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Al₂O₃ coating grown on Nafion membranes by atomic layer deposition

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Abstract

Nafion membranes were shown to be suitable substrates for atomic layer deposition (ALD) process. ALD utilising trimethyl aluminum as a precursor leads to well reproducible formation of smooth single-sided Al₂O₃ coating on the membranes. Physicochemical and mechanical properties of the coated membranes were compared to those of the unmodified ones. The coating reduced water uptake and thus also conductivity. Moreover, the Al₂O₃ coating decreased the oxygen permeability of the membrane by 10 % and the methanol permeability 30-50 %. The mechanical properties of the Nafion[®] membrane were improved. The resulting membranes were successfully applied in hydrogen fuel cells, direct methanol fuel cells and microbial fuel cells. In the microbial fuel cell, the Al₂O₃ coated membrane showed stable performance during long-term measurements of more than 100 d and doubled power densities in comparison to a cell equipped with a pristine membrane. The membrane modification strategy has potential for improving the performance of various types of membrane fuel cells and could be used for several types of functional membranes containing active groups for ALD growth.

Keywords

atomic layer deposition, aluminum oxide coating, ion exchange membrane, reactant crossover, microbial fuel cell

1 Introduction

Perfluorosulfonic acid membranes are widely used as the proton conducting media in energy applications such as electrolyzers, fuel cells or flow batteries due to their high proton conductivity and mechanical and thermal stability. These ion exchange membranes also function as a separator between the anode and cathode reactants. However, they still have some drawbacks limiting their commercial application. Perfluorosulfonic acid membranes such as Nafion® have high cost and high methanol permeability. To maintain a high level of performance, the membrane permeability to liquid fuels and gases should be minimized while keeping a high proton conductivity and appropriate mechanical strength. Further development of the membrane materials is critical for an effective fuel cell application [1,2].

The pristine ion exchange membrane material can be modified by coating [3-5], crosslinking [6], preparing multilayer membrane structures [7,8] or adding fillers during synthesis of the membrane [9-14]. Development of a successful modification strategy may also lead to the opportunity of using less expensive base membrane materials if the properties of a membrane that in its pristine form is inferior to Nafion could be improved by the modification method. Coating Nafion membranes with a barrier polymer [3] or polyelectrolyte layers [4,5] has been shown to effectively decrease the methanol permeability. Crosslinking [6] has been used to improve mechanical strength and decrease methanol permeability and can reduce phase separation in blend membranes. Decrease in methanol permeability is often coupled with losses in proton conductivity though sulfonic acid groups in the crosslinking agent can help to maintain the proton conductivity. Ion exchange membranes have been also modified by using inorganic fillers [9-14] resulting in lower methanol permeability by increasing the tortuosity of the diffusion path [1]. In addition, if the surfaces of the fillers are modified with acidic groups, the resulting membrane structure has improved proton conductivity [10,11].

Atomic layer deposition (ALD) has been previously employed in fuel cell applications for catalyst preparation by depositing Pt or other metals on carbon materials [15,16]. Aluminum oxide layers grown by ALD have been successfully employed to reduce oxygen permeability on flexible polymer substrates for organic light-emitting diodes (OLEDs) [17] and on polymer-coated paper and board for food packaging [18]. Therefore, they could potentially reduce both gas and liquid fuel permeability of the membrane in a fuel cell.

In an ideal process of ALD, there is a high density of reactive groups, such as OH, on the polymer surface, and the ALD precursors do not diffuse inside the polymer matrix [19]. However, usually ALD on polymers includes sub-surface diffusion, leading to a less well defined and rougher surface structure. However, by adjusting the ALD conditions, for example by extending the exposure time per cycle, the surface formation can be controlled. Even polymers lacking reactive groups can be coated if the absorption and retention of the ALD precursor on the surface is sufficient [20].

Microbial fuel cell (MFC) is an emerging technology which can combine wastewater treatment and energy conversion [21]. In an MFC, exoelectrogenic bacteria catalyze the oxidation of substrates in wastewater, releasing some of the electrons produced from cell respiration to the anode. Electrons flow through an external circuit from the anode to the cathode and meanwhile protons generated in the oxidation reaction are conducted to the cathode through an electrolyte. In a single chamber MFC the electrons and protons react with oxygen at the cathode, enhanced by a catalyst such as platinum, to form water. The maximum potential of the process is ca. 1.2 V on the basis of the potential difference between the electron carrier (the reduced form of nicotinamide adenine dinucleotide NADH) and oxygen. [22]

MFC commercialization is mainly limited by the low power density and high cost [2]. Both factors could be significantly affected by the ion exchange membrane. Membrane permeability is particularly critical in MFCs as the various organic and inorganic components of the wastewater permeating

through the membrane to the cathode poison the catalyst [23]. Oxygen permeability also presents a problem on the anode side as the exoelectrogenic bacteria work in anaerobic conditions and oxygen results in formation of an aerobic biofilm on the electrode. This biofouling hinders mass transfer decreasing MFC performance [24] and therefore, different membrane surface treatments [25-27] have been earlier used to inhibit its formation. Methanol permeability is a good model for the permeability of various organic compounds found in the wastewater due to its small size: if methanol permeation can be inhibited, the larger molecules are likely to be inhibited, too.

In this study, the focus is on studying the ALD coating of Nafion membranes, the most frequently used membranes in fuel cells. The aim is to find out whether such a membrane can be coated using the ALD technique, whether the coating affects some of the critical membrane properties and whether the coated membrane is applicable in fuel cells. In the future, the method could also be applied for less expensive membrane materials with suitable reactive groups. In the structure of Nafion, sulfonic acid and ether groups could be reactive sites for trimethylaluminum (TMA), the precursor for growing an Al₂O₃ layer. The coated membranes were characterized, their oxygen and methanol permeability, water uptake, conductivity and mechanical strength were measured and they were tested in a hydrogen fuel cell, a direct methanol fuel cell (DMFC) as well as in an MFC.

2 Experimental

2.1 Membrane pretreatment

Nafion 115 was obtained from DuPont and was pretreated by boiling in 5 % H₂O₂ for 30-60 min, rinsing with water, boiling in 0.5 M H₂SO₄ for 30-60 min and boiling 3 × 30 min in water. The membranes were dried in a vacuum oven at 80 °C for 2 h for ALD and characterization.

2.2 Atomic layer deposition (ALD)

The deposition of the Al₂O₃ coatings was carried out in a Picosun Sunale R-100 ALD-reactor using trimethyl aluminum (TMA) and H₂O as precursors. Nitrogen (99.999 %) was used both as a carrier and purging gas. Two different deposition sequences were used; for the first one the pulse and purge times for both precursors were 5.0 s and 30 s, respectively, while the second one utilized shorter pulse and purge times of 1.0 s and 10 s, respectively. For both sequences, the deposition temperature was 85 °C, and the number of deposition cycles was fixed at 1000.

2.3 Characterization

Scanning electron microscopy (SEM) and X-ray analysis (EDS) were performed using a JEOL JSM-7500FA analytical field emission scanning electron microscope. The presence of aluminum oxide in the sample was confirmed by EDS analysis. Imaging conditions were adjusted for a nonconductive sample. The acceleration voltage was 2 kV and a gentle beam mode was used. EDS was performed as mapping at a 2000-fold magnification. The thickness of the Al₂O₃ layer on Nafion was determined from a cross-section SEM image. The membrane was broken under liquid nitrogen and the sample was sputtered in the cross-section holder with gold for 2 min using 20 mA current. The acceleration voltage was 2 kV.

