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Examination of the influence of PTFE coating on the properties of carbon paper in polymer electrolyte fuel cells

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Abstract

Polymer electrolyte fuel cells gain momentum due to the attainable high power densities and their relatively simple handling. Because their actual reactive catalytic layer is about < 10 μm, carbon papers are frequently used as additional backing in order to improve the gas distribution and water management in the fuel cell. To avoid flooding of the electrodes by the product water, the carbon paper is usually hydrophobed by partial coating with PTFE suspension. The influence of the PTFE coating and the following sintering time on through paper plane conductivity, gas permeability and paper hydrophobicity is analysed and discussed.

Keywords: Polymer electrolyte fuel cells; Coating; Carbon paper

1. Introduction

The need for highly efficient and low emission energy conversion has focused increased interest on fuel cells. The polymer electrolyte fuel cell (PEFC) is considered the most promising option for powering cars and for small combined power units. This is due to the attainable high power densities and their relatively simple handling [1–5]. Because their actual reactive catalytic layer is in the order of < 10 μm [6–8] carbon papers are frequently used as additional backing in order to improve the gas distribution and water management in the fuel cell. To avoid flooding of the electrodes by the product water, the carbon paper is usually hydrophobed by partly coating with polytetrafluroethylene (PTFE) suspension [9–14]. As part of the ongoing PEFC research in our institute [15,16], a series of experiments has been performed in order to examine the influence of PTFE coating and the sintering time on different paper properties. It should be understood that the experiments performed in this study investigate only whether or not certain preparation-dependent characteristics of PTFE-coated carbon paper have an effect on paper performance, as pertaining to its use in a fuel cell; this is not an optimization study. There are three paper characteristics of interest to the study, which can each affect the overall performance of a fuel cell: paper hydrophobicity (important in avoiding decreasing gas permeability through the paper plane as the result of liquid water saturation), ability of a gas to diffuse through the paper plane (important for fuel throughput and overall maximum cell performance), and paper conductivity (important when considering efficiency and energy losses due to ohmic resistance). Each of the three characteristics were plotted against each of two production-dependent factors: (i) the amount of PTFE coated onto the paper, and (ii) the sintering temperature at which the PTFE was fixed onto the carbon paper's fibres. The desired result was to see simple relationships between the three characteristics relevant to paper performance and the two factors involved in paper preparation.

2. Experimental

2.1. Materials

All samples were prepared using Sigri PE 704 carbon paper (thickness 300 μm) and Hostaflon 5032 (60% solid) PTFE suspension. The individual samples used in the experiments were all circular in shape and 26 mm in diameter. Fig. 1 shows a scanning electron microscope (SEM) picture of the untreated carbon paper.

2.2. PTFE coating

Square 9 cm × 9 cm pieces of the Sigri paper were cut out and allowed to sit in standing acetone for 1 h in order to

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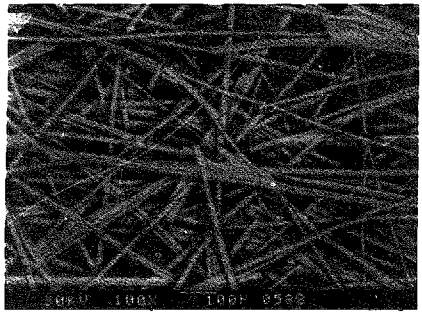

Fig. 1. SEM picture of untreated carbon paper Sigri PE 704.

ensure that the carbon fibres were clean and that the paper was dust free. After briefly rinsing the paper in a cleaner acetone solution for several minutes, the paper was allowed to dry at 80–100 °C. To coat the paper with PTFE, a sample of 9 cm × 9 cm was slowly lowered into the PTFE suspension, never faster than the suspension could adsorb the paper. The paper was left standing in the suspension for 5 min and then removed. To dry the paper, it was laid out flat on a square arrangement of 13 needles (pointed ends up). This enabled the PTFE to dry uniformly across the paper surface and avoided the problem of greater amounts of PTFE drying on one area of the paper, which occurred when samples were hung to dry. Nevertheless, a PTFE migration was observed during drying: higher amounts of PTFE dried on all four edges of the paper in comparison with its centre. However, this was not harmful to the study, as the PTFE content in the centre of the paper was uniform, and it was from this area that samples used in the experiments were cut. The remaining deviation in the PTFE loading of similar prepared pieces was in the range of 3–4% (Fig. 2). This has to be compared with the range of PTFE loadings of 0–200% considered. PTFE wt.% was calculated as $((m_{hydr} - m_{unhydr})/m_{unhydr}) \times 100$ or in other words as the PTFE/carbon paper weight ratio.

