New membranes for direct methanol fuel cells

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Abstract

The performance of direct methanol fuel cells (DMFC) is limited by the cross-over of methanol through the electrolyte. Electrolyte membranes prepared by blending of sulfonated arylene main-chain polymers like sulfonated PEEK Victrex (sPEEK) or sulfonated PSU Udel (sPSU) with basic polymers like poly(4-vinylpyridine) (P4VP) or polybenzimidazole (PBI) show excellent chemical and thermal stability, good proton-conductivity, and good performance in H_2 PEM fuel cells. Furthermore, these materials have potentially lower methanol cross-over when compared to standard Nafion-type membranes.

In this work, membrane electrode assemblies (MEAs) have been prepared from such membranes according to the thin-film method. The catalyst layer was spray-coated directly on the heated membrane using an ink consisting of an aqueous suspension of catalyst powder and Nafion solution. Unsupported catalysts were used for anode and cathode. A rather high catalyst loading was chosen in order to minimize the effects of limited catalyst utilization due to flooding conditions at both electrodes. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Fuel cells are electrochemical energy converters, transforming chemical energy directly into electricity. Due to their numerous benefits such as lower emissions, high efficiencies even at part load and possibly lower requirements for maintenance, they are forming an attractive alternative to combustion engines. Considerable work has been devoted to the development of polymer electrolyte membrane fuel cells (PEFC) for vehicle propulsion [1,2] and independent power generation [2]. Commercial feasibility is expected to be reached in a not too distant future. Yet, these fuel cells are fuelled by hydrogen which is either used pure or prepared on site from carbonaceous precursors such as natural gas or methanol.

Methanol itself is a fuel that possesses significant electroactivity and can be oxidized directly to carbon dioxide and water in so called direct methanol fuel cells (DMFC). Methanol is liquid at room temperature, easy to handle, it has a high energy density and can be generated from a variety of sources such as natural gas, coal and even biomass. Furthermore, it is biodegradable. However, it is

toxic and completely miscible with water, thus, requiring different safety procedures from the ones commonly used with gasoline. The direct use of methanol in a DMFC, therefore, is a topic of considerable interest.

The state of the art in the field of DMFC development was recently reviewed by different authors [3–5]. Since methanol is a liquid completely miscible with water, it is possible to design a DMFC for liquid feed [6–9] or for gaseous feed [10,11] of the fuel. A comparison of DMFC design features was given in [12].

Yet, there are two major obstacles hindering the use of DMFCs:

- limited activity of the anode catalyst;
- methanol cross-over to the cathode, thus, poisoning of the cathode catalyst (Pt) by formation of a mixed potential [3].

The anode activity can be promoted by the use of suitable Pt/Ru-catalysts [3–5,13,14]. Slight activity improvements can be found by the use of multinary catalysts [15–18].

The effects of methanol cross-over have been studied by various authors [19–23]. Methanol cross-over is detrimental since it reduces both the Coulombic efficiency of the fuel cell and the cell voltage. Work by Ren et al. [24] showed a cross-over of methanol equivalent to 80 mA/cm² at a cell current density of 150 mA/cm² using a Nafion electrolyte in a liquid fed DMFC at 80 °C. Furthermore, they showed a

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total water transport to the cathode of 355 mg/(cm^2 h) under these conditions which leads to severe flooding effects of the cathode. The effects of methanol cross-over can be controlled to a certain extent by strictly correlating methanol feed concentration with the actual current demand of the cell [25]. In any case, it is highly desirable to find electrolyte membranes which reduce the methanol and water cross-over significantly.

Considerable effort has been devoted to the development of electrolyte membranes showing reduced methanol cross-over. Membranes containing metallic blocking layers were proposed [26,27]. Organic–inorganic composite membranes containing Zr-phosphonates [28], tin doped mordenites [29,30], zeolites [31] or silica [32,33] were investigated. A reduction of methanol cross-over was observed by doping Nafion with Cs$^+$-ions [34]. Other promising composite membranes are containing polybenzimidazole and phosporic acid [35] or even Nafion [36].