ICP-AES (Inductively coupled plasma atomic emission spectroscopy) (Perkin Elmer 7100 DV) was used to determine the amount of aluminum in the sample. The sample size was 2.09 cm² and it was dissolved in a mixture of HCl, HNO₃ and H₃PO₄.

For *water uptake* measurements membrane pieces with 3 cm² area were soaked in water at room temperature for 20 h. The surface was dried with a lint-free paper and the hydrated membrane was weighed. Subsequently, the membranes were dried in a vacuum oven at 80 °C for 2 h and reweighed to determine the dry mass. The experiment was repeated three times.

Dynamic mechanical analysis were done with TA Q-800 DMA equipment to perform the stress–strain measurements in tension mode using force ramp rate of 1 N/min. Triplicate measurements of pristine or Al₂O₃ coated membranes cut to 4.325 mm width were done at room temperature and RH 46 %. The thicknesses of the samples were 132 μm for the pristine and 125 μm for the coated membrane.

For *conductivity* measurements the membranes were first dried in a vacuum oven at 80 °C for 2 h followed by soaking in liquid water for 15 h. Prior to the conductivity measurements excessive water was removed by blotting the surface and the membrane thickness was determined using a micrometer. The membranes were attached in between two Pt electrodes with a diameter of 5 mm and impedance spectra was measured with an Autolab PGSTAT 20 potentiostat in a frequency range of 400...1 kHz using 5 mV potential stimulus. Resistance of the membranes was determined by extrapolating the intercept of the linear spectrum in the Nyquist plot to the real axis of the complex impedance spectrum. Conductivity, κ , was calculated from the resistance, R , membrane thickness, l , and electrode area,

$$A \kappa = \frac{l}{RA} \quad (1)$$

2.4 Preparation of the membrane-electrode assembly (MEA) for a methanol and H₂ fuel cell

Membranes were hot-pressed at 80 °C using 0.75 t for 2 min with the gas diffusion electrodes (GDE). The gas diffusion electrodes were obtained from Fuel Cells Etc. The anode GDE (FuelCellEtc) had 0.5 mg/cm² of PtRuC (with 60 m-% of metal) and the cathode had GDE (FuelCellEtc) 0.5 mg/cm² of PtC (Pt 60 m-%). The coated side of the membrane was facing the cathode side. To enhance the attachment of the electrodes on the membrane, the electrodes were spray coated with 5 wt-% Nafion® perfluorinated resin solution (Aldrich) and dried in the vacuum oven at 80 °C. The mass of Nafion on the electrodes was between 0.5-0.8 mg/cm². The electrode area was 5.29 cm².

2.5 Performance and permeability measurements in a methanol or H₂ fuel cell

The membranes were studied in a methanol and hydrogen fuelled fuel cell. The performance was characterized by measuring the open circuit voltage, polarization curves, impedance spectra and stability in chronoamperometry at the potential corresponding to the maximum power density. Methanol permeability was also studied in the fuel cell by feeding the anode (RE) side with methanol and the cathode (WE) side with humidified nitrogen and stabilizing overnight followed by measuring a linear sweep voltammetry from OCV to 0.8 V at a sweep rate of 0.1 mV/s. MeOH permeability DK is calculated from the limiting current density i_{lim} as

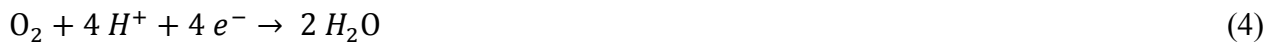
$$DK = \frac{1}{k_{dl}} \frac{i_{lim} l}{6FC_1} \quad (2)$$

where D is the diffusion coefficient of MeOH in the membrane (cm²/s), K is the partition coefficient between the membrane and the liquid (C_m/C_l), l is membrane thickness (cm), F is Faraday's constant (96485 As/mol) and C_1 is the MeOH concentration in the feed solution (mol/cm³). The drag correction factor k_{dl} is taken from the data in ref. [28] as a function of temperature in 1 M MeOH: 0.8592 at 30 °C, 0.8526 at 50 °C and 0.6915 at 70 °C.

Oxygen permeability was also studied in the fuel cell setup. Pt was used as both the anode and the cathode to give the potential window up to -1.2 V which is sufficient to detect the limiting current for oxygen reduction. The GDEs (FuelCellsEtc) had 0.5 mg/cm² PtC (60 % Pt) and were supplied with a Nafion coating. The MEA was prepared by hot pressing at 130 °C for 5 min or 80 °C for 2 min using 0.75 t. Polarization curves were first measured with H₂ as the fuel and O₂ as the oxidant. Then, H₂ was replaced by N₂ in the anode side. The electrodes were reversed such that WE was on the N₂ side and CE/RE on the O₂ side. Overnight stabilization was needed for the OCV to drop close to zero. Then, a linear sweep was measured from OCV to -1.2 V to reduce the oxygen permeating through the membrane at temperatures 30, 50 and 70 °C. Permeability is calculated from Eq 3:

$$D_m C_m = \frac{i_{lim} * l}{nF} \quad (3)$$

where D_m is the diffusion coefficient of oxygen in the membrane (cm^2/s), C_m is the concentration of oxygen in the membrane (mol/cm^3), i_{lim} is the limiting current density for oxygen reduction (A/cm^2), l is membrane thickness (cm), n is number of electrons transferred in the reaction and F is Faraday's constant ($96485 \text{ As}/\text{mol}$). For oxygen reduction reaction (4) on Pt, $n = 4$.



At the end of the O_2 permeability measurements, H_2 was again switched to the anode side and a polarization curve was recorded.

2.6 MFC configuration and operation

The MFC tests were conducted using a single chamber 25 ml MFC reactor with 50 cm^2 active anode and cathode areas. The anode was a woven carbon cloth with a microporous layer (GDL-CT, FuelCellsEtc). The cathode side was open to air and had a GDL-CT with $2 \text{ mg}/\text{cm}^2$ Platinum Black with a Nafion coating (FuelCellsEtc) as an electrode. The current collectors were separate stainless steel meshes. For the Al_2O_3 coated Nafion 115 test current collectors, electrodes and membrane were pressed together by the reactor frame (see Figure 1). The coated side of the membrane was facing the anode side. The pristine Nafion 115 reference tests were measured using commercial ready-made MEAs (FuelCellsEtc) consisting of same materials: GDL-CT, Nafion 115 and GDL-CT with $2 \text{ mg}/\text{cm}^2$ Platinum Black with a Nafion coating.

