

# A modified Nafion membrane with in situ polymerized polypyrrole for the direct methanol fuel cell

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## Abstract

Nafion membranes were modified by the in situ electrodeposition of polypyrrole inside the membrane pores and on the anode side only, in order to prevent the cross-over of methanol in the direct methanol fuel cell (DMFC). Pretreated Nafion membranes were first immersed in 0.1 M sulphuric acid containing the pyrrole monomer and subsequently removed from this solution and placed in a two-electrode solid-state electrochemical cell, where the polypyrrole was formed galvanostatically. The modified membranes were studied in terms of morphology, electrochemical characteristics and methanol permeability. FTIR and SEM confirmed the presence of the polypyrrole on the anode side of the Nafion membrane. SEM shows the polymer to be present both on the membrane surface and inside the membrane pores. It was found to be deposited as small grains, with two distinct sizes, the smallest particles have a diameter of around 100 nm, while the larger particles have diameters of around 700 nm. Methanol permeability was determined electrochemically and was shown to be effectively reduced. Cyclic voltammetry was performed in sulphuric acid, in pure methanol and in 50 vol.% methanol. The untreated Nafion membrane showed CV curves which were similar in all electrolytes with electroactivity only at the extreme ends of the curve. The Nafion/Ppy membrane showed typical polypyrrole curves, with current densities lowest in sulphuric acid, and highest in the 50 vol.% methanol, respectively. For the methanol containing electrolytes, an additional oxidative peak appears in the CV, which may be related to electrocatalytic activity of the polypyrrole for methanol oxidation.

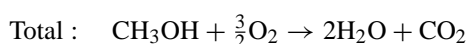
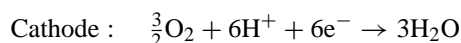
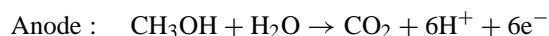
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## 1. Introduction

Fuel cells offer a promising alternative to conventional fossil fuel systems, due to their high efficiency, low environmental impact and flexible application. One of the suggested systems for residential, automotive and portable applications is the direct methanol fuel cell (DMFC), which has a proton conducting polymer membrane as electrolyte. While the fuel used most fuel cells is hydrogen (e.g. in the polymer electrolyte membrane fuel cell: PEMFC), the DMFC uses methanol as fuel. The advantage of methanol is that the existing distribution infrastructure could be used for fuel supply, unlike for hydrogen.

The following overall reactions occur in the direct methanol fuel cell:



The proton conducting membrane generally used in the PEMFC and DMFC is the Nafion (Dupont) membrane, a perfluorosulfonic acid. It has excellent chemical, mechanical and thermal stability and high protonic conductivity in its hydrated state. While it has shown very good performance in the PEMFC, in the DMFC there exists the problem of cross-over of methanol from the anode to the cathode side, leading to secondary reactions, mixed potentials, decreasing energy and power densities, and hence a reduced performance. This cross-over is caused by permeation of methanol due to a concentration gradient, indirectly dependent on the operation current, and by molecular transport due to electro-osmotic drag, directly related to proton migration through the membrane which increases with increasing current density [1,2].

Two different pathways exist to solve this problem of methanol cross-over, the first being the development of ion-conductive membranes based on alternative polymers or polymer composites, the second being the modification

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of the existing Nafion membrane, in order to prevent cross-over.

Composite membranes of Nafion with polypyrrole have been prepared by electrodeposition of polypyrrole on a Nafion-coated electrode [3–5]. The typical electrochemical switching behaviour of the Ppy was found at lowered, more negative, potentials [4]. During the electrode position, the Ppy grows from the electrode side into the ionic areas of the Nafion [5].

Studies of the interaction of methanol with polypyrrole were performed for applications in sensors [6–8] and it was reported that methanol adsorption and desorption in the polypyrrole, results in a conductivity change of the material. For volatile chemicals such as methanol, polypyrrole lowers its conductivity and there is a change in relative permittivity, i.e. capacitance increase [9].