A further promising alternative are composite membranes made from blends of acidic and basic polymers [37]. These membranes are made by blending acidic polymers such as sulfonated polysulfones (sPSU), sulfonated polyetherketones (sPEK) or sulfonated polyetheretherketones (sPEEK) with basic polymers such as poly(4-vinylpyridine) (P4VP), polybenzimidazole (PBI) or a basically substituted polysulfone (bPSU). In these materials, electrostatic forces from salt formation between acidic and basic groups achieve reversible cross-linking of the polymer, which is also clearly visible in IR-spectroscopy [37–39]. The materials show excellent thermal, mechanical, chemical and dimensional stability. Membranes of this type are called polyaryl membranes in the following.

For the work described in this paper, a DMFC using liquid fuel feed has been chosen since it allows for a simple system, allows operation at temperatures up to 130 °C requiring no or only limited cathode humidification. Furthermore, in a complete system cooling can be achieved by the fuel loop. In order to compete in efficiency with reformate fed PEFCs, a power density of 250 mW/cm^2 should be reached at a single cell voltage of 500 mV. Furthermore, the methanol losses should be less than 50 mA/cm^2 equivalent at a power density of 250 mW/cm^2.

2. Experimental

2.1. Pretreatment of the electrolyte membrane

The preparation of electrode membrane assemblies (MEA) was carried out according to the method described by Wilson [40]. Nafion 105 membranes were boiled in 3% H$_2$O$_2$ for 1 h in order to remove organic contaminants. This treatment was followed by washing in acid and boiling three times for 1 h in de-mineralized water. Polyaryl type membranes were washed in acid and boiled in de-mineralized water.

2.2. Preparation of the catalyst ink

Catalyst powder (1 g) was dispersed in 10 ml de-mineralized water. Johnson Matthey platinum black (fuel cell grade) was used for the cathode. The anode ink was made from unsupported Pt/Ru (50%) from Johnson Matthey. Alcoholic Nafion solution (ion power) was added to a content of 10–15% in the dry mixture. This mixture was stirred magnetically for at least 72 h at room temperature. The catalyst ink was kept under constant stirring. However, it should be used within another 10 days in order to minimize morphology changes due to stirring.

2.3. MEA preparation

Wet membranes were fixed in an aluminum frame, allowed to dry and covered by a mask (5 cm × 5 cm). The catalyst ink was dispersed on the membranes by an air brush in multiple layers. In each layer, approximately 1 mg/cm^2 of catalyst was deposited. The loading was determined by weighing the dried MEA. Membrane coating was carried out at a temperature of 120 °C for Nafion membranes, polyaryl type membranes sometimes required lower coating temperatures. Nafion-based MEAs were hot pressed at 130 °C at 140 bar for 3 min. The anode loading typically was 5 mg/cm^2 Pt/Ru, the cathode loading was approximately 6 mg/cm^2 Pt.

Toray graphite paper (TGP 60) was used as a media diffusion layer. At the cathode side teflonized (25 wt.% PTFE) TGP 60 was used.

2.4. Determination of current–voltage curves

All measurements were carried out in a graphite cell housing using serpentine type flow fields of 1 mm depth and width. The distance between channels was 1 mm. Current–voltage curves were determined galvanostatically. Aqueous methanol solution (1 mol/l) was fed by mass flow controllers at a flow rate of 4 ml/min. The anode pressure was 2.5 bar. The solution was preheated to cell temperature by heated tubing. Air was fed at a flow rate of 1.5 l/min at a pressure of 4 bar. CO$_2$ evolution at the cathode was measured by a Fisher–Rosemound infrared analyzer as a measure for methanol cross-over. No correction has been applied for CO$_2$ diffusion through the electrolyte membrane [41].