2.3. Sintering

Samples were placed into the sintering oven at temperatures below 200 °C; the oven was then heated to the desired temperature, a process that lasted as long as 10 min. Once the desired temperature had been reached, time was marked. When the marked time reflected the desired sintering time, the oven was rapidly cooled (2–3 min) to 150–200 °C and the sample was removed. In order to ensure the best uniformity in PTFE content possible, entire 9 cm × 9 cm pieces were sintered after coating with PTFE, and then to cut into individual samples from the sintered square. Sinter time for the samples with different PTFE loadings was 20 min at

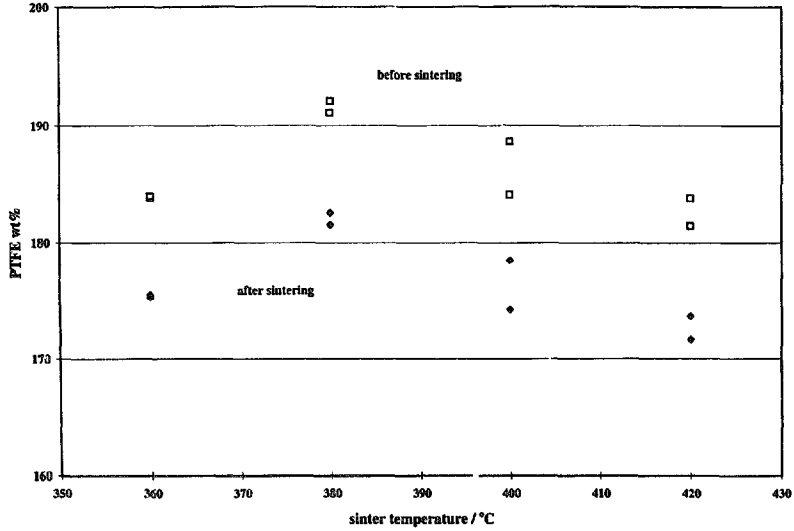

Fig. 2. PTFE wt.% of identical prepared samples before and after sintering.

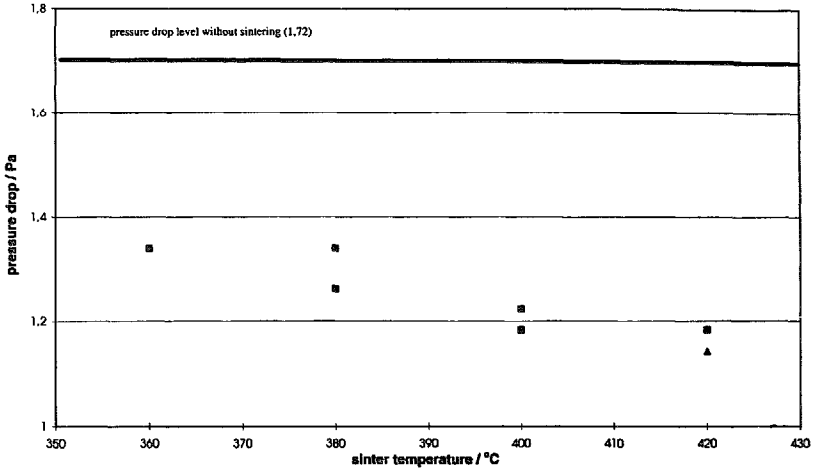

Fig. 3. Pressure drop of gas flow over samples with different sinter temperatures; flow rate: 20 SLPM, PTFE: 180 wt.%, sample area: 3.14 cm^2).

390 °C. Sinter time for the samples of different sinter temperature was 15 min.

