

# Effects of Membrane Cation Transport on pH and Microbial Fuel Cell Performance<sup>†</sup>

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Due to the excellent proton conductivity of Nafion membranes in polymer electrolyte membrane fuel cells (PEMFCs), Nafion has been applied also in microbial fuel cells (MFCs). In literature, however, application of Nafion in MFCs has been associated with operational problems. Nafion transports cation species other than protons as well, and in MFCs concentrations of other cation species ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ ) are typically  $10^5$  times higher than the proton concentration. The objective of this study, therefore, was to quantify membrane cation transport in an operating MFC and to evaluate the consequences of this transport for MFC application on wastewaters. We observed that during operation of an MFC mainly cation species other than protons were responsible for the transport of positive charge through the membrane, which resulted in accumulation of these cations and in increased conductivity in the cathode chamber. Furthermore, protons are consumed in the cathode reaction and, consequently, transport of cation species other than protons resulted in an increased pH in the cathode chamber and a decreased MFC performance. Membrane cation transport, therefore, needs to be considered in the development of future MFC systems.

## Introduction

Chemical energy can be converted to electrical energy in a direct and efficient way by applying fuel cell technology. Due to their high power density, fast startup time, and flexible power output, polymer electrolyte membrane fuel cells (PEMFCs) have received much research attention (1). PEMFCs have been designed for conversion of relatively simple fuels, such as hydrogen. The electrochemical oxidation of hydrogen at the anode of PEMFCs produces protons and electrons. An electrical circuit transports the electrons to the cathode, where the electrons are consumed in the reduction reaction of oxygen. To sustain this process, electroneutrality needs to be observed, i.e., transport of electrons to the cathode needs to be compensated by transport of an equal amount of positive charge to the cathode chamber. In PEMFCs, electroneutrality is observed by transport of protons through

a cation exchange membrane, which, therefore, is often referred to as proton exchange membrane (PEM). The cation exchange membrane is one of the most critical components in the PEMFC configuration. It provides a separation between fuel and oxidizer, but at the same time facilitates transport of positive charge to compensate for transport of electrons. The perfluorosulfonic acid membrane Nafion (product of DuPont) has been known for its good performance as a cation exchange membrane in PEMFCs (2). The morphology and properties of Nafion have extensively been reviewed by Mauritz and Moore (3). Nafion consists of a hydrophobic fluorocarbon backbone to which hydrophilic sulfonate groups ( $-\text{SO}_3^-$ ) are attached (4). The high cation conductivity of Nafion can be explained from the high concentration of these negatively charged sulfonate groups in the membrane ( $[-\text{SO}_3^-] \approx 1.13 \text{ mol/L}$ ) (5, 6).

Due to its good reputation, Nafion has recently become widely applied in microbial fuel cells (MFCs) as well (7–15). MFCs are considered a promising new technology for efficient production of electrical energy from wastewaters (16). In an MFC, electrons are generated from the oxidation of dissolved organic material by electrochemically active microorganisms (16). Current densities achieved in MFCs are typically  $10^3$  to  $10^4$  times lower than those achieved in PEMFCs, so the process is much less demanding with respect to transport of positive charge through the cation exchange membrane. One would expect, therefore, that Nafion, with its excellent cation conductivity, is more than suitable for application in MFCs.

In the literature, however, application of Nafion in MFCs has been associated with operational problems. During operation of a two-chamber MFC, Gil et al. (8) observed a decreasing pH in the anode chamber and an increasing pH in the cathode chamber, because proton transport through the Nafion seemed to be slower than the proton production rate in the anode chamber and the proton consumption rate in the cathode chamber. In another study, Liu and Logan (13) operated a single-chamber MFC in the presence and absence of a Nafion 117 membrane and observed a reduced power output when Nafion was present ( $262 \pm 10$  vs  $494 \pm 21 \text{ mW/m}^2$ ). Potential measurements showed that the anode potential was identical in the presence and absence of a Nafion 117, but that the cathode potential was  $0.177 \pm 0.012 \text{ V}$  lower when Nafion was present.

