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Hydrofluoric acid and sodium hydroxide production by bipolar membrane electrodialysis

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ABSTRACT

The purpose of this study was to offer an alternative new eco-friendly and easily implemented process for the production of hydrofluoric acid and sodium hydroxide. The production of hydrofluoric acid and sodium hydroxide from sodium fluoride was carried out by bipolar membranes electrodialysis. The process feasibility was tested using a laboratory electrodialysis cell. The behavior of the process was investigated for 0.05, 0.025 M concentration and 5, 7.5, 10 V potential. In conclusion, the current efficiencies were obtained up to a value of 98.51 at the applied potential of 10 V and 0.05 M, and the purities were found to be 99.7% and as 99.1% for hydrofluoric acid and sodium hydroxide, respectively. These high purities of acid and base were obtained without any harmful waste material or side product. When in terms of both production technique and environmental impact were compared to hydrofluoric acid production by the reaction of acid-grade fluorspar (CaF_2) with sulfuric acid (H_2SO_4) and sodium hydroxide in chlorine-alkali process, the process was found to have potential for being commercially feasible process for HF and NaOH production from NaF solution.

Keywords: Hydrofluoric acid; Sodium hydroxide; Electrodialysis; Bipolar membrane

1. Introduction

Hydrofluoric acid is generally manufactured by the reaction of acid-grade fluorspar (CaF_2) with sulfuric acid (H_2SO_4) via the following reaction [1–5]:

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF \quad (1)$$

The environmental negative impact of this commercial HF production processes is relatively high [6,7]. In a report prepared by the US Environmental Protection Agency (EPA), the environmental impacts of this process were presented in a detailed manner [8]. HF is a hazardous air pollutant. HF is produced in two different forms, as aqueous HF and anhydrous HF. The general form of manufactured HF is a colorless liquid or gas. The largest usage area of HF is as polishing agent in glass and aluminum industry. The other usage areas of HF is petroleum alkylation, uranium

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processing, stainless steel pickling, and manufacturing of resins, solvents, stain removers, surfactants, and pharmaceuticals [1,9]. To avoid acid streams with low pH level to the environment, the processed disposal options have been considerably reduced by new strict legislation by EPA.

NaOH is usually obtained from the chlorine-alkali process, using Cl_2 gas and mercury, which causes serious environmental pollution [10]. Depending on the operation conditions, mercury mixes into the air, water, waste, and side products. The pollutant of most concern from the chlor-alkali industry is mercury, which is specific to the mercury cell technology. Due to the process characteristics, mercury can be emitted from the process through air, water, wastes, andside products. In 1998, the total mercury emission to air, water, and products from chlor-alkali plants in Western Europe was determined 9.5 tonnes, ranging from 0.2 to 3.0 g Hg/tonne of chlorine capacity at the individual plants [11].

Bipolar membrane is a kind of combination of membranes of a cation-selective layer and an anion-selective layer [12]. Bipolar membrane electrodialysis (BPMED) is a technique well adapted to convert salts into its conjugated acids and bases [13]. It is mainly based on the use of a bipolar membrane to split water to give H^+ and OH^- [14].

Some researchers studied to regenerate concentrated organic and inorganic acids such as acetic acid and sodium hydroxide [15], gluconic acid [16,17], phosphoric acid and sodium hydroxide [18], and formic acid [19] by BPMED. The studies on the similar processes have shown that the electrodialysis (ED) processes, involving bipolar membranes, have economic potential for recovering inorganic, organic, or amino acids [20]. In this ED process, the bipolar membranes are used together with commercial homopolar cation and anion exchange membranes.

The purpose of this study was to offer an alternative new eco-friendly and easily implemented process for the production of hydrofluoric acid and sodium hydroxide.

2. Experimental

2.1. Materials

The chemicals such as NaF, HF, NaOH, and TİSAB III (total ionic strength adjustment buffer) used in the analysis and production were purchased from MERCK. The commercial ion exchange membranes used in the electrodialysis cell were provided from PCCell GmbH-Heusweiler/Germany [21]. The characteristics of the membranes are given in Table 1. The solutions were circulated through the compartments by using pumps, and flow rate of the solutions was adjusted with flowmeters. The temperature of the solutions was kept constant by employing thermostats with circulation. The scheme of the experimental setup is schematically illustrated in Fig. 1.