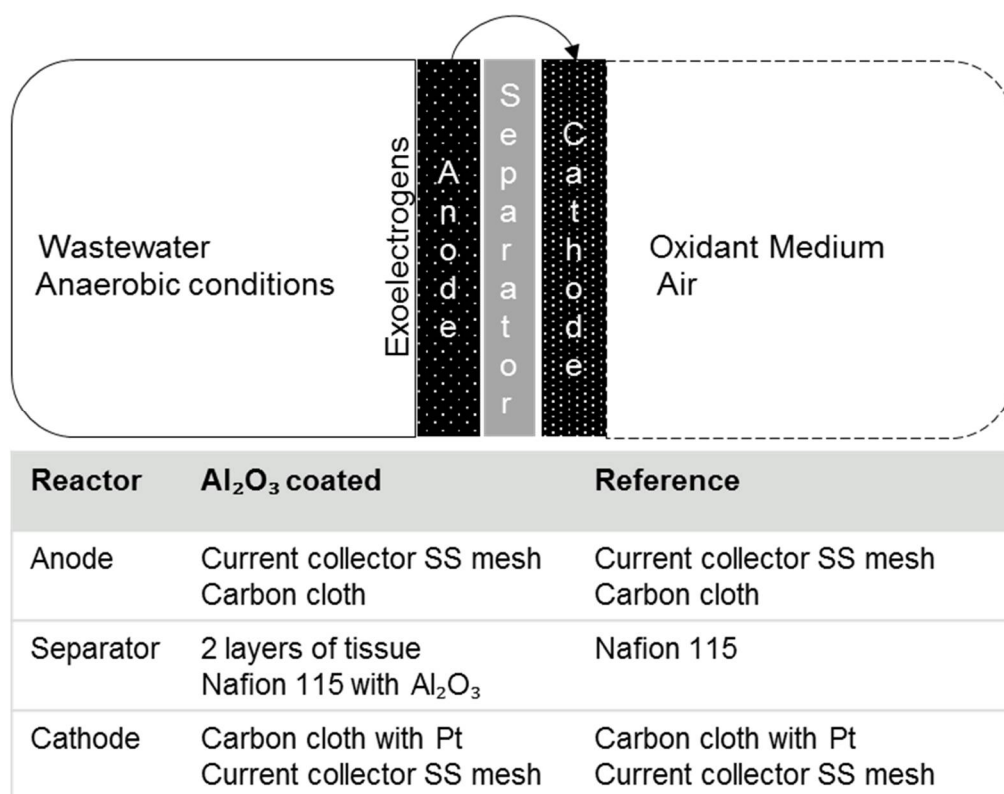


Figure 1. Schematic of the configurations of MFC with Al₂O₃ coated Nafion 115 with an insulating layer and the reference MFCs with a commercial Nafion 115 MEA.

The temperature in the reactor room was 28.0±1.3 °C. The reactors were inoculated with a mixed culture of unknown composition using a mixture of a fresh MFC effluent and unbuffered pre-fermented brewery wastewater. The mixture was recirculated into anode chamber. After inoculation, the reactors were moved to continuous feed of unbuffered pre-fermented brewery wastewater. The average characteristics of the wastewater were: soluble COD 2300 mg/l, conductivity 2.4 mS/cm, pH 7.7. The main components in the wastewater were short chain fatty acids, ethanol and sugars.

The MFC with Al₂O₃ coated Nafion 115 was short-circuited, so an insulating layer was added between the anode and the membrane 15 days after inoculation. The insulation consisted of two layers of cellulose based lab grade tissue.

Anode and cathode were connected by a variable resistor, initial value of the resistor was set at 500 Ω . Resistor value was changed to maximize power based on potential measurements and latest results of linear sweep voltammetry. This assessment was carried out weekly.

2.7 MFC characterization

Potentials of the MFCs at closed circuit conditions were measured every 10 minutes. Open circuit potentials were measured once a week. The performance was also characterized by linear sweep voltammetry scans using a scan rate of 0.5 mV/s

After disassembling the MFCs steady-state voltammetry was performed for i) a piece of the cathode of the MFC with Al₂O₃ coated Nafion 115, ii) for a piece of the MEA of the pristine Nafion 115 reference and iii) for an unused piece of the cathode material. Voltammograms were measured from 400 mV to -400 mV vs. Ag/AgCl (sat. KCl) using 100 mV steps every 2 minutes in 100 mM phosphate buffer with pH 7.

3 Results and Discussion

3.1 Structural characterization

In the SEM image of the pristine Nafion 115 membrane (Figure 2 a), chain-like and spherical structures are observed on the membrane surface. In general, Al₂O₃ coating with ALD results in an amorphous and smooth surface with good barrier properties. This kind of even coating is also observed for Nafion (Figure 2 b) although some distinct granules on the surface and some features underlying the Nafion membrane surface are observed. A relatively smooth surface of a polymer membrane coated with the ALD technique indicates a well distributed film in contrast with the rough globular, structures on inert and hydrophobic polymers such as PTFE [29]. These features results from lack of active groups for nucleation of TMA and the membrane hydrophobicity. In the case of

Nafion, using a shorter pulse sequence of 1 s clearly resulted in a higher density of spherical features indicating that the extent of the reaction was not optimal for obtaining a smooth surface (Figure 2 c). The sample also had more cracks especially at the edges due to the sample preparation which also indicates poorer adhesion. The SEM images confirm that the structure of a Nafion membrane with the sulfonic acid and ether groups is active for TMA nucleation and the pulse length of 5 s was chosen for further studies.

The elemental composition of the surface was analyzed with EDS (Table 1). In the EDS analysis of the pristine membrane, only the elements of the fluorocarbon backbone are detected. The EDS analysis confirms the presence of aluminum oxide on the coated membrane. The elements of the fluorocarbon backbone are still detected after the coating but their signal is significantly weakened compared to ones obtained for the pristine membrane. This is expected as the coating is relatively thin. The remaining of the Al_2O_3 layer on the membrane surface even after the rather harsh sample preparation conditions indicates that the layer is tightly attached to the surface.

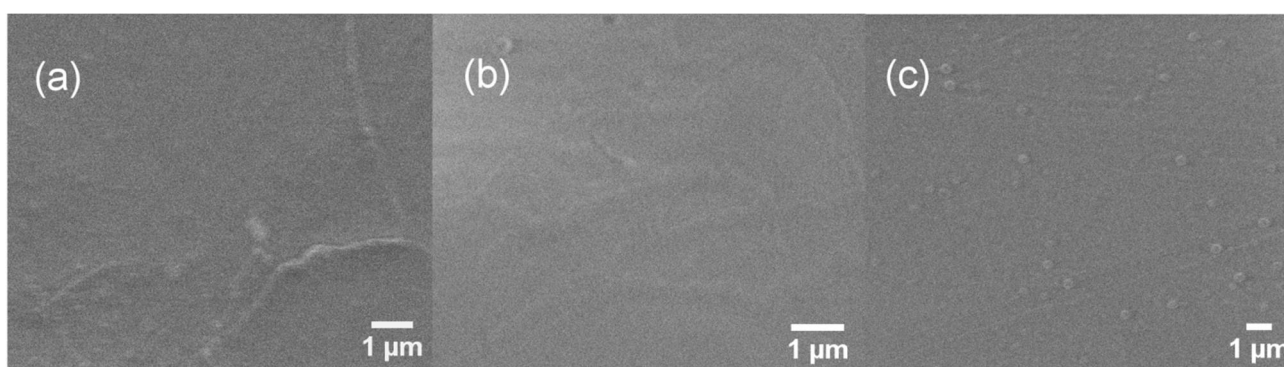


Figure 2. SEM images of the surfaces of the pristine (a) and Al_2O_3 coated (b,c) Nafion 115. The pulse sequence was in (b) TMA 5.0 s, N_2 30 s, H_2O 5.0 s, N_2 40 s and in (c) TMA 1.0 s, N_2 10 s, H_2O 1.0 s, N_2 10 s. The longer pulse in (b) results in smooth coverage of the Nafion surface whereas the shorter pulse in (c) results in globular features.

