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Enhancement of counter-ion transport through ion-exchange membranes in electrodialytic processes

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ABSTRACT

Ion-exchange membranes (IEMs) are ionic conducting materials. They have various applications such as: fuel cell (PEMFC), electrochemical synthesis (Cl_2/NaOH), desalination, purification, separation, and environment. Despite these applications, several aspects are still unknown, such as: the membrane structure, the conduction mechanisms, and concentration polarization. The main obstacle in electro-membrane processes such as electrodialysis is the concentration polarization phenomenon, which remains one of the incomprehensible phenomena in IEM transport. This phenomenon is common to all systems operating a selective ionic transfer through an interface; it arises from the difference in ions mobility in the solution and in the membrane. A better understanding of concentration polarization can help to improve the membrane performance, the process efficiency, and in the reduction the process operation cost. In this research, we studied the effect of the ammonia buffer (NH_3/NH_4^+) on the counter-ion transfer through the anion- and the cation-exchange membranes AMX and CMX, respectively. The results show that the ammonia addition facilitates the counter-ion transfer in both cases and gives a total elimination of the system polarization, but with different behaviors of CMX and AMX membranes. The classical concentration polarization theory remains insufficient to explain the obtained results.

Keywords: Ion-exchange membrane; Limiting current density; Over-limiting current; Electrodialysis; Concentration polarization; Water dissociation

1. Introduction

An ion-exchange membrane (IEM) is defined as a permselective barrier between two phases. Under the influence of a driving force, some components of a feed mixture can permeate while others are retained [1–3]. IEMs are widely used in various fields such as electrodialysis (ED) [2–7], electrodeionization [4–7], diffusion dialysis [8], membrane capacitive deionization [9,10], for energy generation by mixing fresh and salt water in reverse electrodialysis [1,11–15], from wastewater in microbial fuel cells (MFC) [16], or in other types of fuel cells such as proton exchange membrane fuel cells [17], or direct methanol fuel cells [18].

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ED is an electrical potential driven process to concentrate and/or to remove ions from an electrolyte solution through alternately cation-and anion-exchange membranes [5,6]. When an electric current is passed through an IEM, salt concentration on the desalting surface of the membrane is decreased due to the concentration polarization and reduced to zero at the limiting current density (Fig. 1) [24]. In this case, there are no more salt ions available to carry the electric current.

In practice, if the applied current density exceeds the limiting one, operational problems occur, such as inorganic salts precipitation on the membrane surface, destruction of the membranes, and an increase in the energy consumption decreasing the process efficiency. Thus, in order to avoid these problems, a current density of about 80% of the limiting current value is generally applied. The current above the limiting current density is called the over-limiting current (*C*), and it has been one of the incomprehensible phenomena in IEM systems [19–24]. A better understanding of concentration polarization can help in order to improve the membrane performance, the process efficiency, and the reduction of the process operation cost. One of the most important parameter in membrane ionic transport is the membrane surface properties [19,25] that can determine the concentration polarization conditions and therefore the process efficiency. Several papers dealing with the effect of the membrane surface on the transport properties have been published in the literature. Moon et al. [26,27] investigated the influence of the degree of heterogeneity on the membrane electrochemical behaviors, they concluded that the heterogeneous membranes have a smaller conducting region than the homogeneous ones as well as the heterogeneity may lowers the membrane conductivity and the limiting current density.

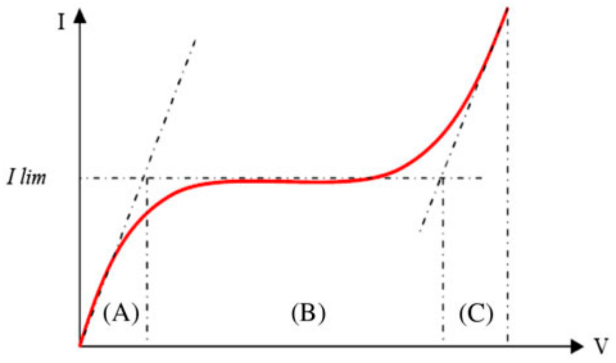

Fig. 1. Typical current–voltage curve of a mono-polar IEM. (A) the ohmic region, (B) the limiting current density, and (C) the over-limiting current region.

