

Porous lignosulfonate membranes for Direct Methanol Fuel Cells

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Abstract

Porous lignosulfonate membranes were prepared and considered for their potential application in direct methanol fuel cells (DMFC). Membranes were characterized by impedance spectrometry and water uptake measurement. Both their ion exchange capacity (IEC) and water uptake capacity affected porous membrane conductivity. Membrane conductivities were in the range 5-12 mS/cm at 80°C. Membrane electrode assemblies (MEAs) based on lignosulfonate membranes were also prepared and characterized in a single cell in order to determine whether they can be used in a DMFC. The current density at 300 mV was of 42 mA/cm² at 80°C.

Keywords: porous membrane, lignosulfonate, proton conductivity, membrane electrode assembly, single cell performance

1. Introduction

For polymer electrolyte membrane fuel cells (PEFC) operating on hydrogen or methanol, Nafion[®] is the standard proton conducting membrane. Its sulfonic acid groups form micro ion channels where the proton is transported together with its solvating water [1-4]. Based on the same concept, one of the main material developments for DMFC is sulfonated polymer and such blends as sulfonated polysulfone, sulfonated polystyrene and sulfonated poly(ether ether ketone). Both inorganic and organic materials are used as blending composite. With SiO₂, TiO₂ and ZrO₂ in the polymeric network, the membrane can be applied in DMFC operated at temperatures above 100°C [5-10]. Other research groups fill the phosphate and other acids into the polymeric matrix to generate membranes with better proton conductivity [10-14,]. Rigid and hydrophobic polymers are chosen to yield hybrid membranes with less methanol permeation [10, 15-21].

In this study, we prepared a type of porous membrane using polysulfone (PSU) and lignosulfonate (LS) blends. PSU is a hydrophobic, chemically resistant polymer which functions as a methanol barrier and membrane structure support. LS is also called sulfonated lignin. It is a highly crosslinked polyphenolic polymer that contains sulfonic acid groups and is a waste product of the pulping and paper making industry. Every year a huge amount of sulfonated lignin is produced all over the world, but only 1% of it is used. It is still a burden to the environment and needs to be explored further. If membranes were to consist of the LS that is not used today and a standard technical polymer such as PSU, they would be much cheaper than the present standard material Nafion. It is generally accepted that polymers containing a perfluorinated main chain and polymers containing a fully aromatic main chain are more stable under fuel cell conditions than polymers containing CH₂-groups in the main chain. However, other

polymers containing aliphatic components in the main chain have previously been tested successfully under fuel cell conditions [22].

In previous research, we prepared LS membranes under different conditions. Morphology analysis showed that LS was incorporated into the PSU matrix and no obvious phase separation was detected. The pores in the membranes were closed [23]. In the present paper, we characterize the electrical resistance of the LS membrane by impedance spectroscopy. The factors that influence membrane conductivity were investigated. At the same time, we prepared membrane electrode assemblies (MEAs) from the LS membrane. The MEAs were characterized in a DMFC at 80°C.

2. Experimental

2.1 Lignosulfonate membrane preparation

PSU (Mw. 35,000) was purchased from Aldrich and LS (Mw. 7000) was provided by Lignotech Borregaard. The casting solution was prepared by dissolving 1-3 wt.% LS (see Table 1) and 15 wt.% PSU in N,N-Dimethylformamide (DMF) at 35°C. Then the casting solution was spread by a coating machine onto a glass surface in a controlled thickness film. After it had been immersed in various precipitation bath solutions, the wet film formed a solid membrane.

2.2 Water uptake measurement

Membrane samples were cut to the size of 42mm×42mm and weighed after 2h in a 130°C oven. Then membrane samples were put into a water bath at 60°C and 80°C for 2

h and the bath was allowed to cool to room temperature. The membrane was immediately weighed and its dimension was measured after the membrane surface had been wiped dry with filter paper. Finally, the water uptake was calculated by

$$uptake(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \quad (1)$$

2.3 Membrane protonation

Membrane samples were put into 3.0 M H₂SO₄ solution at 60°C for 1h. Then they were rinsed with deionized water, and put into deionized water at 80°C for 1h. Finally, the protonated membranes were rinsed with deionized water and stored in deionized water.

