to the presence of the N_2O_4 species, which is red at 21°C when it is in equilibrium with NO_2 gas. In the second and third hours, the change in color was from dark brown to dark green (45–55 w/w%). This was probably due to the presence of species such as NO_2OH , since

in amounts of less than 2%, it produces a greenish blue solution. As the concentration fell, the catholyte turned light blue (35–45%). Finally, at a concentration of 25%, the solution was slightly pink. These changes in coloration were due to a complex mixture of nitrogen oxides.

This change in catholyte color could be avoided by protecting the cathode with a cationic membrane. In an experiment carried out in a three-compartment cell, hydrogen ions migrated from the middle nitric acid compartment towards the cathode through the cationic membrane where the solution in contact with the cathode was only sulfuric acid. Therefore, it was assured that the cathodic reaction was simply the evolution of hydrogen. A cationic Raipore 4010 membrane in contact with a sulfuric acid 1 M solution protected the cathode. In the middle compartment, the azeotropic mixture was in contact with the cationic membrane (catholyte side) and with an AW anionic membrane (anolyte side). In this case, no changes in color in the catholyte were observed. The changes in acid concentration were similar to the changes observed in a three-compartment cell as shown in Fig. 4. It should be emphasized, however, that the concentration of nitric acid in the catholyte dropped faster in a two-compartment cell due to cathodic reduction.

3.3. Selection of membrane for the EED of nitric acid

Several anionic membranes used in the EED of nitric acid are compared in Table 1. In all experiments, the starting concentration of both the catholyte and the anolyte was between 65 and 70%. All the membranes transported nitrate ions so that the concentration of the anolyte surpassed the azeotropic value (68.5%) as can be seen from the column of maximum concentration in Table 1. The DCE varied with the concentration difference and the first column in Table 1 shows the DCE for each experiment when the difference in concentration between the anolyte and the catholyte was approximately 20%. Table 1 also shows the fluxes in NO_3^- , H^+ , and H_2O , calculated from a mass balance during the experiment. From these values, it is possible to evaluate the number of water molecules per nitrate ion that migrated through the membrane. It should be noted that hydrogen and nitrate ions traveled across the membrane as solvated ions; therefore,

Table 1
Comparison of different anionic membranes^a

Membrane	DCE	Flux NO ₃ ⁻ (mol m ⁻² s ⁻¹)	Flux H ⁺ (mol m ⁻² s ⁻¹)	Flux H ₂ O (mol m ⁻² s ⁻¹)	H ₂ O/NO ₃	Maximum [HNO ₃] M (%)	E _s (kW h kg ⁻¹)
AFN7	0.27	0.0087	-0.023	0.021	2.4	16.0 M: 71%	3.54
ARA	0.41	0.0129	-0.019	0.023	1.7	16.5 M: 73.4%	4.66
Raipore 5035	0.48	0.0152	-0.016	0.023	1.5	17.0 M: 75.4%	3.10
ACS	0.52	0.0165	-0.015	0.025	1.5	16.4 M: 73%	2.86
AW	0.60	0.0192	-0.0124	0.025	1.3	17.9 M: 78.9%	1.77
Raipore 6030	0.83	0.0262	-0.0163	0.026	1.0	18.0 M: 79.3%	1.41

^a The initial concentration of the catholyte and the anolyte for all the cases was between 65 and 70%. The DCE was calculated when the concentration difference was 20%. The current density was 300 mA cm⁻².

the ratios H₂O/NO₃⁻ and H₂O/H⁺ provide an estimation of the number of water molecules accompanying each ion as they migrated. The minus sign in the protons' column indicates that H⁺ ions migrated from the anolyte to the catholyte. The cell potential and the current efficiency were used to calculate the specific energy, E_s, during the process. As can be seen from Table 1, the energy consumption varied within the range 1.41–4.66 kW h kg⁻¹. The E_s values for electrochemical processes such as the removal of Cr(IV) and the Monsanto process (hydrodimerization of acrylonitrile) are 11.0 and 6.7 kW h kg⁻¹, respectively, whereas the desalination of water is 1.4 × 10⁻³ kW h kg⁻¹ [34]. Although the E_s values in Table 1 are within the same order of magnitude as in an electrochemical process, they are high in comparison with the desalination of water, which is an ED process.