Table 1
Main characteristics of homopolar membranes used in study

Specification		PC acid 60	PC SK
Transference number	(a) 0.1/0.5 N	>0.95	>0.95
KCl acid	(b) 0.7/3 N	55	
Resistance	Ω cm^2	~2	~2.5
Water content	wt%	~17	~9
Ion exch. capacity			
Strong basic	Meq/g	ca 1.14	n/a
Weak basic	Meq/g	ca 0.45	

Note: (a) Calculated from potentiometric measurements and (b) observed current efficiencies.

The analysis of fluorine was performed by Metler Toledo multi meter, and the analysis of sodium was carried out by flame photometer (Sherwood 410).

2.2. Methods

The experimental cell was composed of nine membranes. Each of the membranes had 64 cm^2 surface areas. The cathode and the anode were made of stainless steel, and Pt/Ir alloy coated with titanium, respectively. The dimensions of the cathode and anode were 110 mm × 110 mm.

The operation was carried out in a three-compartment bipolar membrane arrangement. The operating principle of the process, the circulation of the solution through the chambers, and the transport of the ion across membranes are shown in Figs. 1 and 2. NaF solution was fed between anion exchange and cation exchange membranes, and this region is called the salt compartment. The region in which F^- ions transferred across the anion exchange membrane and combined with H^+ ions, thus producing HF in this region, is called the acid compartment. The compartment in which Na^+ ions transferred across the cation exchange membrane and combined with OH^- ions, thus producing NaOH in this regions, is called the base compartment [22].

When expressed in a simple way, the reactions occurred in the cell can be written as follows:

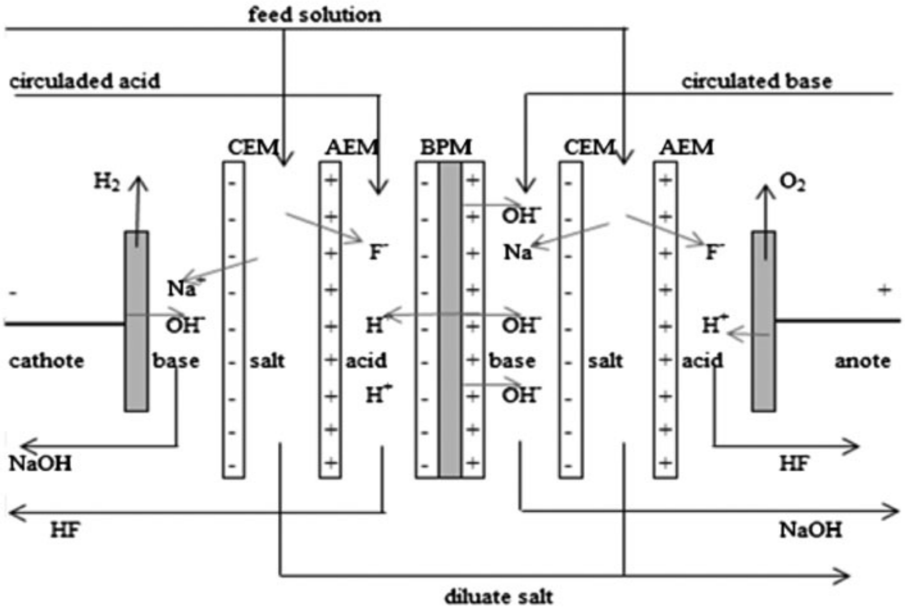

Fig. 1. Scheme of laboratory cell for hydrofluoric acid and sodium hydroxide production by BPMED.