Table 1. Elemental composition (mol-%) of the coating for pristine and Al₂O₃ coated Nafion 115 from the EDS analysis.

sample	C	F	O	Al
pristine Nafion	19.6	80.4	-	-
Al ₂ O ₃ coated Nafion	3.0	18.4	52.7	25.9

Figure 3 shows the cross-section image of the Al₂O₃ layer (white on the left) on Nafion (grey on the right). The thickness of the layer determined from the cross-section image was ca. 150 nm resulting in a growth rate value of ca. 1.5 Å per ALD cycle. Using the same deposition parameters, the same growth rate is observed also on Si(100) used as a reference substrate. This indicates that the nucleation rate is similar on both the surfaces. Compared to the previously reported growth rate value of ca. 1.3 Å/cycle at 80 °C [30], the growth rate in the present study is apparently slightly higher. However, effect of the growth condition is outside the scope of this study and was not studied further. Anyhow, the applied ALD process proved to be well reproducible as we carried out all the experiments at least with two parallel samples and no notable differences between the samples were observed.

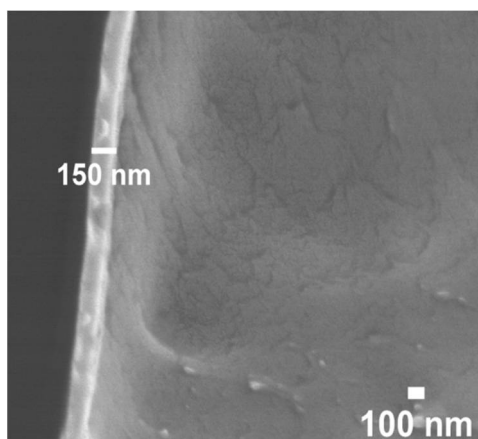


Figure 3. A cross-section SEM image of a 150 nm thick Al₂O₃ layer on Nafion.

The average amount of aluminum in the sample determined by ICP-AES from two parallel samples was 330 mg/m². Assuming that all Al₂O₃ is in the 150 nm thick layer, the density of Al₂O₃ is higher (4.2 g/cm³) than previously reported (2.5 – 3.0 g/cm³) [30] suggesting the presence of Al₂O₃ also in the membrane structure and/or on the backside of the membrane. The average water uptake of the membranes in three parallel measurements was 23.5 % for pristine Nafion and 18.5 % for Al₂O₃ coated Nafion. It is well known that membrane water uptake is strongly dependent on the conditions and water uptake 38 % reported by the manufacturer [31] is higher compared to our measurement as it is obtained after boiling of the membranes. Here, equilibration at room temperature was chosen to avoid any changes occurring in the coating. Reduced water uptake could be attributed to the filling of the polymer structure by the Al₂O₃ coating. Also, a coated membrane is likely to be more rigid and more resistant to swelling. This is also observed when dipping a dry coated membrane in water: it rolls towards the coated side, also indicating that the coated side is more resistant to swelling.

Conductivities of the membranes are 26 mS/cm for the coated and 45 mS/cm for the pristine one. The rather low conductivity value for pristine Nafion results from the low water uptake of the dried membrane in room temperature. The decrease in the conductivity of the coated membrane can be partly explained by the decrease in the water uptake. The number of water molecules per sulfonic acid group (λ) was calculated and average values of 14 and 11 for the pristine and coated membranes,

respectively, were obtained. These values roughly correspond to RH values 100 % and 95 % and the expected conductivities would therefore be 55 mS/cm and 40 mS/cm [32,33]. Therefore, the conductivity decrease attributed to the decreased water uptake would be 30 %. However, the conductivity decrease from our results is 40 % suggesting that the Al₂O₃ layer also inhibits the proton conductivity.

The stress-strain curves (Figure 4) show that Al₂O₃ coated Nafion has improved mechanical properties compared to pristine Nafion. The Young's modulus determined from the slope of the elastic part gives the average values of 176 MPa for pristine and 268 MPa for coated Nafion. The value for pristine Nafion correlates well with the value reported for a pre-treated Nafion 112 (~160-175 MPa) [34] at RH 50 % and 25 °C. Also, the critical strain at break is increased for the coated samples. The change in the mechanical strength can be due to the decreased water uptake of the coated membrane; this is indicated also by the lower thickness of the coated sample. Improvement of the mechanical strength is particularly important in the used microbial fuel cell setup where the MEA is tightened between the current collectors only at the edges. In a DMFC, the MEA is tightly sandwiched between the current collector and the flow channel plates, and therefore the improvement in mechanical strength is of less importance.

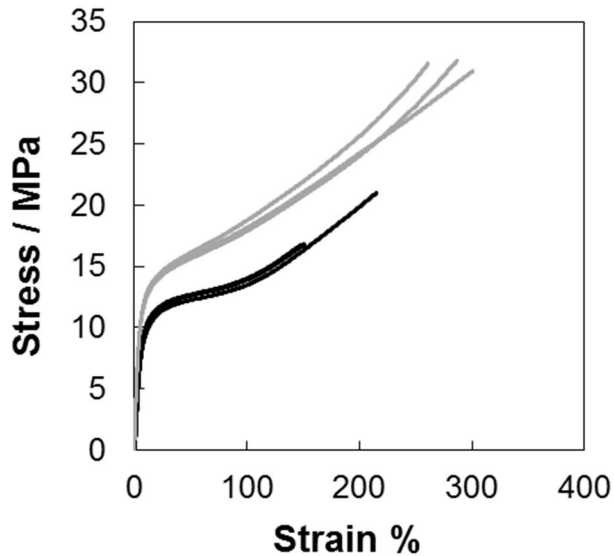


Figure 4. Stress strain curves in three parallel measurements for pristine pretreated Nafion 115 (black lines) and Al₂O₃ coated Nafion 115 (grey lines) at room temperature and RH 46 %.

3.2 Crossover measurements in a fuel cell

Linear sweep voltammograms for oxygen permeability were measured in a fuel cell setup where the CE/RE side was fed with O₂ and the WE side with N₂. The diffusion limited current for oxygen reduction was determined. Examples of voltammograms of coated and pristine Nafion are shown in Figure 5 a. Lower diffusion limiting current with a coated membrane indicates that the coating reduces oxygen permeability but the decrease is very small. The average values for oxygen permeability DC in the two separate tests with different MEA preparation conditions are plotted in Figure 5 b as a function of temperature. The values are in excellent agreement with the values reported for Nafion 117 [35].

