Journal of Power Sources 187 (2009) 103–111

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

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

Ulrike Krewer[a,*], Jun-Young Park[a], Jin-Hwa Lee[a], Hyejung Cho[b], Chanho Pak[b], Dae Jong You[b], Yoon-Hoi Lee[b]

[a] Energy 1 Team, Energy R&D Center Samsung SDI Co., Ltd., 575 Shin-dong, Yeongtong-gu, Suwon-si, Gyeonggi-do 443-391, Republic of Korea
[b] Energy and Environment Lab, Samsung Advanced Institute of Technology, P.O. Box 111, Suwon 440-600, Republic of Korea

ARTICLE INFO

Article history:
Received 7 May 2008
Received in revised form 23 July 2008
Accepted 26 October 2008
Available online 5 November 2008

Keywords:
Sub-zero storage
Freezing
Deactivation
Reactivation
Performance loss prevention
Hydrocarbon membrane

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 °C and 60 °C under different experimental conditions. Storage at 60 °C exhibited negative effects on an MEA's performance only when storing the MEA at a 4 M CH_3OH solution. Here, application of a reverse current for 10 s was found to reinstall the original performance. The effect of storage at −10 °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 °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 °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.

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 °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® membranes [6] and on freezing water in hydrocarbon membrane materials [7]. The Nafion® membrane showed a high amount of freezing water which could damage the membrane at temperatures below −10 °C [6]; after storage at −10 °C, however, no change in the conductivity of the membrane material had been identified. In contrast to Nafion®, 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 °C. Hence, the freezing of the product water would have taken place in the catalyst layer

* Corresponding author. Present address: Max Planck Institute for Dynamics of Complex Technical Systems, Sandtorstr. 1, 39106 Magdeburg, Germany.
Tel.: +49 391 6110 443; fax: +40 391 6110 536.
E-mail address: krewer@mpi-magdeburg.mpg.de (U. Krewer).

0378-7753/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpowsour.2008.10.100

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 °C
HC-CCM-1	HC	CCM	Pt-black, ≥4 mg cm^{-2}	PtRu black, ≥5 mg cm^{-2}	Pass
Naf-CCS-2	**Nafion®**	CCS	Pt-black, ≥4 mg cm^{-2}	PtRu/C, ≥5 mg cm^{-2}	**Fail**
HC-CCS-3	HC	CCS	Pt-black, ≥4 mg cm^{-2}	PtRu/C, ≥5 mg cm^{-2}	Pass
HC-CCM-4	HC	CCM	Pt-black, ≥4 mg cm^{-2}	PtRu black, ≥5 mg cm^{-2}	Pass
HC-CCM-5	HC	CCM	Pt-black, ≥4 mg cm^{-2}	PtRu black, ≥5 mg cm^{-2}	Pass
HC-CCM-6	HC	CCM	**Pt/C, ≤2 mg cm^{-2}**	PtRu black, ≥5 mg cm^{-2}	**Fail**
HC-CCM-7	HC	CCM	**Pt/C, ≤2 mg cm^{-2}**	PtRu/C, ≥5 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® and in the binder structure had been observed after being operated at −5 °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 CH_3OH solution has a freezing point of below −10 °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 CH_3OH 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® 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® membrane. The cathode catalyst layer mostly contained Pt black as the catalyst with a loading of 4 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 ≥5 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 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

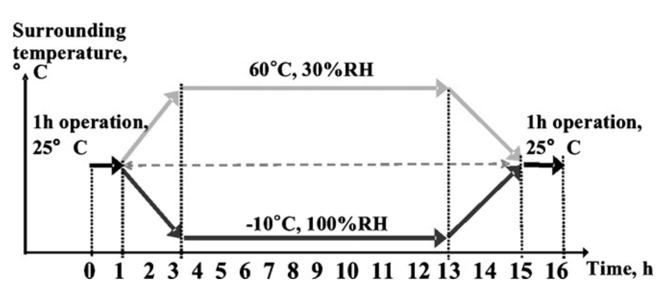

Fig. 1. Procedure for storing MEAs at extreme temperatures including their performance evaluation.