These results indicate that application of Nafion in MFCs is not straightforward. Different working conditions in MFCs compared to those in PEMFCs might be an explanation for this. In PEMFCs, protons are the only cation species present in the system and protons, therefore, are the only cation species transported. In MFCs, however, operating with wastewater at pH neutral conditions, the proton concentration is about  $10^{-4} \text{ mM}$ , whereas concentrations of other cation species (e.g.,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ ) are typically  $10^5$  times higher. Nafion, like all other commercial cation exchange membranes, transports cation species other than protons as well (17, 18). The objective of this study, therefore, was to quantify membrane cation transport in an operating MFC and to evaluate the consequences of this transport for MFC application on wastewaters.

## Materials and Methods

**Electrochemical Cell.** Experimental runs were performed in a two-chamber electrochemical cell (total volume 6.6 L; total liquid volume 6 L) as previously described (19) (see Figure S1, Supporting Information). Graphite felt (surface area  $400 \text{ cm}^2$ , thickness 3 mm; FMI Composites Ltd., Galashiels, Scotland) was used as the anode; a platinum-coated ( $50 \text{ g/m}^2$ )

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**TABLE 1. Experimental Conditions**

run	catholyte (in MilliQ)	cathode chamber pH control?	resistor ( $\Omega$ )
1/2	10 mM phosphate buffer (pH 7)	yes (pH 7)	10
3/4	10 mM phosphate buffer (pH 7)	yes (pH 7)	50
5/6	anolyte without acetate + 10 mM NaCl	yes (pH 7)	10
7/8	10 mM phosphate buffer (pH 7)	no	10
9/10	50 mM phosphate buffer (pH 7)	no	10

titanium mesh electrode (surface area 400 cm<sup>2</sup>, thickness 1 mm, specific surface area 1.7 m<sup>2</sup>/m<sup>2</sup>; Magneto Special Anodes BV, Schiedam, The Netherlands) was used as the cathode. The anode and cathode chamber were separated from each other by a Nafion 117 membrane (surface area 256 cm<sup>2</sup>). Both chambers were equipped with an Ag/AgCl reference electrode and a pH electrode. To prevent interference of pH measurements with potential measurements, the pH electrodes were placed externally to the anode/cathode chamber in a flow cell through which the anolyte/catholyte was continuously pumped at a rate of 250 mL/min. If required, the anode and cathode chamber could be operated pH controlled (Liquisys M CPM 253, Endress + Hauser) by dosing 1 M KOH (anode) or 1 M HCl (cathode).

**Medium and Microorganisms.** The anode chamber of the MFC was continuously fed at a rate of 4.5 mL/min with synthetic wastewater (i.e., anolyte; pH 7) containing (in deionized water) 1.36 g/L NaCH<sub>3</sub>COO·3H<sub>2</sub>O, 0.74 g/L KCl, 0.58 g/L NaCl, 0.68 g/L KH<sub>2</sub>PO<sub>4</sub>, 0.87 g/L K<sub>2</sub>HPO<sub>4</sub>, 0.28 g/L NH<sub>4</sub>Cl, 0.1 g/L yeast extract, 0.1 g/L MgSO<sub>4</sub>·7H<sub>2</sub>O, 0.1 g/L CaCl<sub>2</sub>·2H<sub>2</sub>O, and 1 mL/L of a trace element mixture (20). The anode chamber was inoculated with 500 mL of effluent taken from an active bio-electrochemical cell (19) and operated in batch until a stable MFC system was established. Steady-state conditions were achieved after 5 days of operation (cell voltage 0.14–0.2 V across a 10  $\Omega$  resistor). The anode chamber was operated pH controlled (pH 7) in all experimental runs. The cathode chamber was filled with 3.0 L of catholyte (Table 1) and was operated as a batch system in all experimental runs. The phosphate buffers that were used as catholyte were prepared as a mixture of KH<sub>2</sub>PO<sub>4</sub> and K<sub>2</sub>HPO<sub>4</sub>. The catholyte was kept saturated with oxygen by continuously aerating with humidified air. Cathode chamber pH control varied per experimental run (Table 1).

