



## Low and high temperature storage characteristics of membrane electrode assemblies for direct methanol fuel cells

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### ABSTRACT

This paper investigates changes in the performance of membrane electrode assemblies (MEAs) of Direct Methanol Fuel Cells (DMFC) that are caused by undergoing storage at  $-10^{\circ}\text{C}$  and  $60^{\circ}\text{C}$  under different experimental conditions. Storage at  $60^{\circ}\text{C}$  exhibited negative effects on an MEA's performance only when storing the MEA at a 4 M  $\text{CH}_3\text{OH}$  solution. Here, application of a reverse current for 10 s was found to reinstall the original performance. The effect of storage at  $-10^{\circ}\text{C}$  on an MEA's performance strongly depends upon the MEA's properties. MEAs are grouped into three different categories with regard to their suitability for low temperature storage: not affected, temporarily affected, irreversibly affected. The temporarily affected MEAs could be instantly and completely reactivated by a reverse current. Changes in the MEA properties that had been caused by being stored at  $-10^{\circ}\text{C}$  were investigated for two MEAs using electrochemical methods, scanning electron microscopy and porosity measurements. The following MEA materials and manufacturing methods had been found to be principally suitable to build MEAs tolerant to storage at  $-10^{\circ}\text{C}$ : the manufacturing methods CCM (catalyst coated on the membrane) and CCS (catalyst coated on the substrate), several hydrocarbon membranes, high Pt and Pt-Ru catalyst loadings. By carefully selecting the proper MEA material, MEAs with tolerance towards low and high storage temperatures can be designed.

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### 1. Introduction

The DMFC is seen as a promising power source for portable electronic applications. These devices have to be able to withstand extreme environmental conditions such as shocks, and changes in the humidity and temperature. Of special concern is the stable operability of fuel cell systems after being stored at subzero temperatures or above  $40^{\circ}\text{C}$ . On the system level, evaporation of water at high temperatures or freezing of the balance of plant can lead to problems in the water and temperature management, to damage of the system components, and in extreme cases, to non-operability or damage of the total system. The membrane electrode assembly (MEA) may also be affected as a result of the damage or deactivation of catalyst, the damage of the membrane or the diffusion layer or due to delamination. To the authors' knowledge, no studies on the effect of storage on the performance of MEAs in

DMFCs have been conducted. There has been some research carried out on the low temperature storage and the low temperature operation of polymer electrolyte membrane fuel cells (PEMFC) [1–5], but not on their high temperature storage. Single studies investigated the effect of methanol concentrations on the sub-zero storage of Nafion<sup>®</sup> membranes [6] and on freezing water in hydrocarbon membrane materials [7]. The Nafion<sup>®</sup> membrane showed a high amount of freezing water which could damage the membrane at temperatures below  $-10^{\circ}\text{C}$  [6]; after storage at  $-10^{\circ}\text{C}$ , however, no change in the conductivity of the membrane material had been identified. In contrast to Nafion<sup>®</sup>, hydrocarbon membranes are less likely to be affected by low temperature storage due to the presence of a very low amount of freezing water in the membrane. The large percentage of non-freezing water in the polymers was attributed to the membrane morphology and to the strong interaction between water and the sulphonic acid groups [7]. Studies on the catalyst layer of PEMFCs showed that subzero temperatures can damage the cathode catalyst: after low temperature storage, pore size had increased and the electroactive area had decreased [4]. Ge and Wang [3] highlighted that the freezing point depression inside the catalyst layer is less than  $1^{\circ}\text{C}$ . Hence, the freezing of the product water would have taken place in the catalyst layer

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**Table 1**  
The material and manufacturing properties of the evaluated MEAs.

| MEA       | Type of membrane    | Manufacturing method | Cathode catalyst, loading             | Anode catalyst, loading                 | Storage test at $-10^{\circ}\text{C}$ |
|-----------|---------------------|----------------------|---------------------------------------|---|---------------------------------------|
| HC-CCM-1  | HC                  | CCM                  | Pt-black, $\geq 4 \text{ mg cm}^{-2}$ | PtRu black, $\geq 5 \text{ mg cm}^{-2}$ | Pass                                  |
| Naf-CCS-2 | Nafion <sup>®</sup> | CCS                  | Pt-black, $\geq 4 \text{ mg cm}^{-2}$ | PtRu/C, $\geq 5 \text{ mg cm}^{-2}$     | Fail                                  |
| HC-CCS-3  | HC                  | CCS                  | Pt-black, $\geq 4 \text{ mg cm}^{-2}$ | PtRu/C, $\geq 5 \text{ mg cm}^{-2}$     | Pass                                  |
| HC-CCM-4  | HC                  | CCM                  | Pt-black, $\geq 4 \text{ mg cm}^{-2}$ | PtRu black, $\geq 5 \text{ mg cm}^{-2}$ | Pass                                  |
| HC-CCM-5  | HC                  | CCM                  | Pt-black, $\geq 4 \text{ mg cm}^{-2}$ | PtRu black, $\geq 5 \text{ mg cm}^{-2}$ | Pass                                  |
| HC-CCM-6  | HC                  | CCM                  | Pt/C, $\leq 2 \text{ mg cm}^{-2}$     | PtRu black, $\geq 5 \text{ mg cm}^{-2}$ | Fail                                  |
| HC-CCM-7  | HC                  | CCM                  | Pt/C, $\leq 2 \text{ mg cm}^{-2}$     | PtRu/C, $\geq 5 \text{ mg cm}^{-2}$     | Fail                                  |

CCM: Catalyst coated membrane.

CCS: Catalyst coated substrate.

during its low temperature storage. Volume expansion as a result of the freezing could have caused the observed change in the pore size and the active area. Low temperature storage was also found to damage the interface between the membrane and the catalyst. Interfacial problems like partial delamination and an increase in the Ohmic resistance had been observed [4,5]. Finally, studies on the effect of freezing within the gas diffusion layer (GDL) had also been conducted [5]; while the structure and morphology of the GDL remained the same, some minor changes in the backing layer coating Teflon<sup>®</sup> and in the binder structure had been observed after being operated at  $-5^{\circ}\text{C}$ .

A frequently used method to prevent freezing and the damage of the PEMFC due to the freezing of product water is gas purging of the cathode side prior to low temperature storage [2,4]. Purging of gas through the cathode removes product water from the cathode and from the membrane. This method was found to significantly reduce the performance decrease caused by low temperature storage.

The DMFC MEA has a similar set-up as the PEMFC. Catalyst layer structure, the use of a GDL and the method of the fabrication of the MEA are mostly identical to that of the PEMFC. As the PEMFC was found to be sensitive to low temperature storage, a high risk of performance decrease can also be expected for the DMFC MEA. In contrast to the PEMFC, gas purging of the DMFC MEAs is not a viable option. The anode and the membrane are completely hydrated, while the cathode also holds a significant amount of water due to crossover and cathodic water production. Furthermore, a DMFC system infrastructure is designed for anode liquid transport, not gas transport. A possible option that is available to prevent the liquid from freezing within the DMFC is the application of a high methanol concentration to the MEA in order to decrease the freezing point of the solution inside the MEA. A 4 M  $\text{CH}_3\text{OH}$  solution has a freezing point of below  $-10^{\circ}\text{C}$ . Hence, its use should prevent the freezing of the anode catalyst and the GDL up to this temperature. A further decrease in the freezing point can be reached by increasing the  $\text{CH}_3\text{OH}$  concentration to an even higher concentration. It should be noted, however, that high concentrations can also negatively affect the performance of an MEA due to the occurrence of catalyst poisoning.

