

Effect of the type of ion exchange membrane on performance, ion transport, and pH in biocatalyzed electrolysis of wastewater

R. A. Rozendal, T. H. J. A. Sleutels, H. V. M. Hamelers
and C. J. N. Buisman

ABSTRACT

Previous studies have shown that the application of cation exchange membranes (CEMs) in bioelectrochemical systems running on wastewater can cause operational problems. In this paper the effect of alternative types of ion exchange membrane is studied in biocatalyzed electrolysis cells. Four types of ion exchange membranes are used: (i) a CEM, (ii) an anion exchange membrane (AEM), (iii) a bipolar membrane (BPM), and (iv) a charge mosaic membrane (CMM). With respect to the electrochemical performance of the four biocatalyzed electrolysis configurations, the ion exchange membranes are rated in the order AEM > CEM > CMM > BPM. However, with respect to the transport numbers for protons and/or hydroxyl ions ($t_{H/OH}$) and the ability to prevent pH increase in the cathode chamber, the ion exchange membranes are rated in the order BPM > AEM > CMM > CEM.

Key words | BEAMR, biocatalyzed electrolysis, hydrogen, ion exchange membrane, MFC, microbial fuel cell

R. A. Rozendal
T. H. J. A. Sleutels
H. V. M. Hamelers (corresponding author)
C. J. N. Buisman
Sub-Department of Environmental Technology,
Wageningen University,
Bomenweg 2, P.O. Box 8129, 6700 EV Wageningen,
The Netherlands
Tel.: +31 (0)317 483447
Fax: +31 (0)317 482108
E-mail: bert.hamelers@wur.nl

R. A. Rozendal
T. H. J. A. Sleutels
C. J. N. Buisman
Wetsus, centre for sustainable water technology,
Agora 1, P.O. Box 11138900 CC, Leeuwarden,
The Netherlands

INTRODUCTION

Energy production from wastewater by means of bioelectrochemical conversion has become a rapidly developing research field since the discovery of mediator-less microbial electron transfer to electrodes (Kim *et al.* 1999). Two types of technologies are currently being studied: (i) microbial fuel cells (MFCs) for electricity production (Logan *et al.* 2006), and (ii) biocatalyzed electrolysis (or BEAMR) for hydrogen production (Liu *et al.* 2005; Rozendal & Buisman 2005; Rozendal *et al.* 2006b). With respect to these technologies much progress has been made in a relatively short timeframe. Extrapolating this progress to the future, it is expected that bioelectrochemical systems will eventually be limited by the capabilities of the electrochemically active micro-organisms (Logan & Regan 2006). At the moment, however, the bioelectrochemical system is still limited by the non-biological part of the cell design. Within this scope

ion exchange membranes form an important challenge. Ion exchange membranes separate the biological anode from the cathode reactions, while at the same time facilitating the transport of ions through the membrane in order to maintain electroneutrality in the system. As the cathode reactions of both MFCs and biocatalyzed electrolysis consume protons in equal amounts as electrons, ideally only protons are transported through the ion exchange membrane. In this way electroneutrality is observed without pH changes taking place at the cathode. However, bioelectrochemical systems on wastewater typically apply cation exchange membranes (CEMs) and various studies have shown that in that case mainly cation species other than protons are responsible for the transport of positive charge through the membrane (Rozendal *et al.* 2006a; Zhao *et al.* 2006). This results from the fact that in wastewater the

concentrations of cations other than protons (e.g. Na^+ , K^+ , NH_4^+) are typically 10^5 times higher than the concentration of protons. The transport of other cation species causes a pH increase at the cathode, which can negatively affect the cell performance (Rozendal *et al.* 2006a).

The objective of this study, therefore, was to investigate the effect of alternative ion exchange membranes on ion transport and pH in bioelectrochemical systems running on wastewater (also see Kim *et al.* 2007; Rozendal *et al.* 2007). This was tested in biocatalyzed electrolysis configurations with four different types of ion exchange membranes (Figure 1): (i) a CEM, (ii) an anion exchange membrane (AEM), (iii) a bipolar membrane (BPM), and (iv) a charge mosaic membrane (CMM) (Xu 2005).