**Experimental Procedures and Calculations.** All experimental runs were performed at a temperature of 30 °C. Experimental conditions that were varied are described in Table 1. An experimental run was started by closing the electrical circuit. Every experimental run lasted 96 h and was done in duplicate. Results are reported as means  $\pm$  standard deviation. Every 24 h a 15 mL sample was taken from the influent vessel, anode chamber, and cathode chamber and filtered across a 0.45  $\mu$ m filter. Anion concentrations were determined using an ion chromatograph (Metrohm 761 Compact IC) equipped with a conductivity detector and an anion column (Metrosep A Supp 5 6.1006.520). Ammonium concentrations were photometrically determined using standardized test kits (ammonium cuvette test LCK303, XION 500 spectrophotometer, Dr. Lange Nederland BV, The Netherlands). Other cation concentrations (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup>) were determined using inductively coupled plasma–optical emission spectroscopy (ICP–OES; Perkin-Elmer Optima 3000XL). Cell voltage and potentials of the anode and cathode were logged with a data logger (SQ800, Grant Instruments, England). The current through the electrical circuit was determined from the measured cell voltage according to

$$I = \frac{E}{R} \quad (1)$$

with  $I$  the current expressed in amperes (A),  $E$  the cell voltage expressed in volts (V), and  $R$  the electrical resistance expressed in ohms ( $\Omega$ ). Power output of the system was determined according to

$$P = EI = \frac{E^2}{R} \quad (2)$$

with  $P$  the power output expressed in watts (W).

When calculating charge ( $Q$ ) a distinction was made between transport of negative charge in the form of electrons through the electrical circuit ( $Q^-$ ) and transport of positive charge in the form of the dominantly present cation species in the system (Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup>) through the Nafion membrane ( $Q^+$ ). Transport of negative charge in the form of electrons through the electrical circuit ( $Q^-$ ), expressed in coulombs (C), was determined by integrating current over time. Transport of positive charge in the form of the dominantly present cation species in the system through the Nafion membrane ( $Q^+$ ), expressed in coulombs (C), was determined from the ICP–OES measurements and ammonium tests as follows:

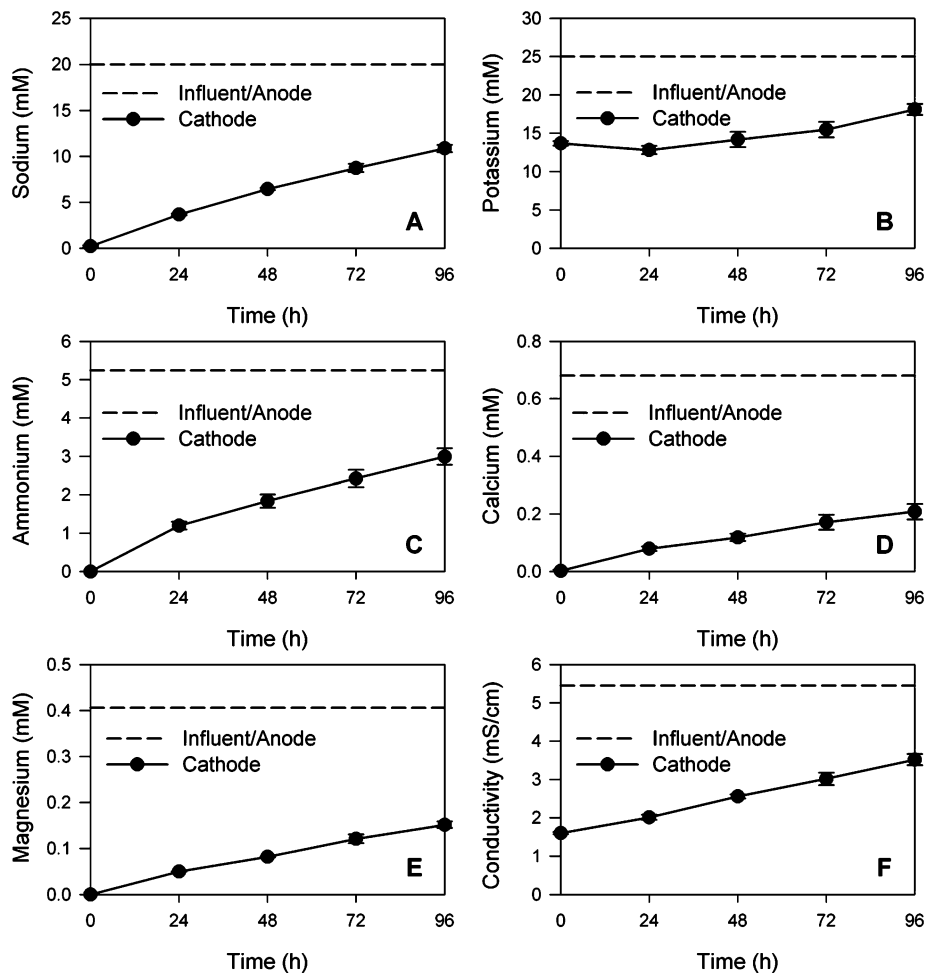
$$Q^+(t) = \sum_{Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}} (x^{cat,t} - x^{cat,0}) Vz^{cat}F \quad (3)$$

