Nitric acid and sodium hydroxide generation by electrodialysis using bipolar membranes

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An electrodialysis process with bipolar membranes was used to generate HNO_3 and $NaOH$ from $NaNO_3$ which can be found in industrial waste waters. The current efficiency of this process is limited by proton leakage through the anion exchange membrane (AEM), co-ion leakage through bipolar membranes (BPM) and water transport through the ion exchange membranes. Three cell configurations using three or two compartment cells with different anion or cation exchange membranes (CEM) in stack series were used and compared. Electrodialysis with three compartments gives the best current efficiencies for nitric acid and sodium hydroxide production from sodium nitrate.

1. Introduction

Bipolar membranes (BPM) are composed of an anion exchange layer, a cation exchange layer and a hydrophilic interface at the junction of the two layers. In this hydrophilic interface, water molecules are split into protons and hydroxide ions. This process allows use of electrodialysis to recover acids and bases from their salts.

Since it allows recovery of acids and bases neutralized during industrial processes, BPM has become an important technique in recycling salts from effluents. For example, sodium nitrate effluents produced from the nuclear industry during the production of uranium hexafluorides from uranium nitrates and sodium hexafluorides can be treated [1]. In the dying industry cadmium nitrate is converted to sulfide according to the following reaction [2]:

$$Cd(NO_3)_2 + Na_2S \longrightarrow CdS + 2NaNO_3$$
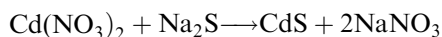
and again the nitrate containing product is amenable to the proposed treatment.

Recent technological improvements in the manufacture of ion exchange membranes have led to the application of electrodialysis in many areas such as the production, purification and reconcentration of acids [3–7]. In electrodialysis with bipolar membranes, the generation of protons and hydroxide ions by water splitting leads to acid and base production directly from the salt [8–10].

Electrodialysers with bipolar membranes commercialized by Aqualytics (a division of the Graver Co.) are attractive devices for production of acid and base from salts extracted from industrial waste waters and mining activities [11]. This technology can also be used to produce acids and bases from mineral salts.

The most important phenomena which limits this process is proton leakage through the AEM and water transport through the ion-exchange membranes. These phenomena have already been described [12–15].

The purpose of this work is to study the production of HNO_3 and $NaOH$ from $NaNO_3$ by electrodialysis with bipolar membranes using an Aqualytics electrodialysis system. A comparison between three and two cell arrangements is proposed.

2. Experimental details

The electrodialyser stack was composed of two electrode compartments between which eight identical cells separated by bipolar membranes were inserted. Three configurations of cell were tested. In the first configuration the cell was composed of three chambers for acid, salt and base separated by the anion and cation exchange membranes, respectively (Fig. 1(a)). In the second configuration, the cell was composed only of two salt and base chambers separated by the cation exchange membranes (Fig. 1(b)). In the third configuration, the two salt and acid chambers were separated by anion exchange membranes (Fig. 1(c)).

When an electrical potential is applied between the electrodes (Fig. 1(a)), the cations (Na^+) and anions (NO_3^-) move in opposite directions across the CEM and AEM, respectively, to form the base and acid by combining with the hydroxide ions and protons generated in the bipolar membrane from water splitting.
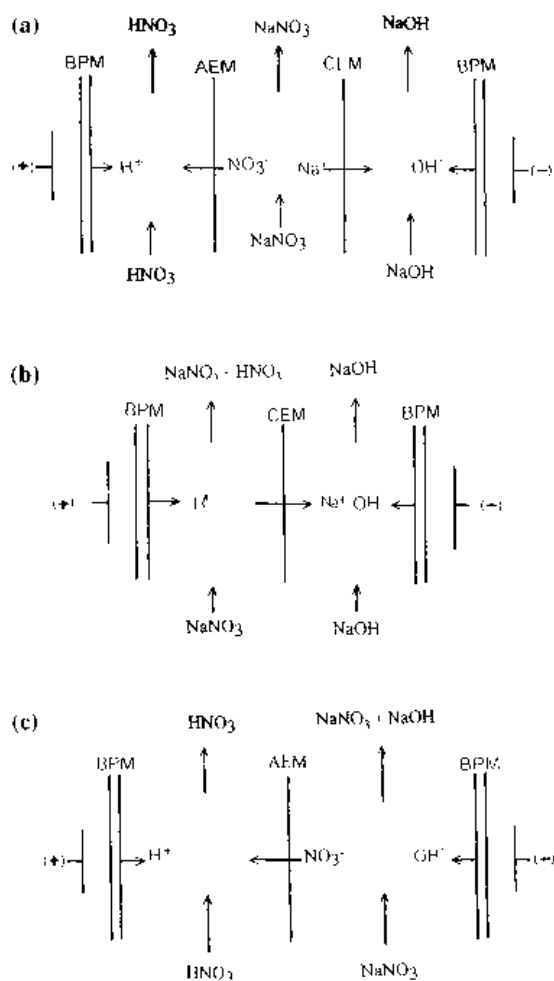
Fig. 1. Cell configurations: (a) with three compartments for acid, salt and base; (b) with two compartments for salt and base; (c) with two compartments for acid and salt.