This work focuses on analysing the effects of sub-zero and high temperature storage on the performance of MEAs for DMFCs. Since no data is available for any such experiment for DMFCs, and in addition DMFC MEAs offered by suppliers employ significantly different material properties, this study is designed to give a first, general overview over which problems could be expected after low or high temperature storage of MEAs employing different materials. In a first step, two MEAs, one containing a Nafion<sup>®</sup> membrane and one containing a hydrocarbon membrane, were tested both for low and high temperature storage. Since low temperature storage had a significant effect on MEA performance, studies on further MEAs were used to investigate more in-depth the effect of sub-zero temperature storage on MEAs for DMFC. In the second step, therefore, low temperature storage experiments were conducted with five

MEAs made of different MEA materials. MEA properties were subsequently correlated to MEA performance, and further measurements such as impedance spectroscopy, cell and anode polarisation, scanning electron microscopy and porosity measurements complete the analysis.

## 2. Experimental set-up and methods

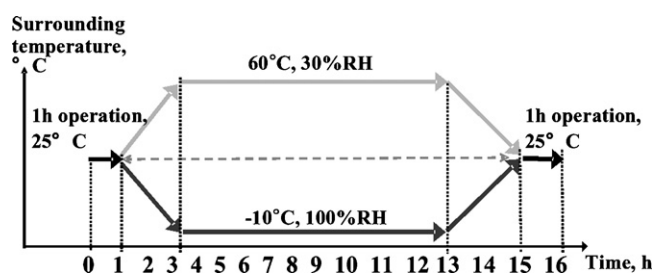
### 2.1. Membrane electrode assemblies (MEA)

MEAs from various manufacturers were evaluated for their suitability for low and high temperature storage. They differed in the materials used for the membrane, the diffusion layers and the catalyst layers as well as in the manufacturing process by which they had been made. Those properties of the MEAs which are open for publication are listed in Table 1. Two manufacturing processes were used to prepare the MEA, the catalyst-coated membrane (CCM) or the catalyst-coated substrate (CCS) process. Six MEAs were prepared using different kinds of hydrocarbon membranes (HC) and one MEA was prepared using a Nafion<sup>®</sup> membrane. The cathode catalyst layer mostly contained Pt black as the catalyst with a loading of  $4 \text{ mg cm}^{-2}$  and above; the MEAs HC-CCM-6 and HC-CCM-7 had a significantly lower Pt loading and were carbon-supported. The anode catalyst of all MEAs consisted of supported or unsupported Pt-Ru with a loading of  $\geq 5 \text{ mg cm}^{-2}$ . Different kinds of diffusion layers were applied; they varied in thickness, polytetrafluoroethylene (PTFE) content, aerial weight and the type of microporous layer used.

All MEAs had an active area of  $25 \text{ cm}^2$  and were assembled in single cells with triple serpentine channels on the anode and the cathode. The assembly torque applied was 7 N m.

### 2.2. Low and high temperature storage procedure

The procedure applied for the low and high temperature storage test is shown in Fig. 1. Before and after low and high temperature storage, the performance of each of the MEAs was evaluated for 1 h at a constant potential of 0.45 V with a WFCTS (WonATech Co., Ltd., Korea). MEAs using a HC membrane were evaluated using a



**Fig. 1.** Procedure for storing MEAs at extreme temperatures including their performance evaluation.

fuel stoichiometry of 2.5, at a cell temperature of 60 °C and with the application of a 1 M CH<sub>3</sub>OH solution; the MEA containing a Nafion® membrane was evaluated at 0.55 M to reduce methanol crossover. After the initial evaluation, the MEAs were gradually cooled or heated to the desired storage temperature over a period of 2 h to prevent shock-freezing and other effects that could result from rapid temperature changes. During this process, the target humidity was adjusted. The storage temperature and the humidity were maintained for 10 h. Subsequently the MEA was gradually cooled or heated to room temperature over a 2 h period at a relative humidity of 30%, and the final evaluation, 1 h of operation at 0.45 V, was then conducted. Reactivation methods as presented in Section 2.4 were applied when the performance decrease after storage was higher than 10%. If a performance drop exceeded this limit, the test was defined as having failed.

The storage conditions of the MEA simulated the state of a stack that had been assembled in a DMFC system: anode outlet and inlet of the single cell DMFC were closed, while the cathode outlet and inlet diameter of the single cell were reduced to 4 mm.

When conducting storage experiments with CH<sub>3</sub>OH concentrations higher than 1 M, the anode side of the single cell had been rinsed with the higher concentrated solution for 10 min at 10 ml min<sup>-1</sup> prior to storage and with a 1 M (or 0.55 M for Naf-CCS-2) methanol solution directly after storage.

### 2.3. Additional MEA characterisation

Cell polarisation curves were recorded at 50 °C, 60 °C and 70 °C using 1 M of CH<sub>3</sub>OH and a fuel stoichiometry of 3. A minimum flow rate was adjusted when operating the cell at low current densities; it was equivalent to a fluid stoichiometry of 3 at 100 mA cm<sup>-2</sup>. The cell polarisation curves were recorded in the galvanostatic mode with a step size of 100 mA being applied every 10 s.

Impedance spectra were recorded at 70 °C, 1 M CH<sub>3</sub>OH, 250 mA cm<sup>-2</sup> and a fluid stoichiometry of 3 with a Solartron equipment (SI1287, 1255B) with booster (1290) in galvanostatic mode. An amplitude of 250 mA/cycle and a frequency range from 10,000 Hz to 0.1 Hz was applied. The same equipment was used to record anode polarisation curves of the MEAs. The operating conditions for the anode polarisation methods were 3 ml min<sup>-1</sup> of 1 M CH<sub>3</sub>OH on the anode, 200 ml min<sup>-1</sup> of H<sub>2</sub> on the cathode and 10 mA s<sup>-1</sup> as scan rate. The supply of such amounts of H<sub>2</sub> on the cathode enables to use the cathode as a reference electrode.

SEM pictures of catalyst layers and GDLs along with a MEA cross-section were achieved with a FE-SEM S-4700 or a FE-SEM S-4500. Adsorption measurements of complete MEAs including GDL were recorded using an ASAP 2020 instrument (Micromeritics) with the adsorption of nitrogen taking place at 77 K. The adsorption isotherms were used to calculate the pore-size distribution according to the Barrett–Joyner–Halenda (BJH) method.

### 2.4. Reactivation methods applied

The reactivation methods investigated the application of a reverse current, anode or cathode side air purging, the constant

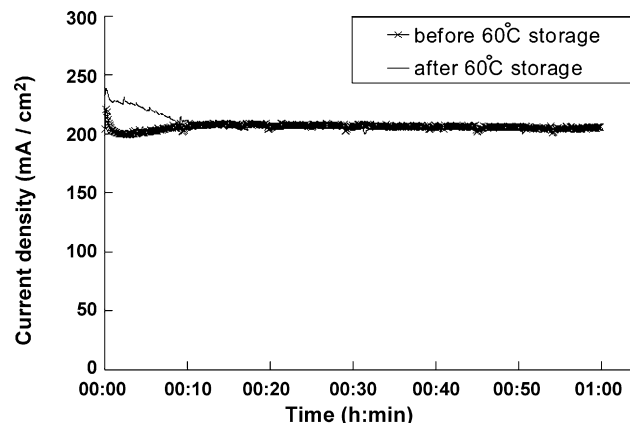


Fig. 2. Performance of HC-CCM-1 at 0.45 V before and after being stored at 60 °C.

operation of the cell at high cathode stoichiometry, and voltage cycling.