with  $x^{cat,t}$  the molar cation concentration of the cation species at time  $t$  expressed in moles per liter (M),  $x^{cat,0}$  the molar concentration of the cation species at the start of an experimental run expressed in moles per liter (M),  $V$  the cathode chamber liquid volume expressed in liters (L),  $z^{cat}$  the valence of the cation species, and  $F$  the Faraday constant (96485 coulombs/mole). Calculated values were corrected for cathode chamber liquid volume reduction caused by sampling ( $\sim$ 0.5% per day).

To evaluate the cation content of the Nafion membrane after use in an MFC, membrane samples were taken after experimental runs 5/6. The membrane samples were first washed with MilliQ water and then analyzed with energy-dispersive X-ray spectrometry (EDX). For the EDX analysis a JEOL JSM-6480LV scanning electron microscope (SEM) equipped with a NORAN System SIX model 300 X-ray microanalysis system (Thermo Electron Corporation) was used. Measurements were done at an acceleration voltage of 10 kV. To test whether detected cation species could be reversibly removed from the Nafion membrane, samples were stored overnight in 35% H<sub>2</sub>O<sub>2</sub>, washed with MilliQ water, boiled in 1 M HCl for 1 h, washed with MilliQ water and then analyzed again with EDX.

## Results and Discussion

**Membrane Cation Transport.** The synthetic wastewater, which was fed to the anode chamber of the MFC, contained 20 mM sodium, 25 mM potassium, 5.2 mM ammonium, 0.7 mM calcium, and 0.4 mM magnesium. At the start of the experimental runs the catholyte consisted of a 10 mM phosphate-buffer solution (run 1/2 in Table 1). Both anode and cathode chamber were kept pH controlled at pH 7 and the proton concentration in the cathode chamber, therefore, remained constant (10<sup>-4</sup> mM) throughout the experimental run. Under these conditions transport of cations to the cathode chamber was studied in an operating MFC in 96 h experimental runs. Average current during the experimental runs was 14.4  $\pm$  1.9 mA across a 10  $\Omega$  resistor (average current density 563  $\pm$  74 mA/m<sup>2</sup> membrane surface area). Figure 1 gives the development of the concentrations of the dominantly present cation species (Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup>)



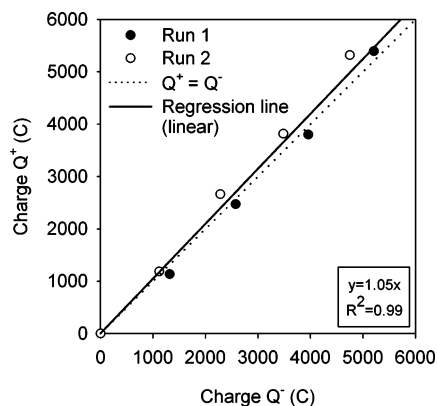
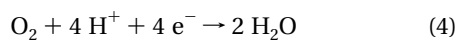
**FIGURE 1.** Development of the cation concentrations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ ) and conductivity in a pH-controlled (pH 7) cathode chamber of a microbial fuel cell (catholyte at  $t = 0$  10 mM phosphate buffer; resistor 10  $\Omega$ ). Bars indicate standard deviations.

and conductivity in the cathode chamber during the experimental run.

