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Short communication

Long term testing of start–stop cycles on high temperature PEM fuel cell stack



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HIGHLIGHTS

- An HT-PEM fuel cell stack was tested for 1562 cycles of start–stop operation (4160 h).
- The longest uninterrupted test run was for 524 cycles (1342 operating hours).
- A start stop procedure resulting in low degradation has been identified.
- The degradation rates were 11 $\mu\text{V}/\text{cycle}$ @ 0.03 A cm^{-2} and 26 $\mu\text{V}/\text{cycle}$ @ 0.25 A cm^{-2} .
- At OCV, a higher degradation rate of 133 $\mu\text{V}/\text{cycle}$ was observed.

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ABSTRACT

A PEM fuel cell with an operating temperature above 100 °C is desired for increasing the kinetics of reactions, reduced sensitivity to impurities of the fuel, as well as for the reduction of the requirements on thermal and water management systems. High Temperature Polymer Electrolyte Membrane Fuel Cells (HT-PEMFC) can effectively be combined with CHP systems to offer a simple system design and higher overall system efficiencies. For HT-PEMFC systems, the development of elaborated start/stop strategies is essential in mitigation of fuel cell degradation during these events. A 5 cell co-flow stack is assembled with BASF P1100W membrane electrode assembly (MEA) with an active area of 163.5 cm^2 . Continuous operation and more than 1500 start stop cycles have been performed in order to study the degradation effects of both continuous operation and of repeated start stops using a protective start–stop algorithm, which is designed to avoid the formation of aggressive cell potentials. The repeated use of this procedure led to a degradation of 26 $\mu\text{V}/\text{cycle}$ at a current density of 0.25 A cm^{-2} and 11 $\mu\text{V}/\text{cycle}$ at a current density of 0.03 A cm^{-2} . At open circuit voltage (OCV), a higher degradation rate of 133 $\mu\text{V}/\text{cycle}$ was observed.

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1. Introduction

In consideration to ecological and energy issues, there is a tendency for transition towards hydrogen energy which assumes wide use of fuel cells for both transport and stationary applications. For allowing a commercial use of these technologies, certain lifetime requirements have to be fulfilled, which is still a developmental issue for some of the possible HT-PEMFC applications. The US Department of Energy (DOE) provided recommendations of about 40,000 h of operation for stationary applications and 5000 h of operation for mobile applications, which leads to a request of a very

limited performance decay. Thus, the degradation of fuel cell components plays a vital role in the performance and lifetime of the fuel cell. Optimal parameters need to be found out in order to operate the fuel cell at its full potential and there involves a significant challenge in improving the lifetime of the HT-PEM fuel cells. Optimization of operation strategies is quite essential in mitigation of fuel cell degradation during start–stop events. Therefore, a profound knowledge both about the influence of decisive operating parameters and the involved degradation mechanisms is required.

For the development of high temperature PEM fuel cells, significant attention has been focused upon fundamentally understanding degradation and in development of strategies to improve fuel cell durability. The start-up strategy developed by Shen et al. [1] includes a nitrogen purge of the anode prior to the introduction

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of the hydrogen fuel. This strategy resulted in low potential difference between the cathode and the anode, which implies lower carbon corrosion by localized corrosive potentials. Shen et al. [1] further found that if a fuel/air boundary cannot be avoided, an introduction of fuel at a higher flow rate was preferable. The higher flow rate still results in a high potential difference, but during a shorter time, which reduces the carbon corrosion.

Another start-up strategy was developed by applying a dummy load as the fuel fills the anode compartment [1–3], where the dummy load lowers the potential difference and thus carbon corrosion is avoided. This type of voltage control reduced the degradation from $\sim 100 \mu\text{V}/\text{cycle}$ to $\sim 4 \mu\text{V}/\text{cycle}$ in a test conducted by Perry et al. [3]. A third strategy has been tested by Jo et al. [4], where the hydrogen is supplied to the anode prior to the introduction of oxygen on the cathode side. This strategy resulted in decreased power loss and a reduced electrochemically active catalyst surface area loss.

Shutdown strategies have also been developed to improve the durability of fuel cells. Kim et al. [2] tested a nitrogen purge strategy on the anode that lowered the potential difference at shutdown and reduced degradation of the MEA. Dummy load strategies where the remaining hydrogen is consumed before shutdown have been developed [1,3]. The dummy load reduces the cell potential which limits the carbon corrosion.

After 244.5 h of OCV tests carried out by Qi and Buelte [5], the crystallite size of cathode Pt increased to as much as 5.3 times of its original value and observed a decline with most of the loss occurred in the first 50 h of exposure to OCV due to the significant increase in cathode activation resistance and the mass transport resistance.