While reactivating by using a reverse current, a negative current of  $-250 \text{ mA cm}^{-2}$  was applied to the MEA for 10 s. Voltages of up to 1.7 V were detected during this time period. Subsequently, for several seconds, open circuit voltages (OCV) of ca. 1 V were observed; they are close to the OCV of PEMFCs and may indicate presence of H<sub>2</sub> at the anode catalyst layer.

## 3. Results and discussion

### 3.1. Storage at 60 °C

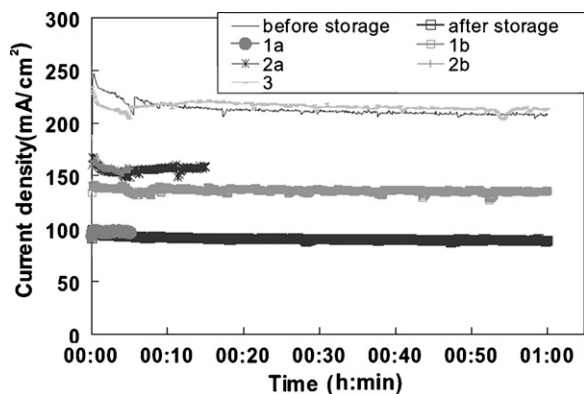
#### 3.1.1. Performance evaluation

Two MEAs were tested for storage at 60 °C under various operating and storage conditions. The expected negative effects of such storage conditions include the deactivation of the cathode due to the evaporation of water and the poisoning of the catalyst due to the long-term, high temperature exposure of the MEA to unreacted methanol. Table 2 lists the performance changes of the MEAs after being stored at 60 °C. Both MEAs showed negligible performance decreases when being operated in the presence of 0.55 or 1 M CH<sub>3</sub>OH concentrations. Fig. 2 illustrates this for the HC-CCM-1 MEA: after a short time span, performance before and after storage was identical. Similar results were obtained when conducting the storage measurements with the cathode inlet and outlet being closed, which had been carried out in order to alter the evaporation rate. In all four measurements, the MEAs showed no change in their performance after high temperature storage. Hence, neither the anode's nor the cathode's performance of these MEAs were affected by high temperature storage. This leads to the conclusion that poisoning of the catalyst did not take place and that the evaporation rate of water from the cathode during the 10 h test was too low to cause a significant amount of drying out and the deactivation of the cathode catalyst.

High CH<sub>3</sub>OH concentrations are mostly applied only to passive DMFCs. To check if poisoning can occur at such concentrations, the

**Table 2**  
Change in the electrochemical performance at 0.45 V of two MEAs after being stored at 60 °C.

| MEA       | Storage test at 60 °C (standard conditions) |                  | Storage test at 60 °C (closed cathode inlet and outlet) |                  | Storage test at 60 °C (storage at 4 M CH <sub>3</sub> OH) |                  |
|-----------|---|------------------|---|------------------|---|------------------|
|           | Reactivation method                         | Performance drop | Reactivation method                                     | Performance drop | Reactivation method                                       | Performance drop |
| HC-CCM-1  | –   | 1%               | –   | 5%               | –   | 57%              |
|           |   |                  |   |                  | Reverse current   | 0%               |
| Naf-CCS-2 | –   | 3%               | –   | 3%               | –   | 1%               |



**Fig. 3.** Performance of HC-CCM-1 before being stored at 60 °C and in a 4 M CH<sub>3</sub>OH solution on the anode, after storage and after various tests to reactivate the MEA: (1a) after air purging on the cathode; (1b) after high cathode stoichiometry and low anode stoichiometry; (2a) after voltage cycling between the OCV and 0.4 V, and the OCV and 0.3 V; (2b) after air purging on the anode; (3) after the application of a reverse current.

MEAs were stored at 60 °C and in the presence of a 4 M CH<sub>3</sub>OH solution on the anode side. In Table 2, it can be seen that the storage in a 4 M CH<sub>3</sub>OH solution did not cause any performance decrease for the Naf-CCS-2 MEA, but it did cause a significant performance decrease of 57% for the HC-CCM-1 MEA. HC-CCM-1 did not show any sign of recovery during the 1 h continuous operation as illustrated in Fig. 3; the new low performance level was stable. It remains to be tested in future more detailed studies, whether such performance decrease at high concentrations can also occur at ambient temperatures, and is hence, is an effect only of concentration. Since both MEAs reacted differently to storage in a high methanol concentration, it was concluded that the MEAs have specific material properties which possess different tolerance levels towards high CH<sub>3</sub>OH concentrations and high temperatures.

### 3.1.2. Evaluation of methods for recovering MEA performance

After HC-CCM-1 failed the storage test, several experimental tests were applied to analyse the cause of this MEA's performance drop and to reactivate the MEA.

Methods categorised into group 1 targeted the removal of excess liquid which could have blocked pores on the cathode side. Excess liquid can be caused by the crossover of the anode water and the oxidation of the crossover methanol. In test (1a), air purging had been applied for 10 min on the cathode side. As seen in Fig. 3, it was not possible to restore the performance of the HC-CCM-1. In the second test (1b), the MEA was operated at 0.45 V under a high cathode ( $\lambda = 4-5$ ) and a low anode ( $\lambda = 1.5-2$ ) stoichiometric reactant supply over the duration of 1 h. These conditions should decrease methanol crossover and increase the penetration of oxygen into the cathode. Hence, they are thought to further remove excess liquid from the cathode. After applying this method, the performance was partly recovered but it was still significantly lower than that observed before storage. Water flooding therefore, does not seem to be the major reason for the observed drop in the performance after being stored at 60 °C and in the presence of 4 M CH<sub>3</sub>OH.

Methods categorised into group 2 targeted the oxidation of strongly adsorbed species on the anode catalyst. Adsorbates on the anode catalyst which may not have been oxidised at a voltage of 0.45 V are more easily removed at lower voltages, which correspond to higher anode potentials. For this reason, 30 min voltage cycling between OCV and 0.4 V, and 30 min voltage cycling between OCV and 0.3 V were applied in test (2a). The voltage was kept at the given minimum level for 4 min. Subsequently, OCV was applied and

the voltage was gradually decreased again to the minimum. This procedure was repeated. As can be seen from Fig. 3, there was no significant improvement after voltage cycling. Although the exact anode potential is not known during these experiments, the anode potential corresponding to the applied voltage might have been insufficiently high to remove strongly adsorbed species such as CO, which is known to be oxidised at anode potentials above 0.4 V [8]. Direct oxidation of CO adsorbates on the anode by air bleeding was found to be beneficial in PEMFCs [9]. Hence, a similar approach to recover the DMFC by oxidising anode adsorbates was applied in test (2b). Instead of methanol, air was fed to the anode side for 10 min. However, as seen in Fig. 3, this treatment had no recovery effect on the DMFC.