In this process, the salt solution must not contain any trace of multivalent metallic cations in order to prevent precipitation of hydroxides within the CEM or on the surface of the bipolar membrane in the two compartment configuration with the AEM.

The working area of the electrodes and of the membranes was 102 cm^2. A predetermined volume of various solutions (2 M NaNO$_3$, 0.1 M HNO$_3$, 0.1 M NaOH) was circulated at a velocity of 11.1 cm s^{-1} in the salt, acid and base compartments, respectively, using an adjustable pump to obtain a continuous flow. The current was maintained at a constant value by a current generator. The selected current densities were 98 mA cm^{-2} in the first configuration and 127 mA cm^{-2} in the two other configurations. The solutions were maintained at 30 °C.

Sampling 10 ml of solution in each compartment enabled the composition to be monitored by pH titration for H$^+$ and OH$^-$, by absorption spectroscopy for Na$^+$ and by HPLC for NO$_3^-$.

3. Results and discussion

3.1. *Electrodialysis with acid, salt and base compartments*

In the electrodialyser shown in Fig. 1(a), 4 dm^3 of electrolyte were circulated in the acid and base compartments loops and 5 dm^3 in the salt compartment loop.

Starting from 0.1 M solutions of NaOH and HNO$_3$, the two concentrations increased markedly with time and tended to steady values after 5 h. The final concentrations were 2.12 M NaOH and 1.92 M HNO$_3$ (Fig. 2). The concentration of acid and base is adversely affected by the transfer of water through the AEM and the CEM. Figure 3 shows the increasing volumes of the two solutions.

The following equations give the concentration as a function of time:

$$C_{(NaOH)} = 0.74\, t^{0.62} + C_{0(NaOH)} \qquad (1)$$

$$C_{(HNO_3)} = 0.64\, t^{0.68} + C_{0(HNO_3)} \qquad (2)$$

Volumes are given by the following relations:

$$V_{(NaOH)} = 4.02 + 0.084\, t \qquad (3)$$

$$V_{(HNO_3)} = 4.14 + 0.15\, t \qquad (4)$$

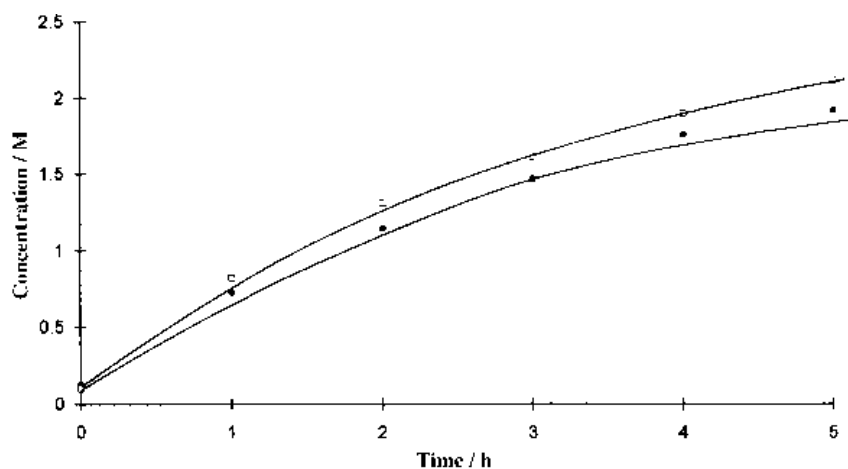The current efficiencies C_E for acid or base are given by

