



Chronopotentiometric evaluation of enhanced counter-ion transport through anion exchange membranes in electromembrane processes

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ABSTRACT

This paper reports the use of chronopotentiometry as a powerful technique to study counter-ion transport properties through ion-exchange membranes. Chronopotentiometry at current values less, equal and greater than the limiting current density has been used to understand the role of ammonia buffer in the reduction and elimination of the concentration polarisation phenomena of ion transport through the Neosepta AMX anion exchange membrane (Tokuyama Soda, Japan). The addition of ammonia led to polarisation chronopotentiograms without transition time. The results show that the water dissociation reaction in the boundary layer is catalytically enhanced by ammonia. It shifted the overlimiting current regions towards the ohmic regions by destruction and elimination of the diffusion boundary layer.

Keywords: Ion-exchange membrane; Chronopotentiometry; Buffer solution; Counter-ion transport; Concentration polarisation; Water dissociation

1. Introduction

Ion-exchange membranes (IEMs) are used in a wide range of chemical and environmental processes, for example, energy generation in proton exchange membrane fuel cells and direct alcohol fuel cells. In reverse electrodialysis to produce electricity from mixing salt and freshwater. For separation and purification in electrodialysis and electrodialysis-derived processes [1–3].

Electrodialysis is one of the various applications of IEMs in separation and/or purification processes where the driving force in the system is the applied electrical potential [4,5]. The system consists of an alternating series of cation and anion exchange membranes separated by spacers and placed

between two electrodes. It is widely used in many fields of chemical engineering such as potable water production from brackish water, in the recovery and reuse of wastewater from metal surface treatment processes, in seawater concentration for salt production, and for desalination and purification of amino acids in biochemical and pharmaceutical industry [1,3,6]. Recently, the combination of IEMs with bipolar membranes or ion-exchange resins led to a large number of new interesting applications such as bipolar membrane electroanalysis [7–9] and electrodeionisation [10–12].

In the previously mentioned electromembrane systems, the applied electrical potential is restricted by the limiting current density due to the occurrence of the concentration polarisation phenomena at the membrane–solution interface. For this reason, the operational current density has to be lower than the limiting current value to avoid several problems such as inorganic salt precipitation on the membrane

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surface, destruction of the membranes, and an increase in the energy consumption decreasing the process efficiency [13–15].

The nature of the concentration polarisation phenomena and the overlimiting current are not well understood, and need further research [16–23]. A universally accepted theory of concentration polarisation and overlimiting current transport has not been reached yet despite many hypothetical explanations, for example, the autocatalytic protonation–deprotonation reaction of water dissociation where the current transport is insured by protons and hydroxyl ions [24–26], and the electroconvection theory where the dissolved salt ions insure current transport [27–31].

Chronopotentiometry has been widely applied as a powerful technique in the studies of counter-ion transport properties through IEMs [32–44]. It can reveal more information about different transport regimes as the system will be functioning at a specific predefined current value for a certain period of time. In previous studies [45–47], we have used buffer solutions and weak electrolytes to chemically reduce the plateau length and eliminate the concentration polarisation phenomena. This work is a continuation of a previous study [47], on the effect of the ammonia buffer on counter-ion transport. Chronopotentiometry at current values less, equal and greater than the limiting current density has been used to investigate and understand the role of ammonia in the reduction and elimination of the concentration polarisation phenomena.

2. Materials and methods

2.1. Chemicals

All solutions were prepared by dissolving analytical-grade reagents in ultrapure water obtained from a water purification system (Millipore, 18.2 MΩ cm). The used chemicals are: potassium sulphate (Aldrich Chemical Co., 98%), acetic acid (Aldrich Chemical Co., Germany, 100%), ammonium chloride (Prolabo, France, 98.5%), ammonium hydroxide (Aldrich Chemical Co., Germany, 30%–33%).

2.2. Anion exchange membrane

The anion exchange membrane used in this work is the AMX anion exchange membrane (Neosepta AMX, Tokuyama Soda, Japan). The membrane was conditioned according to the NFX 45-200 standards of the French Normalization Association (AFNOR) for IEM. The experiments were carried out after a membrane equilibration period of at least 24 h in a solution with the same characteristics, used in these experiments (100 mL/10 cm² membrane). The solutions were prepared by dissolving analytical-grade reagents in distilled water.