Finally, the method categorised into group 3 targeted the reactivation of the anode catalyst by applying reducing conditions. Since the membrane of this MEA was said to be stable at 4 M, the failure of the conducted methods (1 and 2) in reactivating the MEA suggests that the presence of a high storage temperature at 4 M methanol caused either very strongly adsorbed methanol intermediates to generate or a change in the state of the anode catalyst, e.g. via oxidation. To check the effect of the reducing conditions on the anode, a reverse current of  $-250 \text{ mA cm}^{-2}$  was applied to the deactivated MEA for 10 s. Reverse current was previously found to be useful in restoring the performance of fuel cells [10,11]. During the application of a reverse current, electrons and protons are pumped into the anode. It is assumed that gaseous hydrogen is formed on the anode which removes adsorbates or that the anode catalyst is reduced due to the reverse current [11]. On the cathode side, oxidation occurs during application of the reverse current; this is considered to take place through the consumption of crossover methanol or by the electrolysis of water. The oxidation of crossover methanol on the cathode side takes place also during the normal operation of the MEA. Hence, methanol oxidation due to application of reverse current should not cause any changes in the cathode. In addition, the authors expect no instant beneficial effect to result from local water consumption. Short-time application of reverse current is, therefore, thought to mainly have an effect on the anode. After the application of the reverse current to the MEA, OCVs of about 0.9 V were observed for several seconds. Such high OCVs are close to that of PEMFCs and indicate the presence of H<sub>2</sub> at the anode catalyst layer. A subsequently conducted performance test showed that the MEA performance had completely recovered; performance was even slightly higher than before the storage test. The high temperature storage experiment which was run with 4 M of methanol was repeated while using reverse current as the first reactivation mode. The performance drop of the MEA observed after its storage was, again, completely and instantaneously recovered after the application of a reverse current. Hence, applying a reverse current reproducibly and completely recovers the performance of this MEA after its storage in 4 M CH<sub>3</sub>OH at 60 °C. A more detailed analysis of the processes exactly occurring at storage under such specific conditions and during reactivation should be subject of future detailed studies.

## 3.2. Storage at $-10$ °C

### 3.2.1. General performance evaluation and reactivation

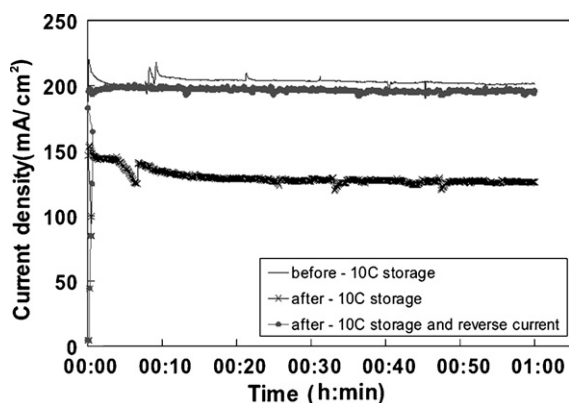
The MEAs HC-CCM-1 and Naf-CCS-2 were evaluated for their ability to be stored at  $-10$  °C under several storage conditions: as described in the procedure given in Section 2.2; cathode in- and outlet were kept closed; storage within the presence of 4 M methanol solutions on the anode. The results are summarised in Table 3. In all of the experiments, the performance decrease of the MEAs after storage was higher than 10%. As illustrated by the storage result for HC-CCM-1 in Fig. 4, the performance loss was

**Table 3**  
Change in the electrochemical performance at 0.45 V of two MEAs after being stored at  $-10^{\circ}\text{C}$ .

| MEA       | Storage test at $-10^{\circ}\text{C}$ (standard) |                  | Storage test at $-10^{\circ}\text{C}$ (closed cathode inlet and outlet) |                  | Storage test at $-10^{\circ}\text{C}$ (storage using 4 M $\text{CH}_3\text{OH}$ at anode) |                  | Storage test at $-10^{\circ}\text{C}$ (storage using 5 M $\text{CH}_3\text{OH}$ at anode) |                  |
|-----------|--|------------------|---|------------------|---|------------------|---|------------------|
|           | Reactivation method                              | Performance drop | Reactivation method   | Performance drop | Reactivation method   | Performance drop | Reactivation method   | Performance drop |
| HC-CCM-1  | –  | 36%              | –   | 42%              | –   | 18%              | –   | –                |
|           | Reverse current                                  | 3%               | Reverse current   | 0%               | Reverse current   | 4%               | –   | –                |
| Naf-CCS-2 | –  | 87%              | –   | 70%              | –   | 84%              | –   | 26%              |
|           | Reverse current                                  | 11%              | Reverse current   | 14%              | Reverse current   | 9%               | Reverse current   | 3%               |

stable. The MEAs showed performance decreases of more than 15% even when freezing of the anode side was prevented by the application of a 4 M  $\text{CH}_3\text{OH}$  solution to the anode previous to storage. The performance decrease of HC-CCM-1 after storage was less significant than at low concentrations, while Naf-CCS-2 showed similar performance losses of around 80% at both concentrations. The storage test of Naf-CCS-2 was repeated with a concentration of 5 M  $\text{CH}_3\text{OH}$  to check if possibly dilution of  $\text{CH}_3\text{OH}$  concentration, e.g. by diffusion of water through the membrane to the anode, lead to freezing of some parts of the anode at 4 M. Performance loss decreased significantly at 5 M, indicating that freezing might have occurred locally when applying 4 M. However, although performance improved when preventing freezing on the anode, this method is not sufficient to secure a performance decrease of less than 10% in both MEAs. The observed performance decrease may, therefore, either be caused by non-destructive changes in the state of the anode, or by problems outside the anode. The first case could have been a result of local dehydration or catalyst poisoning, as was observed during the previously discussed high temperature storage of HC-CCM-1 with 4 M  $\text{CH}_3\text{OH}$  on the anode (Section 3.1.2).

Subsequently, the method which was found to completely reactivate an MEA's performance after high temperature storage at 4 M  $\text{CH}_3\text{OH}$  (Section 3.1.2) was applied to the two MEAs stored at  $-10^{\circ}\text{C}$ : reversing of current for 10 s. Fig. 4 and Table 3 show that the application of a reverse current increases MEA performance up to similar levels observed before sub-zero storage. It is obvious that the performance drop of both MEAs was mainly of temporary nature. The regained performance was found to be stable. Since the application of a reverse current only has a major effect on the anode, as discussed in Section 3.1.2, the observed temporary performance drop is attributed to anode deactivation. Table 3 also shows that reactivating the Nafion<sup>®</sup>-based Naf-CCS-2 by the application of reverse current does not lead to full performance recovery, although the



**Fig. 4.** Performance of HC-CCM-1 at 0.45 V before and after being stored at  $-10^{\circ}\text{C}$ .

**Table 4**  
Change in the electrochemical performance at 0.45 V of further MEAs after being stored at  $-10^{\circ}\text{C}$ .

| MEA      | Storage test at $-10^{\circ}\text{C}$ (standard) |                  |
|----------|--|------------------|
|          | Reactivation method                              | Performance drop |
| HC-CCS-3 | –  | 5%               |
| HC-CCM-4 | –  | 5%               |
| HC-CCM-5 | –  | 6%               |
| HC-CCM-6 | –  | 54%              |
|          | Reverse current                                  | 45%              |
| HC-CCM-7 | –  | 48%              |
|          | Reverse current                                  | 35%              |

Nafion<sup>®</sup>-based Naf-CCS-2 does recover significantly after the application of reverse current. Only storage at concentrations higher than 4 M  $\text{CH}_3\text{OH}$ , which prevent freezing, results in acceptable performance losses of less than 10%. It is therefore concluded that Naf-CCS-2 is permanently damaged by freezing, while HC-CCM-1 is tolerant.