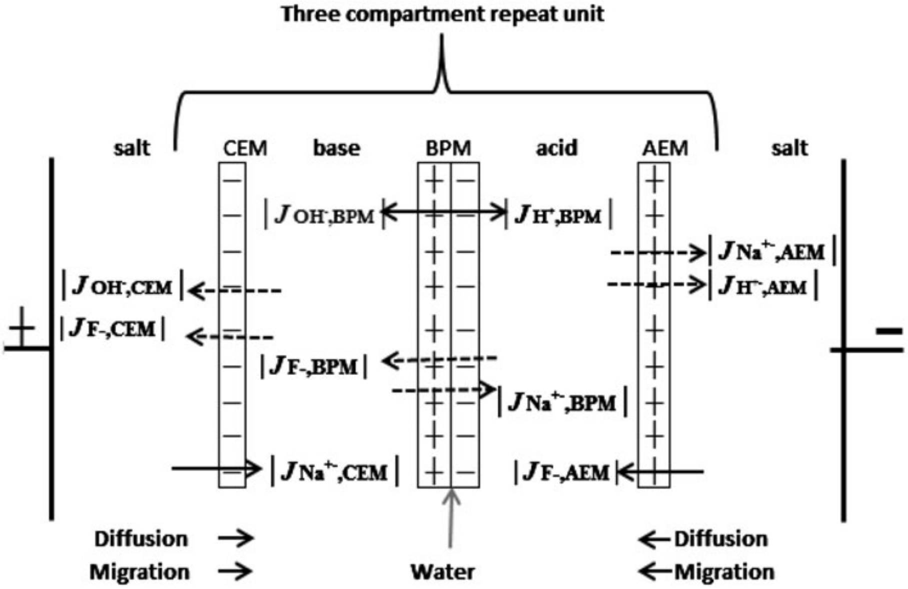

Fig. 2. Material balance of acid, base, and salt compartment for three compartments (the dashed arrows indicate that there is no ion transmission from membrane, and solid arrows indicate that there is ion transmission).

$$\text{Anode reaction}: \quad 2OH^- = 1/2\ O_2 + H_2O + 2e^- \tag{2}$$

$$\text{Cathode reaction}: \quad 2H_2O^+ + 2e^- = H_2 + 2OH^- \tag{3}$$

$$\text{Acid compartment}: \quad H^+ + F^- \rightarrow HF \tag{4}$$

$$\text{Base compartment}: \quad Na^+ + OH^- \rightarrow NaOH \tag{5}$$

$$\text{The overall reaction}: \quad NaF + H_2O \rightarrow NaOH + HF \tag{6}$$

$$J_{H^+} = \frac{J_{app} - \dot{I}_{lim}}{Z_{H^+}F} \tag{7}$$

$$J_{\mathrm{Na}^+} = t^{\mathrm{app}} \frac{J_{\mathrm{app}}}{Z_{\mathrm{Na}^+}F} \tag{8}$$

For two sides of bipolar membrane, when the contribution of the bulk flow is neglected in the boundary layers and membranes, accepting that the flow through the compartments are well mixed, the driving force becomes the sum of the electric field for migration and concentration gradient for diffusion, and the transport of salt ions can be expressed by the following equation based on the Nernst–Planck expression.

$$J_{\mathrm{i}} = J_{\mathrm{i}}^{\mathrm{migration}} + J_{\mathrm{i}}^{\mathrm{diffusion}} = D_{\mathrm{i}}\frac{\mathrm{d}C_{\mathrm{i}}}{\mathrm{d}x} - D_{\mathrm{i}}\frac{Z_{\mathrm{i}}C_{\mathrm{i}}F}{RT}\frac{\mathrm{d}V}{\mathrm{d}x} \tag{9}$$

In the preliminary experiments, it was observed that the membranes was subjected to some deformation when the value of applied potential was exceeded 10 V at the initial salt concentration of 0.05 M. This can be explained by the fact that HF is a strong acid and the reaction is very exothermic. Since the experiments were performed at constant applied potential, sometimes the current values showed high increases, causing split in the bipolar membrane layers. Due to design limitations and size of the cell, the highest feed rate, which could be reached, was determined as 0.38 L/min.

All the experiments were performed at 25˚C temperature, 0.38 L/min flow rate, and 0.1×10^{-6} M initial acid and base concentration. The experiments were carried out for 0.05 and 0.025 M initial NaF concentrations and 5, 7.5, and 10 V applied potentials. The change in the concentration of the solutions in all tanks was checked at 30 min regular intervals. The reproducibility of the experiments was tested, and the maximum standard deviation was evaluated as 0.03 at the end of the reproducibility tests.

