Empirical membrane lifetime model for heavy duty fuel cell systems

Natalia Macauley [a], Mark Watson [b], Michael Lauritzen [b], Shanna Knights [b], G. Gary Wang [a], Erik Kjeang [a, *]
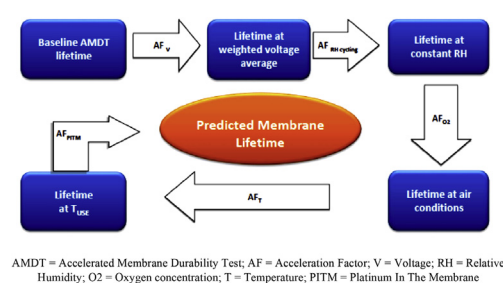
[a] School of Mechatronic Systems Engineering, Simon Fraser University, 250-13450 102 Avenue, Surrey, BC V3T0A3, Canada
[b] Ballard Power Systems, 9000 Glenlyon Parkway, Burnaby, BC V5J5J8, Canada

HIGHLIGHTS

- Accelerated membrane durability tests are performed to generate lifetime data.
- An empirical model is developed to estimate membrane lifetime at use conditions.
- The model is validated using field data from the Whistler, BC fuel cell bus fleet.
- Statistical predictions of membrane leak initiation time and lifetime are reported.

GRAPHICAL ABSTRACT

AMDT = Accelerated Membrane Durability Test; AF = Acceleration Factor; V = Voltage; RH = Relative Humidity; O2 = Oxygen concentration; T = Temperature; PITM = Platinum In The Membrane

ABSTRACT

Heavy duty fuel cells used in transportation system applications such as transit buses expose the fuel cell membranes to conditions that can lead to lifetime-limiting membrane failure via combined chemical and mechanical degradation. Highly durable membranes and reliable predictive models are therefore needed in order to achieve the ultimate heavy duty fuel cell lifetime target of 25,000 h. In the present work, an empirical membrane lifetime model was developed based on laboratory data from a suite of accelerated membrane durability tests. The model considers the effects of cell voltage, temperature, oxygen concentration, humidity cycling, humidity level, and platinum in the membrane using inverse power law and exponential relationships within the framework of a general log-linear Weibull life-stress statistical distribution. The obtained model is capable of extrapolating the membrane lifetime from accelerated test conditions to use level conditions during field operation. Based on typical conditions for the Whistler, British Columbia fuel cell transit bus fleet, the model predicts a stack lifetime of 17,500 h and a membrane leak initiation time of 9200 h. Validation performed with the aid of a field operated stack confirmed the initial goal of the model to predict membrane lifetime within 20% of the actual operating time.

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1. Introduction

There is growing interest in fuel cell cars and buses, due to their promise of improved fuel economy, zero emissions, and quiet operation. However, the light duty fuel cell durability target of 5000 h, and the ultimate heavy duty target of 25,000 h, which corresponds to 12 years or 500,000 miles, are yet to be demonstrated in field operation [1]. Heavy duty transit buses generally operate in revenue service in excess of 10 h per day seven days per week, which is why they require much higher reliability and

durability than passenger cars. In Whistler, BC, some of the buses using Ballard FCvelocity®-HD6 stacks exceeded 10,000 h without failure by the end of the program, whereas the same type of stacks in London have operated for over 20,000 h [2] and a fuel cell system module in Thousand Palms, CA surpassed 20,000 h of operation [3–5]. According to the Clean Urban Transport for Europe (CUTE) program, a total of 56 hydrogen fuel cell buses were deployed across Europe between 2010 and 2016 [6]. By showing long term stability and durability, these buses are paving the way for future hydrogen fuel cell bus programs [7]. Novel solutions for fuel cell catalyst and membrane durability are expected to reach or even exceed the heavy duty lifetime target. Testing of advanced fuel cell systems for transportation is, however, a challenge, as it requires several thousand hours, which is not economically feasible. Instead, accelerated stress tests (ASTs) and accelerated durability tests (ADTs) are used to estimate durability for comparative purposes, and/or benchmark materials for stability in fuel cell systems. ASTs and ADTs induce failure modes observed in the field, in a much shorter time, and are generally of qualitative character. ASTs are generally used as a screening method to quickly eliminate low performers in early stages by exposing the material to much harsher conditions than those experienced during regular fuel cell operation. Good performers are then subjected to an ADT for further evaluation at more realistic conditions, closer to those that can occur during normal operation, generally in-situ, in a single cell or stack [8]. Dynamic ADTs cycle the potential, load, temperature, RH, start/stop events, or apply a bus/car driving cycle [9–11]. Early membrane failure due to degradation-induced perforations, cracks, and pinholes can be a limiting factor for fuel cell durability. Accelerated membrane durability tests (AMDTs) focus on fuel cell membrane failure modes and durability. The primary failure mode of fuel cell membranes is believed to be pinhole formation, which eventually leads to hydrogen leaks that may affect fuel cell performance or exceed a certain safety threshold.