3. Results and discussion

3.1. Cells using Nafion membranes

MEAs using Nafion membranes were used for studying the influence of DMFC operating conditions. Fig. 1 shows a comparison of Nafion 117 and Nafion 105 membranes under similar experimental conditions. It is evident that MEAs made from Nafion 105 are very reproducible. Furthermore, it
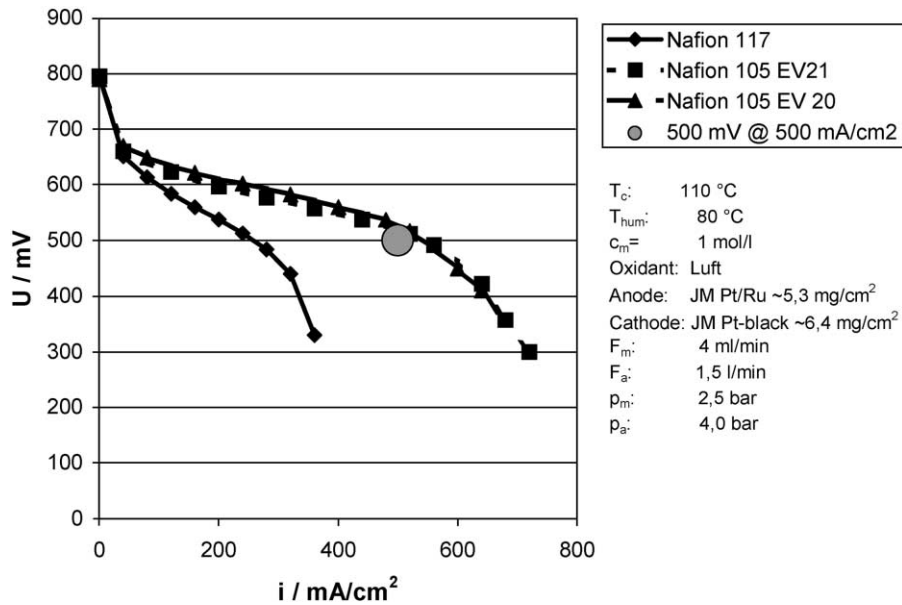
Fig. 1. Comparison of MEAs using Nafion electrolytes. It is evident that better electric performance is achieved using a Nafion 105 electrolyte membrane.

can be seen that significantly better performance can be achieved when Nafion 105 membranes are used. With Nafion 105 electrolyte, power densities above 250 mW/cm² can be achieved at a cell voltage of 500 mV under the experimental conditions shown. Nevertheless, Nafion 105 shows a significantly higher methanol permeation as compared to Nafion 117 (Table 1). Due to the better

Table 1
Comparison of methanol permeation through Nafion-type membranes

Methanol permeation	Nafion 117	Nafion 105
At the rate of OCP (mA/cm²)	163	343
At the rate of 200 mA/cm²	103	257
At the rate of 500 mA/cm²	–	135

electrical performance, Nafion 105 membranes were used in the following experiments.

Fig. 2 shows a comparison of current–voltage curves of MEAs using Nafion 105 electrolyte membranes. Comparing the current densities at 500 mV, it is evident that a significant increase is observed by increasing the anode catalyst loading from 1.1 to 2.1 mg/cm². A further increase to 5.3 mg/cm² shows a less prominent increase. When the current densities at 400 mV are compared, the effects of increasing the catalyst loading are less important. The result is consistent with work by Liu et al. [42] who observed only marginal performance increase at catalyst loadings above 2 mg/cm² when unsupported catalysts were used.