2.3. Electrochemical measurements

The current–voltage curves (CVCs) and the chronopotentiograms are obtained using a two-compartment electrochemical cell as shown in Fig. 1. It is composed of two 25 mL symmetrical half-cells between them the anion exchange membrane is integrated. In both compartments, solutions of identical concentration and composition are used. The circular exposed area of the membrane surface is 0.5 cm².

The potential drop across the membrane is measured using two reference gold-Luggin electrodes. Moreover, all measurements are carried out in galvanostatic mode at a current scanning rate of 10 μA/s. Two graphite electrodes are used to impose the current through the membrane. The system is computer controlled by a VoltaLab PGZ 401 Potentiostat/Galvanostat (Radiometer Analytical SAS) using VoltaMaster4 software. The limiting current density is estimated by taking the current value at the inflection point of the derivative curve in the limiting current region. All experiments are conducted at room temperature without stirring the solutions.

3. Results and discussion

3.1. The effect of NH₄Cl concentration on the CVCs

Fig. 2 shows the CVCs of the AMX anion exchange membrane at different concentrations of NH₄Cl where the three characteristic regions are distinguishable (the ohmic, the polarisation and the overlimiting region). Moreover, the limiting current density increases linearly with the increase of NH₄Cl concentration (not shown here). This behaviour was frequently reported in previous studies using diverse electrolytes [35,38,46], and could be attributed to the fact that at higher concentrations, it is more difficult to reach the zero concentration value at the membrane–solution interface. Thus, higher limiting current density values would be achieved at high concentrations.

3.2. The effect of ammonia concentration on the CVCs

Fig. 3 shows the behaviour of the AMX anion exchange membrane in a buffer mixture of NH₃ and NH₄Cl where the concentration of NH₄Cl remains constant and the

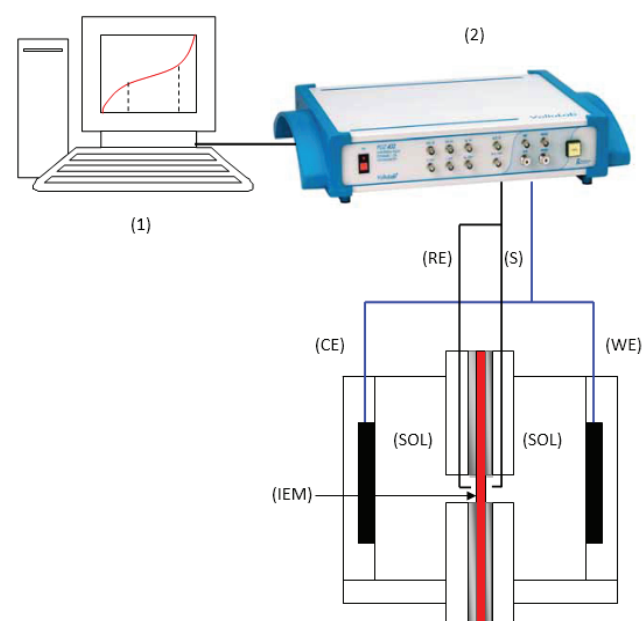


Fig. 1. Schematic description of the experimental setup. RE: reference electrode, S: sensor electrode, CE: counter electrode, WE: working electrode, SOL: solutions and IEM: ion-exchange membrane.

concentration of NH_3 was gradually increased from 0.005 to 0.1 N. It can be seen that, in the ohmic region, the resistance of the system is slightly decreased when NH_3 was added, and then remains constant whatever the NH_3 concentration is. In the limiting current region, the progressive addition of NH_3 reduces the polarisation plateau length and almost eliminates it when the NH_3 concentration reached 0.1 N (blue curve in Fig. 3). In this case, the counter-ion transfers the anion exchange membrane without the occurrence of concentration polarisation. Furthermore, if we continue scanning at higher current densities, to make sure that there is not a higher limiting current density value, the CVC of the system with 0.1 NH_3 does not represent any distinguishable limiting current transport as shown in Fig. 4. The consideration of this unusual behaviour leads to the following question: how does NH_3 eliminate the concentration polarisation phenomenon at the membrane/solution interface and facilitate counter-ion transport through the anion exchange membrane?