Marder et al. [28] used a nonconductive paint to reduce the membrane conducting area to 80, 60, and 45%. The obtained results show that the reduction of the membrane conducting area affects the over-limiting current and the plateau length (region (B) Fig. 1).

Balster et al. [20] investigated the influence of the membrane surface heterogeneity on the plateau length, by preparing membranes with designed undulations and found that the plateau length of the undulated membranes is reduced by up to 60% compared with that of a flat membrane. In addition, the commercial CMX membrane coated with polyethylenimine (PEI) led to a strong increase in the plateau length and a later occurrence of the over-limiting current density. In our previous studies [24,29,30], the effect of weak electrolytes and buffer solutions has been examined. The aim of the present work was to study the effect of the ammonia buffer (NH_3/NH_4^+) on the counter-ion transfer through the AMX and CMX IEMs.

2. Materials and methods

2.1. Ion-exchange membrane

The IEMs used in this work are CMX and AMX IEMs (Neosepta CMX-AMX. Tokuyama Soda, Japan). The experiments are carried out after a membrane equilibration period of at least 24 h in a solution with the same characteristics used in the experiments. The solutions are prepared by dissolving analytical grad reagents in distilled water.

2.2. Electrochemical cell and current–voltage measurements

The current–voltage curves (CVC) are obtained using a two-compartment electrochemical cell as shown in Fig. 2 [24]. This cell is composed of two 25 ml symmetrical half-cells between them, the membrane is integrated. In both compartments, solutions of identical concentration and composition are used and the circular exposed area of the membrane surface is 0.5 cm^2. The potential drop across the membrane is measured using two reference golden Luggin electrodes. Moreover, all measurements are carried out in galvanostatic mode, and two graphite electrodes are used to impose the current density, supplied by a potentiostat/galvanostat (Autolab PGSTAT 30, Ecochemie, The Netherlands) at a current scanning rate of 10 A/s. The limiting current density is estimated by taking the current value at the inflection point of the curve in the limiting current region. All experiments are conducted at room temperature and without stirring the solution.

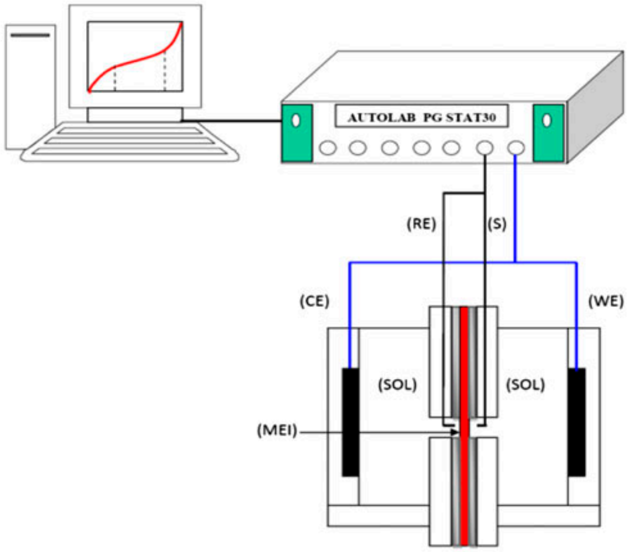

Fig. 2. Schematic description of the experimental set-up, RE: reference electrode, S: sensor electrode, CE: counter electrode, WE: working electrode, SOL: solutions, IEM: ion-exchange membrane.

3. Experimental results and discussion

3.1. CVC obtained during the NH_4^+ and Cl^- transfer

Fig. 3 shows typical CVC obtained for a 0.05 N $(NH_4)_2SO_4$ through the CMX membrane (black) and NH_4Cl through the AMX membrane (blue). As it can be seen, the three characteristic regions can be distinguished. It is also observed that the limiting current densities of both Cl^- and NH_4^+ are approximately the same due to their same ionic motilities under an electrical field.

