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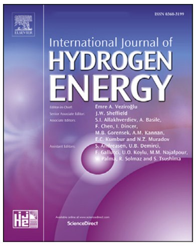

Investigating different break-in procedures for reformed methanol high temperature proton exchange membrane fuel cells

Sobi Thomas[*], *Samuel Simon Araya*[**], *Jakob Rabjerg Vang*, *Søren Knudsen Kær*

Department of Energy Technology, Pontoppidanstraede 111, Aalborg University, Aalborg Øst 9220, Denmark

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The present work focuses on reducing the complexities involved in the mass production of HT-PEM fuel cell systems integrated with a methanol reformer. Different break-in procedures are investigated on a single HT-PEMFC. The work is divided into two parts, the first in which different break-in times are tested in order to reduce the usual break-in time of around 100 h, and the second one, where simulated reformed fuel is tested during and after break-in to understand the impact on degradation over time.

In this study, two set of tests are carried out with different break-in times, the normal break-in (100 h), intermediate break-in (30 and 50 h) and no break-in (0 h). After break-in, all the cells were subjected to a load cycling profile between 0.2 and 0.6 A cm^{-2} with 5 min at each current density. The test was then carried out to compare the cell performance over time when the break-in is carried out with simulated reformed gas having a composition of 64.7% H_2, 21.3% CO_2, 12% H_2O and 2% CH_3OH. The break-in time for this test was 100 h. The cells are operated at 0.2 A cm^{-2} during break-in and thereafter at 0.6 A cm^{-2} under normal operation. The cell performance and impedance change over time is analyzed. The different resistances are deduced using equivalent circuit models and analyzed to understand the changes occurring in the MEA during break-in and how they affect the durability of an HT-PEMFC. The degradation rate for the different operating strategy is calculated from the voltage trajectory over time. The comparison of degradation and break-in time suggests that the normal break-in induces a uniform ohmic resistance changes in the cell over time, while the fast cycling leads to non-uniform changes in resistances. However, the performance and degradation are not significantly affected over ≈750 h test. The test with simulated reformed fuel indicates that the break-in with pure H_2 is important for longer durability when operation thereafter is with reformed fuel. The cell with reformed fuel break-in degrades much faster compared to the cell with H_2 break-in.

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[*] *Corresponding author.*

[**] *Corresponding author.*

E-mail addresses: sot@et.aau.dk (S. Thomas), ssa@et.aau.dk (S.S. Araya).

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Introduction

Fuel cells are energy conversion devices which directly converts chemical energy to electrical energy. They have lower environmental issues as the only by-product on-site is water and heat. Among the various classification of fuel cells, polymer electrolyte membrane (PEM) fuel cell is a promising and mature technology. The research in this field has improved the efficiency, cost and durability.

Among the different kinds of PEMFCs, high temperature polymer electrolyte membrane fuel cell (HT-PEMFC) has various advantages. In a HT-PEM fuel cell, the proton conductor is phosphoric acid (PA) unlike water in LT-PEM fuel cells which facilitates the operation of HT-PEMFC at higher temperatures. The advantage of operating a fuel cell at higher temperature (150 °C–180 °C) includes higher reaction kinetics, increased tolerance to impurities mainly CO in the fuel [1]. Another advantage of HT-PEMFC is reduced water management complexities as the proton conductivity depends on PA distribution and concentration rather than water as in LT-PEM fuel cells [2]. However, HT-PEM fuel cells are also associated with some hurdles in terms of operation and start-up. One such problem associated with mass production of HT-PEMFC is the break-in of membrane electrode assembly (MEA) before installing the stacks to system. The break-in process involves the operation of fuel cell with pure H_2 at 0.2 A cm^{-2} for $\approx$100 h. This leads to an increase in the fuel cell system cost as it is time consuming process and requires pure hydrogen infrastructure.