2.4. Electrical conductivity experiments

The through-plane electrical conductivity of the hydrophobed paper was measured by sandwiching samples between two carefully aligned copper electrodes, and measuring the through-plane electrical resistance of the samples under differing applied pressures (up to a maximum of 540 bar). Values measured represent the change in contact resistance due to hydrophobing the samples. The electrodes used were made of solid copper which were polished before every experiment, both with 22 mm diameter circular contact surface areas. Through-plane resistance was measured using an milliohmmeter (HP 4228A, 4 point measurement at 1 kHz) after verifying the constancy of the short-circuit resistance of the copper electrodes (without a sample in between). Wires to connect the electrodes to the ohmmeter were attached to the back of the electrodes with a conductive silver compound glue.

2.5. Diffusion experiments

Gas diffusion through the paper was evaluated by measuring the pressure drop of gas flowing through the paper plane; as far as trends in data are concerned with respect to how convection and diffusion is affected by sample sinter temperature and PTFE wt.%, these pressure drop experiments reveal the same basic information. Two sections of 20 mm

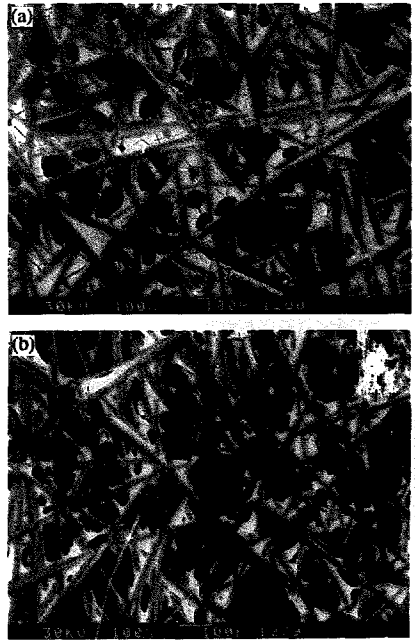

Fig. 4. Carbon paper with same PTFE loading (a) before and (b) after sintering.

internal diameter Plexiglas tubing, placed end to end, formed the main channel for gas flow in this experiment. A small metal plate was placed by the gas inlet at one end of the channel with its plane oriented in order to disrupt any concentrated gas flow currents that might strike the sample surface with too much impact and thus lead to erroneous readings in pressure drop across the paper's plane. A fitting was made where the two sections of pipe meet so that the circular 26 mm diameter samples could be inserted with their planes oriented perpendicular to gas flow. All pipe-pipe and pipe-sample contacts were airtight, and the pressure drop across the paper plane was measured via small holes drilled through the pipe wall on either side of the sample, each connected to opposite ends of a U-shaped tube containing ethanol. The

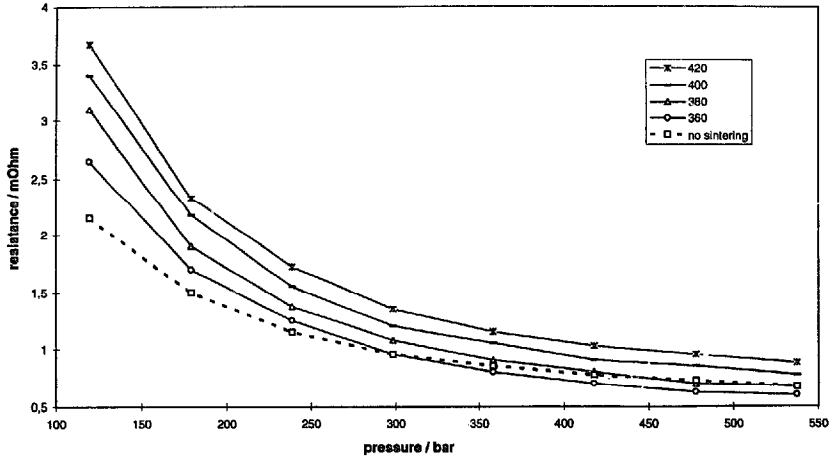

Fig. 5. Through-plane electrical conductivity measurements at samples prepared with different sinter temperatures; PTFE: 180 wt.%, surface area: 3.8 cm^2.