2.4 Proton conductivity measurement

Two cells were used to measure the membrane conductivity. Cell 1, a four-point probe conductivity measuring cell [24] made of Teflon, was used to measure the conductivity under different humidities and temperatures. It consisted of two platinum current-carrying electrodes (distance 3 cm) and two platinum potential-sensing electrodes (distance 1 cm). The cell was placed in a home built environmental chamber which allowed the cell temperature and relative humidity to be controlled independently [25].

Cell 2 is shown in Figure 1 and has the same structure as cell 1. The distance between the potential-sensing electrodes is 2 cm and the distance between the current-carrying electrodes is 4 cm. The cell was placed in a water bath and the conductivity was measured at different temperatures.

The testing sample was a piece of membrane about 10 cm long and 1 cm wide and was fixed in the cell. The membrane resistance was measured by Impedance Spectroscopy

(Potentiostat / Galvanostat model 273A, EG&G Princeton Applied Research). The frequency swept from 65535 Hz to 100 Hz. The data were analyzed by Z plot software.

The conductivity was calculated using

$$\sigma = \frac{d}{RS_c} \quad (2)$$

where σ , d , R , S_c refer, respectively, to proton conductivity (S/cm), the potential-sensing electrode distance (cm), the membrane resistance (Ω) and the membrane cross-section area (cm^2).

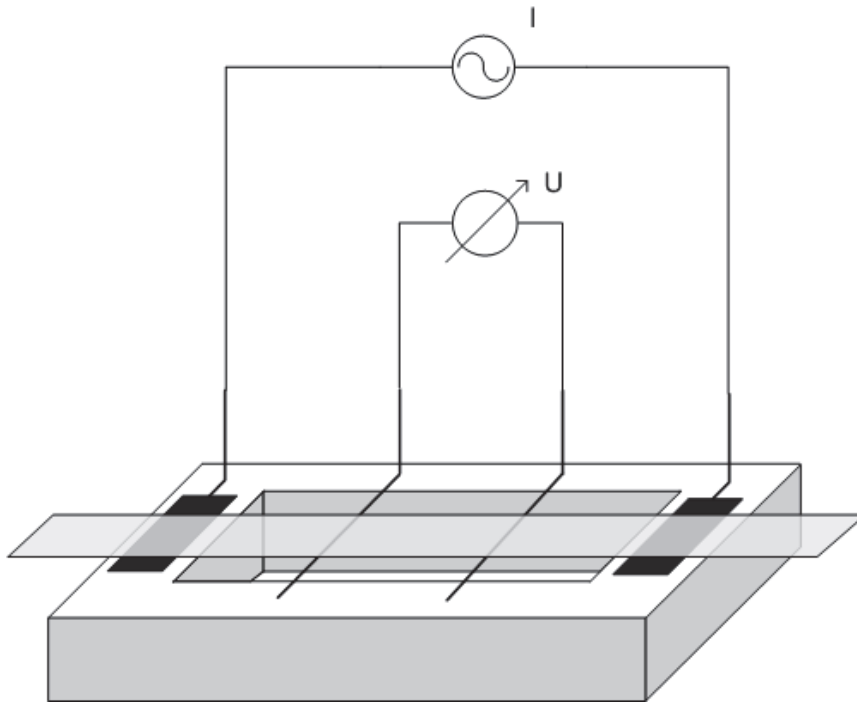


Figure 1. 4-Electrode AC-Impedance measurement cell

2.5 Fabrication of the membrane electrode assembly (MEA)

2.5.1 Catalyst ink preparation

The catalyst ink for the cathode was prepared by proportionally mixing 57.2% Pt/C (Johnson Matthey Hispec 9100) with deionized water, 5% Nafion solution (Fluka Chemika) and isopropanol (IPA). The catalyst ink for the anode was prepared by proportionally mixing 40% PtRu/C (Heraeus) with deionized water, 5% Nafion solution and IPA. The suspension was mixed by ultrasound for 10 min at room temperature. The suspension was then further mixed by ultraturrax (High shear rotor-stator system).