METHODS

Electrochemical cell. All experiments were performed in two-chamber electrochemical cells (total volume 6.6 liter) as previously described in (Rozendal *et al.* 2006a) with an anode of graphite felt (surface area: 400 cm^2 , thickness: 3 mm – FMI Composites Ltd., Galashiels, Scotland) and a cathode of platinum coated (50 g/m^2) titanium mesh (surface area: 400 cm^2 , thickness: 1 mm, specific surface area: $1.7\text{ m}^2/\text{m}^2$ – Magneto special anodes BV, Schiedam, The Netherlands). The electrodes were electrically connected to an adjustable power supply (ES 030-5, Delta Elektronika BV, The Netherlands). Both the anode and the cathode chamber were equipped with an Ag/AgCl reference electrode for measuring potentials. The chambers were

separated from each other by means of an ion exchange membrane. In the experiments four types of membranes (surface area 256 cm^2) were tested for their ion transport properties: (i) a CEM (Nafion[®] 117), (ii) an AEM (Fumasep[®] FAB, FuMA-Tech GmbH), (iii) a BPM (Fumasep[®] FBM, FuMA-Tech GmbH), and (iv) a CMM, (Dainichiseika Color & Chemicals, Co. Ltd., Japan). Conductivity and pH in the chambers were measured outside the electrochemical cells in a flow cell through which the anolyte/catholyte was continuously pumped at a rate of 340 ml/min.

Experimental Procedures & Calculations. All experiments were performed at 303 K. The anode chambers of the electrochemical cells were continuously fed (4 mL/min) with synthetic medium containing (in deionized water): 0.6 g/L CH_3COOH , 0.74 g/L KCl, 0.58 g/L NaCl, 0.68 g/L KH_2PO_4 , 0.87 g/L K_2HPO_4 , 0.28 g/L NH_4Cl , 0.1 g/L $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.1 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and 1 mL/L of a trace element mixture (Zehnder *et al.* 1980). Acetic acid was always available in excess and never limited current generation. The anode chamber was operated at pH 7 during all experiments by dosing 33% NaOH (Liquisys M CPM 253, Endress + Hauser). The electrochemical cells were started up by inoculating the anode chambers with 250 mL effluent taken from an active biocatalyzed electrolysis cell running on acetate (Rozendal *et al.* 2007). After stabilization at an applied voltage of 1.0 V, membrane ion transport was studied in duplicate 48 h experimental runs at an applied voltage of 1.0 V. Prior to every run the cathode chamber was flushed 3 times with potassium phosphate buffer (10 mM, pH 7) and then filled with exactly 3 L of the same buffer. Subsequently, the cathode chambers were

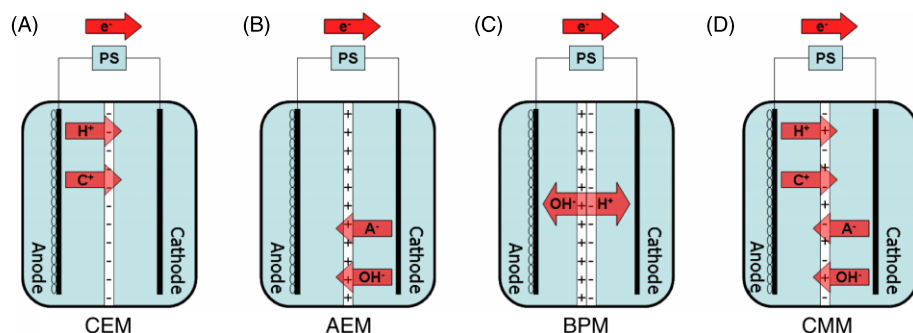


Figure 1 | Theoretical working principle of membrane charge transport in four different types of ion exchange membranes used in biocatalyzed electrolysis: (A) CEM – through the transport of cations (ideally protons) from anode to cathode; (B) AEM – through the transport of anions (ideally hydroxyl ions) from cathode to anode; (C) BPM – through water splitting into protons and hydroxyl ions inside the membrane; (D) CMM – through the transport of cations (ideally protons) from anode to cathode AND/OR anions (ideally hydroxyl ions) from cathode to anode. PS = power supply, C^+ = Cations, A^- = Anions.