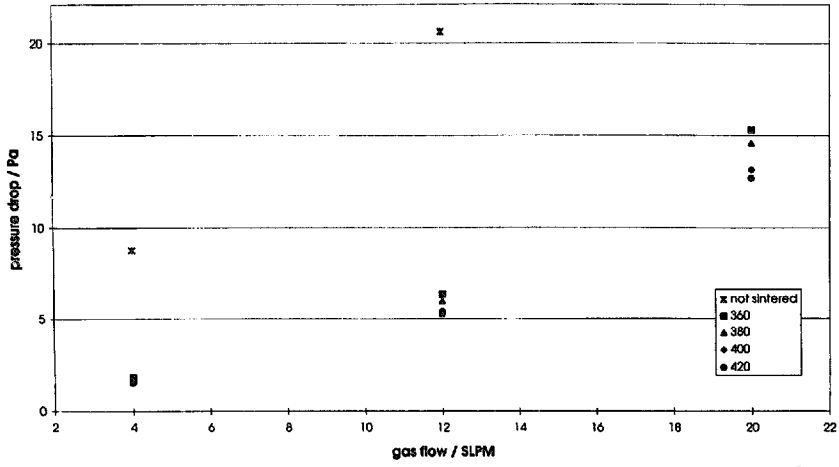

Fig. 6. Pressure drop over pressed carbon paper prepared with different sinter temperatures; PTFE: 180 wt.%, sample area: 3.14 cm^2.

difference in height between the two ethanol columns in the U-shaped tube resulting from the pressure drop across the paper plane measured the pressure drop directly; use of ethanol yielded column height readings that were higher and easier to read than what would have been seen with a more dense fluid like water. Gas flow was adjusted by the inlet pressure of the measurement gas (oxygen).

2.6. Hydrophobicity experiments

Indications for paper hydrophobicity were observed by immersing samples in demineralized water under pressure for 10 min; by comparing sample weights taken both before and immediately after immersion, a determination of the quantity of water taken up by the sample could be made. Samples were

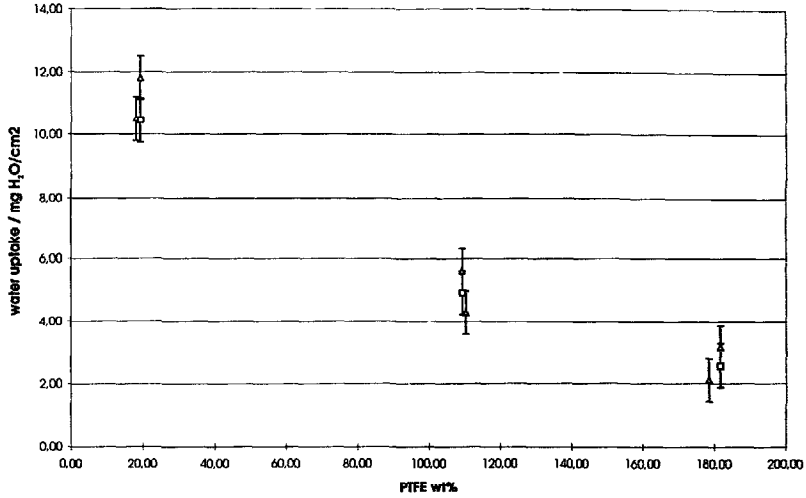

Fig. 7. Water uptake of samples with different PTFE loadings (3 series of measurements).

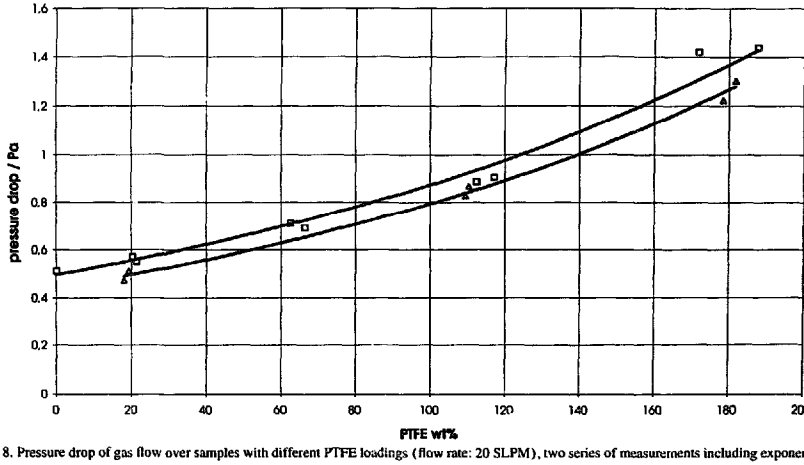

Fig. 8. Pressure drop of gas flow over samples with different PTFE loadings (flow rate: 20 SLPM), two series of measurements including exponential fit.