The calculations were carried out using the following equations:

$$\text{Average current density} = \frac{\int i\,dt}{tA} \tag{10}$$

where $\int i\,dt$ the amount of the current during the time (amp min). $m_{\mathrm{theoretical}}$ was calculated on the basis of Faraday's law.

$$m_{\mathrm{theoretical}} = \int_a^b \frac{Mi\,dt}{nF} \tag{11}$$

The current efficiency was calculated from the measurements of the salt concentration in the tank after the test, using the following equation:

$$\text{Current efficiency} = \frac{m_{\mathrm{used}}}{m_{\mathrm{theoretical}}} \tag{12}$$

3. Results and discussion

Fig. 3 shows the effect of the applied potential on the current for the same initial concentration at a temperature of 25˚C and flow rate of 38 L/min. For a process time of 180 min, the current values 111, 583, and 1,104 mA were observed, 111, 583, and 1,104 mA, corresponding to the applied potentials of 5, 7.5, and 10 V, respectively. This period corresponds to the maximum point of 10 V curve. Since the solution has not enough ions for the process to continue and the amount of transferred ions was decreased in solution, the current was sharply reduced as the process proceeded, the current reached at a minimum value, and almost no current was observed after 300 min. The curve for 5 V also tends to reach a stagnant value after 200 min. These behaviors can be attributed to the decrease of the ions in the salt solution and can be an indication that the amount of the active ions in the salt solution was a strong driving force for the process. Since the concentrations of the ions in the salt solution have not yet reached below the critical value, the curves for the other remaining two applied potentials do not exhibit maximum following by a decrease in current.

Fig. 4 shows the effect of the applied potential again, but for a different initial salt concentration of 0.05 M, double of the previous one. For a process time of 300 min, it was found that, for the applied potentials of 5, 7.5, and 10 V, the current is 170, 735, and 1,190 mA, respectively, for 300 min. Due to high initial concentration, the decrease in the current–potential curve is not observed in this case since the concentration of the ions

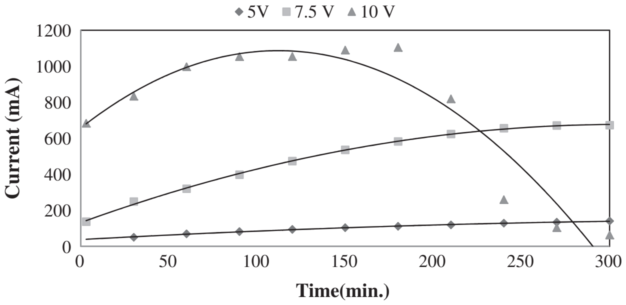

Fig. 3. Time dependence of current at various cell voltages (25˚C, 0.38 L/min flow rate, 0.025 M initial NaF concentration).

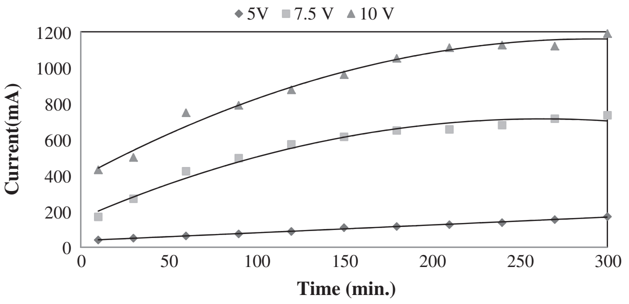

Fig. 4. Time dependence of the current at various cell voltages (25°C, 0.38 L/min flow rate, 0.05 M initial NaF concentration).

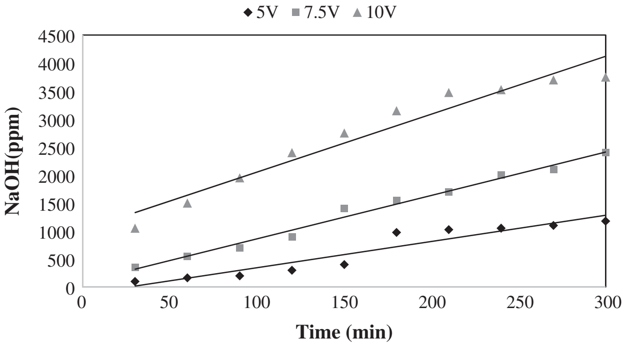

Fig. 5. NaOH concentration in base compartment at various applied potential as a function of time (25°C, 0.38 L/min flow rate, 0.025 M initial NaF concentration).