The electrocatalytic activity of metallic nanoparticles in a conductive polymer matrix for methanol oxidation has been studied in several reports [10–12]. Enhanced electrocatalytic activity is ascribed to the increased specific surface area of the metal particles. However catalytic activity of polypyrrole for methanol oxidation has also been reported [10,13]. Furthermore, polypyrrole was reported to have high catalytic activity for the oxygen reduction reaction and for the hydrogen evolution reaction [14,15]. Also, the presence of polypyrrole in composite Nafion membranes was reported to be able to increase the proton conductivity [16,17]. A composite membrane of Nafion, silicotungsten acid and thiophene was reported to have improved water uptake, higher ionic conductivity and higher current densities in fuel cell operation [18].

In this project we synthesized a thin layer of polypyrrole inside the nanopores of the existing Nafion membrane, in order to minimize the diffusion of methanol through the membrane. Pretreated Nafion membranes were immersed in an acid electrolyte containing the monomer, and subsequently the polypyrrole was formed galvanostatically in a solid-state electrochemical cell, on the anode side only. The modified membranes were studied in terms of morphology, stability, electrochemical characteristics and methanol permeability.

## 2. Experimental

### 2.1. Membrane preparation

Nafion 117 and 115 membranes were cleaned by boiling for 45 min in 3% hydrogen peroxide, followed by boiling for 45 min in 1 M sulphuric acid, and finally 15 min in deionized water (repeated twice). Between each step the membranes were rinsed in deionized water. After cleaning, the membranes were stored in deionized water until further use.

Before polymerization of the pyrrole, the membranes were first dried at a temperature of 130 °C for 3 min, then immersed in a solution of 0.1 M pyrrole monomer and 0.1 M sulphuric acid in deionized water for half a minute. Then,

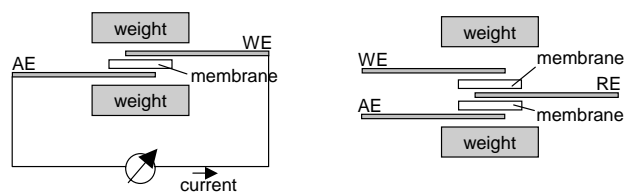


Fig. 1. Set-up of solid-state electrochemical cell as used for polymerization (left) and characterization (right), with WE the working electrode, AE the auxiliary electrode and RE the reference electrode.

the membrane was removed from this solution and, while still wet, placed as electrolyte in a solid-state electrochemical cell (see Fig. 1). This cell comprised of two stainless steel electrodes, between two metal blocks (isolated from the electrodes), which served as weights to provide good contact between the stainless steel electrodes and the hydrated solid electrolyte.

The monomer was polymerized galvanostatically at a current of  $0.4 \text{ mA cm}^{-2}$  during 5, 10 or 20 min, corresponding to 0.12, 0.24 and  $0.48 \text{ C cm}^{-2}$ . This would give a uniform polypyrrole layer of 0.68, 1.36 and  $2.72 \mu\text{m}$  at the used surface area of  $12.25 \text{ cm}^2$  [4], or at a given membrane porosity of around 40% of 1.7, 3.4 and  $6.8 \mu\text{m}$  inside the pores of the membrane. However, the polymer was found not to deposit in a very uniform way.

After polymerization the membrane was dried at 150 °C for 5 min to remove excess pyrrole monomer and subsequently stored in deionized water. Some photo-oxidation of the monomer during this last process could however not be avoided, as observed from a slight colour change of the entire membrane from transparent to transparent brown.

### 2.2. Analysis

For cyclic voltammetry a Radiometer PGZ301 potentiostat was used. The Nafion 117 membrane was first immersed in the test solution for 24 h, after which the wetted membrane was placed in the solid-state cell as described above, between porous Toray carbon paper electrodes. A narrow, thin strip of carbon paper was used as reference electrode, placed between two pieces of membrane, as shown in Fig. 1 (left). All potentials measured are versus the carbon reference electrode. The carbon paper was shown to be inert in the specific circumstances of the test.