Similar experimental arrangement was used to measure methanol crossover. The voltammograms for methanol oxidation and the calculated methanol permeability are shown in Figure 6. The values for Nafion 115 are close to the values reported for Nafion 117 [36]. The decrease in methanol

permeability with the coated membrane is more pronounced than in oxygen permeability. The coating shows a promising trend in reducing the permeability of the membrane for both liquid and gaseous reagents. Oxygen permeability decreased after the Al_2O_3 coating in two parallel tests at three different temperatures in average by 10 %. Methanol permeability of Nafion 115 decreased after the Al_2O_3 coating by 50 % at 30 °C and 30 % at 50 °C and 70 °C. The decrease in methanol crossover is attributed to the lower liquid uptake in the coated membrane in comparison the pristine Nafion (see discussion above). Water and ion exchange groups of the membrane form water channel network through the membrane which morphology is strongly affected by the amount of the absorbed water [33]. More water results in better connectivity between the channel and presence of even bulk like water in the channels enhancing transport through the ion exchange membrane. Therefore, decrease in the liquid water uptake impedes methanol transport through the coated Nafion. Methanol diffusion coefficients and permeability have also been earlier shown to decrease with the decreasing water uptake of an ion exchange membrane [28]. Similar trend has been observed for oxygen transport through Nafion as it is faster through the hydrophilic water channel phase than through the another phase of the membrane comprising of the hydrophobic backbones of the Nafion molecule chains [37]. In any case, the decrease in oxygen permeability is quite small and consequently, unlikely contributes to performance improvement in a DMFC, but the decrease in methanol permeability may have a larger effect as methanol penetrating from the anode to the cathode reacts readily at the high voltage of the Pt cathode inducing voltage losses.

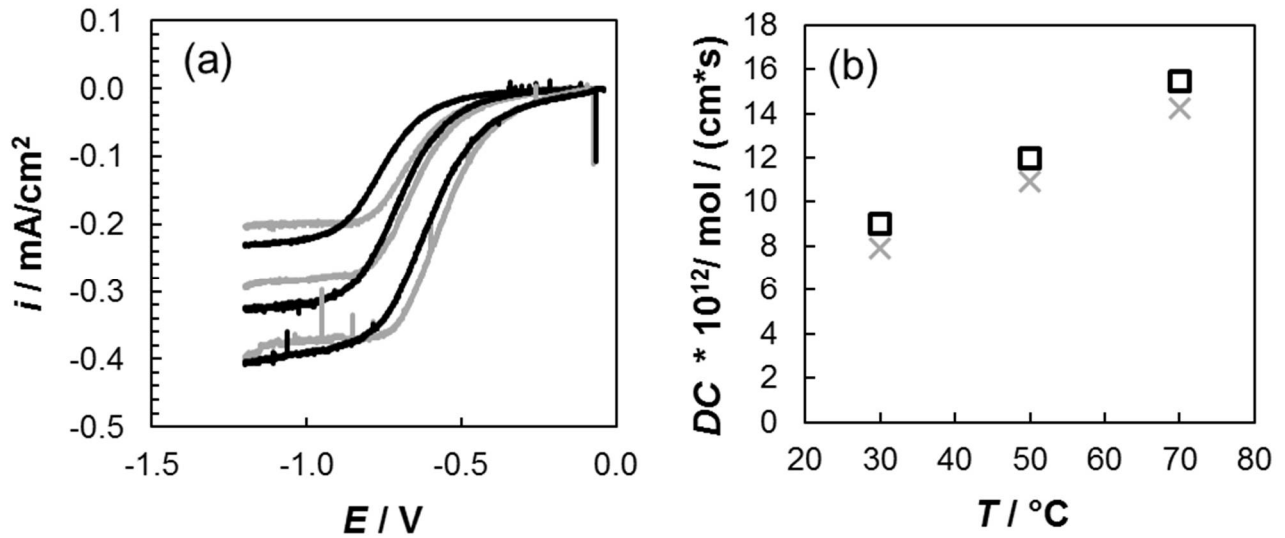


Figure 5. Oxygen permeability measured in a fuel cell setup with Pt as both the anode and cathode catalyst. Anode feed : N₂, cathode feed: O₂. (a) an example of linear sweep voltammograms at scan rate of 0.1 mV/s with Al₂O₃ coated Nafion 115 (grey) and pristine Nafion 115 (black) at temperatures 30, 50 and 70 °C (from top to bottom) and (b) the calculated oxygen permeability as the average value from 2 individual measurements for Al₂O₃ coated Nafion 115 (grey) and pristine Nafion 115 (black).

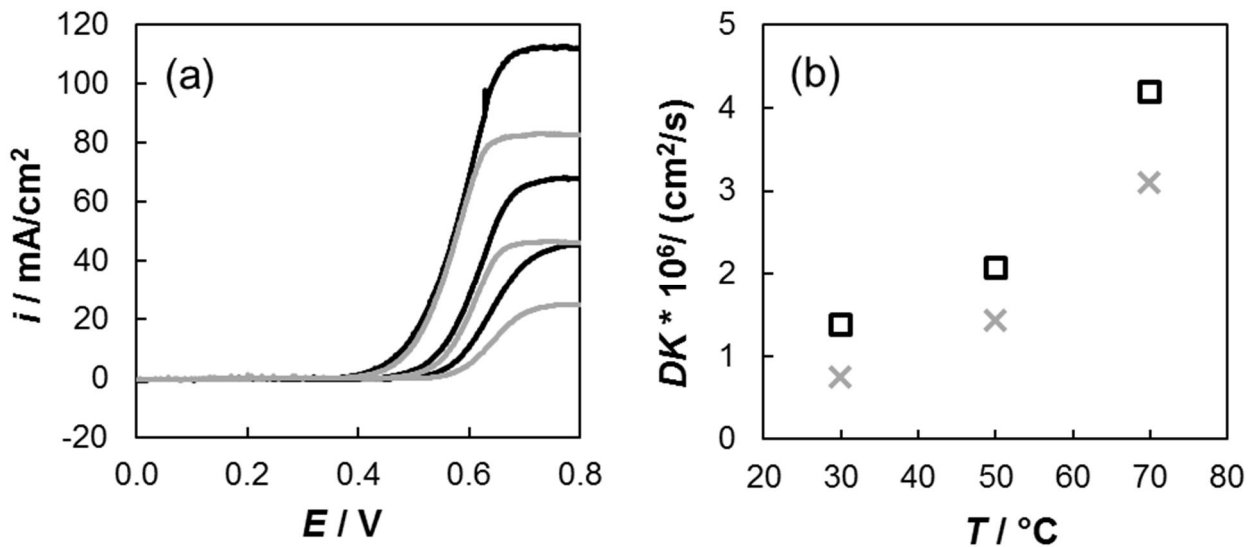


Figure 6. Methanol permeability measured in the fuel cell setup. Anode feed: 1 M MeOH, cathode feed: N₂. (a) linear sweep voltammogram at scan rate of 0.1 mV/s with Al₂O₃ coated Nafion 115

(grey) and pristine Nafion 115 (black) at temperatures 30, 50 and 70 °C (from bottom to top) and (b) the corresponding calculated methanol permeability.

3.3 DMFC and H₂|O₂ fuel cell performance

The coated membranes were successfully applied in a H₂ fuel cell, a DMFC and an MFC. The performance of the coated membrane was comparable to the pristine one in a H₂ fuel cell (not shown) and in a DMFC. Top performances of two parallel DMFC tests are reported in Figure 7 a and the average values in Table 2.