Air pressure and flow rate are a very prominent factor to influence the DMFC performance. Fig. 3 shows the
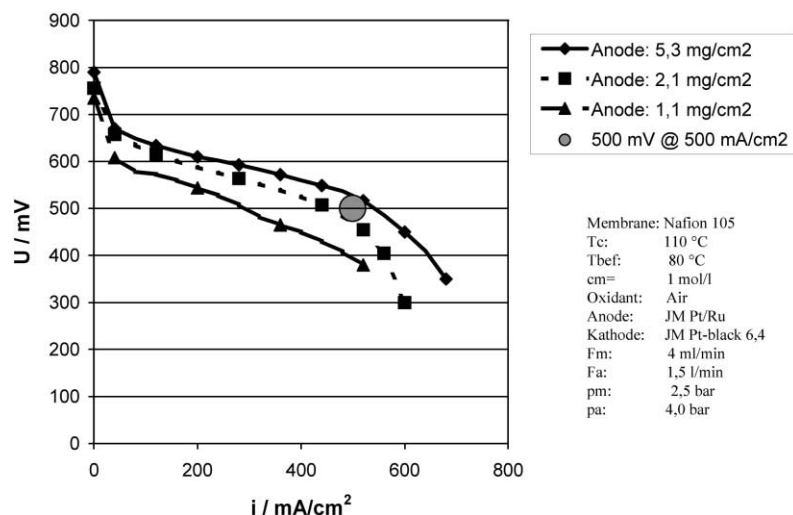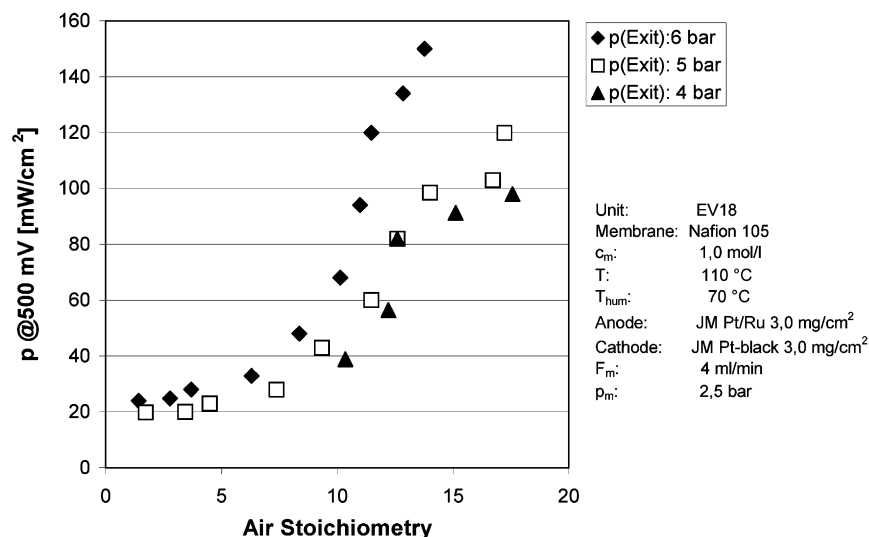

Fig. 2. Comparison of anode catalyst loading.

Fig. 3. Dependence of DMFC performance on pressure at the cell exit and air stoichiometry.

influence of pressure at the cell exit, and of air stoichiometry on the power density at 500 mV. It is evident that for the kind of MEA used in this investigation, air stoichiometries between 10 and 15 show significantly increased performance. Above an air stoichiometry of 15 the cell performance no longer increases noticeably. Furthermore, it is evident that high air stoichiometry is particularly beneficial at high pressure. The results reported here are consistent with the observations of Shukla et al. [9] at lower pressure and air stoichiometries.

Electron microscopy of liquid nitrogen fractured Nafion based MEAs showed good adhesion of the catalyst layer to membrane. No de-lamination could be observed.

3.2. Cells using polyaryl membranes

In the experiments using polyaryl type electrolyte membranes, anode loadings of 5 mg/cm^2 and constant air flow of 1.5 l/min at a pressure at the cell exit of 4 bar were used. All polyaryl type membranes were stable to thermal decomposition above a temperature of 200 °C. However, membranes containing PBI as a basic polymer proved to be most stable against mechanical stresses under fuel cell operating conditions. Addition of a basically substituted PSU (bPSU) proved to be possible. Therefore, MEAs made from membranes consisting of acidic polymers (sPEEK and sPEK) using PBI and different bPSU materials were studied. The details of membrane preparation were described in [39]. Table 2 shows some properties of the membranes used in this work. Structure formulas of the polymers used are depicted in Fig. 4.