lowered into the water, a pressure of 10 bar was applied and the entire setup was allowed to stand for 10 min. This experiment was previously attempted using lower pressure levels, and though they all initially yielded similar trends in results, these results could never be reproduced well when the same samples were used twice.

2.7. Order of experiments

Each of the three paper properties investigated in this study ((i) paper hydrophobicity; (ii) the pressure drop of flowing oxygen through the paper plane, and (iii) through-plane conductivity of the paper) were plotted against the two factors involved in sample production: the amount of PTFE coated onto the paper, and the sinter temperature. The order of experiments conducted for any sample in the study was: (i) paper hydrophobicity; (ii) pressure drop of oxygen flowing through the paper plane; (iii) through-plane paper conductivity, and (iv) pressure drop of oxygen flowing through the paper plane, performed in a second test to observe any differences from the first time due to the 'squashing' effects of the conductivity experiment, in which samples are pressed under high pressure between electrodes. Each measurement was repeated at least two times with two different samples.

2.8. Assumptions made

Treatment of data required one assumption to be made. The recording of sample weights was towards calculating PTFE wt.% and the quantity of water taken up by samples during hydrophobicity experiments. These calculations, however, all start with a sample's original untreated weight — the weight of a circular piece of Sigri carbon paper (26 mm diameter) without PTFE. The value for this assumed untreated weight was established by taking the average weight of 12 untreated pieces of the Sigri paper, each cut into the same appropriate sample size and shape. By viewing the single highest and lowest weights within these 12 untreated samples as minimum and maximum limits for a sample's untreated weight, maximum errors of 5% are possible in calculating the PTFE wt.% of treated samples.

3. Results and discussion

3.1. Structural gains through sintering

One advantage of coating carbon paper with PTFE is seen in the structural advantages gained from the binding ability of the PTFE, which holds broken paper fibres together very well. Though no formal measurements were made with respect to these observations, the effects were clear. Untreated samples placed between the copper electrodes (for measuring through-plane conductivity) and subjected to as little as 120 bar of pressure broke down completely into carbon powder. Treated samples, however, underwent as much as 540 bar pressure without breaking apart; the PTFE coating kept the sample together, though most fibres had been broken into smaller pieces. Additionally, more force was required to cut sintered samples as opposed to unsintered samples, indicating further structural gains through sintering.

3.2. Paper characteristics versus sinter temperature

Sinter temperatures of 360–420 °C were chosen as the range in which to conduct this part of the study. A small amount of the PTFE evaporates during sintering (from about 8 wt.% at 360 °C to 10 wt.% at 420 °C, see Fig. 2), but in comparison with the wide range of PTFE wt.% examined in this study (0–200%), the deviation of the PTFE wt.% can be neglected. In order to exclude that the weight loss is due to evaporation of remainders of liquid components from the Hostaflon suspension several samples were dried at 100 °C for 1 h after being dried at room temperature. There was no detectable change in weight.

No conclusive results have been obtained concerning the influence of sinter temperature on sample hydrophobicity. The results fluctuated randomly when plotted against sinter

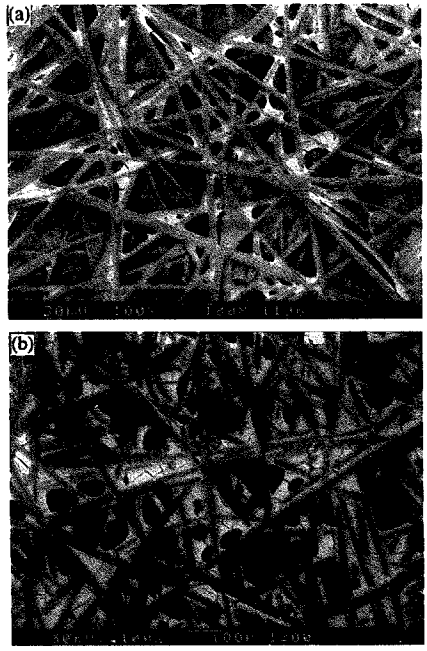

Fig. 9. SEM pictures of carbon paper before sintering: (a) with 25 wt.%, and (b) 60 wt.% PTFE loading. (Fig. 9 (b) is identical with Fig. 4 (a)).

temperature and there was no reproducibility with the equipment used.