The impedance measurements in the DMFC showed no significant difference between the pristine and coated samples indicating that the coating has little effect on the cell resistances (Figure 7 b). Durability of the coated membrane in a 24 h chronoamperometry test was comparable to pristine Nafion and no significant differences were observed (Figure 8 a). Moreover, the coated membrane also showed good durability in a 10 d measurement (Figure 8 b) indicating that that the Al₂O₃ layer is strongly attached on the membrane surface. The coated membrane also performed as well as the pristine membrane at temperatures of 50 and 70 °C (not shown).

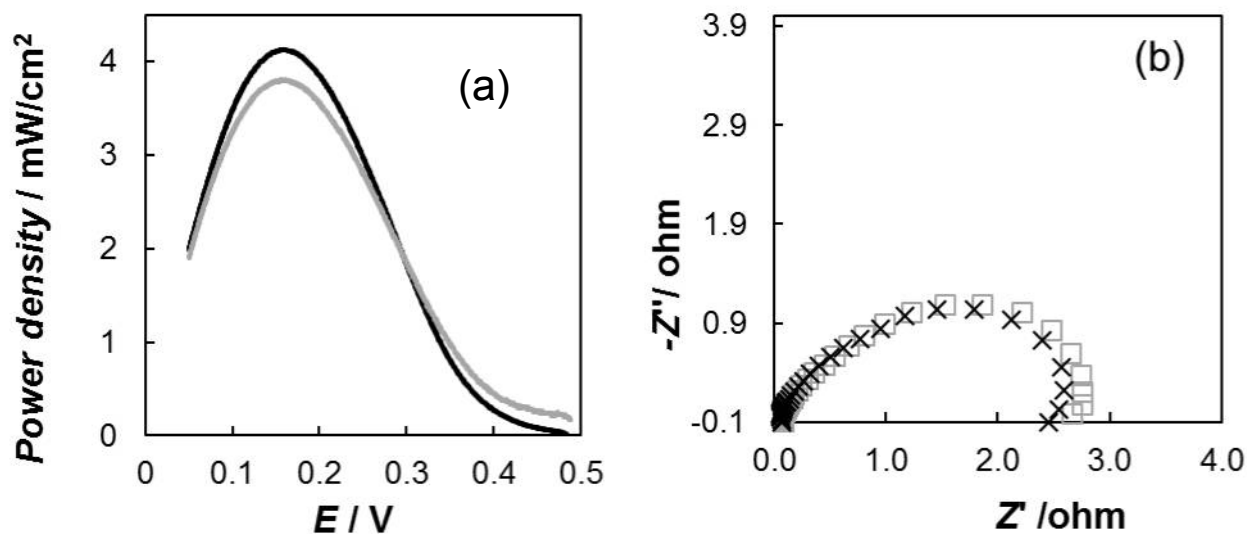


Figure 7. Power density plots for the top performance with pristine Nafion 115 (black) and Nafion 115 with Al_2O_3 coating (grey) and impedance plots at 50 mA for pristine Nafion 115 (black cross) and Nafion 115 with Al_2O_3 coating (grey square) in a DMFC. Catalyst content: 0.5 mg/cm^2 , fuel: 1 M MeOH, oxidant: air, $T = 30 \text{ }^\circ\text{C}$.

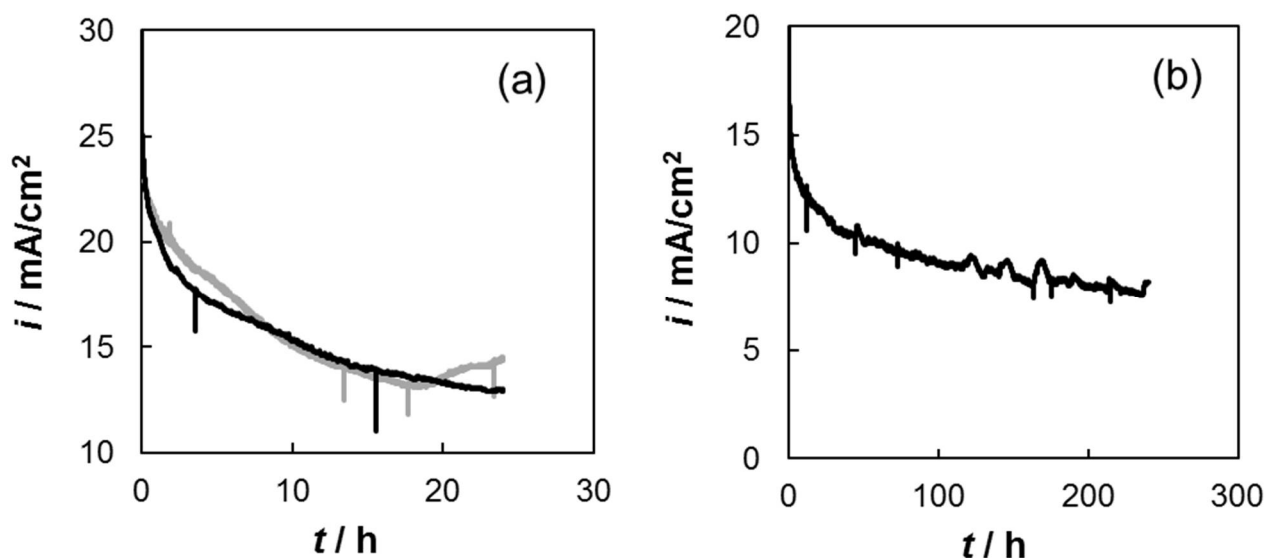


Figure 8. Chronoamperometry at the potential corresponding to the maximum power density (a) in a 24 h experiment for pristine Nafion 115 (black) and Nafion 115 with Al_2O_3 coating (grey). (b) in a 10 d experiment for Nafion 115 with the Al_2O_3 coating.

3.4 MFC test results

MFCs performance with the pristine membranes was recorded for 77 d and with the Al_2O_3 coated membrane for more than 100 d. MFC equipped with coated Nafion 115 was short-circuited for the first 14 days. The MFC currents calculated as daily averages between operation days 14-77 are shown in Figure 9. MFC voltages were regulated to ca. 0.3 V to maximize power. The MFC with the coated membrane was able to maintain a closed circuit voltage of ca. 0.3 V with a smaller resistor than the reference MFCs which can be observed as a higher current. Also the power density curves (Figure 10) show notable improvement in the performance as the peak power density is double to the MFC equipped with the coated membrane in comparison to cell with the pristine membrane.