2.5.2 Gas diffusion electrode preparation

Gas diffusion electrodes (GDE) were prepared by spraying catalyst ink on top of the diffusion layer (Vulcan XC 72, Cabot Corp. and PTFE, Dyneon) [26]. Then, the wet electrode was dried at 60°C for 2 h. Before use, GDE was sprayed with 5% Nafion solution, and then dried at 60°C. Nafion loading on GDE was about 1 mg/cm². This Nafion layer on top of the electrode was necessary to obtain a good contact between the electrodes and the membrane without hot-pressing.

2.5.3 MEA preparation

The membrane was pretreated by spraying 5% Nafion solution on both sides, and then it was dried at 130°C. Very thin Nafion dense layers formed on the surfaces of the LS membrane. Nafion loading was around 2 mg/cm². The Nafion layers on the membrane also helped to improve contact between the membrane and the electrodes. Furthermore, the Nafion dense layers sealed the surface of the LS membrane and significantly reduced the risk of pin-holes.

MEA was formed by directly placing GDEs, the pre-treated membrane and the sealing material in a single measure cell. During operation, the GDEs stuck to the treated membrane surface and thus the MEA was formed in situ. Standard MEA-preparation procedures including a hot-pressing step could not be used because they destroyed the membrane.

2.6 Single cell performance and methanol permeation

All MEAs were characterized in a test rig with a single titanium cell. The flow-field had a grid-structure. The channels were 1.0mm deep, 1.0mm wide and spaced 1.0mm from each other. The electrode area was 20cm². The anode compartment was fed with 1.0M methanol under 1.0 bar pressure, and the cathode compartment was fed with air under 1.5 bar pressure. The flow rates were 664 ml_N/min of air at the cathode and 249 ml/h of methanol solution at the anode. The operation temperature was 80°C. Methanol permeating to the cathode was mostly oxidized directly on the cathode. In order to ensure complete conversion of permeated methanol to CO₂ a catalytic converter was placed in the cathode exhaust. Then the total CO₂ in the cathode exhaust was measured by an IR-detector. The amount of CO₂ enabled the amount of permeated methanol to be calculated and from this the current density that could have been generated was calculated (loss current) [27]. The corresponding methanol permeability (P , cm²/s) was calculated as

$$J_{\text{methanol}} = \frac{i}{6F} \quad (3)$$

$$P = \frac{J \times l}{C_{\text{methanol}}} \quad (4)$$

where, F is Faraday constant, i (A/cm²) is the current density, $J_{methanol}$ (mol/cm²s) is the crossed methanol flux, l (cm) is the membrane thickness, $C_{methanol}$ (mol/cm³) is the methanol concentration of the anode, which was consider as 1.0×10^{-3} mol/cm³ in our case.

3. Results and discussion

3.1 Membrane and properties

Several membranes were formed and their density, thickness and IEC are listed in Table 1.

1. The theoretical gravimetric IEC (meq/g) was calculated as

$$IEC_{gravimetric} = \frac{LS_{content} \times Acid_{content}}{M_{acid}} \times 1000 \quad (5)$$

where, LS content refers to the LS content in the dry membrane, $Acid_{content}$ refers to the sulfonic acid groups content (8.4 wt.%) which was provided by Lignotech Borregaard, M_{acid} (g/mol) refers to the molecular weight of the sulfonic acid.

The theoretical volumetric IEC was calculated by multiplying the theoretical gravimetric IEC with the density of the dry membrane.