Figure 1 shows that all five dominantly present cation species in the anolyte were transported through the Nafion 117 membrane resulting in an increased concentration of these cation species in the catholyte. Variations in the concentration of anion species in the cathode chamber during the experimental runs were negligible ( $<0.1$  mM). An exception to this was the chloride concentration, which increased due to hydrochloric acid dosing for pH control. Increase in conductivity, therefore, was a combined effect of increased cation and chloride concentrations.

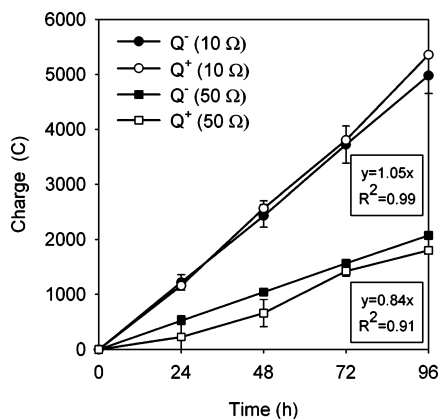
To quantify the contribution of the transport of cation species other than protons in relation to the total transport of positive charge to the cathode chamber, the total measured amounts of these cation species were expressed in coulombs (see Materials and Methods) and plotted against the integrated current (Figure 2).

As can be seen from Figure 2 a linear correlation exists between the transport of electrons through the electrical circuit and the transport of positive charge in the form of dominantly present cation species through the membrane. The slope close to unity (1.05) indicates that mainly cation species other than protons were responsible for the transport of positive charge through the membrane. This was also confirmed by chloride concentration measurements. The oxygen reduction reaction consumes protons equimolarly with electrons as follows:



**FIGURE 2.** Transport of positive charge in the form of the dominantly present cation species ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ ) through the Nafion 117 membrane ( $Q^+$ ) to a pH-controlled (pH 7) cathode chamber of a microbial fuel cell (catholyte at  $t = 0$  10 mM phosphate buffer; resistor 10  $\Omega$ ) against the integrated current ( $Q^-$ ). The box gives the result of the linear regression of  $Q^+$  as a function of  $Q^-$  of all acquired data points of the duplicate runs.

To keep pH constant, one molecule of hydrochloric acid, therefore, needs to be dosed for every positive charge in the form of cation species other than protons that is transported through the membrane. Indeed, the total amount of hydrochloric acid dosed was confirmed to be in the same range as the total amount of transported positive charge in the form of the dominantly present cation species ( $49.7 \pm 9.0$  mmol vs  $56.2 \pm 0.6$  mmol, respectively).



**FIGURE 3.** Influence of the electrical resistance on the integrated current ( $Q^-$ ) and the transport of positive charge in the form of the dominantly present cation species ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ ) through the Nafion 117 membrane ( $Q^+$ ) to a pH-controlled (pH 7) cathode chamber of a microbial fuel cell (catholyte at  $t = 0$  10 mM phosphate buffer). The boxes give the result of the linear regression of  $Q^+$  as a function of  $Q^-$  of all acquired data points of the duplicate runs. Bars indicate standard deviations.

To exclude the possibility that the observed linear correlation was coincidental, the experimental runs were repeated with a 50  $\Omega$  resistor in the electrical circuit (run 3/4 in Table 1; Figure 3). At this higher electrical resistance, less current flows (average current  $6.0 \pm 0.2$  mA; average current density  $234 \pm 8$  mA/m<sup>2</sup> membrane surface area) and consequently a reduced transport of the dominantly present cation species is expected.

Figure 3 shows that also when a 50  $\Omega$  resistor was used, the transport of positive charge in the form of dominantly present cation species through the membrane was linearly related to the transport of electrons through the electrical circuit. Again, the slope of the linear regression line between  $Q^+$  and  $Q^-$  was close to unity (0.84), which indicated that also in this case mainly cation species other than protons were responsible for the transport of positive charge through the Nafion membrane.