In general, it was observed that the values of DCE diminished upon increasing the concentration in the anolyte for all the experiments. Fig. 5 shows the change in concentration for the anolyte and the catholyte for the EED carried out with the Raipore 6030 membrane; the inset in the figure shows the changes in both ICE and DCE. The efficiencies decreased as the concentration difference increased, the DCE decreased rapidly which was an indication of the instant performance of the membrane, whereas the ICE was the accumulative value of the efficiency from the beginning of the experiment.

Clearly, the Raipore 6030 membrane from Pall showed a higher DCE and a higher nitrate ion flux than the rest of the membranes under the conditions used. It exhibited three times more nitrate flux than the AFN7 membrane, which had the lowest flux. In addition, a mass balance for the ratio H₂O/NO₃

demonstrated that the acid concentration within the membrane was the highest. On the contrary, the anionic membrane AFN7 had the lowest acid concentration inside the membrane and the lowest DCE. In addition, proton leakage in the AFN7 membrane was 1.4 times higher than in the Raipore 6030 membrane. Thus, it made the AFN7 membrane more suitable for a dialysis process, since high proton leakage is necessary for dialysis. The flux of water towards the anolyte across the membranes remained practically constant, differing only by a factor of 1.2 among these two extreme membranes.

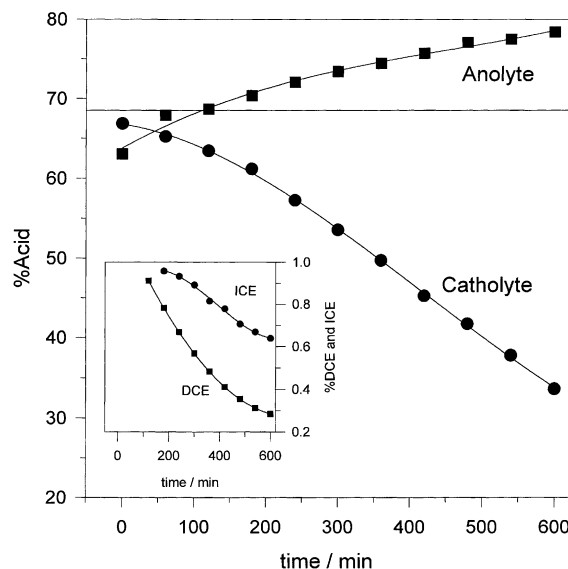


Fig. 5. Change in the acid concentration with time in both anolyte and catholyte. The inset shows the current efficiencies ICE and DCE for an electrolysis at a current density of 300 mA cm⁻² using a Raipore 6030 membrane from Pall.

Table 2
Experiments with a Raipore 6030 membrane (300 mA cm^{-2})

Experiment	Catholyte initial (%)	Catholyte final (%)	Anolyte initial (%)	Anolyte final (%)	DCE ($\Delta 9 \text{ M}$)	Duration (h)	Accumulative time (h)
(a) Constant catalytic concentrations							
1	25	25	61	66	0.00	6	6
2	35	35	64	72	0.20	7.2	13.2
3	45	45	61	71	0.50	6.5	19.7
4	55	55	62	74	0.65	6.4	26.1
(b) Comparison of new and used membranes							
Used	65	50	74	86	0.55	13	39.1
New	64	50	68	77	0.80		

3.4. Experiment at constant catholyte concentration

Since the Raipore 6030 membrane showed the highest nitrate ion flux, it was then chosen to carry out a series of long-term experiments with different constant catholyte concentrations, in order to determine the degree of membrane degradation. In each experiment, the catholyte concentration was kept at the following constant values: 25, 35, 45 and 55%, whereas the initial concentration of the anolyte was approximately 60% for each experiment. The experiments were carried out using the same piece of membrane, starting with the lowest acid concentration. The results are shown in Table 2a. As can be seen from the table, the DCE values depended on the initial catholyte concentration; the DCE increased as the concentration difference between the catholyte and the anolyte diminished. This series of experiments showed that the concentration of the anolyte overcame the azeotropic value (68.5%) only when the catholyte concentration was higher than 35% (Experiment 2). However, in this case, the DCE value was only 0.20, with a final concentration difference of approximately 35%. The highest DCE value was 0.65 with a final concentration difference of 20% at the end of the fourth experiment, i.e., after 26 h of operation at 300 mA cm^{-2} . The experiments suggested that, if the concentration of catholyte and anolyte differed by more than 25%, a staged process would be necessary.