The applied potential range for cyclic voltammetry was between 1.2 and  $-1 \text{ V}$ , starting from 0 V in anodic direction, with a scanrate of  $50 \text{ mV s}^{-1}$ .

SEM was performed on a Philips XL30 ESEM microscope in BSE mode. FTIR was done on a Perker-Elmin Spectrum GX in ATR mode.

Methanol permeability was measured electrochemically. The (modified) Nafion 115 membrane was used to divide the two compartments of an electrochemical cell. One compartment had an electrolyte of 0.5 M sulphuric acid, and in this electrolyte the working electrode and the reference

electrode, using a Luggin probe, were placed. In the other compartment, an electrolyte of 0.5 M sulphuric acid with 1.0 M methanol and the auxiliary electrode were placed. Both compartments were de-aerated by continuously bubbling with nitrogen. The auxiliary and working electrode were platinum mesh electrodes, while the reference electrode was a standard calomel electrode. Cyclic voltammetry was performed every half hour with a scan-rate of  $50 \text{ mV s}^{-1}$ . This allowed to monitor the passage of methanol through the membrane towards the working electrode. The height of the methanol oxidation peak is assumed to be proportional to the amount of methanol permeated through the membrane.

### 3. Results and discussion

#### 3.1. FTIR

FTIR results are shown in Fig. 2. The spectra for the untreated Nafion sample and for the cathodic side of the polypyrrole treated sample are identical, and show typical peaks for Nafion at  $1200$ ,  $1147$ ,  $1056$ ,  $981$  and  $969 \text{ cm}^{-1}$  [19]. The spectrum for the treated sample taken on the anode side (drawn line) shows some small additional peaks, at  $805$ ,  $929$  and  $1559 \text{ cm}^{-1}$ , corresponding to polypyrrole, specifically to C–H out-of-plane bending, C–H out-of-plane deformation and C–C stretching vibrations in the ring, respectively [20,21]. These results confirm that polypyrrole was successfully deposited and on the anode side only.

#### 3.2. SEM

SEM images (Fig. 3) show the surface of a Nafion 117 membrane with  $0.12 \text{ C cm}^{-2}$  polypyrrole. The presence of typical polypyrrole grains can be clearly observed, with grains having diameters of  $100\text{--}700 \text{ nm}$  approximately. The arrows indicate pores in the membrane with polypyrrole deposited around and inside the pore. The deposit on the surface was found to be slightly inhomogeneous, and there appear to be two distinct groups of polypyrrole grains. The smallest grains (around  $100 \text{ nm}$  diameter) appear to be found

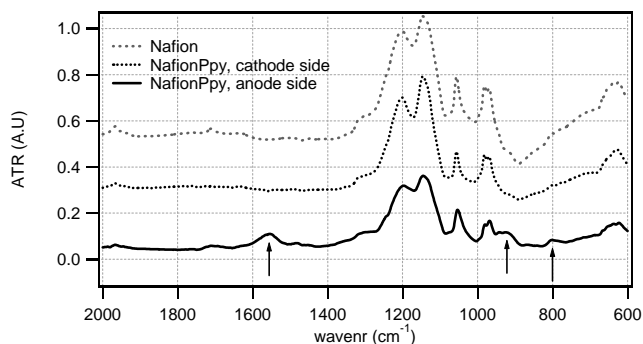


Fig. 2. FTIR spectra for Nafion and Nafion/Ppy.

