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Review

A review on performance degradation of proton exchange membrane fuel cells during startup and shutdown processes: Causes, consequences, and mitigation strategies

Yi Yu[a,b], Hui Li[a,*], Haijiang Wang[a,**], Xiao-Zi Yuan[a], Guangjin Wang[b], Mu Pan[b]

[a] Institute for Fuel Cell Innovation, National Research Council Canada, 4250 Wesbrook Mall, Vancouver, BC, Canada V6T 1W5
[b] State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, PR China

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ABSTRACT

Performance degradation during startup and shutdown is considered an important issue affecting the durability and lifetime of proton exchange membrane fuel cells (PEMFCs). Due to the high potentials experienced by the cathode during startup and shutdown, the conventional carbon support for the cathode catalyst is prone to oxidation by reacting with oxygen or water. This paper presents an overview of the causes and consequences of performance degradation after frequent startup–shutdown cycles. Mitigation strategies are also summarized, including the use of novel catalyst supports and the application of system strategies to prevent performance degradation in PEMFCs. It is found from the literature review that improvements in catalyst supports to prevent oxidation come at the expense of high cost, and the novel supports developed to date are not sufficient to completely prevent carbon oxidation in fuel cell engines. System strategies, including potential control and reaction gas control, have been developed and applied in fuel cell engines to alleviate or even avoid performance decay. This review aims to provide a clear understanding of the mechanisms related to degradation behaviors during the startup and shutdown processes, thereby helping fuel cell material or system developers in their efforts to prevent performance degradation and prolong the lifetime of PEMFCs.

Contents

* Corresponding author. Tel.: +1 604 221 3000.
** Corresponding author. Tel.: +1 604 221 3038.
E-mail addresses: hui.li@nrc.gc.ca (H. Li), haijiang.wang@nrc.gc.ca (H. Wang).

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1. Introduction

A fuel cell is an electrochemical device that can directly convert hydrogen energy to electricity. Among the various types of fuel cell, the proton exchange membrane fuel cell (PEMFC) is considered one of the most promising clean energy sources of the twenty-first century for transportation and stationary applications, due to its high energy conversion efficiency and power density, fast startup, and low/zero emission level [1,2]. Considerable research over the past few decades has significantly advanced PEMFC technology. However, some technological "bottlenecks" have limited its further commercialization. For example, the relatively short lifetime of PEMFCs, induced by materials degradation, is still unsatisfactory for stationary and automotive applications. The U.S. Department of Energy (DOE) lifetime targets for 2015 are 5000 h for transportation power systems and 40,000 h for stationary power systems [3], but current PEMFC technology yields only 1700 h and 10,000 h, respectively [4]. Insufficient fuel cell system durability is caused by degradation of the fuel cell components. The durability of each component in a PEMFC is affected by many internal and external factors, including material properties, fuel cell operating conditions (such as humidification, temperature, cell voltage, etc.), impurities or contaminants in the feeds, environmental conditions (e.g., subfreezing or cold start), operation modes (such as startup, shutdown, potential cycling, etc.), and the design of the components and the stack.

For automobile applications, PEMFCs must operate under various conditions, such as load changing cycles, high power conditions, idling conditions, and startup and shutdown cycles. Among these various dynamic conditions, startup and shutdown processes present a unique challenge for PEMFC systems, as they cause the cathode potential to become abnormally high, at which point the catalyst support is prone to be oxidized, resulting in adverse effects for fuel cell durability. Pei et al. investigated the durability of a PEMFC and evaluated its lifetime under startup and shutdown conditions [5]. The results suggested that performance decay under frequent startup and shutdown cycles is very serious, but the effect of startup and shutdown cycles on fuel cell lifetime can be ignored if the stack voltage is promptly dispelled after the fuel cell stops operating. However, quickly and completely dispelling the stack voltage is not easy, due to residual gas in the flow field after shutdown.

The recent literature contains several review papers on PEM fuel cell durability/reliability issues. Wu et al. [6] published a comprehensive review on PEMFC degradation mechanisms and mitigation strategies, in which durability tests under steady state [7–17] and dynamic state [18–30] conditions were also briefly summarized. In addition, Wu et al. [6] also discussed the major failure modes and mitigation strategies of different components in PEMFCs. Borup et al. [2] published an important review paper contributed by 56 researchers from national laboratories and universities in the United States and Japan who participated in a PEMFC Durability Workshop funded by the United States Department of Energy (DOE). This review provided comprehensive discussions on fundamental and scientific aspects of PEMFC durability, such as operational effects on fuel cell durability, but its main focus was on the degradation of components, including the membrane, catalyst layer, and gas diffusion layer. Vahidi et al. [31] in their review introduced the main parameters influencing the long-term performance and durability of PEMFCs. Zhang et al. [32] provided a review of Pt-based catalyst layer degradation in PEMFCs, including a very detailed discussion of the carbon corrosion mechanisms under gross fuel starvation and the air/fuel boundary; mitigation strategies were also introduced, among them carbon support improvement and system strategies.

All these reviews have touched on performance degradation and carbon oxidation during the startup and shutdown cycles, but there is no comprehensive review of PEMFC durability studies and mitigation strategies under startup and shutdown conditions. Over the last few years, in an effort to enhance the lifetime of PEMFC systems for automobile applications undergoing frequent startup and shutdown, significant progress has been made in the development of novel catalyst supports. In addition, various system strategies for tackling startup and shutdown issues have been developed and reported through a considerable number of papers and patents. There is thus a need for a detailed review of degradation mechanisms and all known mitigation strategies, including materials improvement and system strategies for startup and shutdown processes, to help fuel cell material developers or fuel cell system developers in their efforts to prevent performance degradation and prolong the lifetime of PEMFCs for automotive applications.

The purpose of this review is therefore to summarize the studies conducted by academic and industrial researchers on the durability of PEMFCs during startup and shutdown. First, a description of startup and shutdown processes is provided for a clear understanding of what happens to fuel cells during these processes. Second, accelerated lifetime tests under startup–shutdown cycle conditions, conducted by both academic and industrial researchers, are summarized and discussed. In addition, the major failure modes and root causes of degradation during startup and shutdown processes are discussed in detail. The review concludes with a detailed introduction of recently developed mitigation strategies, including materials improvement and system strategies, based on an exhaustive survey of journal papers and patents.

2. Startup and shutdown processes

Both startup and shutdown are dynamic processes that a fuel cell inevitably must confront in automobile applications. Compared to steady-state processes, startup and shutdown processes experience different profiles under operating conditions. For example, the cell temperature, gas humidity, and local gas mixture are different than under steady-state conditions—for example, increasing temperature and humidity during startup, and decreasing temperature and humidity during shutdown. However, the major feature during startup and shutdown, a feature that is also the major cause of performance degradation during those processes, is the local gas mixture at the anode, which is commonly called the hydrogen/air interface or the fuel/air interface. To clearly understand the accelerated lifetime tests and degradation mechanisms associated with startup and shutdown processes, a brief introduction to these processes is given below and a schematic graph is presented in Fig. 2.

2.1. Startup process

The startup process for the fuel cells referred to in this paper excludes cold start below freezing temperatures. In the normal operation of fuel cell engines, air fills the anode flow field after