Regarding the pressure drop of gas flowing through the paper plane, data indicated that the pressure drop decreases with increasing sinter temperatures (Fig. 3). This was attributed to higher sinter temperatures causing available PTFE to coat paper fibres more thoroughly, moving PTFE from spaces between fibres to the fibres themselves, thus allowing easier gas flow through those spaces. It was found, that the higher is the PFTE loading, the greater is the difference in the pressure drop due to the different sintering temperatures. Fig. 4 shows SEM pictures of the same sample (60% PTFE) before and after sintering. Before sintering there are many areas in which the PTFE suspension forms a closed film between the fibres and which only have small cracks. After sintering most of these areas have vanished. Only in areas with a very high PTFE accumulation the space between the fibres is still closed.

Through-plane electrical conductivity was clearly negatively affected by higher sinter temperatures (Fig. 5), probably due to better coating (and therefore better insulating) of paper fibres with PTFE. The fact that some unsintered samples are less conductive than some sintered samples at higher pressure range, we attribute this to the instrumental limitations at these very low resistance levels.

Finally, pressure drop measurements taken after the conductivity experiments show a mild dependence on sinter temperature (higher temperatures yielding lower pressure drops) (Fig. 6). But the data are most useful in conveying the importance of sintering a PTFE-coated sample: by being pressed between electrodes, the PTFE contained in unsintered samples forms a film which hinders extremely gas penetration in comparison with sintered samples, which would lead to a significant reduction in fuel throughput in an actual fuel cell.

3.3. Paper characteristics versus PTFE loading

PTFE amounts ranging from 0 to 190% of a sample's untreated weight were used for this part of the study. This great range was chosen in order to distinguish clearly the different effects and to be out of the range where systematical errors are greater than the effect. The typical commercially available PTFE-treated carbon papers contain about 100–120 wt.% PTFE. Samples showed a clear tendency towards increased hydrophobicity with increasing PTFE wt.% (Fig. 7); this result was expected since PTFE is a very hydrophobic material.

With respect to the pressure drop of oxygen flowing through the sample plane, the pressure drop increases with increasing PTFE wt.% (Fig. 8). Again, this was expected; increasing the PTFE content fills a greater number of the spaces between individual carbon fibres in the paper, and therefore reduces the gas flow through the plane.

This assumption is supported by SEM pictures. Fig. 9(a) shows a paper with 25 wt.% PTFE loading, Fig. 9(b) a paper with 60 wt.% loading. The different amounts of closed pores can clearly be seen.

Electrical conductivity decreased with increasing PTFE wt.%, as higher amounts of PTFE coat and insulate the paper fibres more completely (Fig. 10); attempts to lightly sand