Table 1. Membrane properties

Membrane	LS content	Casting conditions		Dry	Average	Theoretical gravimetric IEC meq/g	Theoretical volumetric IEC meq/cm ³
	in the dry membrane wt. %	LS content in the casting solution wt. %	Precipitation bath solution	membrane density g/cm ³	membrane thickness μm		
LS6	6.25	1	Water	0.2731	86	0.054	0.0148
LS12	11.70	2	Water	0.2593	89	0.102	0.0264
LS17	16.70	3	Water	0.2143	110	0.144	0.0309
LS17/IPA	16.70	3	IPA	0.3063	77	0.144	0.0438
LS17/IPAW	16.70	3	50%IPA/Water	0.1833	155	0.144	0.0265
Nafion 117	-	-	-	1.98	178	0.909	1.8

From table 1, we see that LS content and precipitation bath solution influence the membrane density. When the precipitation bath solution was water, a high LS content reduced the membrane density. When the precipitation bath solution was isopropanol (IPA), the membrane had higher density. When it was precipitated in a 50% IPA/water bath solution (IPAW), the membrane was more porous. The gravimetric, and particularly the volumetric, IEC were much lower than the standard material Nafion 117.

3.2 Water uptake measurement

To determine the water uptake, we used Nafion 1135 as a reference because it was as thick as the LS membranes. The results are listed in table 2. Since no dimensional change was observed for all the tested LS-membranes after the swelling experiments, we can conclude that LS membranes took water into its pores other than dimensional swelling, which was due to its porous property and rigid and hydrophobic PSU chains. Nafion 1135 swelled by 8-10% in each direction, because of the more flexible backbone of the Nafion polymer. Higher temperatures increased the water uptake for LS membranes and Nafion 1135. This and the fact that even the swollen LS membranes have densities of less than 1 g/cm³ indicates that some pores are not accessible at 60°C but become accessible at 80°C while other pores are not accessible even at 80°C.

The membrane density is related to the water uptake capacity. Low density membranes contain more pores, which results in high water uptake.

Table 2. Membrane water uptake at different temperatures

uptake%	60°C	80°C
LS6	131.76	156.62
LS12	162.71	185.44
LS17	245.03	282.95
LS17/IPA	89.18	93.03
LS17/IPAW	313.55	321.98
Nafion 1135	23.67	31.45

3.3 Proton conductivity

We tested the conductivities of LS17 membranes using cell 1 under different humidities and temperatures. The results are presented in Figure 2. Membrane conductivity increases as the humidity and temperature increase.

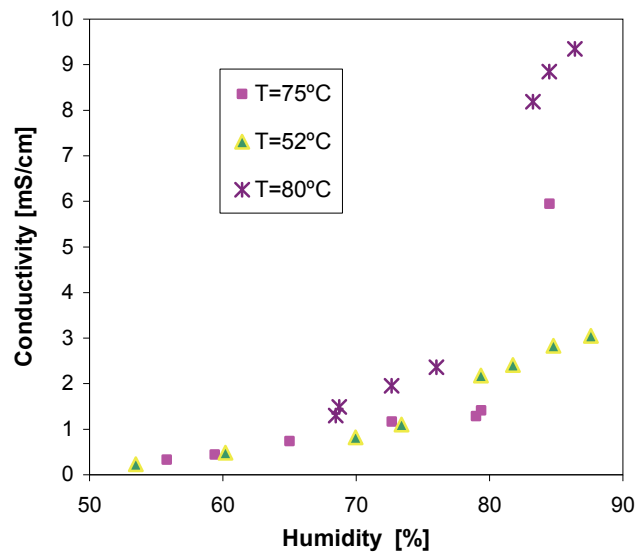


Figure 2. The effect of humidity on the proton conductivity of a protonated LS17 membrane at different temperatures

After immersing the membrane in the water bath, we measured membrane conductivity over time by using cell 2. Figure 3 shows that membrane conductivity improved slightly with the equilibration time in water. After two hours, membrane conductivity reached a plateau. This suggested that the conductivity of LS membranes depends on the water uptake, which agrees with the conductivities measured under different humidities.