Fig. 5 shows a current–voltage curve of a MEA using membrane sample 442. It is evident that this material shows excellent methanol blocking properties. However, the electrical performance was limited.

Table 2
Properties of polyaryl type membranes

Sample	Composition (g)	Swelling (%)	Thickness (μm)	IEC (meq./g)	$R_{sp}^{H^+}$ (Ω cm)
442	3 sPEEK[a], 0.15 PBI[b], 0.2 bPSU(I)[c]	27.7	95	1.18	36
447	4.5 sPEEK, 0.225 PBI, 0.225 bPPO[d]	27	89	1.2	26.3
504	PEK[e], PBI, bPSU(I)	22.7	60	0.7	66.6
511	PEK, PBI	33.7	108	0.8	18.31
519	PEK, PBI, bPSU(II)[f]	31.5	90	1.2	24.6
526	sPEK, bPSU(I)	32.8	115	1.48	21.5
527	sPEK, PBI, bPSU(III)[g]	31	101	0.99	21.6
528	sPEK, PBI, bPSU(I)	24.7	96	1.2	38

[a] Sulfonated poly(etheretherketone), IEC = 1.75 meq./g.
[b] Polybenzimidazole Celazole® (producer: Celanese).
[c] PSU with one group C(OH)(4-diethylaminophenylene)$_2$ per repeating unit.
[d] Polyphenyleneoxide with 0.4 groups C(OH)(4-diethylaminophenylene)$_2$ per repeating unit.
[e] Sulfonated poly(etherketone), IEC = 1.8 meq./g.
[f] PSU with two groups C(OH)(2-pyridyl)$_2$ per repeating unit.
[g] PSU with two groups C(OH)(4-diethylaminophenylene)$_2$ per repeating unit.
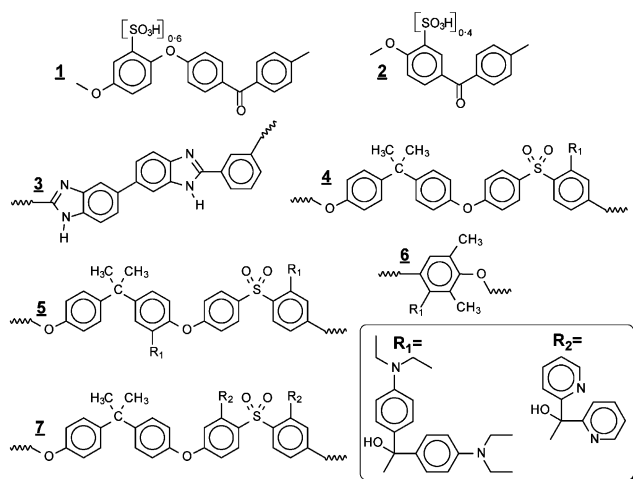
Fig. 4. Arylene main-chain polymers used for the preparation of the acid–base blend membranes: (1) sulfonated poly(etheretherketone) with 0.6 sulfonic acid groups per repeating unit; (2) sulfonated poly(etherketone) with 0.4 SO₃H groups per repeating unit; (3) polybenzimidazole Celazole® PBI; (4) polysulfone modified with one group R₁ per repeating unit; (5) polysulfone modified with two groups R₁; (6) poly(phenyleneoxide) modified with 0.4 groups R₁ per repeating unit; (7) polysulfone modified with two groups R₂ per repeating unit.