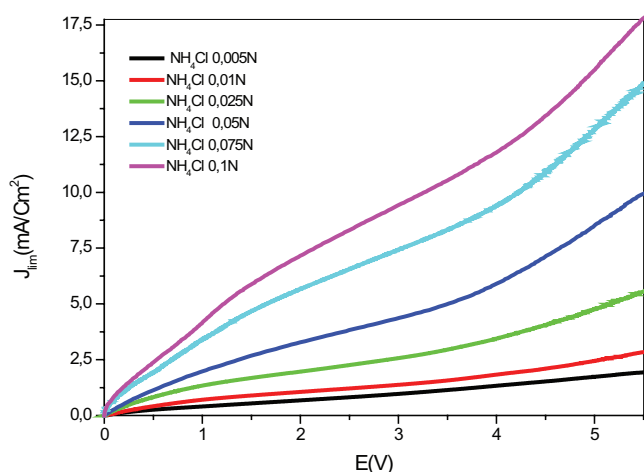


Fig. 2. Current–voltage curves of the AMX anion exchange membrane at different potassium sulphate concentrations.

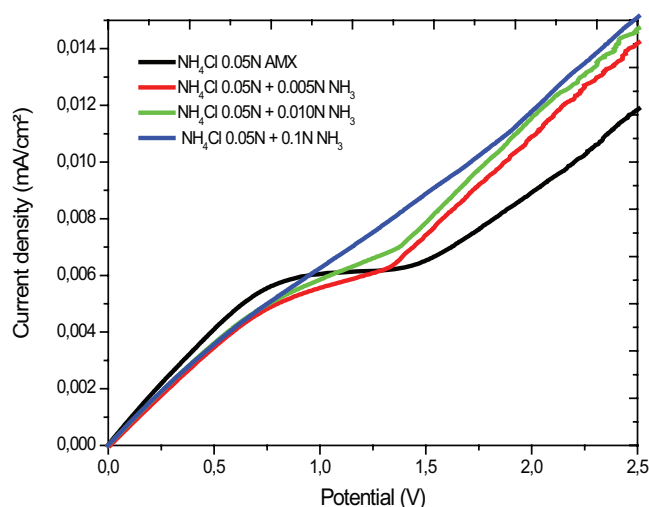


Fig. 3. Current–voltage curves of 0.05 N ammonium chloride solution without (black) and with (others) ammonia as a function of ammonia concentration (adapted from [47]).

3.3. Chronopotentiometry of NH_4Cl at different current values

In order to understand the role of ammonia in the elimination of the concentration polarisation plateau, constant-current chronopotentiometry has been used to characterise the counter-ion transport at different current regimes. The transient process of the system to reach its steady-state potential at a constant operational current density could be studied by measuring the potential drop across the membrane as a function of time. Fig. 5 shows the obtained chronopotentiograms of the AMX anion exchange membrane in 0.05 N NH_4Cl solution at the ohmic (black), the limiting (red) and the overlimiting (blue) current regimes, respectively.

A full description of a chronopotentiogram with all the characteristic regions could be obtained at current densities equal to or greater than the limiting current value. As we can see on the red curve (limiting current) of Fig. 5, it first

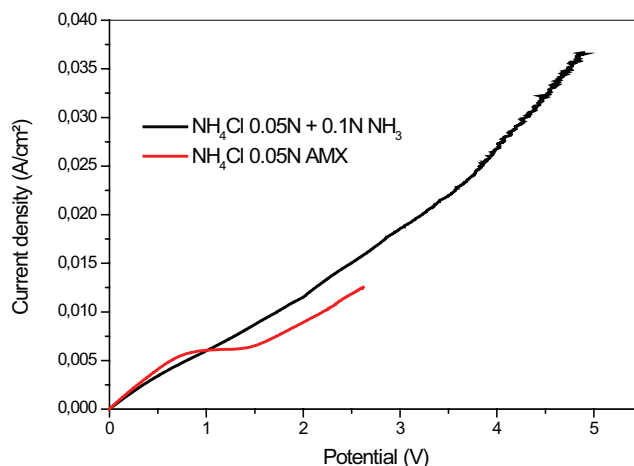


Fig. 4. Current–voltage curves of 0.05 N ammonium chloride solution without (red) and with (black) 0.1 N ammonia at higher current values.