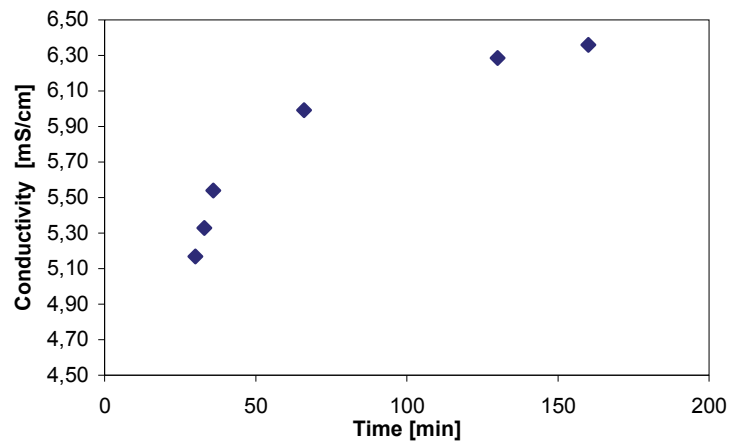


Figure 3. The influence of water uptake time on membrane conductivity at 40°C

Figure 4 shows the conductivities of LS membranes and Nafion 117 measured by cell 2 at different temperatures. Higher temperatures led to higher conductivities for all the membranes. It is also clear that Nafion 117 showed higher conductivity than LS membranes because its IEC was higher. Likewise, LS membranes with higher IEC showed increased conductivity. Therefore, increasing the LS content in the membrane will improve membrane conductivity.

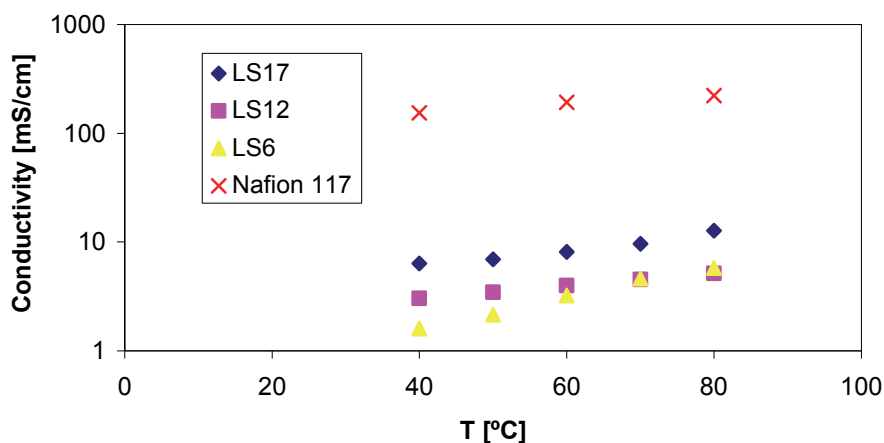


Figure 4. Logarithmic Plot of Proton conductivity of LS membranes and Nafion 117 at different temperatures

LS membrane conductivity also depends on the precipitation bath solution (Figure 5). At the same LS content, the conductivity of the membranes precipitated in a water bath was higher than the conductivity of those precipitated in other solutions. As we observed when measuring the water uptake with IPA as the precipitation bath solution, the membrane was denser and took up much less water, which resulted in lower conductivity. However, LS17/IPAW showed lower conductivity than LS17 although LS17/IPAW took more water than LS17. Obviously the IEC, water uptake and precipitation solvent all play a role in membrane conductivity. It should be pointed out that the conductivity of the LS17 membrane is fifteen times lower than that of Nafion, while the volumetric acid group density is sixty times lower. The general expectation is that conductivity should be reduced more than the acid group density, because even if only a few acid groups are removed, some conduction pathways will be broken. This leads us to conclude that by choosing the right precipitation solvent, the acid groups can be directed into a very favorable steric arrangement.