The PA doped MEA when assembled in a cell leads to a non-uniform distribution of acid within the membrane electrode assembly. The process taking place during the break-in of an HT-PEMFC is not well known. However, it is supposed to improve the performance, as a result of uniform distribution of phosphoric acid, increased catalyst activity by impurity removal and improved membrane conductivity after a break-in of 80–100 h at 0.2 A cm^{-2}. Thus, it is suggested to carry out break-in at 0.2 A cm^{-2} for 100 h before drawing maximum output power [3,4].

Ref. [5] studied the process taking place in an HT-PEM fuel cell during activation. They used different characterization techniques like polarization, electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) to understand the various phenomena taking place within the cell during break-in. It was reported that the ohmic resistance improves in the presence of water, but the cathode degrades by PA removal in the presence of excess water. Galvanostatic break-in was suggested to draw higher performance. To break-in an HT-PEMFC rapidly and to ensure repeatable baseline performance different strategies were investigated by Tingelöf and Ihonen [6]. They reported potential cycling after 100 h of 0.2 A cm^{-2} did not contribute much to reach a stable repeatable performance. They suggested a higher temperature of 200 °C operation under galvanostatic mode for 24 h followed by 48 h operation at 160 °C is the best to achieve reproducible performance from an HT-PEMFC system. Rastedt et al. [7] proposed a rapid and flash test procedure to quantify the quality of the MEAs from different batches and/or manufacturers. The rapid test involved a operation of 65 h and the flash test lasted only for 8 h. The rapid test was able to identify the variations among different batches of MEAs from different manufacturers. They suggest that a short duration test would be sufficient to determine the quality of the MEAs.

Eberhardt et al. [8] investigated the cause of degradation in an HT-PEM fuel cell under operation using synchrotron based X-ray tomographic microscopic imaging. The focus was on understanding the dynamic re-distribution of PA under load cycling operation. The tests quantified the migration of PA from the cathode to anode at high current density and vice-versa at low current density (i.e., migration of PA from the anode GDL and flow field to membrane). They attributed the phenomenon to electrochemical pumping, resulting from the non-zero transport number of hydrogen phosphate anions, which drags the electrolyte from the cathode to anode [9]. The migration was observed to be fast under high current density and slow at low current density. A comparison of degradation as an effect of start-stop cycle and reformed fuel, mainly CO concentration in the fuel, was investigated and the results suggests start-stop cycle leads to faster degradation when the anode fuel has 2% CO. However, when the CO concentration is 0.5% the effects are minimal [10].

In this paper, different strategies are employed to reduce the break-in time and at the same time investigate the long-term implications of the break-in procedure on the durability of HT-PEMFC. The tests are subdivided into three test sequences. The first two were with different break-in times and the third one was break-in with simulated reformed fuel. The objective was to obtain a stable and reproducible performance with a rapid break-in strategy. As known from literature [3,5], one major factor influenced during break-in was the acid redistribution which improves the ohmic resistance and also reduces the mass transport resistance as a result of uniform redistribution of phosphoric acid during break-in. Also, acid movement was reported to be a function of current density [8]. Thus, based on these knowledge in this study, the cells were subjected to current cycling procedure to redistribute the acid faster. The reformed fuel break-in was also investigated to do away with the intermediate step of HT-PEMFC stack break-in with H_2 before integrating to a reformer in a reformed methanol HT-PEMFC system.

Experimental

Test setup

The tests as described in Table 1 was carried out using an in-house built test set-up and is shown in Fig. 1. It consists of five single cells in parallel with the hardware capable of carrying out IV curves and EIS measurements. The mass flow controllers (MFC) are from burkert (H_2-8711, Air -8712). The flow rates are 0–1 L min^{-1} for H_2 and 0–2 L min^{-1} for air. The test with simulated reformed fuel was carried out using a similar setup with the provision of an evaporator and pump unit to supply CH_3OH and H_2O, and also additional MFC for CO_2 supply.

The MEA used for the experiments were provided by Serenergy. The active area of the MEA was 45 cm^2 and thickness of the MEA was 860 μm. The gaskets were 300 μm on the anode and 350 μm on the cathode. The compression force applied was 7 kN. This was controlled using springs. The anode flow field was two channel serpentine while the cathode was 3 channel

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