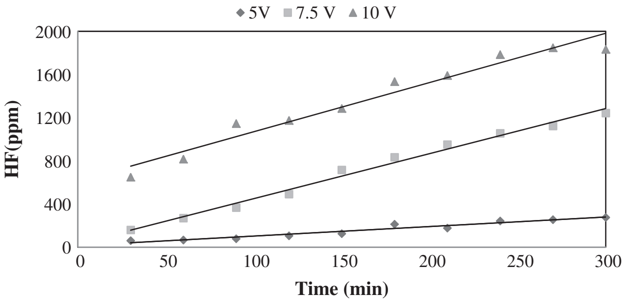

Fig. 6. Hydrofluoric acid concentration in acid compartment at various applied potential as a function of time (25°C, 0.38 L/min flow rate, 0.025 M initial NaF concentration).

have not reached yet at the critical value for the present working conditions. But currents seem to reach at a stagnant value for all applied voltages after 200 min. These results also confirm that the applied potential is one of the most important parameters on the acid–base production by BPMED [23].

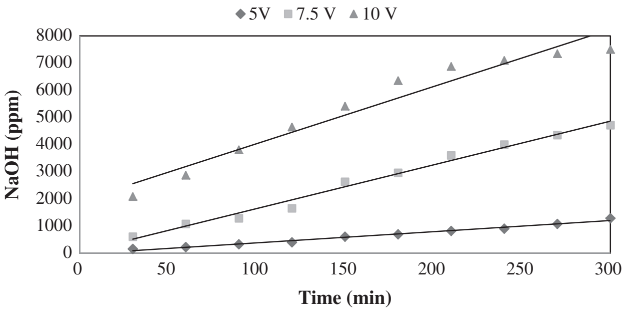

Fig. 7. NaOH concentration in the base compartment at various applied potential as a function of time (25°C, 0.38 L/min flow rate, 0.05 M initial NaF concentration).

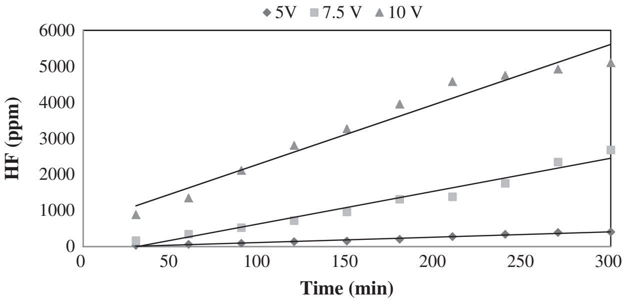

Fig. 8. Hydrofluoric acid concentration in acid compartment at various applied potential as a function of time (25°C, 0.38 L/min flow rate, 0.05 M initial NaF concentration).

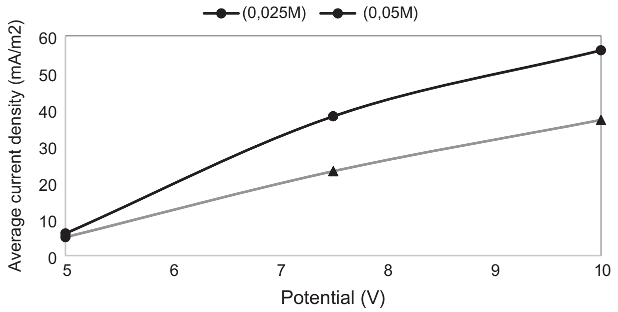

Fig. 9. Average current density–potential curves for different initial NaF concentration.

For an applied voltage of 5, 7.5, and 10 V at 0.38 L/min, 25°C and 0.025 M initial salt concentration, the concentration–time curves for HF and NaOH are shown in Figs. 5 and 6. It can be seen from Fig. 3 that the current through the stack initially increases for all the values of the applied voltage. When Fig. 3 is compared with Figs. 5 and 6, for the applied voltage of 10 V, it can be clearly seen that the formation of the

Table 2
Current efficiencies and product purities

Potential (v)	Concentration (M)	Current efficiency	Time (min)	Acid purity	Base purity
5	0.05	0.9918	300	0.951	0.963
7.5	0.05	0.9694	300	0.988	0.986
10	0.05	0.9851	300	0.997	0.991
5	0.025	0.9384	300	0.965	0.975
7.5	0.025	0.9621	300	0.972	0.973
10	0.025	0.9671	300	0.987	0.988

products at about 200 min tends to reach at a constant value, which is the result of reducing current value due to decreasing concentration of the salt ions. If the experiments were performed for longer times, similar behavior observed for the curve of 10 V at the initial salt concentration of 0.025 M would be observed for the other experimental conditions as well. The change in current values with time depends on applied potential and initial salt concentration.