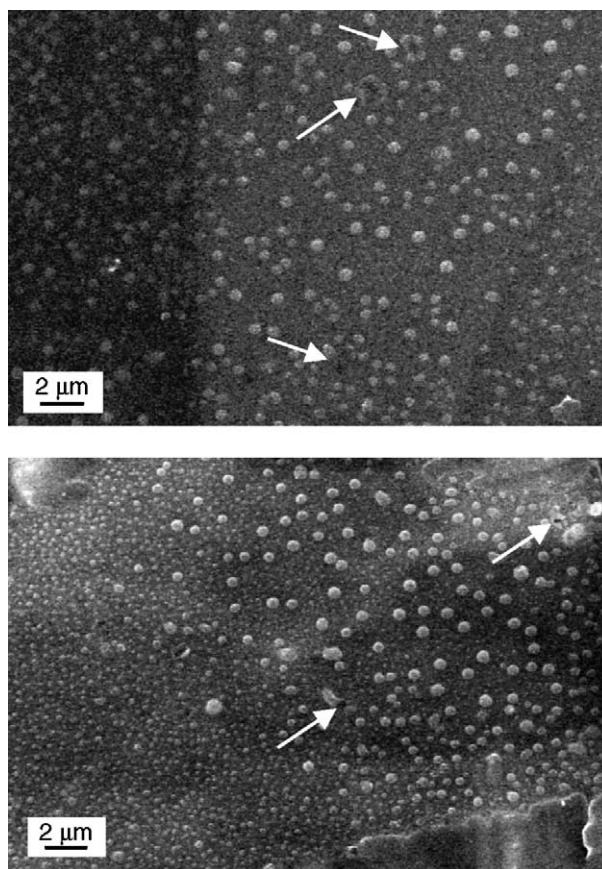


Fig. 3. SEM micrographs of Nafion/Ppy membrane.

over the entire surface, while the larger grains are concentrated in specific areas. Possibly, the largest grains are deposited only on the outside of the membrane surface, while the smallest deposits are present both on the surface and inside the membrane pores. Small pores may have been completely blocked by the polypyrrole.

The amount of polypyrrole visible on the membrane surface in the SEM micrographs, does not correspond with the calculated layer thickness of the deposited polypyrrole of  $0.68 \mu\text{m}$  (see Section 2). This again indicates that part of the polypyrrole was deposited inside the membrane.

#### 3.3. Methanol permeability

Fig. 4 (top) shows the results for four different membranes: pretreated Nafion 115, and Nafion 115 with subsequently  $0.12$ ,  $0.24$  and  $0.48 \text{ C cm}^{-2}$  polypyrrole, after 2 h in the cell. The methanol oxidation takes place between  $0.2$  and  $0.8 \text{ V}_{\text{SCE}}$  with a maximum at  $0.5 \text{ V}$  at the upward scan, while at  $0.4 \text{ V}$  at the downward scan. Results indicate that the unmodified membrane has the highest methanol permeability (an increase in the peaks indicating increased passage of methanol), while the membrane with  $0.12 \text{ C cm}^{-2}$  polypyrrole shows lowest permeability. The membranes with more polypyrrole deposited have intermediate permeabilities, possibly due to the inhomogeneous deposition.