To test whether the transport of cation species other than protons would stop when cation concentrations in the catholyte become identical to those in the anolyte, membrane cation transport was quantified in case the cation concentrations in the catholyte at the start of the experimental runs were identical to those in the anolyte (run 5/6 in Table 1; see Figure S2, Supporting Information). Even under these conditions mainly cation species other than protons were responsible for the transport of positive charge through the membrane. During the experimental runs (average current  $14.2 \pm 2.0$  mA across a 10  $\Omega$  resistor; average current density  $555 \pm 78$  mA/m<sup>2</sup> membrane surface area) the sodium concentration in the catholyte increased with  $24 \pm 7\%$ , potassium with  $51 \pm 3\%$ , ammonium with  $25 \pm 2\%$ , and conductivity with  $36 \pm 2\%$ . Again, the slope of the linear regression line between  $Q^+$  and  $Q^-$  was close to unity (0.90). This shows that membrane transport of cation species other than protons to the cathode chamber does not even stop when the cation concentrations of the anolyte are reached. This means that the MFC is performing electrodialysis (21). In electrodialysis processes liquid streams are concentrated or desalinated under the influence of an electric field. In case of the MFC this electrical field is generated internally.

**Sulfonate Group Occupation.** The experimental runs described above have demonstrated that under typical MFC working conditions, electroneutrality is sustained mainly by transport of cation species other than protons through the Nafion membrane. This can be explained from the relative abundance of these other cation species compared to protons

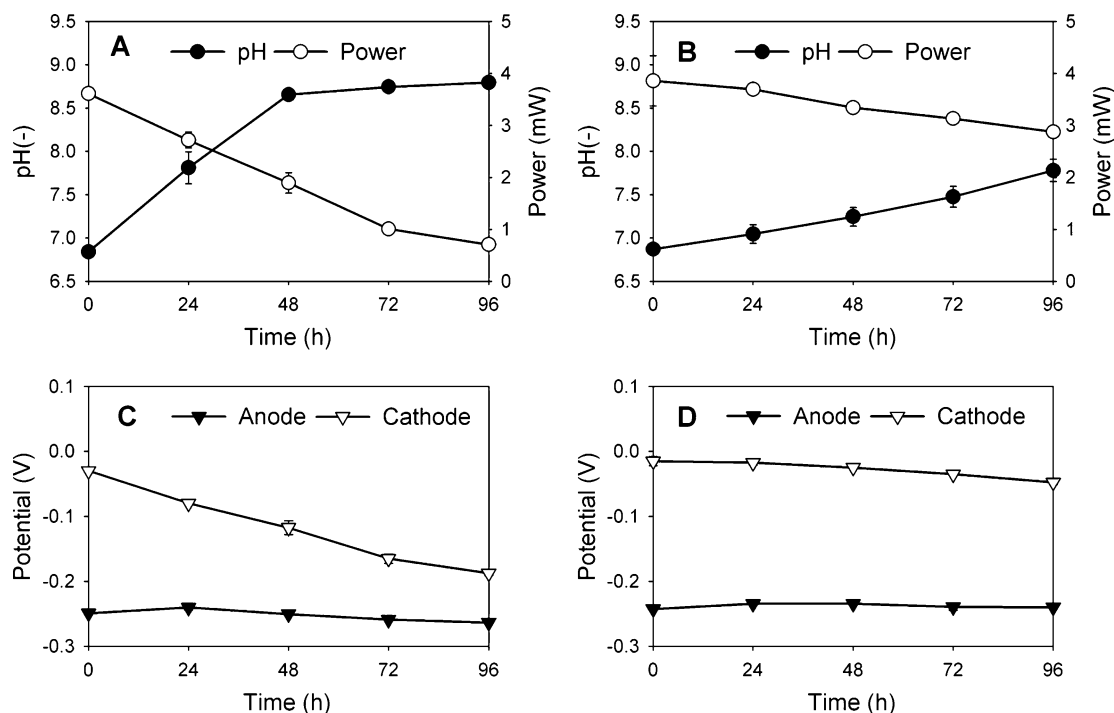
in the system. In the MFC, the Nafion membrane equilibrates with the cation species present in the anolyte and catholyte. This equilibration rapidly turns the membrane from its proton form to a form in which mainly other cation species ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ ) occupy the negatively charged sulfonate groups. Considering that concentrations of other cation species in (synthetic) wastewaters ( $\sim$ pH 7) are typically  $10^5$  times higher than the proton concentration ( $\sim 10^{-4}$  vs  $\sim 10^{-7}$  mM) and that the sulfonate groups in Nafion have a higher affinity for most other cation species than for protons (5, 6, 22), it can be calculated that over 99.999% of the sulfonate groups will be occupied by cation species other than protons. Although the diffusion coefficient of protons in Nafion is up to 4.4 times (17) higher than that for sodium and up to 6.2 times (18) higher than that for potassium, the low proton concentration in solution and in the membrane cause the transport rate of protons to be about  $10^4$  times lower than the transport rate of other cation species. This makes proton transport negligibly small compared to the transport of other cation species, which explains the observed results.