Figs. 7 and 8 also show the produced amount of acid and base with time for the initial concentration of 0.05 M. In Figs. 5–8, it is seen that increasing initial NaF concentration increased the produced amount of acid and base. Even the concentrations of acid and base solutions seem not to increase in the similar rate when expressed in the concentration unit of ppm, they have equal concentration values if the concentration is expressed in mol units. In the first stage, the amount of the Na^+ and F^- ions in the salt solution was excessive and so the current increase was very rapid. If the amount of the ion diminishes, it also slows down. After certain time, when the amount of the ions reduces to under a certain level, transfer becomes very slow and concentration stayed stable.

The current efficiency is generally taken as the first criterion for the electrodialysis performance [13]. The current efficiency is the ratio of practically obtained material amount to that which should theoretically be obtained. From the experimental data calculated, the average current density and current efficiency are shown in Fig. 9 and Table 2.

The results of the average current densities are given in Fig. 9. The average current density increased almost with increasing applied potential. The current efficiency values and product purities are shown in Table 2. The current efficiency values are between 0.9384 and 0.9918 depending upon the experimental conditions. The product purity values changed between 0.951 and 0.997. Taking into consideration these experimental findings, it can be said that the optimal working conditions for the present work are the initial concentration of 0.05 M and the applied potential of 10 V.

The highest current efficiency was found to be 99.18% for 0.05 M initial NaF concentration and 5 V working potential. Under these conditions, the average current density was calculated as 5.66 mA/cm^2. This value is very important to avoid the energy losses in electrodialysis studies. The highest product purity was calculated to be 99.7% for HF and 99.1% for NaOH.

In light of the above experimental results, BPMED can be considered as an alternative technique for acid and base production from salts, avoiding the use of strong acids. Furthermore, the large amounts of chemical wastes in production of acid and base with conventional methods would also be eliminated [24]. Because of membrane life shortening at high acid concentrations, maximum HF concentration was restricted at 0.05 M in the present work. In conditions of the present work, no damage happened to the membranes.

When taking into consideration of the harmful and toxicant waste produced, and the difficulty of controlling the reactions in the conventional production of NaOH and HF [1,8,11], it can be concluded that BPMED process can have an serious potential for future industrial applications with advantageous of no harmful waste, being a single stage operation, and high current efficiency.

4. Conclusions

Under the light of the results presented above for the production of hydrofluoric acid and sodium hydroxide using BPMED, the main characteristics of the present work can be summarized as follows:

(1) A low energy consumption of average current density 5.66 mA/cm^2 and a relatively high current efficiency 99.17% were achieved.
(2) Increasing the applied potential and concentration has an increasing effect on the production rate.
(3) Highest product purity was found to be 99.7% for HF and 99.1% for NaOH.
(4) The production of sodium hydroxide and hydrofluoric acid by BPMED does not produce any harmful waste material.

(5) The above-summarized advantages show that this process can be very attractive for the production of HF.

The negative aspect of this process is the fact that at the high acid and base concentrations, the membranes were damaged. Therefore, for the productions in such processes, the concentrations of the strong acids should be kept low.

Nomenclature

A^{M} — total active membrane area (m^2)
AEM — anion exchange membrane
BPM — bipolar membrane
C — concentration (mol/L)
CEM — cation exchange membrane
C_{H^+} — salt proton concentrations in the acid chamber (mol/L)
C_{Na^+} — salt cation concentrations in the acid chamber (mol/L)
D_i — ion diffusion coefficients (m^2/s)
F — Faraday constant (F = 96,485 A s/mol)
i_{app} — applied current density (A/m^2)
i_{lim} — limiting current density (A/m^2)
J — ion flux across the membrane (mol/m^2 s)
J_{H^+} — proton concentrations fluxes (mol/m^2 s)
J_{Na^+} — cation concentrations fluxes (mol/m^2 s)
M — molecular weight (g/mol)
$m_{theoretical}$ — theoretical amount of the substance released on the electrode (g)
n — valency effect
Q — volume stream of product (m^3/s)
R — universal gas constant (8.314 J/mol K)
T — cell temperature (K)
t — time (s)
t^{app} — actual transport number
V — electric potential (V)
x — dimension perpendicular to membrane (m)
Z_{H^+} — electrochemical valence of the proton
Z_{Na^+} — valence of the Na^+ ion

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