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Accelerated Life-time Tests including Different Load Cycling Protocols for High Temperature Polymer Electrolyte Membrane Fuel Cells

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ABSTRACT

The purpose of this work is to identify new accelerated life-time (ALT) test protocols for polymer electrolyte membrane fuel cell (PEMFC), which function at conditions of high temperature and low humidity (under 120 °C 40%RH). A design of accelerated life protocols was studied to observe degradation phenomena under different load step cycling conditions, compared with the constant voltage test at 0.6 V. The effects of changes in frequency and potential range are explored, and different degradation rates are revealed. The test protocol of constant voltage test, load step cycling and with different potential range show total performance decay rates of 5.3 $mA \cdot cm^{-2} \cdot h^{-1}$, 8.4 $mA \cdot cm^{-2} \cdot h^{-1}$ and 10.2 $mA \cdot cm^{-2} \cdot h^{-1}$, respectively, while the highest total decay rate of load step cycling with frequency change is 17.0 $mA \cdot cm^{-2} \cdot h^{-1}$ including a rapid decrease of current density after 450 cycles under 120 °C 40%RH. In respect to the operation of 500 cycles (35 h), material degradation failure mechanisms are investigated according to the electro- and physico-chemical characteristics of the MEA. The performances assessed by the life-time evaluation methods are strongly related to the increase in the membrane resistance and the release of the sulfate and fluoride ions, dominated more at a higher cycling frequency. Furthermore, in the contrast to the starting MEA, Pt aggregations of the catalysts and a decline in the electrochemical surface area (ECSA) are clearly observed at the end of the testing especially with a wider sweeping range, corresponded to the decrease in the electrochemical properties.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are promising candidates for transportation, stationary and portable electric power generations due to their simplicity, high energy density and easy recharging [1–3]. Nowadays, one of the challenges in the PEMFC is the operation under medium or high temperature (above 120 °C) [4,5]. Increasing the temperature up to 120 °C would improve the catalyst behavior, as it enhances the reaction kinetics, alleviates flooding by liquid water at the cathode electrode, and increases the tolerance to CO contained in the hydrogen from the reforming process or chloride, which may come from the water. Furthermore, high temperature operation will reduce the size of the thermal subsystem, and could potentially be co-generated using hot water ambient heat in the stationary system. This would simplify the architectural design and result in an overall increase of system efficiency, thereby advancing the commercialization of the fuel cell system [6–9]. For these reasons, the department of Energy (DOE) funds multiple projects intended to modify the chemical structure of the high temperature membrane to enable high conductivity and durability for a future plan with a target of up to 120 °C and relative humidity under 40% [10,11]. Therefore, the minimum operation condition of 120 °C and relative humidity 40% was selected to design a tests for high temperature fuel cells.

Among commercialization issues, such as performance, cost, reliability and long-term performance, for high temperature fuel cell, long-term durability is one of the most critical problems. Recently, DOE announced also the long-term durability target as >500 h for automobile applications, and as more than 20,000 h for stationary applications in order to represent the full range of external environment conditions [12–14]. Most existing studies on PEM fuel cells focus on the durability of degradation mechanism using different failure modes due to the additional demands. Recently, accelerated life-time test (ALT) spotlighted in the field of the degradation test because life-time tests under normal operation conditions are impractical [15–17]. ALT is a more preferred method, since it significantly reduces the experiment time and subsequent post-mortem analysis, while still providing

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critical information to expedite failures or degradation mechanisms by loading a stress severer than that of the normal operation conditions. There are various acceleration factors when examining the serious causes from different running atmosphere, which include (1) operation conditions such as temperature (-30∼120 °C), gas flow, water management and humidity; and (2) operation models such as mechanical vibration, open circuit voltage (OCV) operation, load/potential (current/voltage/power) cycling, on-off cycling and freeze/thaw cycling [18–21]. This kinds of durability test methods open up discussions regarding pinholes, gas crossover, mechanical stability, polymer decomposition at the membrane and carbon support corrosion, Pt dissolution, agglomeration at the electrode chases in morphology, chemical degradation, and other degradation mechanisms via different electro- and physicochemical characterization of the fuel cell compounds [22–26]. In general, these degradations are exacerbated at elevated temperatures [4–9]. However, the lack of understanding of the degradation mechanism as well as the difficulty of performing made the condition of the operating at high temperature and low humidity requiring more effort.

