Journal of Power Sources 257 (2014) 102–110

Contents lists available at ScienceDirect

Journal of Power Sources

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

Membrane degradation during combined chemical and mechanical accelerated stress testing of polymer electrolyte fuel cells

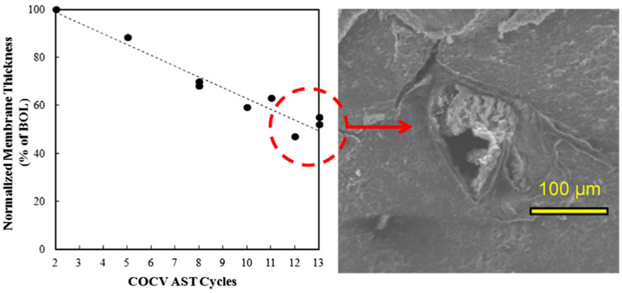
C. Lim[a], L. Ghassemzadeh[b], F. Van Hove[a], M. Lauritzen[c], J. Kolodziej[c], G.G. Wang[a], S. Holdcroft[b], E. Kjeang[a],*

[a] *School of Mechatronic Systems Engineering, Simon Fraser University, 250-13450 102 Avenue, Surrey, BC V3T0A3, Canada*
[b] *Department of Chemistry, Simon Fraser University, 8888 University Drive, Burnaby, BC V5A1S6, Canada*
[c] *Ballard Power Systems, 9000 Glenlyon Parkway, Burnaby, BC V5J5J8, Canada*

HIGHLIGHTS

- A combined chemical/mechanical membrane accelerated stress test is applied.
- Membrane failure via pinhole formation is generated in 160 h.
- NMR and fluoride emission data show both side chain and main chain degradation.
- Membrane degradation is intensified by periodic chemical and mechanical stressors.
- Insight is provided into the conjoint chemical/mechanical degradation mechanism.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 26 June 2013
Received in revised form
6 November 2013
Accepted 22 January 2014
Available online 2 February 2014

Keywords:
Fuel cell
Membrane
Accelerated stress test
Durability
Mechanical degradation
Chemical degradation

ABSTRACT

A cyclic open circuit voltage (COCV) accelerated stress test (AST) is designed to screen the simultaneous effect of chemical and mechanical membrane degradation in polymer electrolyte fuel cells. The AST consists of a steady state OCV phase to accelerate chemical degradation and periodic wet/dry cycles to provide mechanical degradation. The membrane degradation process induced by COCV AST operation is analyzed using a standard MEA with PFSA ionomer membrane. The OCV shows an initially mild decay rate followed by a higher decay rate in the later stages of the experiment. Membrane failure, defined by a threshold convective hydrogen leak rate, is obtained after 160 h of operation. Uniform membrane thinning is observed with pinhole formation being the primary cause of failure. Mechanical tensile tests reveal that the membrane becomes stiffer and more brittle during AST operation, which contributes to mechanical failure upon cyclic humidity induced stress. Solid state ^{19}F NMR spectroscopy and fluoride emission measurements demonstrate fluorine loss from both side chain and main chain upon membrane exposure to high temperature and low humidity OCV condition.

1. Introduction

Membrane durability is an important factor for fuel cell lifetime. Evaluating the durability of a polymer electrolyte fuel cell under normal operating conditions requires several thousand hours of operation which makes the process inconvenient due to its high

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* Corresponding author. Tel.: +1 778 782 8791; fax: +1 778 782 7514.
E-mail address: ekjeang@sfu.ca (E. Kjeang).

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http://dx.doi.org/10.1016/j.jpowsour.2014.01.106

cost and long duration. Accelerated stress test (AST) methods are preferred to facilitate rapid degradation and failure of specific membrane electrode assembly (MEA) components such as electrocatalyst, catalyst support material, and membrane. To define failure modes and understand degradation mechanisms of the MEA components, it is essential to avoid significant interactions between different components and degradation mechanisms while maximizing the sample throughput and minimizing the experimental time.

Standard AST protocols for membrane degradation were developed by the US Department of Energy (DOE) [1]. Two individual, well-established AST protocols are currently employed for accelerating membrane chemical degradation and mechanical degradation, respectively. Many factors contribute to the chemical degradation of polymer electrolyte membrane including reactant gas crossover, transition metal ion contamination, and changes in the potential and operation temperature [2–5]. These factors can directly or indirectly increase the risk of radical formation in the MEA. The reaction of oxidative radicals such as hydroxyl (•OH) and hydroperoxyl (•OOH) with the polymer electrolyte is known to be the main cause of chemical degradation. It has been shown that open circuit voltage (OCV) operation accelerates chemical degradation, and therefore, OCV conditions are often employed in accelerated stress tests to increase the rate of chemical degradation [6].