Moçotéguy et al. [6] tested a single cell and 24 cells stack $500 \text{ W}_{\text{el}}$ with constant current density of 0.2 A cm^{-2} and 0.4 A cm^{-2} and 160°C over a total of 500 h, including additional sections with dynamic operation under simulated reformat and air with respective hydrogen and oxygen over-stoichiometric ratios of 1.4 and 2. After 500 h of operation, the degradation rate of the single cell ranged from 41 to $149 \mu\text{V h}^{-1}$, whereas the 24 cell stack after 658 h of operation was stopped due to worst cell performances. The ageing effect also strongly varied with dependence on cell position with some cells exhibiting an average degradation ranging around $20 \mu\text{V h}^{-1}$, while some others exhibited degradation rates above $100 \mu\text{V h}^{-1}$.

Long term stability of PBI-based HTPeMFC has been demonstrated for more than 17,000 h under steady state condition ($T = 150^\circ\text{C}$, $\lambda_{\text{H}_2} = 1.2$, $\lambda_{\text{air}} = 2$, $i = 0.2 \text{ A cm}^{-2}$, with pure hydrogen and air) with a voltage decay rate of around 10% during a single cell test. Oono et al. [7] discovered that the degradation is due to agglomeration of the electrode catalyst particles in the early stages, and due to the depletion of phosphoric acid in the latter stages.

Based on the commercial Celtec-P1000 MEA, Schmidt and Baurmeister [8] reported $11 \mu\text{V h}^{-1}$ degradation rate after a period of 6300 h with 260 cycles (a 12 h operation at 160°C followed by 12 h shutdown period) under mild conditions operation at 160°C on hydrogen and air with respective stoichiometric ratios of 1.2 and 2. Start/stop cycles did not impact significantly the cell ohmic resistance or the oxygen reduction kinetics but ohmic resistance slightly increased beyond 2500 h of ageing. Mass transfer limitations at the cathode increased with ageing and were magnified by the start/stop cycling.

During dynamic tests with thermal, load and shutdown–startup cycling, the amount and the vapor pressure of the water product varies and thinning of phosphoric acid might be involved. In addition, the shutdown–startup or/and temperature cycling cause thermal and mechanical stresses to the membranes and cell components as well as the volume expansion and contractions of the acid in MEAs. Another important mechanism of the cell

degradation involved in these dynamic tests is the corrosion of carbon support and sintering of noble metal catalysts [9].

In this paper, we have studied the impact of start/stop cycling induced performance degradation of a 5 cell Celtec-P 1100W stack under the conditions of CHP applications for 1562 cycles. A protective start-up and shutdown strategy has been chosen in order to increase the lifetime of the fuel cell. After activation, the stack is progressively operated according to the protective start–stop algorithms shown in Section 3.1. The algorithms for analyzing the fuel cell degradation are also presented in the following section.

2. Experimental procedure

This section explains the experimental setup and equipment used for testing the aging of fuel cells. A 5 cell co-flow stack with an active area of 163.5 cm^2 is assembled using BASF P1100W MEAs. A leakage test using forming gas (95% nitrogen, 5% hydrogen) showed overall leakage rates of less than 7 N ml min^{-1} .

2.1. Fuel cell test bench

For the characterization of both performance and degradation of the fuel cell stack, a test bench with additional capabilities for gas analysis has been used. The test bench is equipped with:

- Flow controllers for hydrogen (5 Nl min^{-1}), nitrogen, carbon dioxide (anode side) and air (20 Nl min^{-1}), oxygen and nitrogen (cathode side).
- Mass spectrometer (Pfeiffer GSS 300) for measurement of inlet and outlet gas concentrations for both anode and cathode side.
- Thermo oil based heating and cooling system (Julabo HC) for active cooling and stack heating up to a temperature of 200°C .
- Electronic load (Höcherl & Hackl DS 1006) for adjustment and measurement of both cell voltage and current.
- Yokogawa data acquisition system with 30 individual channels and 8 Hz maximal acquisition frequency for single cell voltages.
- SIEMENS PLC 200 unit for test bench control and measurement of flow rates and temperatures, including proprietary data acquisition and control software (start/stop, characteristic curve recording under galvanostatic or potentiostatic control, constant power operation, gas flow control for constant media utilization, minimum gas flow rates, temperature control, data storage).

2.2. Fuel cell test and operation procedures

Heat up of the stack is performed with a rate of 2.5 K min^{-1} under nitrogen (N_2) purge to avoid start–stop induced carbon corrosion. During operation, simulated reformat ($\text{H}_2/\text{CO}_2/\text{CO}$ 74.8/25/0.2 Volume % or H_2/N_2 80/20 Volume % mixture) was used as an anodic fuel at a minimum gas flow rate equivalent to a stoichiometric ratio of 1.25 (anode) and 2.5 (cathode) at a current density of 0.25 A cm^{-2} throughout the experiment to improve the repeatability and to ensure the reliability of the results. Reactant gases were kept dry throughout the experiment.

The voltage at the given current density was recorded for 3 min and determined by the average value excluding transient periods. However, the stay duration at lowest current densities and at OCV was limited to 1 min to avoid cell degradation caused by high cathodic potentials.

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