In this study, alternative PSFA membranes and ionomer with the tradename of Aquivion™ from Solvay-Solexis was used as a reference since Nafion® membrane has undeniable drawbacks including deterioration of water retention, proton conductivity and cell performance at high temperature and low humidified conditions [27,28]. Among these membranes, a short side chain perfluorosulfonic ionomer (SSC-PFSA, Aquivion™) shows high glass transition temperature of 127 °C (long side chain ionomer: Nafion® of 67 °C at the same equivalent weights) in dry form [29]. Furthermore, larger crystallinity is observed in short side chain ionomers than in long side chain ionomers, resulting in more reliable properties at a high temperature than Nafion®. It is proven in the reference that the Aquivion™ membranes appeared to perform significantly better under high temperatures with lower ohmic loss resistance, hydrogen cross-over, and a better electro catalytic activity, which can be explained by the better properties at high temperature [29–31]. Furthermore, SSC-PFSA polymer have a good balance between transport properties and stability. The shorter side-pendent chains and the absence of the ether group of the tertiary carbon also gives better chemical and mechanical properties, making them more suitable for working at harsh conditions in fuel cell systems [32]. The other reasons for the better properties of the SSC-PFSA were not only due to the good chemical properties but also due to the effective water sorption polymer structure, especially at an elevated temperature, which was characterized by the motion of water within proton conducting membranes [33]. However, there are no systematic works regarding functional durability under the conditions of high temperature and low humidity using both SSC-PFSA membrane and ionomer.

The purpose of this work is to provide valuable information regarding the PEMFC durability and membrane electrode assemblies (MEAs) degradation under 120 °C 40%RH using new ALT test protocols operating at harsher conditions than the normal constant voltage test. For the high temperature operation, all MEAs of the single cells are based on Aquivion™ to focus on only to the degradation by the different protocols. ALT protocols include load step cycling with different frequencies and voltage range to evaluate the degradation patterns of the MEAs. The performance drops during the ALT protocols were monitored while IV curve, electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were periodically

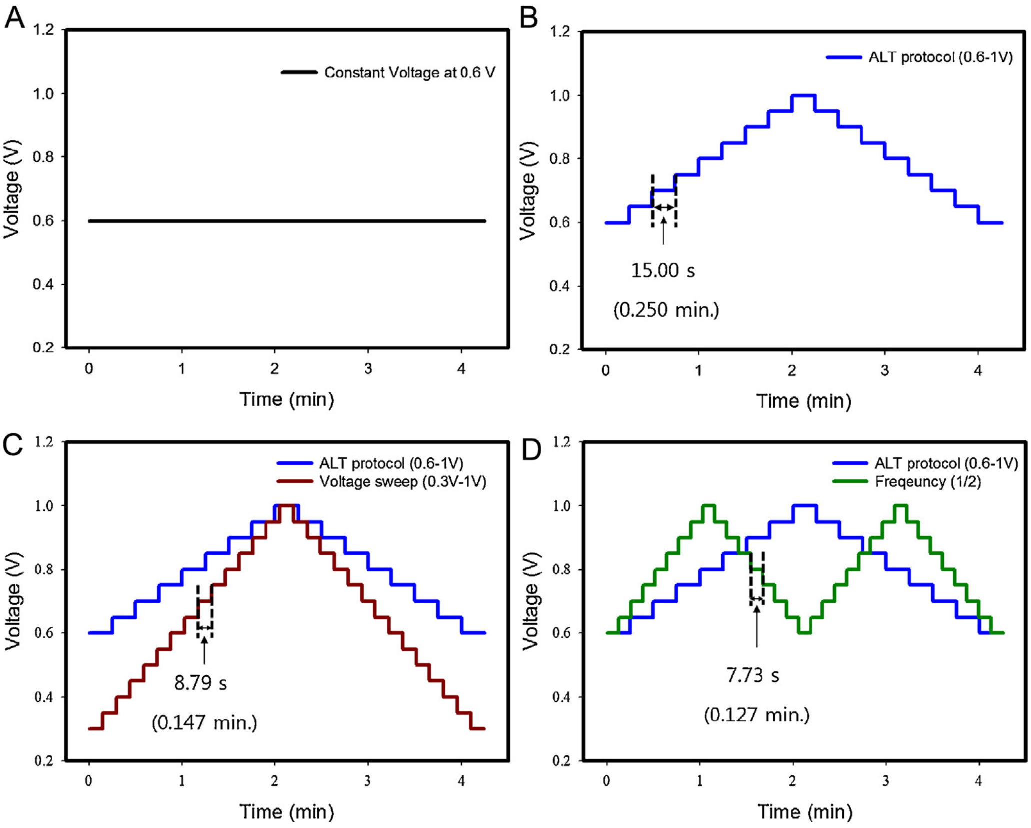

Fig. 1. Accelerated life-time test protocols in one cycle for single MEAs consisted of Aquivion E87-05 S under 120 °C 40%RH: A. mode 1, B. mode 2, C. mode 3, D. mode 4.