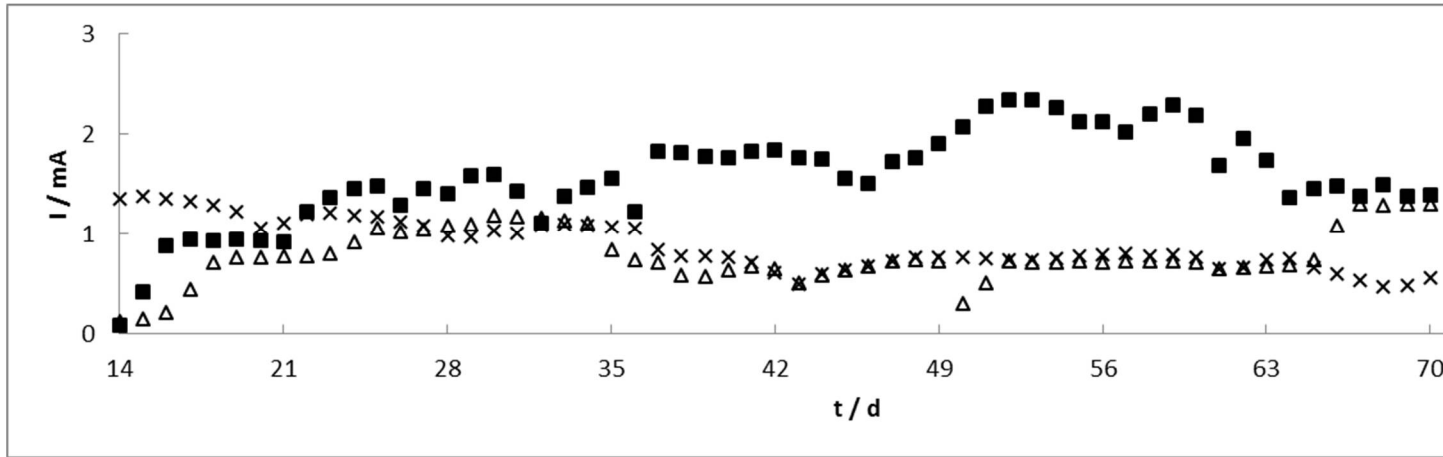


Figure 9. Calculated daily average currents of the MFCs with voltages adjusted to ca. 0.3 V for cells with pristine Nafion 115 (Δ ref test 1, \times ref test 2) and Al_2O_2 coated Nafion.115 (\blacksquare)

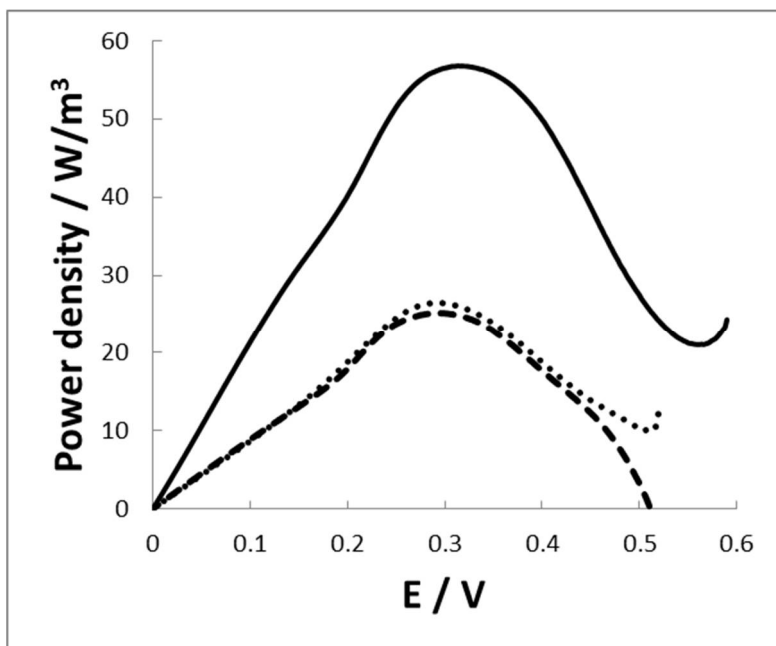


Figure 10. P – V plot of the scans for the highest power point density during days 14-77 with pristine Nafion 115 (\cdots ref test 1, $---$ ref test 2) and Nafion 115 with the Al_2O_3 coating ($---$). Catalyst content: 2.0 mg/cm^2 , fuel: brewery wastewater, oxidant: air, $T_{\text{average}} = 28 \text{ }^\circ\text{C}$.

The MFC results are also reported as a frequency distribution of continuous power density measurement (Figure 11) as the distribution plot clarifies the difference between MFCs as variation is significant. Typical reasons for this variation include maturity of the biofilm and the quantity and quality of organic substrates in wastewater. These graphs reveal clearly an improved performance of the MFC with the coated membrane in comparison to two reference tests with pristine Nafion.

The enhancement in the MFC power density is attributed to combination of two enhancing effects of the Al_2O_3 coating: reduction in substrate crossover and antibacterial properties. As to the former, the cathode Pt catalyst is non-selective and therefore, it readily oxidizes substrates transferred through the membrane from the anode to the cathode. This creates mixed potentials in the cathode reducing the MFC performance. Because of the lower crossover of the substrates (see crossover results above) this effect is diminished in the MFC equipped with the coated membrane. This conclusion is supported by the higher open circuit potential (OCP) obtained with the MFC equipped with the coated membrane (Figure 12). At the OCP no current is drawn from the cell and the substrates are not consumed and therefore, crossover has a significant effect on the measured potential. This effect can be observed for the whole duration of the long-term experiment confirming once again the stability and strong bonding of the coating to the membrane structure.

On the other hand, when disassembling the MFCs after the test, the cathode was clearly in a better condition in the case of the coated membrane. To confirm this observation, the MFCs tested cathodes were investigated with the steady-state voltammetry (see Figure 13). For the cathode facing the coated membrane similar cathodic current to an unused cathode material is observed whereas the cathodes used with pristine Nafion showed clearly lower currents. This indicating that the Al_2O_3 coating protects the cathode catalyst layer against contamination. This effect is attributed to the antibacterial properties of the Al_2O_3 coating [38,39] reduced biofilm growth into the membrane in addition to reduction in the crossover.

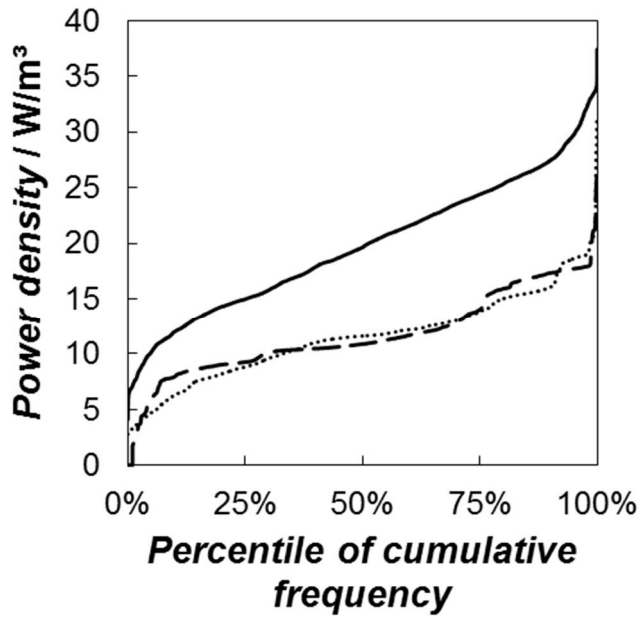


Figure 11. MFC power density distribution plots with pristine Nafion 115 (⋯⋯ref test 1, --- ref test 2) and Nafion 115 with the Al₂O₃ coating (—). The power plot is percent of measurements equal to or less than the indicated value of a continuous measurement. Amount of the measurements for Nafion with Al₂O₃, Nafion ref 1 and Nafion ref 2 are 16270, 8393 and 9111, data points, respectively. Catalyst content: 2.0 mg/cm², fuel: brewery wastewater, oxidant: air, $T_{\text{average}} = 28$ °C