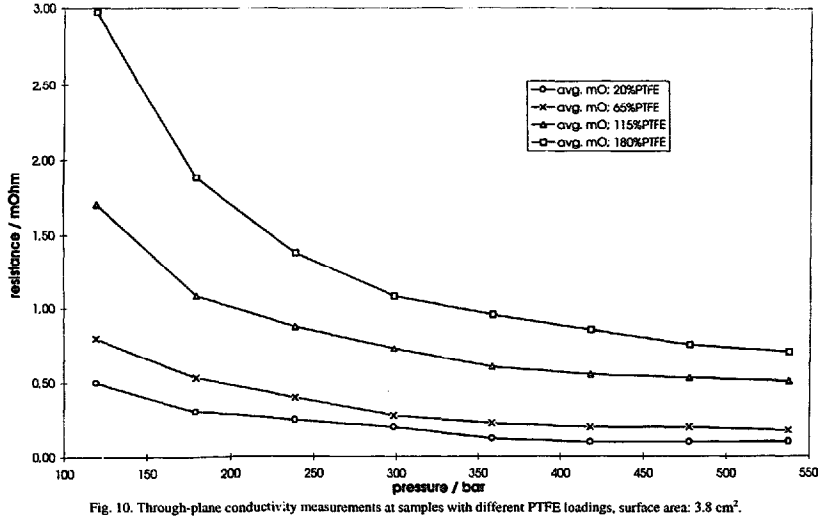

Fig. 10. Through-plane conductivity measurements at samples with different PTFE loadings, surface area: 3.8 cm^2.

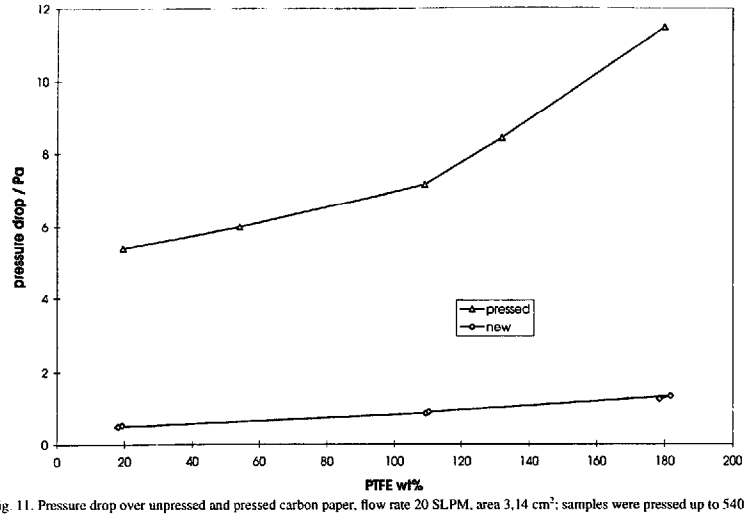

Fig. 11. Pressure drop over unpressed and pressed carbon paper, flow rate 20 SLPM, area 3,14 cm^2; samples were pressed up to 540 bar.

the sample surface proved ineffective in increasing its conductive properties and applicable readings were not able to be taken for untreated samples because without the binding presence of PTFE, samples disintegrated into carbon dust during the experiment.

Finally, a dramatic difference was seen between newly produced samples and samples which had already been pressed between electrodes for electrical conductivity measurement in terms of their abilities to allow gas to flow through their planes: as can be seen in Fig. 11, pressure drop measurements are much higher for samples which have experienced compression between electrodes, which forces PTFE to flatten out and fill spaces between paper fibres, making the paper more like a thin film and therefore more resistant to gas flow through its plane. This is important with regard to the carbon papers used in fuel cells where the paper is also exposed to pressure in order to minimize the contact resistance.

4. Conclusions

This study is meant to elucidate the principal influences of different PTFE loadings and sintering times on carbon papers when used as backing in polymer electrolyte fuel cells. We are aware of the fact that the quantity of the reported effects will differ from paper to paper due to different porosity and different carbon fibre sizes. But the general trend should be similar in all cases and the performed experiments give an idea of the magnitude of the effects. Perhaps most clear in this study is the tradeoff between hydrophobicity and conductivity. Higher PTFE content, higher sinter temperatures during sample preparation, or a combination of the two led to better hydrophobicity. But in all of these cases, electrical conductivity suffers; PTFE content and sinter temperature both correlate negatively with conductivity — that is, an increase in either will lead to poorer conductivity. For the third property observed — pressure drop of gas flowing through the paper plane, indicative of diffusion properties of the carbon paper — PTFE content and sinter temperature correlate oppositely. Diffusion correlates positively with sinter temperature, but negatively with PTFE content. So diffusion is caught directly in the middle of the tradeoff between hydrophobicity and conductivity. No recommendations can be made by this study as to which of these tradeoffs is more important in achieving an optimal paper for use in a fuel cell. This must be done by an individual optimization analysis with special regard to the existing fuel cell hardware, the gas distribution structure, the properties of the catalytic layer and especially the used carbon paper.

Acknowledgements

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