The effect of radicals on the chemical structure of the polymer electrolyte is often discussed in terms of attack on polymer at the main chain carboxylic acid end group sites (formed in small quantities during the polymer manufacturing process), or by the attack of sulfonic acid groups in the side chain [7–12]. In both cases, radical attack can induce a change in ionomer morphology and decrease its ion exchange capacity, which diminishes its proton conductivity in the earlier stages and leads to a less durable material in advanced stages. The most frequently reported evidence for radical attack and chemical degradation is fluoride release and membrane thinning. Another important consequence of chemical degradation is dehydration of the membrane, resulting in a decrease of proton conductivity and corresponding increase of ohmic loss. Humidity cycling can also cause severe degradation to the ionomer due to high gas crossover in dry conditions [13].

Mechanical degradation of fuel cell membranes is exacerbated by excessive swelling and shrinking. At room temperature, perfluorosulfonic acid (PFSA) ionomer membranes have been found to shrink ~10% from their fully saturated state upon exposure to 50% RH [14]. A membrane, constrained by electrodes and gas diffusion layers (GDLs) and indirectly by flow field plates, is subjected to in-plane compression due to swelling caused by high RH conditions and in-plane tension due to shrinkage during low RH conditions. Repeated high and low RH cycles, which are a natural consequence of dynamic fuel cell power demands, impose cyclic stress and strain upon the membrane, leading to catastrophic mechanical failures such as pinholes [15–19] and cracks [20,21]. Huang et al. [17] measured tensile properties of MEAs subjected to two different RH cycling conditions, and demonstrated that the strain-to-failure of an 80–120% RH-cycled MEA decreased faster than that of a 30–80% RH-cycled MEA, due to higher cyclic swelling of the membrane. The mechanical properties of the membrane are affected not only by the chemical degradation of the ionomer, but also by accumulated damage due to RH and temperature cycling. Membrane failure is believed to be a consequence of combined chemical and mechanical stress, but this has not been explicitly shown.

While established AST protocols are important in terms of evaluating durability at the material and component level, complex interactions exist that complicate degradation processes at the fuel cell stack level [22]. Therefore, the standard AST protocols may not be sufficiently comprehensive to evaluate the effects of all operating conditions and duty cycles that are typically encountered during actual fuel cell operation, particularly for automotive applications. During vehicle operation, the stack is subjected to frequent idling and changes in humidity of the fuel/oxidant feed. In addition, stressor modes of the chemical and mechanical degradation occur simultaneously in the membrane due to fluctuations in load demands of the vehicle.

To better represent fuel cell stack operation, a combined chemical and mechanical AST protocol was developed at Ballard Power Systems to evaluate the durability of the membrane [23,24]. The protocol is based on a cyclic open circuit voltage (COCV) AST that intensifies the effects of residence time at high voltage (that occurs during automotive idling conditions) and RH cycling (that occurs during the acceleration/deceleration of the vehicle), mimicking environmental fluctuations of the operating parameters but also promoting failure in a fraction of the time normally required. The objective of the present work is to benchmark the COCV AST protocol for standard PFSA ionomer membranes and examine its capability of accelerating the combined chemical and mechanical stressors during fuel cell operation. In addition, an MEA sample extraction strategy is designed to investigate membrane degradation processes and associated changes in membrane structure/properties during accelerated degradation. The results of this study provide insight into coupled chemical and mechanical membrane degradation mechanisms that occur during field operation of fuel cell stacks.

2. Experimental

2.1. Membrane electrode assembly (MEA) fabrication

Catalyzed gas diffusion electrodes (GDEs) were fabricated by coating a micro-porous layer made of polytetrafluoroethylene (PTFE) and carbon black on a non-woven carbon paper gas diffusion layer substrate, followed by coating a catalyst layer consisting of carbon-supported platinum catalyst and perfluorosulfonic acid ionomer [25]. MEAs were prepared by hot-pressing a standard perfluorosulfonic acid ionomer membrane with anode and cathode GDEs. The peripheral area of the MEA was covered with one-sided adhesive plastic films on both sides to minimize local electrochemical and mechanical damage during operation.

2.2. Stack assembly

Research-scale stacks were built using Ballard Power Systems' standard test hardware consisting of five cells separated by graphitic bipolar plates designed to achieve close to uniform conditions over the active area. The flow field plates had co-flow parallel straight channels and high gas flow conditions, ensuring minimum pressure drop and minimum changes in reactant composition from stack inlet to outlet. The AST stack consisted of five 45 cm^2 MEAs. A pressurized bladder was used to ensure uniform compression between MEAs and bipolar plates after stack assembly. Prior to installation on a test station, external and internal gas leak tests were carried out by pressurizing dead-ended fluid compartments and measuring any gas transfer to other compartments.

2.3. Fuel cell test station

A Ballard test station was the primary tool used to operate the research-scale stacks, consisting of fully computer-controlled mass flow controllers (MFCs), back pressure control system, pre-heated water circulating coolant loops, and electronic load. The test