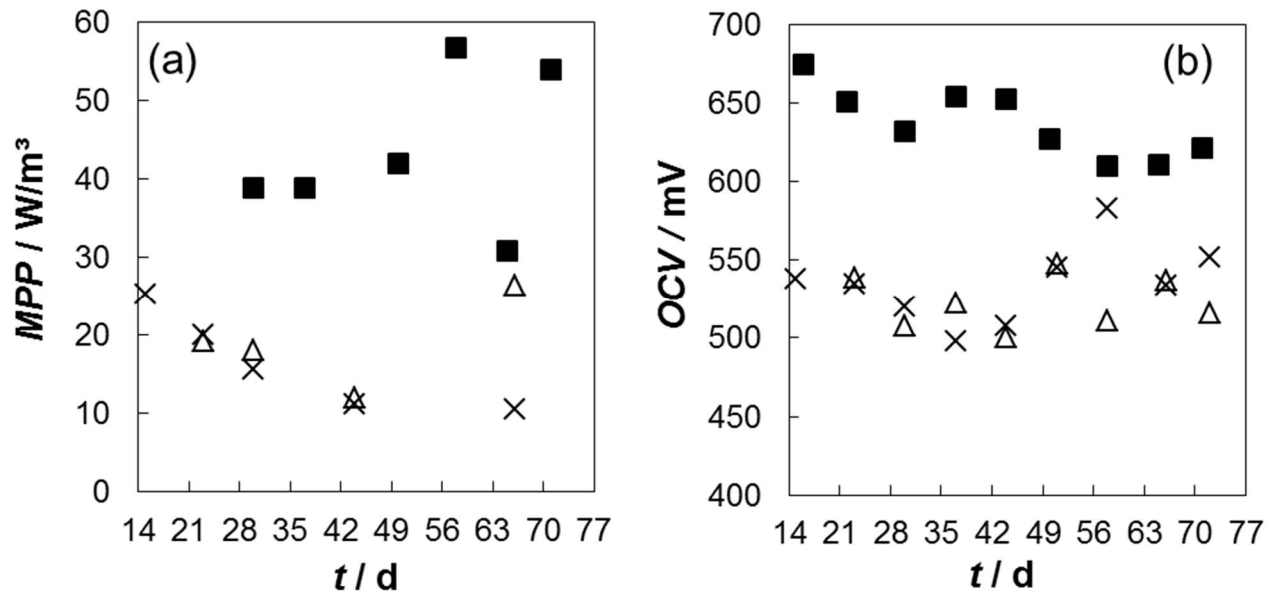


Figure 12. (a) MFC maximum power point (MPP) results of two electrode linear sweep voltammetry scans and b) MFC open cell potential results over operation time with pristine Nafion 115 (Δ ref test 1, \times ref test 2) and Nafion 115 with the Al_2O_3 coating (\blacksquare). Catalyst content: 2.0 mg/cm^2 , fuel: brewery wastewater, oxidant: air, $T_{\text{average}} = 28 \text{ }^\circ\text{C}$.

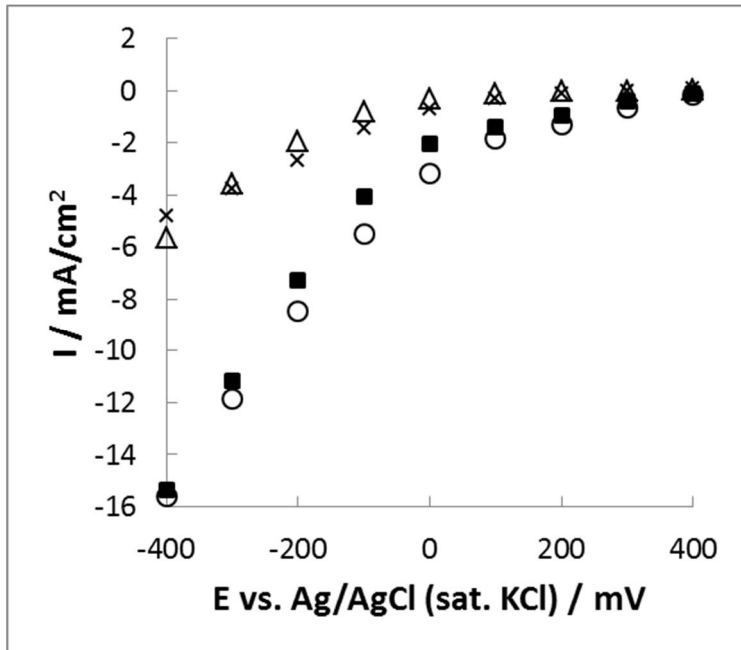


Figure 13. Steady-state linear sweep voltammetry with the cathodes of the used pristine Nafion 115 MEAs (Δ ref test 1, \times ref test 2) and the cathode of Nafion 115 with the Al_2O_3 coating (\blacksquare) and an unused cathode (\circ).

3.5 Summary

The results are summarized in Table 2. The average maximum power density for the DMFC is obtained from a five-day test. The average maximum power density for the MFC is calculated from the maximum power density results in Figure 12 a. The coating resulted in improvement of the Young's modulus indicating higher rigidity and lower permeability of oxygen and methanol. In contrast, the water uptake and conductivity decreased with the coating. Overall, the coating proved to be advantageous as higher average power density in both the DMFC and MFC is obtained. The improvement of the power density was small in the DMFC but remarkable in the MFC and this difference is contributed to the antibacterial properties of Al_2O_3 .

Table 2. Water uptake, conductivity (κ), Young's modulus (Y), oxygen permeability (DC), methanol permeability (DK), average maximum power density in DMFC (P_{ave}) and average maximum power density in MFC (MPP_{ave}) for pristine and Al_2O_3 coated Nafion 115.

Sample	Water uptake %	κ mS/cm	Y MPa	DC (O_2) $\times 10^{12}$ at 30 °C mol/cm \times s	DK (MeOH) $\times 10^6$ at 30 °C cm ² /s	P_{ave} (DMFC) mW/cm ²	MPP_{ave} (MFC) W/m ³
Nafion 115	23.5	45	176	9	1.4	3.3	26.4
Nafion 115 + Al_2O_3	18.5	26	268	7.9	0.7	3.4	56.8

4 Conclusions

The surface of a Nafion membrane is active for TMA nucleation and can be coated with Al_2O_3 using the atomic layer deposition method. The Al_2O_3 coating on Nafion reduced the permeability of both oxygen and methanol, methanol permeability being a more significant factor. It also reduced the water uptake and improved the mechanical strength. The coated membrane can be applied in a H_2 fuel cell, a DMFC and an MFC. The coating reduced the conductivity but the coated membrane still performed as well as the pristine one in a H_2 fuel cell and in a DMFC. With further development of the coating process, potential improvements in the DMFC performance can be achieved. In a microbial fuel cell, the power density doubled with the Al_2O_3 coating and this improvement is attributed to combination of decreased crossover and antibacterial properties of the Al_2O_3 coating. Membrane permeability to gases and liquid fuels is an issue in several types of fuel cells and membrane modifications are one possible solution to improve fuel cell performances. ALD coatings as a modification method

improving permeability or mechanical strength could also open opportunities for using inexpensive membrane base materials which would be active as ALD substrates.

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