Fig. 4 shows the differential $\Delta V/\Delta I$ curves of the CVC as a function of the current density. The peak in the figure corresponds to the inflection point of the CVC that determines the limiting current density value (I_{lim}) in more accurate way than the Cowan–Brown method [31].

3.2. The effect of the ammonia buffer (NH_3/NH_4^+) on the counter-ion transfer

3.2.1. Through the CMX cation-exchange membrane

In this case, the NH_4^+ counter-ions are the carriers of the current, the weak electrolyte is ammonia (NH_3) and the buffer mixture (NH_3/NH_4^+) will maintain the pH of the solution at a constant value (pH = pKa = 9.25). Fig. 5 shows the CVC of $(NH_4)_2SO_4$ 0.05 N without (black), and with ammonia from 0.01 to 0.1 N. The obtained results showed that the addition of ammonia does not affect the limiting current density and has no effects on the first ohmic region. It can be also seen that the plateau length decreases and its slop increases with increasing the concentration of ammonia in the system. When we add 0.1 N of NH_3 to the system, the polarization has been totally eliminated, and we have a linear CVC where the current continues to increase as we increase the electrical potential driving force.

3.2.2. Through the AMX anion-exchange membrane

Fig. 6 shows the obtained CVC for a 0.05 N NH_4Cl and a AMX membrane. As it can be seen, the presence of ammonia slightly increases the resistance of the ohmic region. Also, the plateau length decreases and its slop increases with increasing the concentration of ammonia in the system but in a different way of the CMX membrane. The polarization has been totally eliminated when the concentration of ammonia was 0.075 N.

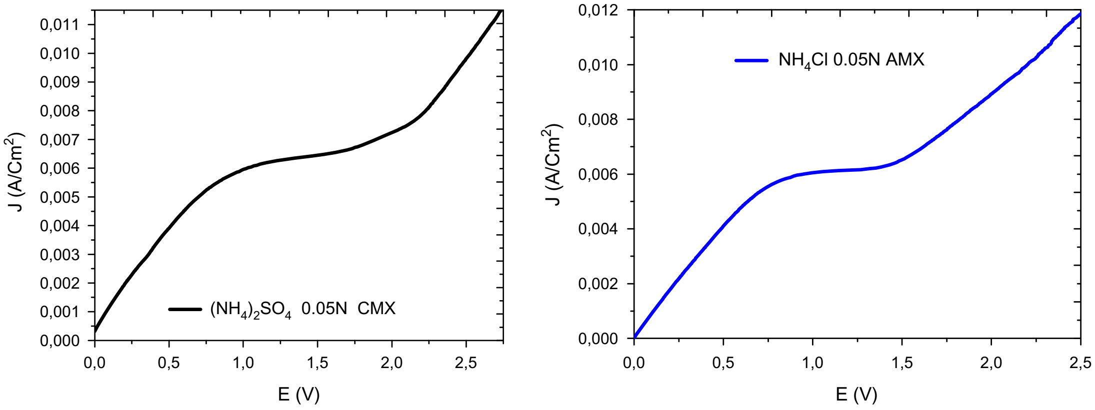

Fig. 3. CVC of 0.05 N $(NH_4)_2SO_4$/CMX (black) and 0.05 N NH_4Cl/AMX (blue).