A comparison of new and used membranes is given in Table 2b using data obtained with both new and used Raipore 6030 membranes. The used membranes had been submitted to a density current of 300 mA cm^{-2} in the experiment in the previous section, for 26 h.

The initial catholyte conditions were the same for both experiments; however, the initial anolyte concentration was different, that is, 74%, for the used membrane and 68% for the new membrane. As a result, at the end of the experiments, the anolyte with the used membrane reached 86% concentration and the anolyte with the new membrane reached 74%. However, the DCE values in both cases were different; the new membrane had a current efficiency of 0.80, whereas the used one had 0.55 under the same conditions. It is clear that, during electrolysis, certain degrees of degradation occurred inside the membranes, probably due to the loss of ionic sites.

3.5. Sorption experiments

The Raipore 6030 membrane was tested in a series of experiments to determine its sorption characteristics. Known weights of a new and a used dry membrane were soaked in nitric acid at 25°C for 24 h at different concentrations. The used membrane had already been used for 40 h of EED for the experiment in the two previous sections. Once the membranes were well impregnated with the acid, they were washed thoroughly with water to remove all the surplus acid from the surface, and dried with a dry clean cloth. The membranes were placed in a container at a low pressure (near 1 mm Hg), in order to desorb all the acid and water adsorbed in the membrane. The acid and water extracted were collected in a cold trap and analyzed by standard volumetric analysis. Table 3 shows the calculated ratio of grams of HNO_3 , H_2O , and $\text{HNO}_3 + \text{H}_2\text{O}$ per gram of dry membrane for the new and used membranes. Regardless of whether the membrane had been

Table 3
Data from sorption experiments using a Raipore 6030 membrane^a

[HNO ₃] (%)	New membrane (weight specie/weight of dried membrane)				Used membrane (weight specie/weight of dried membrane)			
	(%) in solution	HNO ₃ / membrane	H ₂ O/ membrane	HNO ₃ +H ₂ O/ membrane	% in membrane	HNO ₃ / membrane	H ₂ O/ membrane	HNO ₃ +H ₂ O/ membrane
51	0.08	0.049	0.129	62.1	0.057	0.034	0.091	62
57.7	0.08	0.055	0.135	59.3	0.048	0.059	0.087	55.2
62	0.097	0.041	0.138	70.2	0.054	0.022	0.076	70.6
69	0.157	0.054	0.212	74.1	0.112	0.047	0.159	70.4
74.5	0.166	0.054	0.220	75.4	0.109	0.036	0.145	75.2
79	0.177	0.043	0.220	80.4	0.103	0.025	0.128	80.1
84.9	0.252	0.009	0.261	96.5	0.157	0.046	0.203	77.4
92	0.185	0.020	0.205	90.3	0.098	0.016	0.114	89.4

^a Column 1 shows the concentration of acid used for soaking. Columns 2, 3, 6 and 7 show the ratio between nitric acid and water per gram of membrane. Columns 4 and 8 show the total mass of components inside the membrane per gram of membrane. Columns 5 and 9 show the acid concentration inside the membrane.

used or not, the ratio of acid per unit weight of membrane increased with the concentration of the acid, where the membrane had previously been stabilized. The relationship was always smaller for a used membrane. This confirmed the fact that the used membrane lost some ionic or active sites during electrolysis. On the other hand, as was expected, the sorption of water became less as the acid concentration increased.

3.6. Reaching a high nitric acid concentration by EED

In another experiment, a new Raipore 6030 membrane was used to investigate the possibility of reaching 100% nitric acid concentration. The catholyte was replaced three times when its concentration diminished to 50% for a new 68.5% solution. The concentration in the anolyte increased to up to 92%. Fig. 6 shows the change in the anolyte volume versus anolyte concentration. It can be seen that, at the beginning of electrolysis, the volume increased steadily; however, it reached a maximum when the acid concentration was 80%. This increase in volume was followed by a rise in the anolyte concentration, indicating that the moles of nitrate rose faster than the moles of water in the anolyte. The back diffusion of nitrate ions to the catholyte increased after the acid concentration reached 80%, due to the large difference in concentration between the two compartments. At below 80%, the NO₃(H₂O)_n⁻ species was believed to have been

transported through the membrane towards the anolyte by electrodiffusion. However, with more than 80% of acid in the anolyte, the back diffusion equalled the electrodiffusion of nitrate ions, and after this point, the concentration of acid increased only due to the consumption of water in the anode. This competitive process caused the flow of water to change direction.