Fig. 2. Variation of NaOH and HNO$_3$ concentrations as a function of time in the base and acid compartments, respectively. Key: (●) HNO$_3$ and (□) NaOH.
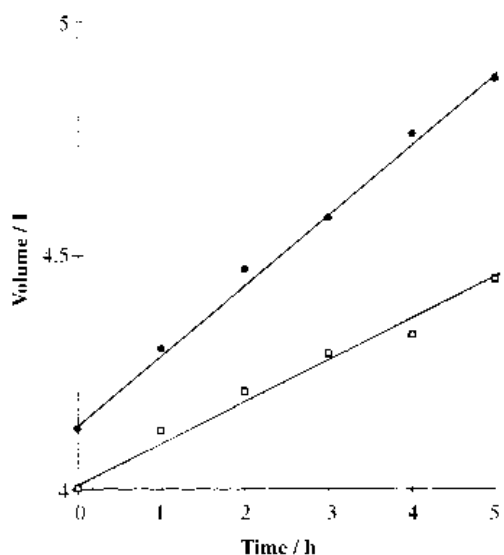
Fig. 3. Variation of the volume of acid and base solutions against time. Key: (●) HNO$_3$ and (□) NaOH.

$$C_E = 100 \frac{(C_f V_f - C_i V_i)}{8 I \Delta t} \qquad (5)$$

In this relation $(C_f V_f - C_i V_i)$ is the variation with time of the amount of acid and base in moles, F is the Faraday number, I the applied current, t the time and '8' the number of cells in the electrodialyser stack.

Figure 4 shows that current efficiencies for NaOH and HNO$_3$ decrease with increasing concentrations of acid and base which limits the product concentrations. These variations can also be obtained from the following equations:

$$C_{E(NaOH)} = 120 - 29.5\, C_{NaOH} \qquad (6)$$

$$C_{E(HNO_3)} = 100 - 20.7\, C_{HNO_3} \qquad (7)$$

The lower values of $C_{E(HNO_3)}$ relative to those of $C_{E(NaOH)}$ can be attributed essentially to proton

leakage through the AEM which is higher than the co-ion leakage through the CEM and BPM.

The decreasing slopes in Fig. 4 can be attributed to the following factors: (i) proton leakage through the AEM; (ii) OH$^-$ leakage through the CEM; and (iii) co-ion leakage through the BPM (Fig. 5).

Proton leakage through the AEM induces a decreasing C_{Na^+}/C_{H^+} ratio in the salt compartment (Fig. 6) given by

$$\frac{C_{Na^+}}{C_{H^+}} = 190 - 165\, t^{0.087} \qquad (8)$$

where t is the duration of experiment.

This decrease leads to a decrease in $C_{E(NaOH)}$ in the base compartment because of the competition between H$^+$ and Na$^+$ during their transfer through the CEM membrane.

Taking into account the normal fluxes of counter ions and these different leakages we can write the flux equations for the CEM and AEM membranes.

In the CEM, the current density can be related to the three ionic (Na$^+$, H$^+$ and OH$^-$) fluxes with the following relation:

$$\frac{i}{F} = \left| J_{Na^+}^C \right| + \left| J_{H^+}^C \right| + \left| J_{OH^-}^C \right| \qquad (9)$$

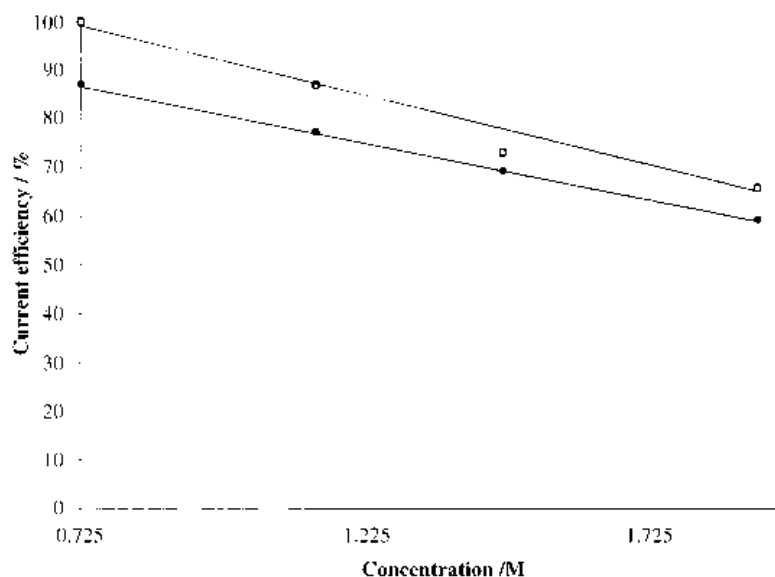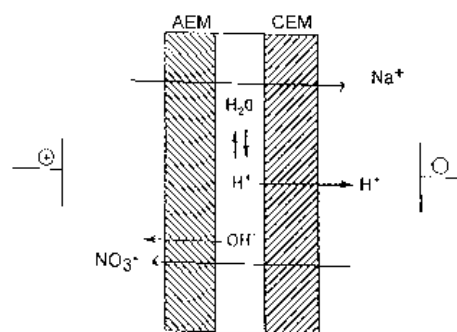Fig. 5. Co-ion leakage through the BPM membrane.