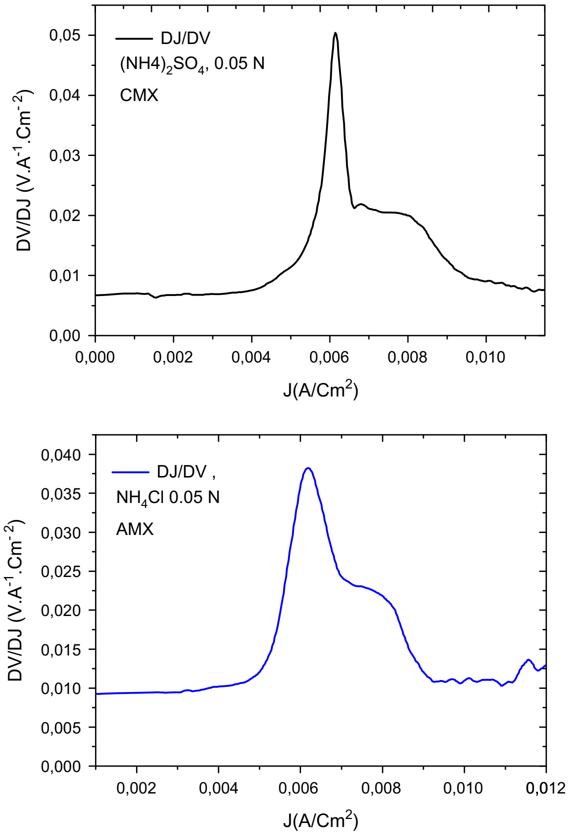

Fig. 4. The instantaneous differential $\Delta V/\Delta I$ value at a given current density of $(NH_4)_2SO_4$ (black) and NH_4Cl (blue).

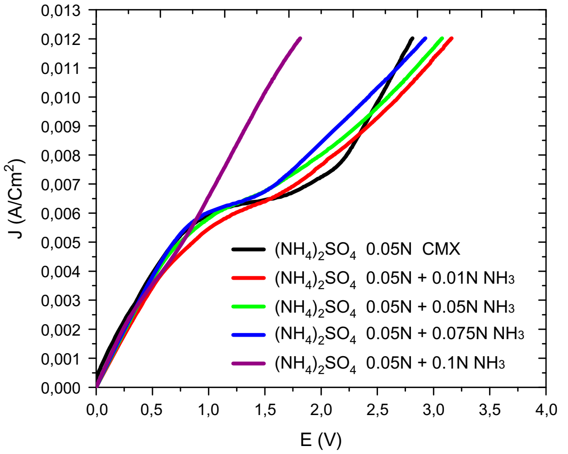

Fig. 5. CVC of 0.05 N $(NH_4)_2SO_4$/CMX without (black), and with ammonia from 0.01 to 0.1 N.

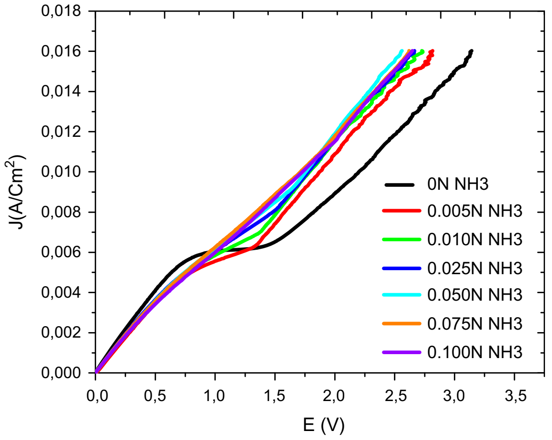

Fig. 6. CVC of 0.05 N NH_4Cl/AMX without (black), and with ammonia from 0.005 to 0.1 N.

The obtained results show that the addition of ammonia facilitates the counter-ion transfer in both cases and gives a total elimination of the system polarization but with different behaviors of CMX and AMX membranes, the difference should be associated to:

- The chemical properties (acid–base) of the functional groups of the membrane.
- The penetration of the buffer couple: In the case of the CMX membrane, the buffer couple NH_3/NH_4^+ can pass through the membrane, but with the AMX membrane, only NH_3 can pass through, the co-ion NH_4^+ will be rejected by the functional groups of the same positive electrical charge, thus limits its effect on the membrane surface.

According to the classical concentration polarization theory described by the depletion of the diffusion boundary layer and according to the electro-convection theory proposed by I Rubenstein and co-workers [32–34], that is the most adapted in electro-membrane polarization and over-limiting current origin, the reduction and the elimination of the concentration polarization plateau could not be expected in such conditions.