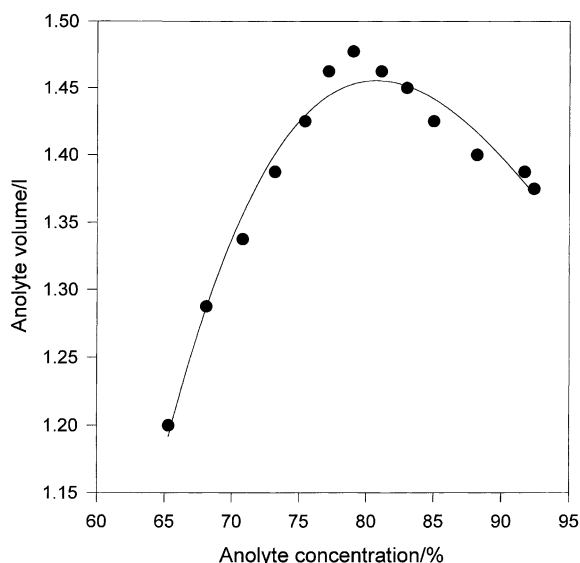


Fig. 6. Volume changes in the anolyte with the change in the anolyte concentration, when the anolyte concentration increased up to 92%. The electrolysis was carried out at a density current of 300 mA cm⁻² using a Raipore membrane 6030 from Pall.

The change in moles of water in the anolyte per Faraday was

$$\text{DCE} \cdot n\text{NO}_3^- = -(1 - \text{DCE})n\text{H}^+ - 0.5$$

where $n\text{NO}_3^-$ is the number of moles of water associated with each nitrate ion transported through the membrane; $n\text{H}^+$ is the number of moles of water associated with each proton transferred through the membrane.

The 0.5 value arises from the consumption of 1/2 mol of water per Faraday based on the assumption that the evolution of oxygen was the only anodic reaction. If $n\text{NO}_3^- = 3$ and $n\text{H}^+ = 1$, the point of zero change in volume was at the DCE value of 0.375. The experimental DCE at 80% of HNO_3 was 0.36 showing that, at this concentration, the amount of water dragged by each NO_3^- ion to the anolyte less the loss of water by back diffusion (due to each H^+ ion) equalled the water consumed in the anodic process.

The nitric acid–water mixtures are complex systems in which molecules of acid, its ions and the hydrate and non-hydrate species are all present together along with free water. Investigations on the absorption of infra-red and ultraviolet light by these mixtures [4] showed that, at 80% concentration, the $\text{NO}_2\text{OH}\cdot\text{H}_2\text{O}$ and $\text{NO}_2\text{OH}\cdot 3\text{H}_2\text{O}$ species account for 70% of the fraction of total HNO_3 , the anhydrous NO_2OH species for 25%, and the ions H^+ and NO_3^- only for 5%. This may suggest that the ionic species of the acid at these concentrations contribute very little to the back migration.

At 300 mA cm^{-2} , the evolution of O_2 in the anolyte was $6.1 \times 10^{-3} \text{ mol min}^{-1}$. Thus, the rate at which the water reacted at the anode, neglecting the density changes, was 0.0131 h^{-1} . This change corresponds approximately to the 20% change in volume presented in Fig. 6, assuming that the evolution of oxygen was the only anodic reaction.

An interesting fact noted when characterizing the membrane was the comparison between the diffusional and electrodiffusional flows. The change in acid concentration due only to dialysis in the Raipore 6030 membrane was approximately 0.3 mol h^{-1} . At an applied current density of 300 mA cm^{-2} , the change in concentration was approximately 1.2 mol h^{-1} in the direction of the anolyte at a DCE of 0.80. Thus, the diffusional flow was approximately 20% of the electrodiffusional flow.

4. Conclusions

The cathodic reaction of concentrated nitric acid produced a complex mixture of nitrogen oxides such as N_2O_4 , N_2O_3 , and NO_2^- . The cathodic reduction of nitrate ions could be avoided using a three-compartment cell.

It was possible to break the nitric acid azeotrope mixture using any of the anionic membranes tested including (a) AFN7, (b) ARA, (c) Raipore 5035, (d) ACS, (e) AW, (f) Raipore 6030, when the difference in concentration between catholyte and anolyte did not exceed 5 M. The transportation of nitrate ions through these membranes increased in the same order in which they are listed above. The most efficient membrane was the Raipore 6030. However, the membrane needs to be tested in a series of long-term experiments.

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