Fuel cell membrane degradation originates in thermal, chemical, and mechanical degradation mechanisms. Thermal membrane degradation can be caused by decomposition of side chain groups in the ionomer at high temperature; membrane blistering from the heat of reactions of crossover gases in a leaky membrane; or membrane deformation due to ice formation at subfreezing temperatures [12]. Chemical degradation is caused by radical attack of the ionomer, whereby the hydroxyl (OH•), hydroperoxyl (HOO•), and hydrogen (H•) radicals have been identified as potentially harmful to the membrane [13]. Radicals can form in the catalyst layers or as a result of hydrogen peroxide decomposition in the presence of Fenton's reagents such as Fe^{2+} in the membrane [14,15]. Hydrogen peroxide may form as an intermediate of the oxygen reduction reaction (ORR) at the cathode and from crossover oxygen that meets hydrogen at the anode [16–21]. The electrochemical reaction for hydrogen peroxide (H_2O_2) formation via the two-electron ORR in the catalyst layers is [22]:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad E_{2e} = 0.695V \; vs. \; SHE \quad (1)$$
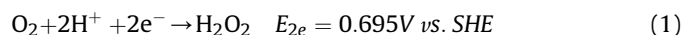
H_2O_2 formed at the electrodes can diffuse into the membrane and decompose into OH• via the Fenton's reaction in the presence of a ferrous iron, Fe^{2+}:

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + OH^{\cdot} + H_2O \quad (2)$$
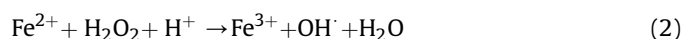
Direct formation of hydroxyl radicals can also occur on Pt surfaces, without peroxide intermediates [23]. Polymer side chain degradation in chemically stabilized perfluorosulfonic acid (PFSA) ionomer membranes is predominantly due to OH• radical attack on the first ether bond in the $\alpha-OCF_2-$ group [24]. Attack by H• may occur to a smaller extent at the tertiary carbon C–F bond on the main and side chains, while attack by OH• occurs solely on the side chain, specifically at the α-O–C bond [25]. Cell voltages close to open circuit voltage (OCV) are known to lead to high levels of chemical degradation [26], resulting in a gradual loss of membrane material, evidenced by general membrane thinning and fluoride release in effluent water [8]. The recently proposed iron redox cycle in the membrane, which has been shown to control the harmful Fe^{2+} concentration in the membrane through reaction-transport phenomena of mobile and redox active iron ions, elucidated the fundamental mechanism of increased chemical membrane degradation at high voltages [27]. Furthermore, membrane hydration levels influence reactant partial pressures, permeability, and thickness [28]. Fuel cell operation at dry conditions leads to increased membrane degradation due to increased anode H_2O_2 production [29]. Thus, adequate humidification of the membrane is crucial for membrane health and durability. Chemical stabilization of PFSA polymer end groups [30] and use of additives, such as cerium and manganese radical scavengers, are promising mitigation strategies for chemical degradation [31,32]. Chemical membrane degradation has been shown to have a strong impact on mechanical membrane properties. Nafion® membrane samples degraded under OCV conditions exhibited a decline in fracture stress and strain due to molecular weight reduction caused by chemical degradation [33]. Furthermore, membrane ductility decreases more significantly when exposed to chemical degradation compared to mechanical degradation [34].

Mechanical stress is a result of the membrane's response to humidity and temperature changes in a constrained fuel cell, which can eventually lead to mechanical membrane degradation in the form of polymer fatigue and creep [35]. Mechanical stress from frequent swelling and shrinking results in a decrease in membrane stiffness and strength [36], as well as the formation of pinholes, cracks, and tears on the surface or in the bulk of the membrane [37]. Non-uniform stress distribution due to temperature gradients induces localized bending stress, which causes delamination between the membrane, electrodes, and gas diffusion layers [38]. Physical membrane reinforcement with a porous polymer matrix, fibers, or inorganic materials are ways to enhance mechanical endurance in membranes [39].

Coupled chemical and mechanical stress exacerbates membrane degradation more than chemical and mechanical degradation applied separately [16]. Membrane fracture, cracks, rips, tears, and pinholes are likely to form faster in the presence of underlying chemical degradation [40]. Results of mechanical testing show a rapid reduction in CCM ductility and fracture strain together with a significant decrease in ultimate tensile strength as a function of cyclic OCV (COCV) AST cycling [40,41], which applies coupled chemical and mechanical stress. Both stressors are present during fuel cell operation, which is why coupled chemical and mechanical degradation successfully generates typical membrane failure modes observed in the field such as local membrane thinning, crack and pinhole formation, or delamination from the catalyst layers [42].

Fuel cells can experience local potential spikes at the cathode during start-ups from an air-air state and during shut-downs, leading to Pt dissolution, corrosion of carbon support, and migration of platinum from the cathode catalyst layer into the membrane [43–45]. A protective platinum oxide (PtO) film forms on the catalyst surface at potentials above 0.9 V. The PtO film is stripped away as the potential cycles below 0.9 V, causing instability of Pt–Pt bonds in the first and second atomic layers, and exposing them to dissolution [46]. Dissolved Pt ions are chemically reduced by crossover H_2 permeating through the membrane from the anode, resulting in Pt particle deposition in the membrane and the formation of a densely packed Pt band at a specific distance from the