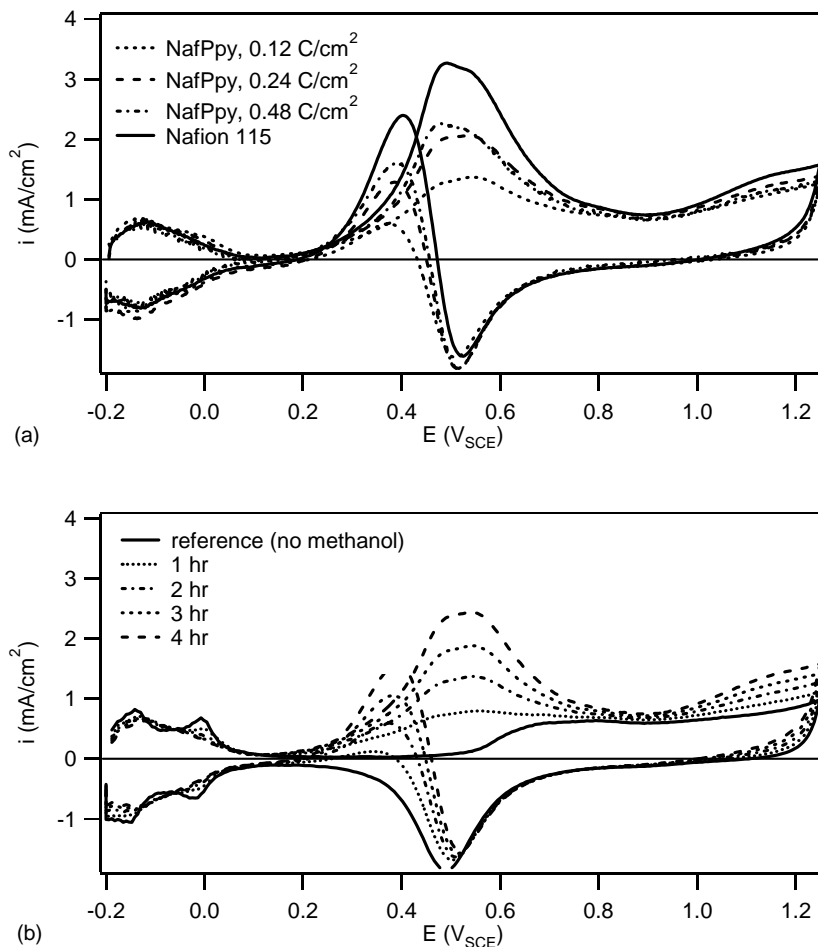


Fig. 4. Results for methanol permeability tests for four different Nafion 115 membranes (a) and for the  $0.12 \text{ C cm}^{-2}$  Ppy membrane (b).

Fig. 4b shows the permeabilities for Nafion 115 with polypyrrole ( $0.12 \text{ C cm}^{-2}$ ) at different times of immersion, as compared to a reference test in which no methanol was present in the electrolyte. The peak for methanol oxidation increases with time, indicating that the amount of diffused methanol continues to increase with time.

### 3.4. Cyclic voltammetry

Results are shown in Figs. 5–7 for Nafion 117 samples previously immersed for 24 h in 0.1 M sulphuric acid, in pure methanol and in a mixture of methanol/distilled water (50/50 vol.%, 12.5 M), respectively. In all cases there is a clear difference between the modified and unmodified samples, with higher current densities for the Nafion/polypyrrole (Nafion/Ppy) samples. Peaks of polypyrrole oxidation and reduction are seen in sulphuric acid and in methanol, while additional peaks appear in methanol, possibly due to methanol oxidation.

Fig. 5 shows cyclic voltammograms of membranes previously immersed in 0.1 M  $\text{H}_2\text{SO}_4$  (24 h). For the untreated Nafion sample, at high potentials oxygen evolution is seen. At low potentials ( $-0.2$  to  $-0.7 \text{ V}$ ) small current densities correspond with the reduction of oxygen, while below po-

tentials of  $0.7 \text{ V}$  larger current densities are due to hydrogen evolution.

For the Nafion/polypyrrole sample, the curve is typical for polypyrrole, with oxidation and reduction of the polypyrrole (and consequently the transport of  $\text{SO}_4^{2-}$  ions in and out of the polypyrrole) during the first 2 cycles (at  $0.50$  and  $-0.60 \text{ V}$ , respectively). After longer cycling the process becomes reversible.

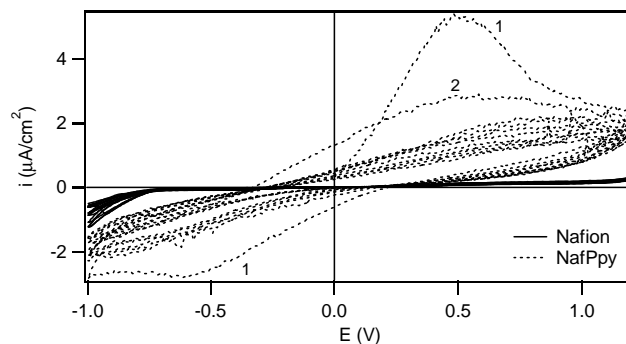


Fig. 5. Cyclic voltammograms of Nafion and Nafion/polypyrrole membranes in 0.1 M sulphuric acid. Numbers 1 and 2 refer to the first and second cycle, respectively.