To confirm that cation species other than protons indeed mainly occupied the negatively charged sulfonate groups, the Nafion membrane used in experimental runs 5/6 (Table 1) was subjected to EDX analysis (see Figure S3A, Supporting Information). A quantitative analysis of this spectrum identified 1.33% of the atoms as sulfur (S), which originate from the negatively charged sulfonate groups in Nafion. Sodium and potassium represented 0.30% and 0.68% of the atoms respectively, which indicated that these two cation species alone already occupied an important fraction (74%) of the negatively charged sulfonate groups. The other dominantly present cation species in the system ( $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ ) were below the detection limit of the EDX analysis, but were expected to occupy most of the remaining sulfonate groups. All detectable cation species could be reversibly replaced by protons by storing the membrane overnight in 35% hydrogen peroxide and boiling it for 1 h in 1 M HCl (see Figure S3B, Supporting Information).

**Effects on pH and MFC Performance.** Protons are consumed equimolarly with electrons in the oxygen reduction reaction in the cathode chamber (eq 4) and consequently, in the absence of pH control the pH will increase in the cathode chamber if protons are not replenished through the membrane. This was tested in the MFC (resistor 10  $\Omega$ ) with a 10 mM phosphate buffer (pH 7) as the catholyte (run 7/8 in Table 1; Figure 4A and C) and with a 50 mM phosphate buffer (pH 7) as the catholyte (run 9/10 in Table 1; Figure 4B and D).

As predicted, the pH in the cathode chamber started to increase straight from the beginning of the experimental runs due to transport of cation species other than protons through the Nafion membrane. Due to the higher buffer capacity of the catholyte with 50 mM phosphate buffer, pH increase was slower than when the catholyte with 10 mM phosphate buffer was used. Figure 4A and B show that an increase of pH in the cathode chamber was associated with a decrease in power output of the MFC. From Figure 4C and D it becomes clear that this decrease in performance was mainly caused by the decrease of the cathode potential. The anode potential, on the other hand, remained constant throughout all experimental runs and was close to the theoretical potential for acetate oxidation of  $-0.28$  V at pH 7 (19).

**Implications for MFC Application on Wastewaters.** By quantifying membrane cation transport, this study has provided an explanation for the operational problems, mentioned in the literature, associated with the application of Nafion in MFCs. The pH effects as mentioned by Gil et al. (8), i.e., a decreasing anode pH and an increasing cathode pH, can now be explained from membrane cation transport. In an operating MFC, electroneutrality is sustained mainly



**FIGURE 4.** Development of the pH in the cathode chamber, power output, and anode and cathode potentials (vs NHE) during operation of a microbial fuel cell (resistor 10  $\Omega$ ). A/C: 10 mM phosphate buffer (pH 7) as the catholyte; B/D: 50 mM phosphate buffer (pH 7) as the catholyte. Bars indicate standard deviations.