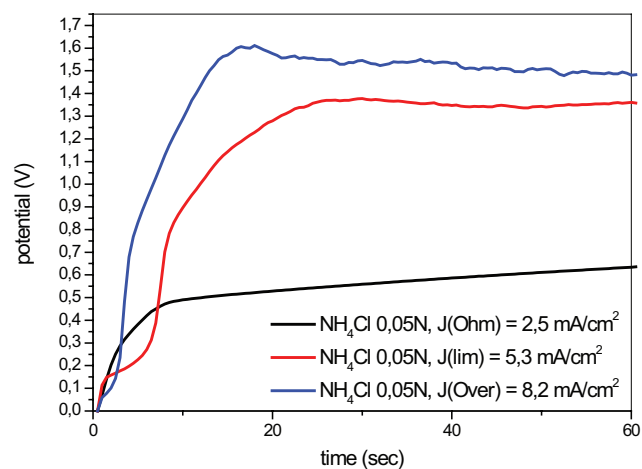


Fig. 5. Chronopotentiograms of the AMX anion exchange membrane in 0.05 N NH_4Cl solution at different current densities: $J_{\text{Ohm}} = 2.5 \text{ mA/cm}^2$ (black), $J_{\text{lim}} = 5.3 \text{ mA/cm}^2$ (red) and $J_{\text{over}} = 8.2 \text{ mA/cm}^2$ (blue).

starts with an instantaneous increase of the potential across the membrane due to the ohmic resistance of the system. Followed by a slow increase until the electrolyte concentration at the membrane–solution interface reaches zero where a highly resistant diffusion boundary layer (DBL) is formed. The formation of the DBL leads to a rapid increase of the electrical potential. The time corresponds to the inflection point where this increase starts is called the transition time (τ). It is an important characteristic in the study of electrochemical interfacial phenomena. Finally, the system reaches its steady state (equilibrium potential) after about 30 s where the potential remains constant with time. The same zones could also be noticed on the overlimiting chronopotentiogram (blue curve) with a less important transition time due to the occurrence of other transport phenomena at the overlimiting current region. On the other hand, the ohmic chronopotentiogram (black curve) does not show a transition time because the DBL has not been formed yet and the current transport is only insured by ion migration.

3.3.1. Chronopotentiometry of NH_4Cl with different NH_3 concentrations

3.3.1.1. At the ohmic current regime The effect of ammonia on ammonium chloride transport through the AMX anion exchange membrane has been studied by chronopotentiometry at the ohmic, limiting and overlimiting currents where the ammonia concentration was progressively increased from 0.005 to 0.1 M. Fig. 6 shows the obtained chronopotentiograms at the ohmic current regime where the current density was fixed at 2.5 mA/cm^2 for all the curves abstained at various ammonia concentration. As expected, the chronopotentiograms do not show a transition time due to the dominance of ionic migration at the expense of diffusion. At the ohmic current regimes, the ion migration is faster through the membrane than from the bulk solution. Thus, each ion reaches the membrane/solution interface will be immediately transferred through the membrane to the other desalination compartment.