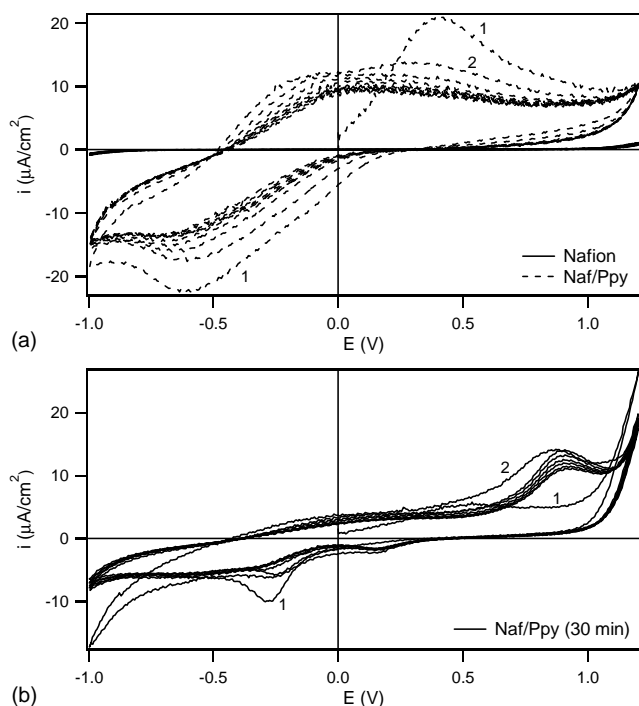


Fig. 6. Cyclic voltammograms of Nafion and Nafion/polypyrrole membranes in a pure methanol after 24 h immersion in test solution (a) and Nafion/Ppy after 30 min in pure methanol (b). Numbers 1 and 2 refer to the first and second cycle, respectively.

Cyclic voltammetry (Fig. 6) of membranes previously immersed in methanol during 24 h shows for the Nafion sample a curve which is nearly identical to that in sulphuric acid (Fig. 5). For the Nafion/Ppy sample the curve is typical for polypyrrole (Fig. 5) but it shows higher current densities and there are additional peaks. Polypyrrole oxidation and reduction takes place principally at 0.40 and  $-0.60$  V during the first cycle. The additional peaks at around 0 V (anodic) for prolonged cycling most likely correspond to oxidation of methanol [10,13], while the high cathodic current densities around  $-0.6$  V probably correspond to reduction of the produced products trapped at the surface in the sandwich-type cell. The high current densities again indicate a possible

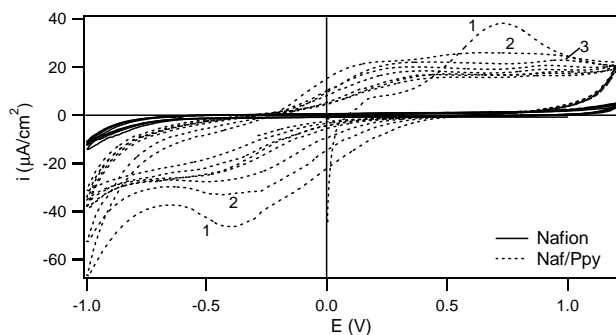


Fig. 7. Cyclic voltammograms of Nafion and Nafion/polypyrrole membranes in a methanol–water mixture after 24 h immersion in test solution. Numbers 1, 2 and 3 refer to the first, second and third cycle, respectively.

catalytic activity of polypyrrole for methanol oxidation. Such an additional catalytic effect of conductive polymer deposited on the anodic side of the Nafion membrane, would aid to reduce the cross-over of methanol even more.