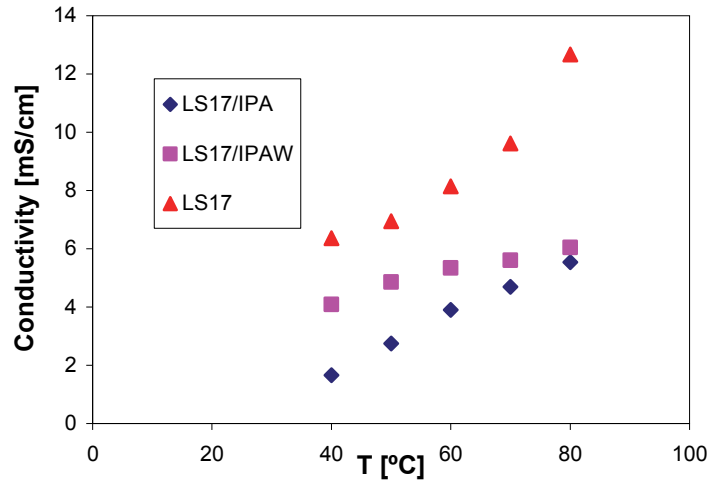


Figure 5. Effect of the precipitation bath solution on membrane conductivity

3.3 Methanol crossover and single cell performance

Three MEAs (Table 4) were formed and measured in a single cell test rig. Cell performance and methanol permeation are presented in Figures 6 and 7. MEA 1 and MEA 2 show very similar performances in spite of the difference in membrane conductivity. This may be an indication of non-perfect proton transfer between Nafion-based catalyst layers and the LS-based membrane. At 300 mV, the current density reached in both cases was around 42mA/cm², while Nafion 117 based MEA usually obtains a current density of 214mA/cm². This is because the conductivity of Nafion 117 is better than that of LS membranes and also Nafion has better contact with GDEs.

Table 4. List of MEAs prepared

MEA	Membrane	Anode catalyst loading mg/cm ²	Cathode catalyst loading mg/cm ²
1	LS17	1.77	2.38
2	LS12	1.77	2.30
3	Nafion 117	2.70	2.01