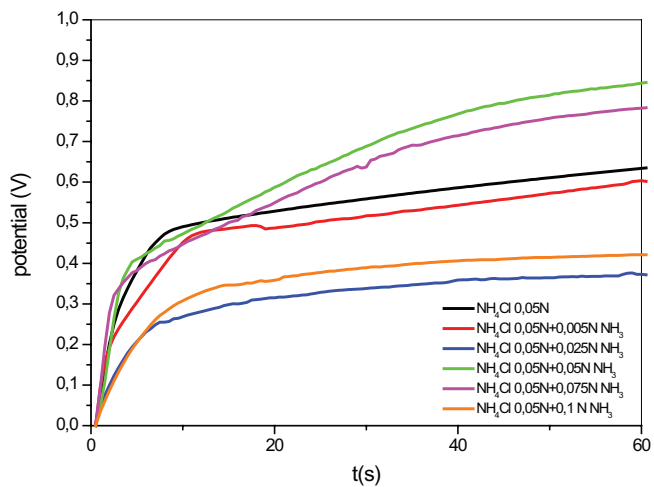


Fig. 6. Chronopotentiograms of the AMX anion exchange membrane in 0.05 N NH_4Cl solutions with different NH_3 concentrations (from 0 to 0.1 N) at the ohmic region current density ($J_{\text{ohm}} = 2.5 \text{ mA/cm}^2$).

However, the addition of ammonia significantly decreases the equilibrium potential values for concentrations $<0.05 \text{ M}$. This 0.05 M ammonia concentration corresponds to an equimolar mixture of $\text{NH}_4^+/\text{NH}_3$. At this value, the equilibrium potential increases instantly to reach a maximum of 0.75 V (Fig. 7). Then, decreases when the ammonia concentration exceeded 0.05 M. It is also worth mentioning that the equilibrium potential of the system with equimolar proportions is greater than the equilibrium potential without any addition of ammonia. This suggests that the addition of ammonia increases the membrane resistance at the ohmic region by diffusing through the membrane matrix, due to the electroneutrality of ammonia molecules.

3.3.1.2. At the limiting current regime Fig. 8 shows the obtained chronopotentiograms at the limiting current regime

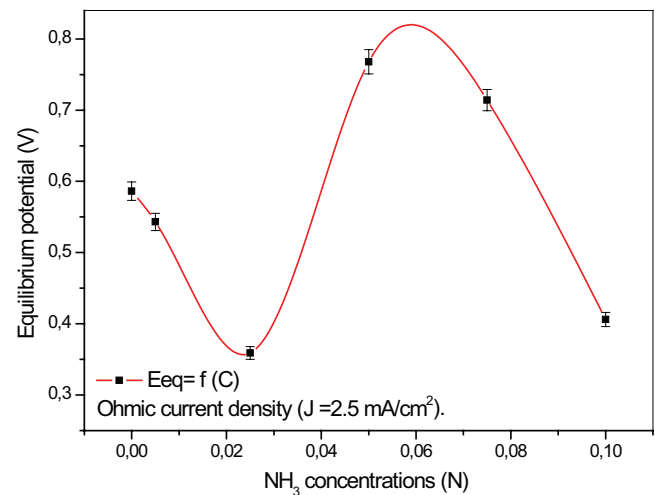


Fig. 7. Equilibrium potential after 40 s (E_{eq}) as a function of ammonia concentration at the ohmic current density ($J_{\text{ohm}} = 2.5 \text{ mA/cm}^2$).

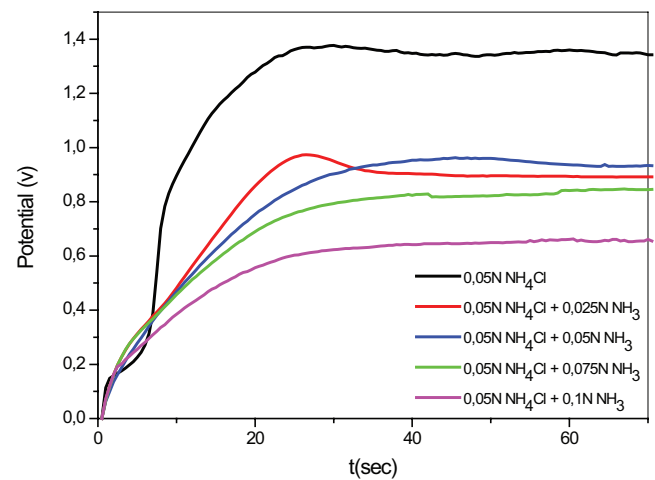


Fig. 8. Chronopotentiograms of the AMX anion exchange membrane in 0.05 N NH_4Cl solutions with different NH_3 concentrations (from 0 to 0.1 N) at the limiting current density region ($J_{\text{lim}} = 5.3 \text{ mA/cm}^2$).

