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Accelerated life-time test protocols for polymer electrolyte membrane fuel cells operated at high temperature

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ABSTRACT

Durability of high temperature fuel cells with low humidity has been receiving attention for its commercialization into the automobile. Therefore, advanced durability protocols are designed to evaluate the membrane electrode assembly (MEA) composed of short-side-chain conducting polymer (Aquivion™) at the high temperature of 120 °C and low humidity of 40%RH. Accelerated life time tests (ALTs) of on–off cycle test with the duration time of 10 min and load cycle test with a voltage sweep of 0.6 V–1.0 V and a duration of 4.25 min, are developed to induce different stresses. The different degradation behaviors of the MEAs are monitored and compared to the normal constant voltage mode of 0.6 V. The decay rate using the on–off cycle test is 0.113 mA/(cm^2 min) whereas a slightly slower decay rate of 0.096 mA/(cm^2 min) is obtained for the load cycle test. The electrochemical analyses of membrane electrode assembly (MEA) are confirmed periodically during the tests for each protocol using polarization curve, impedance spectroscopy and cyclic voltammetry. The characterizations of the MEA are carried out before and after the durability tests to verify the material degradation and failure mechanisms. Although both protocols show similar degradation on the MEA materials, the membrane degradation is more dominant after the on–off test while more catalyst degradation is observed after the load cycling test. Nafion® is also tested by the developed load cycle test to observe the difference between short-side-chain and long-side-chain conducting polymer.

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Introduction

High temperature fuel cell has been highlighted for its use in the wide range of the applications because of its simplified system due to easier integration and high energy efficiency [1,2]. The operating condition of high temperature, which is expected to over 120 °C and low humidity, is now a stimulating area of study due to its advantages including improvement in the catalyst behavior, better water and thermal management, and tolerance to CO or chloride that may come from the reactants or water [3–5]. Moreover, lower relative humidity (RH) operation offers quicker start-ups and better freeze cycle operation [6,7]. However, there exists a technical barrier for the acceptance of the high temperature fuel cell system as a practical power generation because of durability issues under various operating conditions. The requirements for fuel cell life-time are presented by the department of Energy (DOE) with the target of >5000 h for cars, >20,000 h for buses and more than 40,000 h for stationary applications [8–10]. Although the life-time target for the automobile is lower than the stationary applications, various durability operation modes, such as dynamic load cycling, on–off and freeze-thaw, are challenges facing the current fuel cell technology. Most studies for the durability of the PEM fuel cells focuses on accelerated life-time test (ALT), since the life-time test under normal operating conditions is impractical [11–18]. ALT is more concrete method because it significantly reduces the experiment time and subsequent post-mortem analysis, and yet still provides critical information to expedite failures or degradation mechanisms by loading stresses severer than the normal operating conditions. Among these operating modes, the dynamic load cycling and on–off cycling test are significantly more important for the high temperature fuel cell system. As is the case with automobiles, the on–off cycle seriously deteriorates the materials in the membrane electrode assembly (MEA) due to local hydrogen starvation [19–23]. Furthermore, it has been acknowledged by many research groups that load cycling drastically impacts performance compared to constant load conditions [24–26]. Both ALT protocols may result in the physical degradation by the oxidant starvation, local hotspots, material loss at the membrane or carbon support corrosion, Pt dissolution and agglomeration at the electrode, thereby cause serious degradation of performance [27–30]. However, the lack of understanding of the degradation mechanism, as well as the difficulty of conducting operated in high temperature and low humidity, made this conditions required more effort to utilize it to the real industry.

The current benchmark membrane is Nafion®, a long side chain perfluorosulfonic acid (LSC-PFSA) copolymer made by Dupont, which is widely utilized for the low temperature membrane under high humidity [31,32]. Nafion® exhibits high proton conductivity along with a thermal and chemical stability under the temperature of 90 °C. However, this membrane is limited in application at high temperature and low humidity due to its deterioration of water retention and loss of conductivity. Therefore, a short side chain perfluorosulfonic (SSC-PFSA) ionomer with the tradename of Aquivion™ from Solvay-Solexis is considered, since it shows high glass transition temperature and larger crystallinity, which result in more reliable properties at a high temperature than Nafion® [33–38]. 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 and of the tertiary carbon also gives better chemical and mechanical properties, making them more suitable for working at harsh conditions in fuel cell systems [39]. It is proved in the papers that Aquivion™ membranes appeared to perform significantly better under high temperature, and had better properties at high temperature compared to Nafion® membrane [35–37]. The reasons for the better performance 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 [40]. However, there is no systematic work on MEA durability that can function at high temperature and low humidity conditions using both SSC-PFSA membrane and ionomer.

In this work, we demonstrate advanced durability tests to provide valuable information regarding the operation of the high temperature fuel cell at low humidity based on Aquivion™ and Nafion®. An on–off test and load cycling test were designed to investigate the effect of the different stress conditions under 120 °C 40 %RH, and these were compared to the normal constant voltage test of 0.6 V. The performance drops during the accelerated life-time test (ALT) protocols were periodically monitored with IV curve, electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were analyzed. Furthermore, post-test characterizations of SEM, TEM and XRD were conducted to observe the degradation of the membrane, electrode and interfaces between them.

Experimental

Preparation of membrane electrode assembly (MEA)

A catalyst ink for the MEA fabrication was prepared by mixing 0.3 g of carbon supported Pt catalyst (Johnson Matthey, 40 wt.% Pt on carbon black), 1.2 g de-ionized water, 0.8 g of Aquivion™ ionomer solution (15 wt.% solution in lower aliphatic alcohol/ H_2O mix, EW = 870, Solvay Solexis) and 3.6 g of isopropyl alcohol (Aldrich). The catalysts ink was mechanically stirred and ultrasonicated to allow well-mixing of ionomer and Pt particles for five times repeatedly. Then, the slurry was sprayed onto the Aquivion™ E87-05S membrane (Solvay solexis, 50 ± 1 μm) with the active surface area of 1 cm^2 and catalyst loading of 0.4 mA/cm^2 at both sides. The catalyst coated membranes were dried at 100 °C for 1hr to remove residual solvent. The MEA was fabricated by stacking, without hot-pressing, the catalyst-coated membrane, gas diffusion media (SGL 10BC) and Teflon gasket. The same process was used for the MEA based on the Nafion® ionomer and 212 membranes.

Single cell operation and test protocols

The single cell tests were carried out at a PEMFC station (Fuel cell technology, USA). Pure H_2 and O_2 were fed into the cell as