Fig. 4. Variation of the current efficiency for HNO$_3$ and NaOH production against concentration of generated acid and base. Key: (●) HNO$_3$ and (□) NaOH.
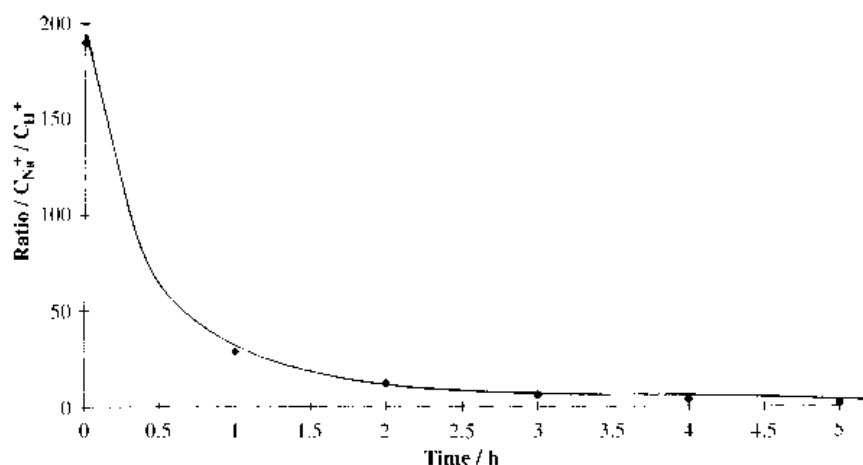
Fig. 6. Variation of C_{Na^+}/C_{H^+} ratio against time in the salt compartment.

where $\left|J_{H^+}^C\right|$ is the flux of H$^+$ through the CEM due to proton leakage through the AEM and $\left|J_{OH^-}^C\right|$ is the flux of OH$^-$ ions through the CEM (OH$^-$ leakage) when the concentration of NaOH becomes significant in the base compartment.

In the same way for the AEM:

$$\frac{i}{F} = \left|J_{NO_3^-}^A\right| + \left|J_{H^+}^A\right| + \left|J_{OH^-}^A\right| \tag{10}$$

$\left|J_{H^+}^A\right|$ is the proton leakage through the AEM, $\left|J_{OH^-}^A\right|$ is the OH$^-$ flux through the AEM due to OH$^-$ leakage through the CEM.

In the same way taking into account the different leakages through the BPM (Fig. 5), the fluxes through the anion exchange and cation exchange layers of the BPM, give the following relations:

$$\frac{i}{F} = \left|J_{OH^-}^{ABPM}\right| + \left|J_{NO_3^-}^{ABPM}\right| + \left|J_{Na^+}^{ABPM}\right| \tag{11}$$

$$\frac{i}{F} = \left|J_{H^+}^{CBPM}\right| + \left|J_{NO_3^-}^{CBPM}\right| + \left|J_{Na^+}^{CBPM}\right| \tag{12}$$

The NO$_3^-$ leakage through the cation exchange layer of the BPM and the Na$^+$ leakage through the

anion exchange layer of the BPM contribute to the limitation of concentrations in the base and in the acid compartments respectively. Figure 7 shows the increasing current efficiencies of NO$_3^-$ and Na$^+$ against time.

3.2. Electrodialysis with base and salt compartments (Fig. 1(b))

Circulation in the loops of base and salt compartments were 3.0 and 3.5 dm^3, respectively.