Table 3
Temperature dependence current density (in mA/cm^2) achieved at a cell voltage of 500 mV

	25 °C	70 °C	90 °C	110 °C
EV20 (Nafion 105)	28	167	309	528
E442	11	120	186	302
E447	13	85	126	193
E504	25	176	300	476
E511	19	149	225	320
E519	18	155	254	320
E526	9	88	121	178
E527	22	129	198	326
E528	24	114	196	250

materials were used. Fig. 7 shows a plot of the current density at 500 mV and the methanol losses at a current density of 200 mA/cm^2 at an operating temperature of 110 °C. Nafion 105 and E504 are showing the best electrical performance. However, E504 shows reduced methanol losses. The lowest methanol losses were observed for E442.

Electron microscopy of polyaryl type MEAs fractured under liquid nitrogen showed frequent de-lamination of the catalyst layer, thus, showing limited adhesion of the catalyst layer to the membrane electrolyte.

In general, MEAs made from polyaryl type membranes required higher cathode humidification for optimum performance than Nafion based MEAs, thus, indicating the modified methanol and water transport across the membrane.

No clear correlation could be found between membrane composition, MEA-performance and methanol blocking properties. However, preparation and electrode adhesion could have major influence on the overall performance of the MEA.

Fig. 6 shows the performance of a MEA made from membrane sample 504. Its electrical performance is comparable to the one achieved with Nafion 105. The electrical performance reaches almost the target of 500 mV at the rate of 500 mA/cm^2. However, the methanol cross-over for this membrane is comparable to the one observed for Nafion 117. At a current density of 500 mA/cm^2, the methanol cross-over amounts to an equivalent of approximately 90 mA/cm^2.

Table 3 shows a comparison of the current densities achieved at different temperatures, when different membrane
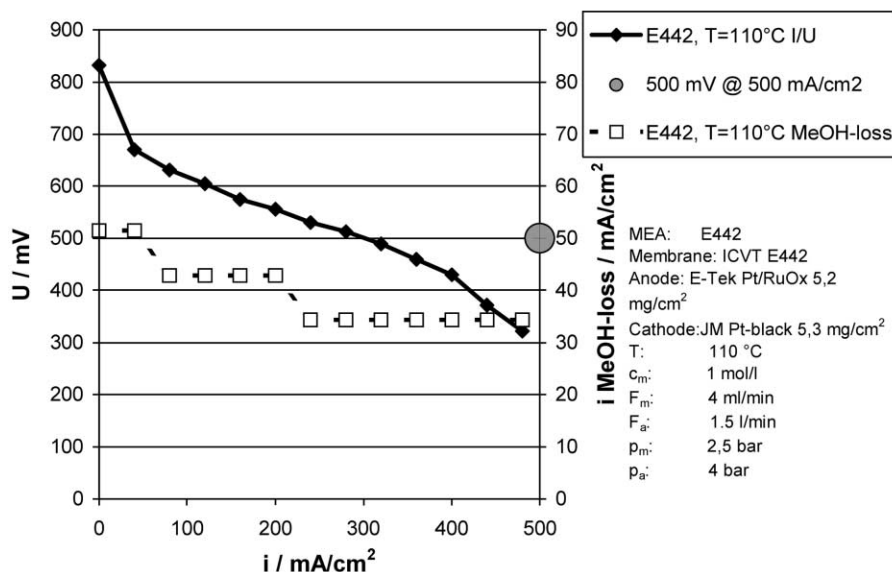