where the current density was fixed at 5.3 mA/cm^2 for various ammonia concentrations. In this case, the curve of ammonium chloride without ammonia (black) shows a clear inflection point corresponds to the transition time of the system. As the concentration of ammonia increases progressively, the transition time in the curves disappears. This could be explained by the destruction and elimination of the DBL while the system is reaching its equilibrium potential. It is the physical proof that the addition of ammonia destructed and eliminated the DBL even at the limiting current regime. It was also observed that the equilibrium potential decreases as the concentration of ammonia increases with a slight increase when it reaches the equimolar fraction (Fig. 9).

3.3.1.3. *At the overlimiting current regime* Fig. 10 shows the obtained chronopotentiograms at the overlimiting current regime where the current density was fixed at a value of 8.2 mA/cm^2 for various ammonia concentrations. In this

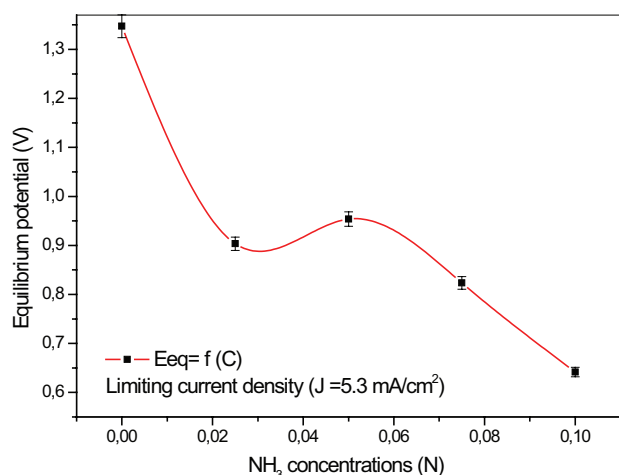


Fig. 9. The equilibrium potential after 40 s (E_{eq}) as a function of ammonia concentration at the limiting current density ($J_{lim} = 5.3 \text{ mA/cm}^2$).

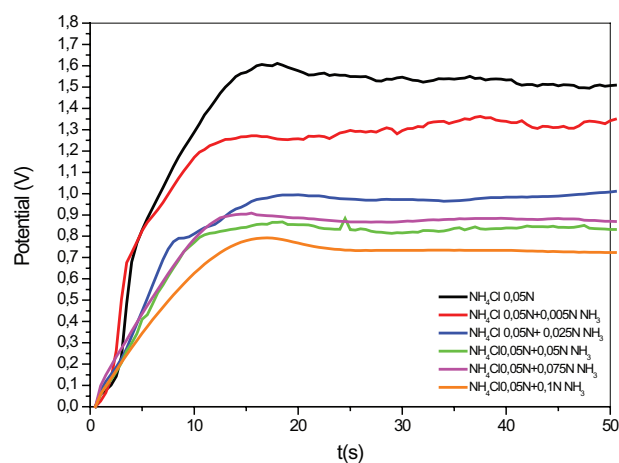


Fig. 10. Chronopotentiograms of the AMX anion exchange membrane in $0.05 \text{ N NH}_4\text{Cl}$ solution at the overlimiting current density ($J_{over} = 8.2 \text{ mA/cm}^2$).

case, the same chronopotentiometric response of the limiting current density was obtained. The transition time of the chronopotentiograms could be only seen in the case ammonium chloride without ammonia addition.

It was observed that the equilibrium potential of the system decreases as the concentration of ammonia increases (Fig. 11). Like in the ohmic regime, the highest equilibrium potential value is that of the system without addition of ammonia. The decrease of the equilibrium potential as the ammonia concentration increases could be associated to the fact that ammonia was chemically transformed to other electroactive species in the limiting and/or the overlimiting current regime where the water dissociation reaction takes place.