by transport of cation species other than protons through the membrane, because these other cation species are more dominantly present. As suggested by Gil et al., buffers can compensate for lack of proton transport, but this compensation, however, can be only temporary. The buffer strengths as applied in the catholytes in our experimental runs are similar to those used in many other MFC studies (8, 14, 15, 23). In short experiments these buffers are sufficiently strong to keep a reasonably constant performance. However, as our results show, if experiments take longer than a few days, i.e., which is more realistic compared to practical conditions, the cathode chamber will suffer from an increasing pH. In our experiments this increasing pH was associated with a decrease of the MFC performance. Furthermore, if also the anode chamber is operated in batch, a decrease of the anode chamber pH can be expected as well. A decrease of the anode chamber pH can inhibit the microbial consortium, which will also negatively influence MFC performance (8).

This study also provides an explanation for the cathode potential loss as reported by Liu and Logan in their study on a single-chamber MFC operated in the presence and absence of a Nafion 117 membrane (13). At open circuit conditions, the cathode potential loss caused by the presence of the Nafion 117 membrane was  $0.177 \pm 0.012$  V and remained constant over the complete measuring range (up to  $1.4$  A/m<sup>2</sup>). This potential loss is too high to be explained from the area resistance of the membrane. The reported area resistances for Nafion 117 are in the range  $0.09$  to  $0.35$   $\Omega$ cm<sup>2</sup> (4) for protons and  $1.5$   $\Omega$ cm<sup>2</sup> for cations in general (24). Assuming the highest value applies to Nafion in MFCs, the cathode potential loss due to the area resistance of the Nafion at the current densities, as reported by Liu and Logan, cannot have been higher than  $0.00021$  V ( $=1.4 \times 10^{-4}$  A/cm<sup>2</sup>  $\times$   $1.5$   $\Omega$ cm<sup>2</sup>). Alternatively, the results of this study suggest that lack of protons in the membrane due to equilibration with the anolyte (pH 7.3–7.6), was the most important reason for the cathode potential loss. Transport of protons through Nafion markedly decreases when the amount of cation species other

than protons occupy over 50% of the sulfonate groups (5, 6, 25). In an MFC, over 99.999% of the sulfonate groups are expected to be occupied by cation species other than protons. This lack of protons, therefore, is likely to limit proton transport through the membrane. In a single-chamber MFC, the cathode chamber is omitted by applying a gas diffusion electrode (GDE). Consequently, the protons required for the oxygen reduction reaction need to be supplied from the anolyte through the Nafion membrane. As lack of protons in the membrane limits the proton transport through the membrane, a pH increase at the cathode side of the membrane can be expected. From the Nernst equation (26) it can be calculated that this negatively influences cathode potential. If the pH at the cathode side of the membrane increases only 3 pH units (e.g., from pH 7 to 10) the cathode potential will already decrease 0.18 V, which comes close to the value reported by Liu and Logan.

Despite the excellent performance of Nafion in PEMFCs, application of Nafion as a cation exchange membrane in MFCs is not straightforward, because the membrane transports cation species other than protons as well. Although not demonstrated for other types of cation exchange membranes, such as Ultrex (27–29), similar results can be expected there. In the literature, operational problems associated with the use of cation exchange membranes in MFCs are not generally acknowledged, but the effects for long-term operation of MFCs on wastewater can be problematic. Buffers offer only a temporary solution and permanent cathode chamber pH control is too costly as for every mole of electrons transported, close to one mole of acid needs to be dosed. In principle, only membranes that are truly 100% proton selective can prevent the described pH effects, but these types of membranes are currently not commercially available. Alternatively, membranes can be omitted from the MFC configuration, but only at the cost of a reduced coulombic efficiency (13). None of the available solutions seem to be optimal and membrane cation transport, therefore, is an important issue for the development of future MFC systems.

## Acknowledgments

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## Supporting Information Available

Photo of the experimental setup, figure with the development of  $Q^-$  and  $Q^+$  over time when cation concentrations in the catholyte at  $t = 0$  are identical to those in the anolyte, EDX spectrum of a Nafion 117 membrane used in an MFC experiment. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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