### 3.2.2. Categorising MEAs for suitability to be stored at low temperatures

The two MEAs HC-CCM-1 and Naf-CCS-2 differed in their tolerance to storage at  $-10^{\circ}\text{C}$ . In order to check if DMFC behaviour to storage at  $-10^{\circ}\text{C}$  could be generalised, five further MEAs (HC-CCS-3, HC-CCM-4, HC-CCM-5, HC-CCM-6, HC-CCM-7) were subjected to the storage procedure. Their properties are provided in Table 1. Table 4 lists the performance changes of these MEAs after being stored at  $-10^{\circ}\text{C}$ , as well as their performance after subsequent reactivation. While three MEAs (HC-CCS-3, HC-CCM-4, and HC-CCM-5) showed a negligible performance decrease, two MEAs (HC-CCM-6 and HC-CCM-7) had permanent performance losses of above 10%, which were not recoverable through the application of a reverse current. The comparison of the test results of all of the investigated MEAs shows that the MEA response to sub-zero storage cannot be generalised. This indicates that the ability of a MEA to withstand  $-10^{\circ}\text{C}$  storage strongly depends upon its material properties or the manufacturing procedures associated with its production. MEAs were categorised into three classes: those possessing a largely unaffected performance after storage at  $-10^{\circ}\text{C}$ ; those possessing a performance that is temporarily affected; those possessing a performance that is irreversibly affected. Reactivation methods which proved to be effective in the prevention of performance drops in the MEAs include the application of a reverse current on temporarily affected MEAs, and the combination of reverse current and the usage of anode  $\text{CH}_3\text{OH}$  concentrations of above 4 M during the storage in order to prevent freezing. Due to the short duration of 10 s to reactivate the MEA with reverse current, the first method is seen as being basically suitable for the implementation in real systems.

### 3.2.3. Correlation between MEA properties and tolerance to storage at $-10^{\circ}\text{C}$

MEA material and manufacturing properties that had led to the failure of the MEAs in the storage test will now be further discussed. The properties evaluated and the test results are shown in Table 1. Evaluation of further MEA properties such as catalyst layer thickness or porosity, catalyst particle size, the type of microporous layer (MPL) and gas diffusion layer (GDL) could not be conducted due to the absence of material data.

Several MEAs using hydrocarbon membranes were found to be suitable for low temperature storage. This was exemplified by two MEAs, HC-CCM-4 and HC-CCM-5, which passed the storage test at  $-10^{\circ}\text{C}$  without reactivation. They are from the same manufacturer and differed only in the type of hydrocarbon membrane they were made of. The comparison of the MEAs HC-CCS-3 and Naf-CCS-2, both from the same manufacturer, revealed that the MEA containing a hydrocarbon MEA (HC-CCS-3) had passed the storage test, while the same MEA containing Nafion<sup>®</sup> as membrane material (Naf-CCS-2) had failed. Hydrocarbon membrane material is therefore seen as being principally more suitable than Nafion<sup>®</sup> for the building of MEAs that are to be subjected to storage temperatures as low as  $-10^{\circ}\text{C}$ .

The MEA manufacturing procedure was found to have no significant influence on the MEAs' ability to withstand sub-zero temperature storage. HC-CCS-3 had been produced using the CCS manufacturing procedure, and it showed no performance decrease. Also, several MEAs using the CCM process (HC-CCM-1, HC-CCM-4, HC-CCM5) passed the storage test. Both manufacturing procedures should, therefore, be suitable for the production of MEAs which can tolerate storage at  $-10^{\circ}\text{C}$ .

All of the investigated MEAs made use of high anode catalyst loadings of Pt-Ru  $\geq 5\text{ mg cm}^{-2}$ . The anode material data as given in Table 1 differs significantly only in regards of the carbon support. MEAs with an anode carbon support (HC-CCS-3) and without an anode carbon support (HC-CCM-4, HC-CCM-5) are both tolerant to storage at subzero temperatures. Hence, it is suggested that the presence of a support of the anode catalyst layer does not have a critical influence on a MEA's ability to tolerate storage at temperatures of up to  $-10^{\circ}\text{C}$ .

Finally, an analysis of the cathode's influence on the tolerance to sub-zero temperature storage is discussed. The two MEAs HC-CCM-6 and HC-CCM-7 failed the storage test and could not be sufficiently reactivated. These two MEAs mainly differed from the MEAs that are tolerant to freezing in loading and support of the cathode catalyst. HC-CCM-6 and HC-CCM-7 use significantly less cathode Pt loading than all other MEAs and their catalyst is carbon supported, while that of the others is unsupported. Reverse current application is thought to generally reactivate the anode. It had a positive impact on the temporarily affected MEAs. The fact that HC-CCM-6 and HC-CCM-7 were the only MEAs which were not significantly reactivated by the application of a reverse current and also the only ones with low cathode catalyst loading suggests a correlation between low loading and permanent performance loss.

### 3.2.4. Analysis of MEAs that tolerate storage at $-10^{\circ}\text{C}$

To substantiate the above given MEA correlation between material and tolerance to storage at  $-10^{\circ}\text{C}$ , several MEAs were selected for further in-depth investigations, such as scanning electron microscopy (SEM), pore size distribution measurements and electrochemical measurements. The MEAs were compared to the MEAs of the same type which were not subjected to storage.

Fig. 5 shows SEM cross-sections of MEAs of type HC-CCM-4. The performance of this MEA type was unaffected by low temperature storage. The SEM picture of the stored MEA (Fig. 5, right) did not exhibit any visual damages after having undergone storage five

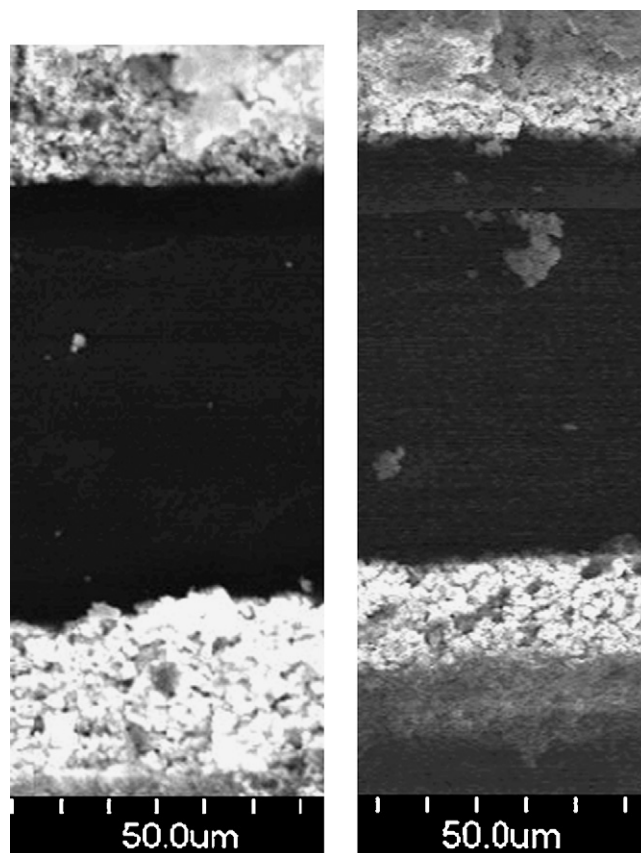


Fig. 5. SEM cross-section of two MEAs of the type HC-CCM-4: left = no storage; right = after  $5\times$  storage at  $-10^{\circ}\text{C}$ . From top to bottom: cathode, membrane, anode.