4. On the mechanism of the elimination of concentration polarisation

The water dissociation reaction in the boundary layer is catalytically enhanced by ammonia. Ammonia plays the role of a water dissociation facilitator at the membrane/solution interface. With its neutral electrical charge, it could easily diffuse through the DBL where the water dissociation reaction takes place (Eq. (1)). It reacts as a weak base with the released protons from the water molecules and allows to the hydroxyl ions to pass through the membrane (Eq. (2)). This property will shift the water dissociation equilibrium to the formation of the products (Eqs. (1)–(3)). Thus, in return, will affect the onset potential of the overlimiting zone that will shift towards lower values (the ohmic zone) reducing the polarisation plateau length according to the following chemical reactions shown in Fig. 12.

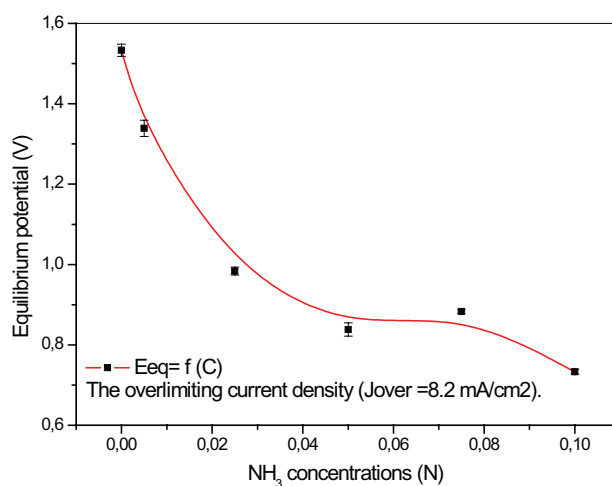
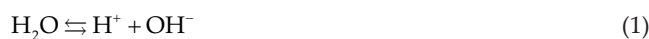


Fig. 11. The equilibrium potential after 40 s (E_{eq}) as a function of ammonia concentration at the overlimiting current density ($J_{over} = 8.2 \text{ mA/cm}^2$).

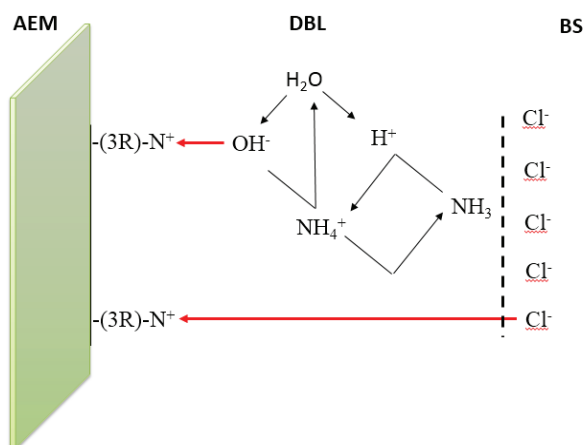


Fig. 12. Schematic description of proposed mechanism. AEM: anion exchange membrane, DBL: diffusion boundary layer and BS: bulk solution.

In a polarised system without ammonia, the applied electrical potential forces the water molecule to dissociate. In the presence of ammonia, the needed energetic barrier to dissociate the water molecule becomes lower and lower as the concentration of ammonia increases. Under these conditions of the applied electrical potential, the presence of neutral ammonia and the functional charged groups of the membrane will all lead to the dissociation of the water molecules faster than the expected rate. This will contribute to the early occurrence of the overlimiting current transport by adding more hydroxyl ions near the membrane/solution interface beyond the accumulation layer of chloride ions. It will also enhance the net current transport of negative charges (chloride and hydroxyl) through the membrane and eliminates the polarisation concentration phenomenon.

5. Conclusion

The role of ammonia in the reduction and elimination of concentration polarisation during the transfer of chloride counter ions through the AMX anion exchange membrane was investigated by chronopotentiometry. The obtained results show that the addition of ammonia destructs the formation of the DBL. The absence of a clear transition time on the chronopotentiograms at the limiting and the overlimiting current regions is the physical proof of this phenomenon. The addition of ammonia in the system allowed the water dissociation reaction to occur at an early polarisation stage reducing the length of the polarisation plateau. These results could be used for further modification and development of novel generation of IEMs operating without limiting the current density in electromembrane processes.

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