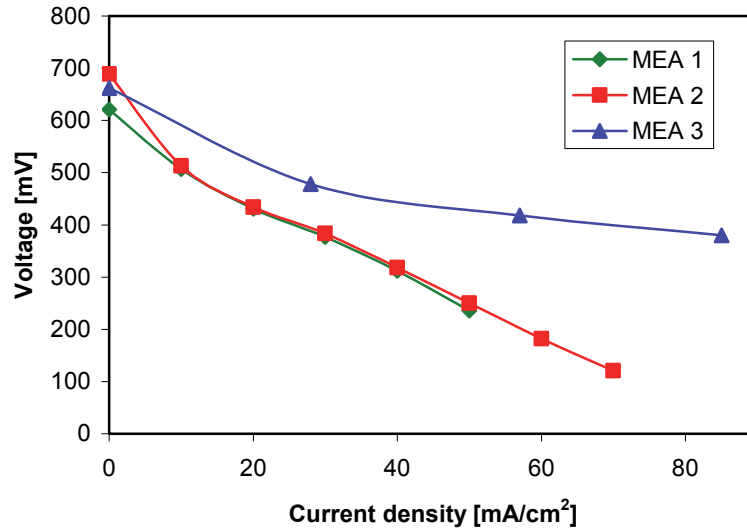


Figure 6. Cell performance curve of MEA1- MEA3

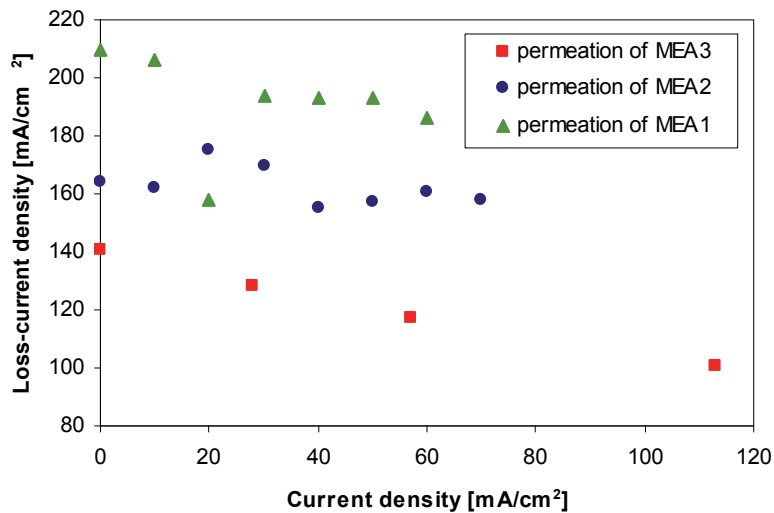


Figure 7. Loss-current density of MEA1, MEA2 and MEA3

Figure 7 shows the loss-current density due to methanol crossover for MEAs based on LS membranes and Nafion 117. The loss-current densities for MEA1, MEA2 and MEA3 were about 210 mA/cm², 160 mA/cm² and 140 mA/cm², respectively. A high loss-current density means high methanol permeation. Using equation (3) and equation (4), we calculated the methanol permeabilities of three MEAs based on the loss-current

density obtained at open cell condition. The methanol permeability of MEA3 based on the Nafion 117 membrane was $4.90 \times 10^{-6} \text{ cm}^2/\text{s}$, and that of MEA1 based on the LS17 membrane was $3.98 \times 10^{-6} \text{ cm}^2/\text{s}$ and that of MEA2 based on the LS12 membrane was $2.45 \times 10^{-6} \text{ cm}^2/\text{s}$. It was clear that MEAs based on the LS membranes showed lower methanol permeabilities comparing to the MEA based on Nafion 117. From this result we can also conclude that our lignosulfonate membranes can separate the anode and cathode reactants effectively. The porous structure is a closed pore structure as shown elsewhere [23]. Therefore the method taken during MEA-preparation to avoid pinholes as described above make these membranes very good separators in spite of their low density.

Although we did not test the life time of the LS-membrane-based MEA, MEAs have operated for over 60h and have shown stable cell performance. This demonstrated that LS membranes are stable during the real cell test. Since membranes made of other aliphatic polymers have also been successfully tested under fuel cell conditions [22], it is reasonable to assume that Lignosulfonate membranes are sufficiently stable under DMFC conditions.

4. Conclusions

This research has focused on the electrical and electrochemical characterization of lignosulfonate membranes for DMFCs and MEAs based on them. Our swelling experiments showed that porous LS membranes took up water into their pores but did not swell in water. Their dimensional stability in water is an advantage to be used in the DMFC. Impedance analysis showed that LS membranes were more resistant than

Nafion 117, which is mainly because of their low IEC. In fact, considering the low IEC, the proton conductivity is remarkably high, so the lignosulfonate in the blend must have a steric distribution which is favorable for proton transport.

MEAs were successfully formed in the single cell build-up. The current density at 300 mV was about 42 mA/cm², which was 5 times lower than that of MEA based on Nafion 117. Membrane resistance plays a crucial role in cell performance. The methanol permeability of LS-based MEA was lower than that of Nafion 117-based MEA. LS-based MEA was stable for 60 hours in the test condition.

As a new type of membrane for DMFC, LS membranes still require further investigation if they are to perform as well as the more expensive Nafion membranes. Especially the membrane preparation process has to be improved in order to obtain membranes with higher IEC and higher conductivity. In spite of the high porosity and high water uptake these membranes show very low methanol permeability, making them highly promising candidates for further development. MEA preparation should also be investigated in the future if cell performance is to be improved.

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