The above finding is of great interest, because the concentration polarization phenomena were the main obstacle of the electro-membrane processes such as ED. It has been eliminated by only ammonia addition, the question is as follows: How can we exploit and use this results to make a new generation of IEMs without polarization and therefore increase the process efficiency and reduce the operation cost of such processes?

4. Conclusions

In the present work, the effect of the ammonia buffer (NH_3/NH_4^+) on the counter-ion transfer through the AMX and CMX IEMs was thoroughly examined. Based on the obtained CVC, the concentration polarization plateau has been completely eliminated in both case of the cation- and the anion-exchange membranes, which is in contrast with the expected result according to the classical concentration polarization theory in electrochemistry. This result revealed that the concentration polarization is a phenomenon that takes place inside the membrane and not necessarily on its surface (boundary layer) and the electro-convection theory remains insufficient to explain this unusual behavior.

References

[1] P. Dlugolêcki, Mass Transport in Reverse Electrodialysis for Sustainable Energy Generation, PhD thesis, University of Twente, The Netherlands, 2009.

[2] Y. Tanaka, Ion Exchange Membranes: Fundamentals and Applications, first ed., Elsevier, Amsterdam, The Netherlands, 2007.

[3] H. Strathmann, Ion Exchange Membranes Separation Processes, first ed., Elsevier, Amsterdam, The Netherlands, 2004.

[4] H. Strathmann, Electrodialysis, a mature technology with a multitude of new applications, Desalination 264 (2010) 268–288.

[5] T. Xu, C. Huang, Electrodialysis-based separation technologies: A critical review, AIChE J. 54 (2008) 3147–3159.

[6] T. Xu, Ion exchange membranes: State of their development and perspective, J. Membr. Sci. 263 (2005) 1–29.

[7] R.K. Nagarale, G.S. Gohil, V.K. Shahi, Recent developments on ion-exchange membranes and electro-membrane processes, Adv. Colloid Interface Sci. 119 (2006) 97–130.

[8] J. Luo, C. Wu, T. Xu, Y. Wu, Diffusion dialysis-concept, principle and applications, J. Membr. Sci. 366 (2011) 1–16.

[9] M.A. Anderson, A.L. Cudero, J. Palma, Capacitive deionization as an electrochemical means of saving energy and delivering clean water. Comparison to present desalination practices: Will it compete?, Electrochim. Acta 55 (2010) 3845–3856.

[10] S. Porada, L. Weinstein, R. Dash, A. van der Wal, M. Bryjak, Y. Gogotsi, P.M. Biesheuvel, Water desalination using capacitive deionization with microporous carbon electrodes, ACS Appl. Mater. Interfaces 4 (2012) 1194–1199.

[11] D.A. Vermaas, M. Saakes, K. Nijmeijer, Power generation using profiled membranes in reverse electrodialysis, J. Membr. Sci. 385–386 (2011) 234–242.

[12] P. Długołęcki, P. Ogonowski, S.J. Metz, M. Saakes, K. Nijmeijer, M. Wessling, On the resistances of membrane, diffusion boundary layer and double layer in ion exchange membrane transport, J. Membr. Sci. 349 (2010) 369–379.

[13] J.W. Post, H.V.M. Hamelers, C.J.N. Buisman, Energy recovery from controlled mixing salt and fresh water with a reverse electrodialysis system, Environ. Sci. Technol. 42 (2008) 5785–5790.

[14] J. Veerman, M. Saakes, S.J. Metz, G.J. Harmsen, Electrical power from sea and river water by reverse electrodialysis: A first step from the laboratory to a real power plant, Environ. Sci. Technol. 44 (2010) 9207–9212.

[15] D.A. Vermaas, M. Saakes, K. Nijmeijer, Doubled power density from salinity gradients at reduced intermembrane distance, Environ. Sci. Technol. 45 (2011) 7089–7095.

[16] Z. Du, H. Li, T. Gu, A state of the art review on microbial fuel cells: A promising technology for wastewater treatment and bioenergy, Biotechnol. Adv. 25 (2007) 464–482.