After only 30 min (Fig. 6b) of immersion in pure methanol the curve for Nafion/Ppy looks quite different. During the first cycle no oxidative peak was seen and there is a reductive peak at  $-0.27$  V, while during the following cycles oxidative peaks are seen at 0.89 V and reduction peaks at 0.15 and  $-0.27$  V. This indicates that due to the short time of immersion of the membrane in the methanol, not all of the water in the membrane was replaced, so that peaks for oxidation and reduction of water appear.

Fig. 7 shows cyclic voltammograms for the membranes in an aqueous mixture of 50 vol.% methanol (12.5 M). While the curve for the Nafion sample remains nearly identical as in sulphuric acid and in pure methanol, for the Nafion/Ppy sample a typical polypyrrole curve at high current densities with additional peaks is seen. This may be related with an improved proton conductivity of the Nafion membrane due to the presence of water, hydrating the membrane. The potentials have shifted around 200 mV compared to the results in pure methanol. The first peak at 0.72 V again corresponds to polypyrrole oxidation, anodic peaks at 0.97 V to oxygen production (oxidation of water), at 0.16–0.32 V to methanol oxidation, while the cathodic peak at  $-0.394$  V corresponds to polypyrrole reduction and reduction of methanol products. The curve shape is very similar to the curve for Nafion/Ppy after 30 min in pure methanol, indicating that after immersion in methanol, the water absorbed in the membrane is only slowly displaced by the methanol.

It can be seen that methanol oxidation takes place at a range of  $-0.4$  to 0.2 V (versus carbon) in pure methanol (Fig. 6) and  $-0.2$  to 0.4 V (versus carbon) in the methanol–water mixture (Fig. 7), corresponding to 0.2–0.8 V<sub>SCE</sub> at a platinum electrode as found in the permeability test (Fig. 4).

Assuming that the peak height of the methanol oxidation peak ( $10 \mu\text{A cm}^{-2}$ ) corresponds entirely to methanol oxidation due to the catalytic activity of the polypyrrole, the catalytic activity can be normalized to polypyrrole mass. Since the membrane contained  $0.12 \text{ C cm}^{-2}$  polypyrrole, corresponding to  $41.9 \mu\text{g cm}^{-2}$  polypyrrole, an oxidation current of  $10 \mu\text{A cm}^{-2}$  corresponds with a current of  $0.24 \text{ A g}^{-1}$  polypyrrole. This value is very low compared to values found for traditional catalysts, such as Pt/C-based catalyst, which have activities of around  $100 \text{ A g}^{-1}$  [22]. However, the use of smaller particles of polypyrrole (nanoparticles) may provide better results.

#### 4. Conclusions

- Nafion membranes were successfully modified by the in situ electrodeposition of polypyrrole inside the membrane pores and on the anode side only, in order to prevent the cross-over of methanol in the direct methanol fuel cell.

- The presence of the polypyrrole on the membrane surface was confirmed by FTIR and SEM.
- SEM shows the polymer to be present both on the membrane surface and inside the membrane pores. The polypyrrole was found to be deposited as small grains, with two distinct sizes of diameters, the smallest particles have a diameter of around 100 nm, while the larger particles have diameters of around 700 nm.
- Methanol permeability was determined electrochemically and was shown to be effectively reduced for the modified membrane, although the passage of methanol could not be completely stopped.
- The cyclic voltammograms for the Nafion/Ppy membrane showed typical polypyrrole curves. Current densities were lowest in sulphuric acid, intermedium in methanol and highest in a methanol/water mixture.
- For the Nafion/Ppy membranes in methanol containing electrolytes, an additional oxidative peak appears in the CV, which may be related to electrocatalytic activity of the polypyrrole for methanol oxidation. The catalytic activity was calculated to be  $0.24 \text{ A g}^{-1}$  polypyrrole.
- The polypyrrole deposition on the surface was not completely homogeneous and part of the polymerization occurred unintentionally by photo-oxidation of the monomer at elevated temperatures. The specific effects on the performance are not known.

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