Figure 8 shows the increasing concentration with time of NaOH generated in the base compartment and of HNO$_3$ generated in the salt compartment. A plateau is reached at 1.1 M after 120 min. The decreasing current efficiency $C_{E(NaOH)}$ against C_{H^+}/C_{Na^+} ratio shown in Fig. 9 is mainly due to competition between H$^+$ and Na$^+$ crossing the CEM membrane. Figure 10 allows comparison of the increase and decrease in sodium concentrations in the base and salt compartments, respectively.
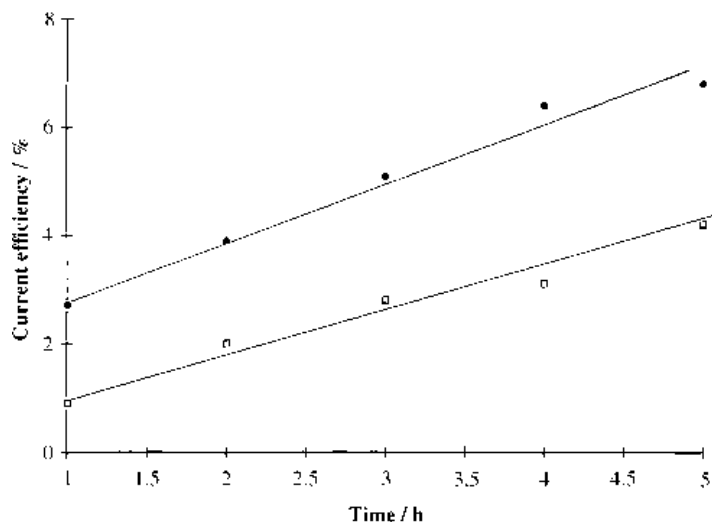

Fig. 7. Increasing of current efficiencies against time for NO$_3^-$ in the base compartment and for Na$^+$ in the acid compartment (NO$_3^-$ leakage through the cation exchange layer and Na$^+$ leakage through the anion exchange layer of the BPM). Key: (□) NO$_3^-$ and (●) Na$^+$.
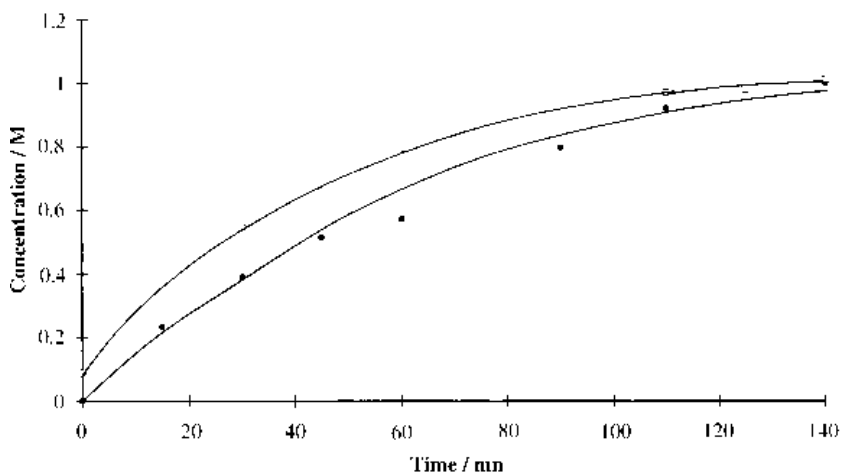
Fig. 8. Increasing NaOH and HNO_3 concentrations against time generated in the base and salt compartments, respectively. Key: (●) HNO_3 and (□) NaOH.
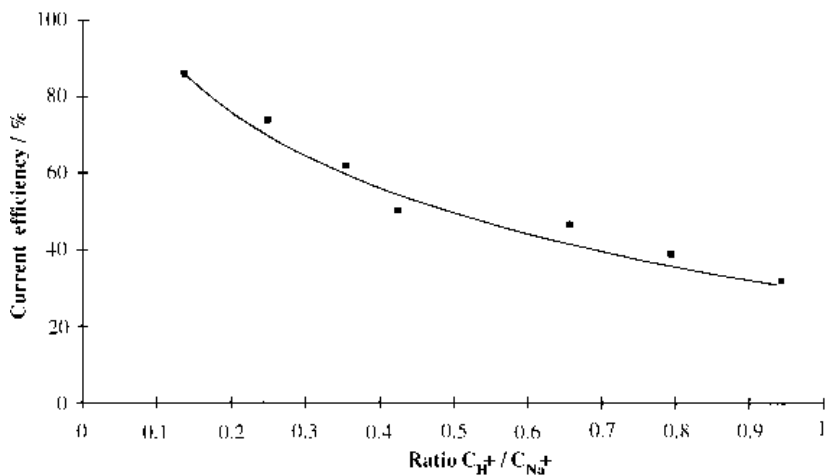