[17] S.J. Peighambardoust, S. Rowshanzamir, M. Amjadi, Review of the proton exchange membranes for fuel cell applications, Int. J. Hydrogen Energy 35 (2010) 9349–9384.

[18] T.S. Zhao, C. Xu, R. Chen, W.W. Yang, Mass transport phenomena in direct methanol fuel cells, Prog. Energy Combust. Sci. 35 (2009) 275–292.

[19] E.I. Belova, G.Y. Lopatkova, N.D. Pismenskaya, V. V Nikonenko, C. Larchet, G. Pourcelly, Effect of anion-exchange membrane surface properties on mechanisms of overlimiting mass transfer J. Phys. Chem. B 110 (2006) 13458–13469.

[20] J. Balster, M.H. Yildirim, D.F. Stamatialis, R. Ibanez, R.G.H. Lammertink, V. Jordan, M. Wessling, Morphology and microtopology of cation-exchange polymers and the origin of the overlimiting current, J. Phys. Chem. B 111 (2007) 2152–2165.

[21] N.A. Mishchuk, Concentration polarization of interface and non-linear electrokinetic phenomena, Adv. Colloid Interface Sci. 160 (2010) 16–39.

[22] Y. Kim, D.F. Lawler, Overlimiting current by interactive ionic transport between space charge region and electric double layer near ion-exchange membranes, Desalination 285 (2012) 245–252.

[23] V.V.R. Nandigana, N.R. Aluru, Understanding anomalous current–voltage characteristics in microchannel–nanochannel interconnect devices, J. Colloid Interface Sci. 384 (2012) 162–171.

[24] R. Zerdoumi, K. Oulmi, K.-E. Bouhidel, The effect of the borate/boric acid buffer on the transfer of potassium counter-ion through a cation-exchange membrane: Current–voltage characteristics, Desalin. Water Treat. 51 (2013) 6179–6183.

[25] N.D. Pismenskaya, V.V. Nikonenko, N.A. Melnik, K.A. Shevtsova, E.I. Belova, G. Pourcelly, D. Cot, L. Dammak, C. Larchet, Evolution with time of hydrophobicity and microrelief of a cation exchange membrane surface and its impact on overlimiting mass transfer, J. Phys. Chem. B 116 (2012) 2145–2161.

[26] J. Choi, S. Kim, S. Moon, Heterogeneity of ion-exchange membranes: The effects of membrane heterogeneity on transport properties, J. Colloid Interface Sci. 241 (2001) 120–126.

[27] H. Lee, M. Hong, S.-D. Han, S.-H. Moon, Influence of the heterogeneous structure on the electrochemical properties of anion exchange membranes, J. Membr. Sci. 320 (2008) 549–555.

[28] L. Marder, E.M. Ortega Navarro, V. Pérez-Herranz, A.M. Bernardes, J. Ferreira, Evaluation of transition metals transport properties through a cation-exchange membrane by chronopotentiometry, J. Membr. Sci. 284 (2006) 267–275.
[29] K. Bouhidel, K. Oulmi, Concentration polarization in electrodialysis: Buffer solutions experimental method, Desalination 132 (2000) 199–204.
[30] K. Bouhidel, S. Benslimane, Ion exchange membrane modification by weak electrolytes and glycine: Reduction and elimination of the concentration polarization plateau in electrodialysis, Desalination 199 (2006) 67–69.
[31] D.A. Cowan, J.H. Brown, Effect of turbulence on limiting current in electrodialysis cells, Ind. Eng. Chem. 51 (1959) 1445–1448.
[32] I. Rubinstein, B. Zaltzman, Extended space charge in concentration polarization, Adv. Colloid Interface Sci. 159 (2010) 117–129.
[33] I. Rubinstein, B. Zaltzman, Electro-convective versus electroosmotic instability in concentration polarization, Adv. Colloid Interface Sci. 134–135 (2007) 190–200.
[34] I. Rubinstein, F. Maletzki, Electroconvection at an electrically inhomogeneous permselective membrane surface, Faraday Discuss. 87 (1991) 2079–2087.