times. There was no obvious change in the electrode or the membrane structure between the stored and not stored MEA (Fig. 5, left) nor did delamination occur at the interface between the membrane and the catalyst. However, there were visible differences in the pore size distribution of the MEA: Fig. 6 shows a significant reduction of micropores with size between 2 and 5 nm for the stored MEA, as well as small changes in pore volume for pore sizes between 5 and 80 nm. Both ranges of pore size are found in the catalyst layers: Reshetyenko et al. reported pore sizes of 5–100 nm [12] while Mao et al. found pore sizes between 2 and 20 nm [13]; GDL and MPL [14,15] have significantly larger pore sizes in the range of  $\mu\text{m}$ , while the membrane pores tend to be smaller, e.g. around 1 nm for Nafion 117<sup>®</sup> [16].

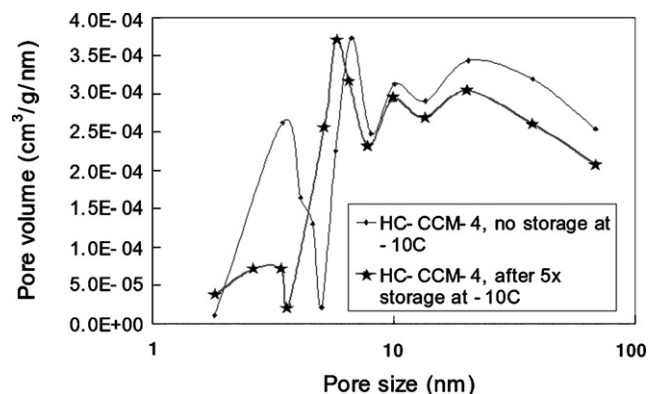
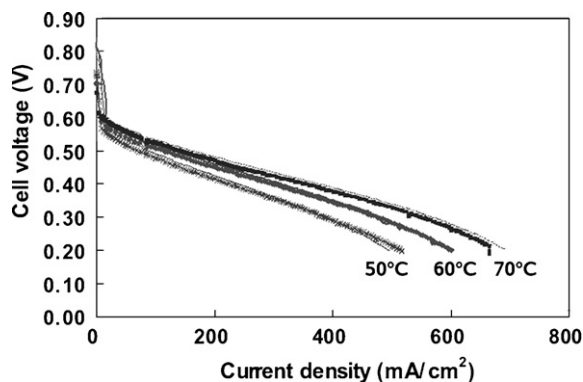


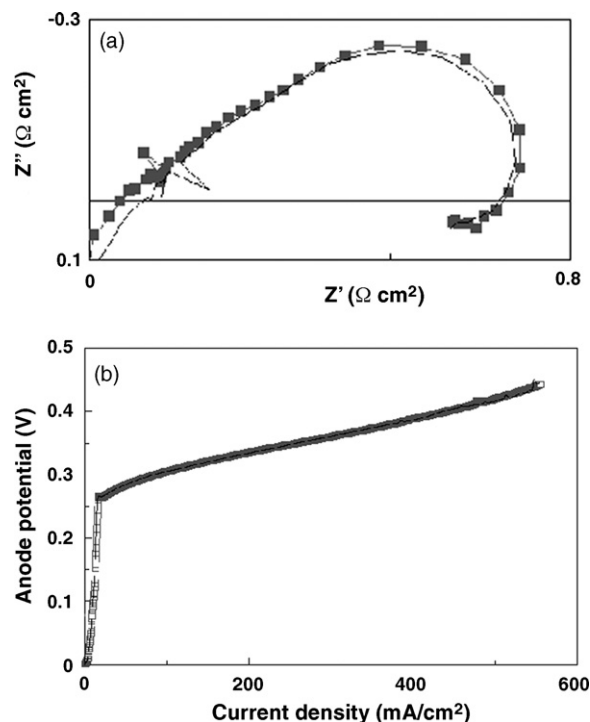
Fig. 6. Pore size distribution of MEA HC-CCM-4 obtained from the adsorption branch of nitrogen adsorption isotherms using the Barrett-Joyner-Halenda method.



**Fig. 7.** Cell polarisation curves of HC-CCM-1 at 50°C, 60°C and 70°C before and after conducting  $-10^{\circ}\text{C}$  storage experiments. Lines: before storage; symbols: after storage.

The significant decrease in pore volume for pores with size 2–5 nm did not cause a change in the electrochemical performance which was evaluated by conducting impedance measurements, anode polarisation measurements and cell polarisation measurements at various temperatures. The results suggest that the damaged pores of sizes between 2 and 5 nm were not active for oxidation or reduction in this MEA. The inactivity could be either caused by the absence of a three-phase-boundary in these pores, or by a low reactant mass transfer inside the small pores of the catalyst layer. Low mass transfer prevents sufficient supply of reactants to the reaction centres located inside these pores and causes therefore low reaction rates.

In addition to the MEA unaffected by storage at  $-10^{\circ}\text{C}$ , HC-CCM-4, an MEA which was affected by low temperature storage, but which was completely reactivated using a reverse current (HC-CCM-1) was investigated. Cell polarisation curves at different temperatures (Fig. 7) confirm that the MEA had the same performance before and after five consecutive sub-zero temperature storage tests: the curves before and after storage are largely overlapping. The charge transfer regime of the electrochemical impedance spectra – observable at lower frequencies – and the anode polarisation data (both Fig. 8) further show that the anode performance is unchanged. Since total polarisation and anode polarisation curves which were recorded after storage are identical to those recorded before  $5\times$  storage, cathode performance and membrane behaviour are also largely unaffected by low temperature storage and application of reverse current. It can be concluded that MEAs such as HC-CCM-4 and HC-CCM-1, which are not or only temporarily

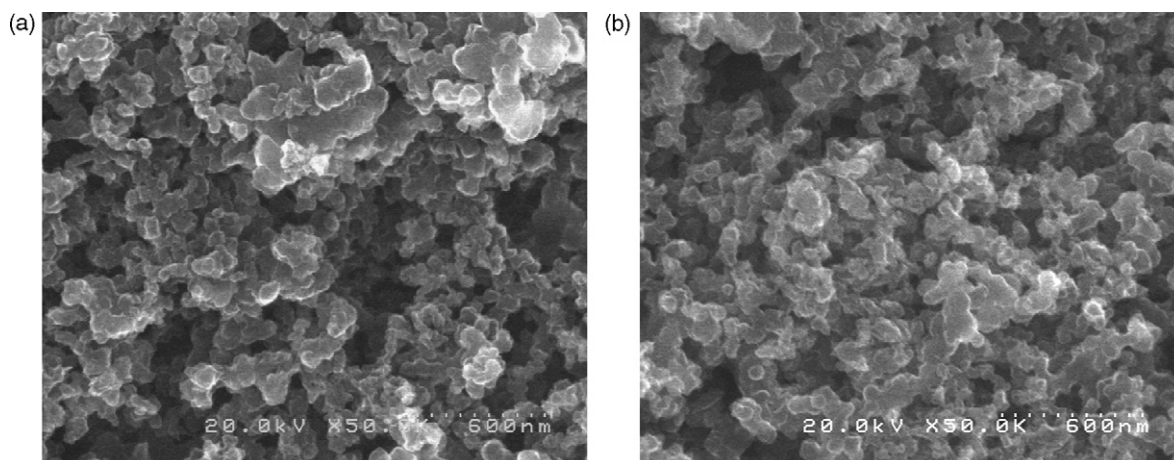


**Fig. 8.** Impedance spectra (a) and anode polarisation (b) of HC-CCM-1 at  $60^{\circ}\text{C}$  before and after conducting  $-10^{\circ}\text{C}$  storage experiments. Lines: before storage; symbols: after  $5\times$  storage.