flushed with water-saturated nitrogen gas (99.999% N₂, Air Products) until the experimental run was started by closing the electrical circuit. During the experimental runs hydrogen accumulated in the headspace of the cathode chamber and left the system through a gas flow meter (Milligascounter[®], Ritter). A data logger (Ecograph T, Endress + Hauser) continuously logged the applied voltage, current, anode potential, cathode potential, cathode pH, cathode conductivity and gas production. At the beginning and at the end of the experimental runs a 50 mL liquid sample was taken from the cathode chamber. The hydrogen fraction in the headspace of the cathode chamber and the ion content in liquid samples were analyzed according to Rozendal *et al.* (2007). The amount of water still left in the cathode chamber after the experimental runs was measured to correct the ion transport data for osmotic loss of water from the cathode to the anode chamber (<3% for all membranes). Total charge production (Q_e), expressed in Coulombs (C), after the 48 h experimental runs was calculated by integration of the current. Total charge production was compared to the transport of charge in the form of specific ions through the ion exchange membrane (Q_{ion}), which was calculated from the cathode chamber ion content data according to:

$$Q_{ion} = (x^{ion} - x^{ion,0}) \cdot V \cdot z^{ion} \cdot F \quad (1)$$

with Q_{ion} the transport of charge in the form of a specific ion through an ion exchange membrane after a 48 h

experimental run expressed in Coulombs (C), x^{ion} the molar concentration of a specific ion after a 48 h experimental run expressed in moles per liter (M), $x^{ion,0}$ the molar concentration of a specific ion at start of a 48 h experimental run expressed in moles per liter (M), V the cathode chamber liquid volume expressed in liters (L), z^{ion} the valence of the specific ion and F the Faraday constant (96485 Coulombs/mole). Transport numbers for cation (t_c), anions (t_A) and, protons and/or hydroxyl ions ($t_{H/OH}$) through the ion exchange membranes were calculated according to Rozendal *et al.* (2007). The transport of protons from anode to cathode and the transport of hydroxyl ions from cathode to anode were lumped together, because in practice no distinction can be made between those kinds of transport. Results are reported as means \pm standard deviation.

RESULTS AND DISCUSSION

Figure 2A shows the current generation of the four biocatalyzed electrolysis configurations during the 48 h experimental runs. As can be seen from this figure the CEM and the AEM configurations outperform the BPM and CMM configurations. As can be expected, this has a significant effect on the cumulative H₂ production during the 48 h experimental runs (Figure 2B). With respect to the performance of the four biocatalyzed electrolysis configurations, the ion exchange membranes are rated in the order AEM > CEM > CMM > BPM.

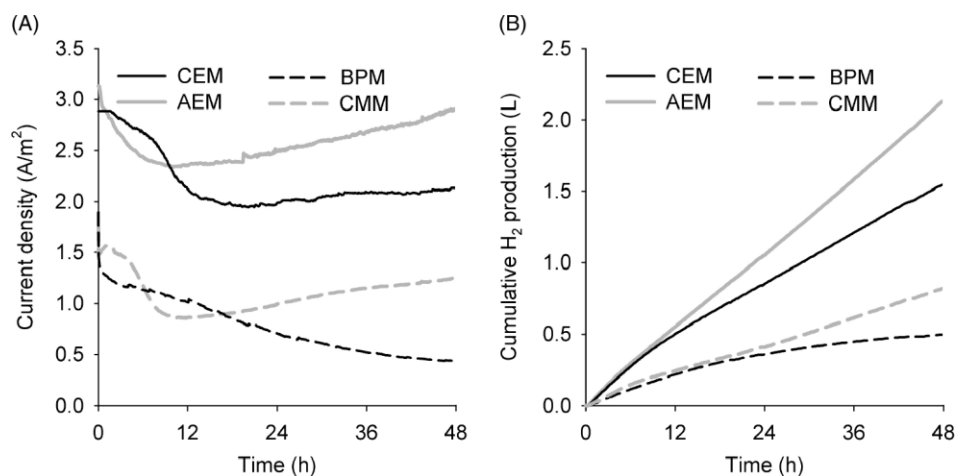


Figure 2 | Performance of the four biocatalyzed electrolysis configurations with different types of ion exchange membranes: (A) current density and (B) cumulative H₂ production during duplicate 48 h experimental runs at an applied voltage of 1.0 V.