Fig. 5. Electrical performance and methanol losses of a MEA using polyaryl membrane E442.
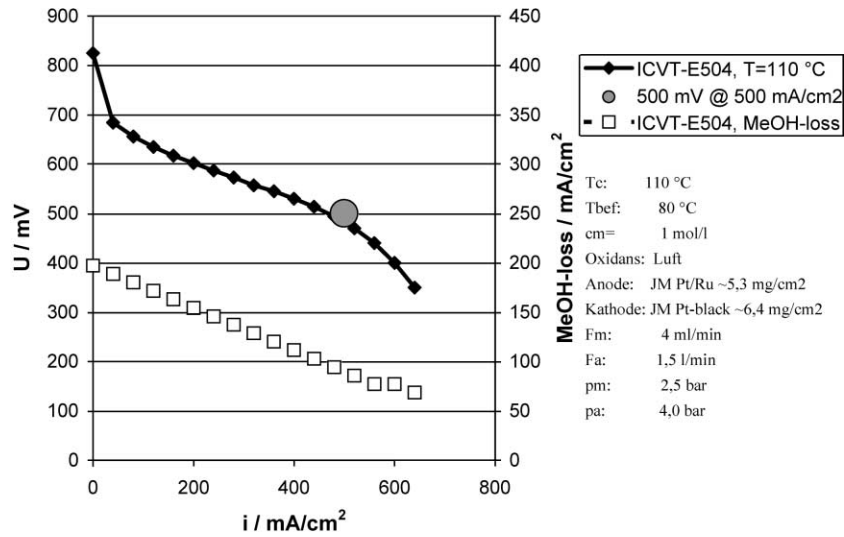
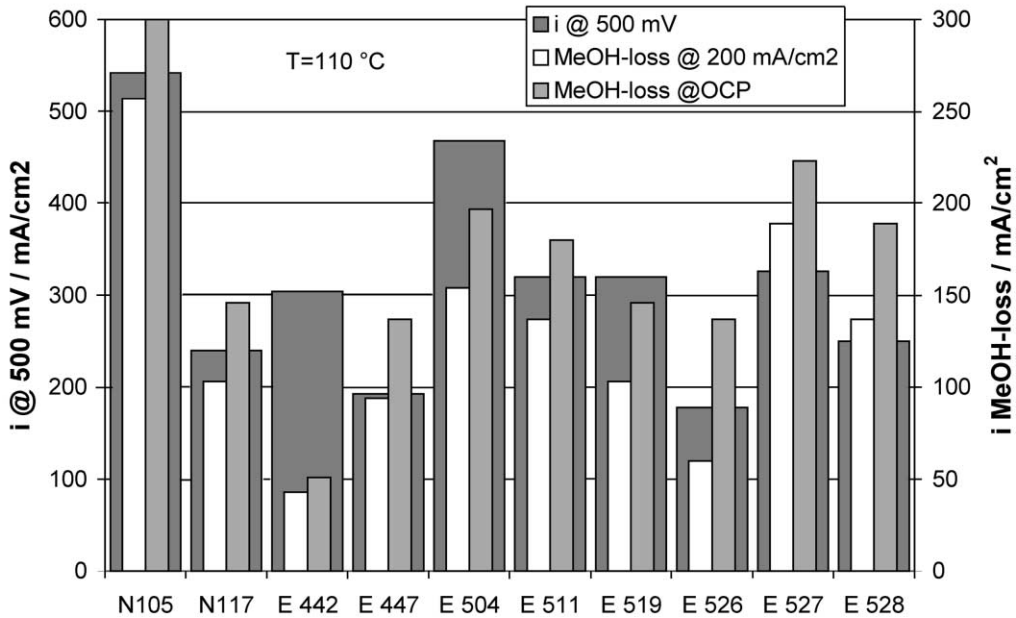Fig. 6. Electrical performance and methanol losses of a MEA using polyaryl membrane E504.

Fig. 7. Electrical performance at 500 mV and MeOH-cross-over at OCP and 200 mA/cm² of different membrane materials.

4. Conclusions

Electrolyte membranes showing similar electrical performance to that of Nafion 105 at levels of methanol permeation typical for Nafion 117 can be manufactured by using polyaryl type membranes. These materials show good thermal, mechanical and dimensional stability. MEAs made from these membranes can achieve electric performance comparable to Nafion membranes despite a non-optimized interface between catalyst and electrolyte membrane due to the use of Nafion as binder in the catalyst layer.

Further work is required to understand the influence of membrane composition and membrane manufacturing procedures to electrical performance and methanol blocking properties of the polyaryl type membranes. Furthermore, work must be devoted to study the transport properties of these new materials and to the optimization of the adhesion between catalyst layer and membrane.

Acknowledgements

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