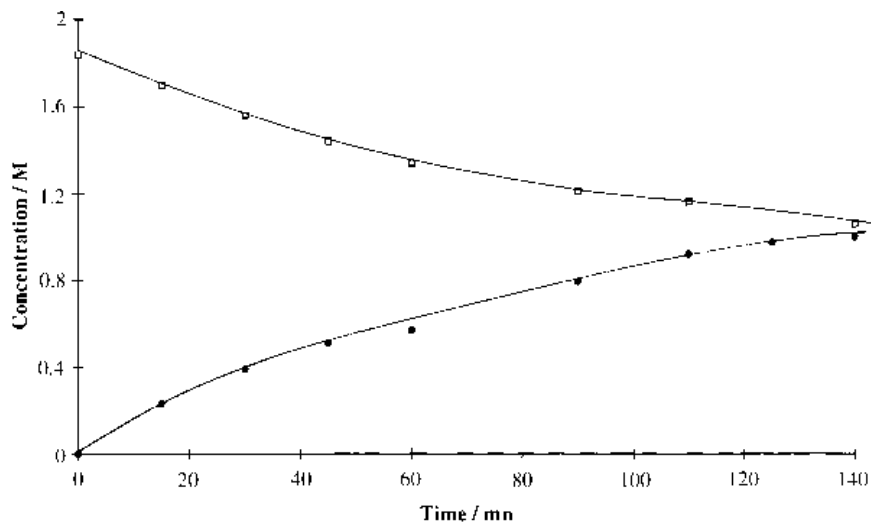Fig. 9. Variation of current efficiencies of NaOH against C_{H^+}/C_{Na^+} ratio.

Fig. 10. Sodium increasing and decreasing concentrations in the base and salt compartment, respectively. Key: (●) Base and (□) salt.

Table 1. Voltage variations between the electrodes for the three configurations of the electrodialysers

Time/h	Three cells electrodialyser (acid, base, salt)/V $I = 98 \, mA \, cm^{-2}$	Two cells electrodialyser (base, salt)/V $I = 127 \, mA \, cm^{-2}$	Two cells electrodialyser (acid, salt)/V $I \approx 0 \, mA \, cm^{-2}$
0	33.0	30.0	∞
1	23.8	16.5	∞
2	22.5	16.0	∞
3	21.5	16.0	∞
4	21.4	16.0	∞
5	31.2	16.0	∞

3.3. *Electrodialysis with acid and salt compartments (Fig. 1(c))*

Circulation in the loops of the acid and salt compartments were 3.0 and 3.5 dm³, respectively. This electrodialysis was also limited by competition between NO_3^- and OH^- (produced by water breakdown) through the AEM. The conductivity of the system is very low which makes this configuration unsuitable for base generation. This is due to the weakly basic vinyl pyridinium groups inside the AEM which are deprotonated as soon as the OH^- concentration increases. In this system it is impossible to establish a noticeable current because the resistance of the system is infinite (see Table 1).

4. Conclusion

This work shows that bipolar membrane electrodialysis using three compartments is a promising process for production of HNO_3 and $NaOH$ from $NaNO_3$. This configuration enables the production of acid and base with good efficiencies. The process can be improved by limiting the co-ion leakage through the membranes especially the proton leakage through the AEM and OH^- leakage through the CEM. This system is more attractive for industrial production than electro-electrodialysis which necessitates a pair of electrodes for each cell as BPM electrodialysis necessitates only one pair of electrodes for many cells.

Generation of acid or base by electrodialysis with two compartments is hindered by competition between the counter-ions through the membranes. The base produced in the case of Fig. 1(b) is not highly pure because of the presence of salt in one of the two compartments inducing NO_3^- leakage through the BPM membranes. In the case of Fig. 1(c), the two compartment system cannot work to produce nitric acid because of the deprotonation of vinyl pyridinium groups inside the AEM with increasing concentration of hydroxide ions. Except for this last case these processes are valuable if there is no need for pure acid or base at high concentration because they can operate with low energy requirement.

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