Potential measurements demonstrated that the difference in performance of the biocatalyzed electrolysis configurations was predominantly caused by the difference in voltage loss across the membrane. This voltage loss across the membrane is included in a measurement of the total voltage difference between the reference electrodes in the anode and cathode chambers (Ter Heijne et al. 2006). At the start of the experimental runs, i.e. when all other conditions in the cathode chamber were still identical, the voltage differences between the reference electrodes in the anode and cathode chambers were -0.27 ± 0.01 , -0.32 ± 0.02 , -0.71 ± 0.01 , and -0.45 ± 0.02 V for the CEM, AEM, BPM, and CMM configurations respectively. It seems unlikely that these differences are caused by the area resistance of the ion exchange membranes, which are typically in the order of $1\text{--}10 \Omega\text{cm}^2$ (Xu 2005). At the current densities as observed in the 48 h experimental runs ($<3.5 \text{ A/m}^2$) this area resistance of the ion exchange membranes can only account for a loss of several mV. The true causes of these differences in voltage loss across the membrane remain a topic of further investigation, but it is obvious that they have a significant effect on the overall electrochemical performance of the four biocatalyzed electrolysis configurations.

An important aspect of the membrane performance is their ability to prevent pH increase in the cathode chamber. Figure 3A shows that the CEM, AEM, and CMM perform very similar in this respect with a rapid cathode pH increase

after only little charge production. The BPM, on the other hand, demonstrated a more slowly cathode pH increase. Figures 3B and 4 show that cathode pH increase results from the membrane transport of ion species other than protons and/or hydroxyl ions. The trends observed in these figures also give an explanation for the large variations observed in the current density plots (Figure 2A). Current density is negatively affected by an increasing pH in the cathode chamber, but at the same time positively affected by an increase of cathode chamber conductivity. Again, the BPM shows deviating behavior as the point of increasing current densities is not yet reached in the 48 h experimental run as a result of the slower cathode pH and conductivity increase.

Figure 4 shows that the membrane charge transport in the CEM configuration was predominantly in the form of cations ($t_C 0.71 \pm 0.04$) and H^+/OH^- ($t_{\text{H}/\text{OH}} 0.30 \pm 0.03$). In the AEM configuration, however, the membrane charge transport was not only in the form of anions ($t_A 0.19 \pm 0.01$) and H^+/OH^- ($t_{\text{H}/\text{OH}} 0.49 \pm 0.01$), but also to a large extent in the form of cations ($t_C 0.32 \pm 0.00$). As expected from the working principle of BPMs (Figure 1), the membrane charge transport in the BPM configuration was predominantly in the form of H^+/OH^- ($t_{\text{H}/\text{OH}} 0.72 \pm 0.02$), but also here cations contributed ($t_C 0.30 \pm 0.01$) to the membrane charge transport, which explains the observed cathode pH and conductivity increases (Figure 3). Interestingly, the membrane charge transport in the CMM configuration was predominantly in the form of cations ($t_C 0.64 \pm 0.00$) and