affected by storage at  $-10^{\circ}\text{C}$ , display no substantial changes in their electrochemical properties and can, therefore, be seen as being suitable for low temperature storage. Hence, DMFC systems employing such freeze-tolerant MEAs may be stored several times without the taking into account of any special measures in order for the MEA to endure temperatures around  $-10^{\circ}\text{C}$ .

### 3.2.5. Analysis of an MEA not tolerant to storage at $-10^{\circ}\text{C}$

An MEA irreversibly affected by low temperature storage, HC-CCM-6, was analysed using SEM, further electrochemical characterisations and pore size distribution measurements, in order to locate changes in the performance of this MEA. Material comparison in Section 3.2.3 suggested that the observed performance loss of HC-CCM-6 was related to its low cathode loading. Both, the MEA stored  $5\times$  at  $-10^{\circ}\text{C}$ , as well as the MEA used under nor-



**Fig. 9.** SEM picture of the cathode of two MEAs of type HC-CCM-6: (a) no storage; (b) after  $5\times$  storage at  $-10^{\circ}\text{C}$ .

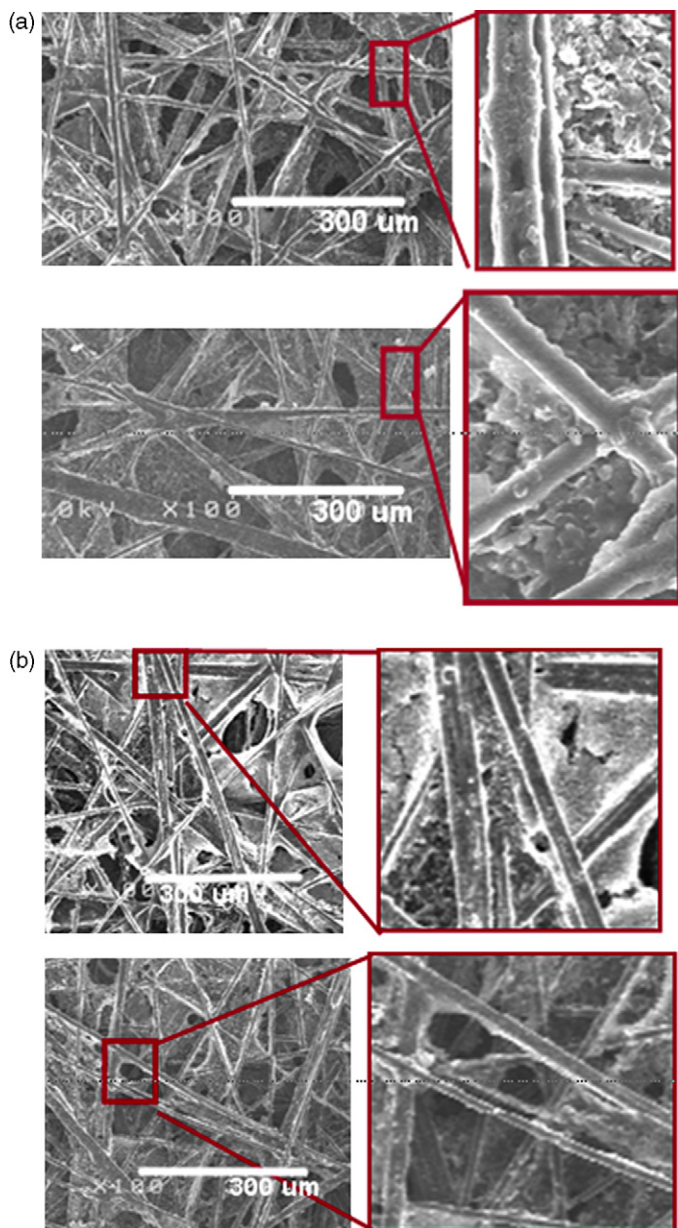


Fig. 10. SEM pictures of the anode GDL (a) and the cathode GDL (b) of MEAs of type HC-CCM-6: top = no storage; bottom = after  $5 \times -10^\circ\text{C}$  storage.

mal operating and storage conditions, showed after disassembly strong delamination of the catalyst from the membrane. Therefore, SEM cross-sectional picture for these MEAs could not be recorded. Instead, SEM pictures were separately recorded for the membrane, the anode, the cathode (Fig. 9) and the anode and the cathode GDL (both Fig. 10). The membrane and anode SEM pictures did not show significant changes and are not presented here. Also, SEM pictures of the cathode of both MEAs did not indicate significant changes as a result of the sub-zero temperature storage (Fig. 9). However, the pore size distribution of the total MEA, HC-CCM-6, in Fig. 11 shows that there were indeed significant morphological changes in the MEA on the nanometre scale: the MEA exposed to sub-zero temperatures displayed an alteration in the pores having a diameter of between 1 and 5 nm, as well as a strong decrease in the total pore volume for those pores having diameters between 5 and 20 nm. The changes in the pores possessing a diameter of below 5 nm did not necessarily affect the MEA performance, as was shown above in the

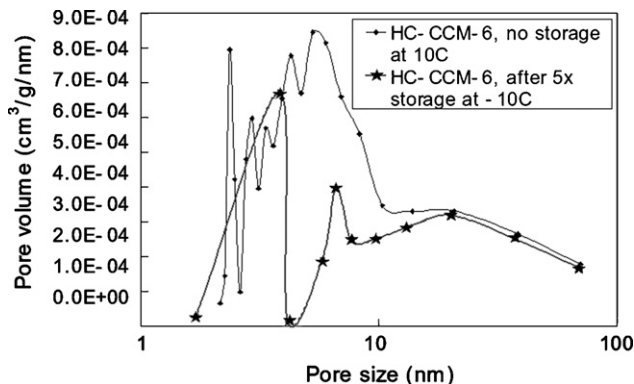


Fig. 11. Pore size distribution of the MEA HC-CCM-6.

discussion of Fig. 6 for the freeze-tolerant MEA. In the latter MEA, however, there were negligible changes in the pores with diameters of between 5 and 20 nm. Hence, the decrease in the pore volume for the pores having diameters of between 5 and 20 nm in the affected MEA, HC-CCM-6, may be related to its decreased electrochemical performance. That pores in the diameter range of 5–20 nm are indeed located in the catalyst layers, and less likely in GDL, MPL or membrane, had shown the literature analysis presented in Section 3.2.4 and is illustrated also for the GDL in Fig. 10.