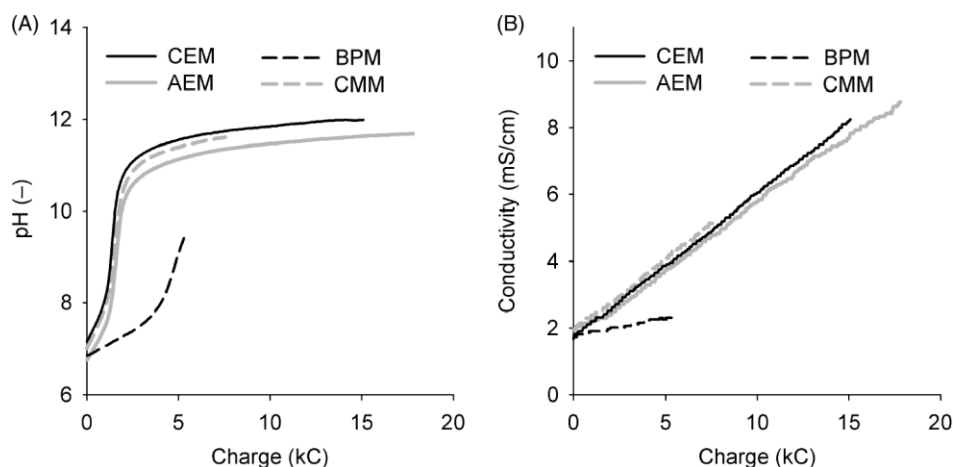


Figure 3 | Ability of the ion exchange membranes to prevent pH and conductivity increase in the cathode chamber: (A) cathode chamber pH and (B) cathode chamber conductivity against the total charge production of the four biocatalyzed electrolysis configurations during duplicate 48 h experimental runs at an applied voltage of 1.0 V.

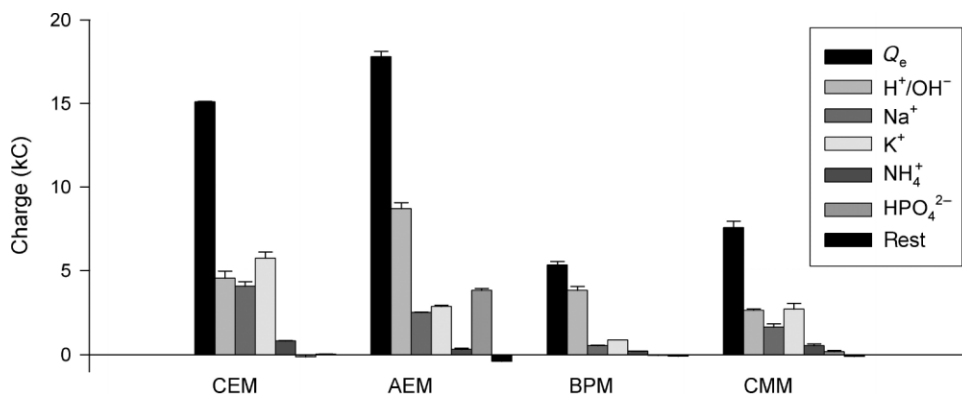


Figure 4 | Comparison of the total charge production (Q_e) to the transport of charge in the form of specific ions through the ion exchange membrane (Q_{ion}) after the duplicate 48 h experimental runs at an applied voltage of 1.0V. The sum of the categories H^+/OH^- , Na^+ , K^+ , NH_4^+ , HPO_4^{2-} , and rest accounts for 100% of the total charge transport through the ion exchange membrane.

H^+/OH^- ($t_{H/OH}$ 0.35 ± 0.03). In contrast to what was expected based on the CMM working principle (Figure 1) anions (t_A 0.01 ± 0.00) almost did not contribute to the membrane charge transport. Therefore, under the conditions of the biocatalyzed electrolysis experiments, the CMM functioned more as a CEM than as a CMM.

On the basis of the results presented in Figures 3 and 4, the ion exchange membranes are rated in the order BPM > AEM > CMM > CEM with respect to the transport numbers for protons and/or hydroxyl ions ($t_{H/OH}$) and the ability to prevent pH increase in the cathode chamber.

CONCLUSIONS

In this paper the effect of the type of ion exchange membrane on ion transport and pH in bioelectrochemical systems running on wastewater was studied. Four types of ion exchange membranes were tested in a biocatalyzed electrolysis cell: (i) a CEM, (ii) an AEM, (iii) a BPM, and (iv) a CMM. With respect to the electrochemical performance of the four biocatalyzed electrolysis configurations, the ion exchange membranes are rated in the order AEM > CEM > CMM > BPM. However, with respect to the transport numbers for protons and/or hydroxyl ions ($t_{H/OH}$) and the ability to prevent pH increase in the cathode chamber, the ion exchange membranes are rated in the order BPM > AEM > CMM > CEM.

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