To further clarify the location of the observed performance decrease of HC-CCM-6, electrochemical measurements were recorded. As is illustrated in the cell polarisation curves in Fig. 12, the MEA performance had significantly and permanently decreased at all temperatures and at all current densities after low temperature storage. The anode polarisation measurement in Fig. 13b shows that changes in the anode were significant only at current densities higher than  $250\text{ mA cm}^{-2}$ . A comparison of the performance drop between anode polarisation and cell polarisation below  $250\text{ mA cm}^{-2}$  illustrates that performance loss observed in the complete MEA was more than ten times larger than that observed only in the anode. Hence, most of the performance loss resulting from the low temperature storage is located on the cathode side or on the membrane. The impedance spectrum in Fig. 13a further narrows the location of performance loss to the cathode: charge transfer impedance, occurring at low frequencies is nearly doubled after storage at  $-10^\circ\text{C}$ . Since the anode is only slightly affected (Fig. 13b), the increase in charge transfer impedance is attributed to the cathode. The membrane itself shows no increase in Ohmic resistance after storage, hence its performance seems not affected by low temperature storage. It is concluded therefore that the major performance decrease of HC-CCM-6 was indeed located at the cathode. Since HC-CCM-6 differed mainly from the

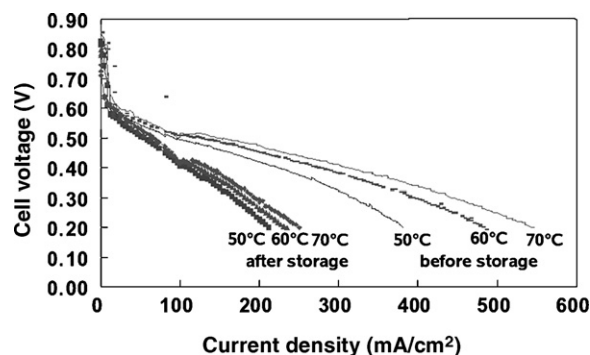
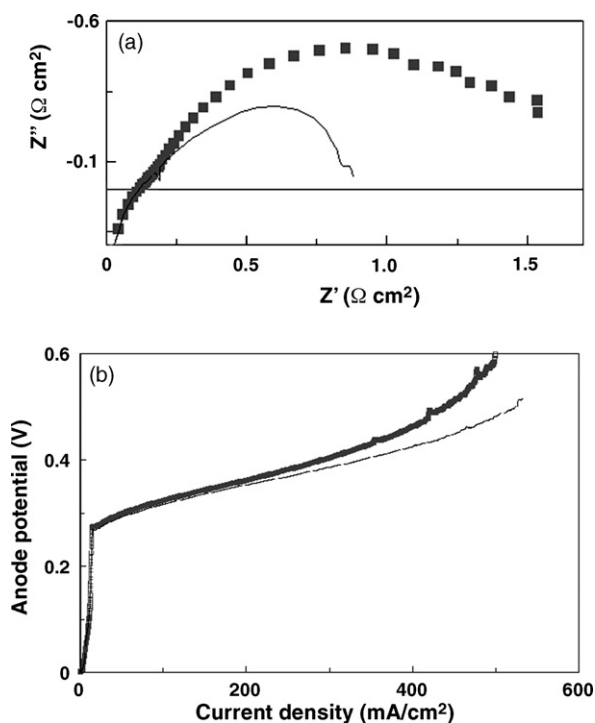


Fig. 12. Cell polarisation curves of HC-CCM-6 before and after conducting  $-10^\circ\text{C}$  storage experiments. Lines: before storage; symbols: after storage.





**Fig. 13.** Impedance spectra (a) and anode polarisation (b) of HC-CCM-6 at 60 °C before and after conducting  $-10^\circ\text{C}$  storage experiments. Lines: before storage; symbols: after storage.

freeze-tolerant MEAs in that it uses significantly less cathode catalyst loading, the cause of the intolerance of HC-CCM-6 to be stored at  $-10^\circ\text{C}$  might be correlated to the low cathode catalyst loading and the resulting differences in layer properties such as thickness, porosity and tortuosity.

Finally, the SEM pictures of the anode and cathode GDL of HC-CCM-6 were analysed to see the effect of sub-zero temperature storage on the diffusion layer of DMFCs. The pictures show that the anode GDL (Fig. 10a) and the cathode GDL (Fig. 10b) were not affected by low temperature storage. There were neither indications of macroscopic damage such as the breaking of fibres nor a change of the surface of the carbon fibres, a phenomenon which has been reported previously in literature [5]. This result is especially noticeable since sub-zero temperatures would lead to ice formation on the anode side, which could cause serious damage. It is assumed that  $\text{CO}_2$  gas prevailing in the anode or an increase in the flexibility of the GDL by PTFE coating may have prevented any damage due to freezing.

Finally, it can be concluded that some MEAs show permanent damage after being stored at  $-10^\circ\text{C}$  and, therefore, are less suitable for sub-zero temperature storage than others. Usage of high  $\text{CH}_3\text{OH}$  concentrations may still enable to store such MEAs with sufficiently low performance loss. However, rinsing the anode cycle of the DMFC system with concentrations of 4 M or 5 M methanol will negatively affect the performance and the fuel utilisation of the total DMFC systems.

#### 4. Conclusions

This paper investigated the performance change of DMFC MEAs after 10 h storage at  $-10^\circ\text{C}$  or  $60^\circ\text{C}$ . The study highlights the signifi-

cant influence of methanol concentration, MEA material properties and reactivation procedure on the performance decrease resulting from the storage.

Storage for 10 h at  $60^\circ\text{C}$  had been found unlikely to affect an MEA's performance when storage was carried out in  $\text{CH}_3\text{OH}$  concentrations of around 1 M, but could affect the MEA's performance when it had been stored in high  $\text{CH}_3\text{OH}$  concentrations. Here, the application of a reverse current for only 10 s proved useful in fully reactivating the affected MEA.

The effect of storage at  $-10^\circ\text{C}$  on an MEA's performance strongly depended upon the MEA properties. MEAs were grouped into three categories with regards to their suitability for low temperature storage: not affected, reversibly affected, and irreversibly affected. Several MEAs were irreversibly damaged; macroscopic changes were not visible from the SEM images, but electrochemical characterisation had indicated a decrease in the cathode performance for some of these MEAs, which was correlated to low cathode loadings. Other MEAs became deactivated after being stored at  $-10^\circ\text{C}$ , but their performance could be reinstated by reactivation: the application of a reverse current led to the instant regaining of the original performance. Storage at high concentrations without the application of a reverse current prevented freezing, but did not prevent performance decreases. Hence, freezing is not the major cause of the decrease in the performance of these MEAs. The following MEA materials and manufacturing methods were found to be principally suitable for the building of MEAs that are to be tolerant against storage at  $-10^\circ\text{C}$ : the manufacturing methods CCM and CCS, several hydrocarbon membranes, supported and unsupported anode catalyst with high PtRu loadings, and high Pt cathode loadings. In contrast, MEAs using Nafion® membranes or a low cathode catalyst loading showed significant, detrimental performance decreases after being subjected to sub-zero temperature storage. By carefully selecting the MEA material, MEAs with tolerance towards low and high temperature storage can be designed.

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