Review

Degradation aspects of water formation and transport in Proton Exchange Membrane Fuel Cell: A review

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HIGHLIGHTS

- The effect of water formation and transport on PEMFC durability varies with cell's designs.
- The effect of water accumulation on PEMFC durability is detrimental at sub-freezing temperatures.
- The impact of water mechanisms on PEMFC durability can be classified as ageing or catastrophic.

ARTICLE INFO

ABSTRACT

This review paper summarises the key aspects of Proton Exchange Membrane Fuel Cell (PEMFC) degradation that are associated with water formation, retention, accumulation, and transport mechanisms within the cell. Issues related to loss of active surface area of the catalyst, ionomer dissolution, membrane swelling, ice formation, corrosion, and contamination are also addressed and discussed. The impact of each of these water mechanisms on cell performance and durability was found to be different and to vary according to the design of the cell and its operating conditions. Overall, the impact of water mechanisms can be classified as aging or catastrophic. Ageing has a long-term impact over the duration of the PEMFC life-time whereas in the catastrophic mechanism the impact is immediate. The conversion of cell residual water into ice at sub-freezing temperatures by the water retention/accumulation mechanism and the access of poisoning contaminants through the water transport mechanism are considered to fall into the catastrophic category. The effect of water mechanisms on PEMFC degradation can be reduced or even eliminated by (a) using advanced materials for improving the electrical, chemical and mechanical stability of the cell components against deterioration, and (b) implementing effective strategies for water management in the cell.

1. Introduction

Fuel cells have the potential to resolve the current energy crisis of the 21st century. These electrochemical energy devices convert the chemical energy of hydrogen fuel into electrical energy efficiently [1]. They offer great flexibility in their design which allows them to be in various configurations and to operate with a wide range of hydrocarbon fuels, features that broaden the scope of their applications. Furthermore, the fact that hydrogen is an abundant source gives fuel cells the advantage to be one of the most sustainable solutions for future energy needs.

The commercialisation of fuel cells is mainly affected by their high cost and the lack of a hydrogen infrastructure. Attempts to reduce the cost of fuel cells and to develop a global hydrogen network for their use are still ongoing. The primary focus is to minimise the loading of Platinum (Pt) in the catalyst of the Membrane Electrode Assembly (MEA) which is considered to be the main contributor to the high cost [2]. Some studies have suggested the use of more effective techniques for Pt deposition onto the catalyst to reduce its loading [3–7], others concentrated on enhancing the polarisation performance of the cell to compensate for further Pt reduction [8–10]. Although some studies [11] claimed that reduction of up to 50% (e.g. 0.15 mg-Pt cm^{-2}) is achievable with marginal compromise to the fuel cell stack efficiency (<1%), further reduction is still needed [12]. The manufacturing cost of fuel cell components, particularly the MEA and the Gas Diffusion Layer (GDL), is another significant contributor to the overall cost [2]. An approach which can make them more affordable is to increase the manufacturing volume of fuel cell stacks and to reduce the complexity of the manufacturing processes of some of their

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components [2]. It is expected that, as fuel cell stacks become commercially viable, hydrogen fuelling infrastructure will be established that is easily accessible for supporting the penetration of fuel cells into the market place [13,14]. This remains a major concern particularly for the transport sector where issues associated with hydrogen production [15,16], safety [17–19], on-board and off-board storage [20–22] have surfaced.

The durability of fuel cells is another obstacle affecting their commercialisation [23]. Currently, PEMFCs can operate for some 2500 h in transportation [24]. Although this timescale has doubled in recent years, it is still inadequate and may need further doubling (∼5000 h) in order to meet the target for year 2015 aimed by the US Department of Energy (DOE), the Japan's New Energy and Industrial Technology Development Organisation (NEDO), and the European Hydrogen and Fuel Cell Technology Platform (HFP). For stationary applications, the life-time requirement for fuel cells extends to 40,000 h [25]. The reason for the longer life period in this case is attributed to the fact that the fuel cell load is more stable than under transport conditions. The rapid change in fuel cell load, usually referred to as dynamic load cycling, affects significantly the degradation rate [26] and the life-time expectancy of the cell [27]. Potential load cycling can severely affect the mechanical and chemical properties of the catalyst and its carbon support leading to an early cell failure [28].

Various durability tests were implemented by fuel cell developers in order to predict their life-time under practical operating conditions. Emphasis on developing accelerated life-time tests, also called accelerated stress tests (ASTs), has increased in recent years to prevent the prolonged test periods and high costs associated with real time tests. The results obtained from those accelerated tests were found not to be consistent and to differ considerably from the real lifetime or steady state measurements [28–34]. This is probably expected as measurements were carried out under different operating conditions and for different fuel cell component designs. Furthermore, some durability measurements [35–42] were made of individual components rather than of the complete cell unit. Thus, the effect of degradation on the neighbouring components which consequently affects the life-time of the entire cell will not be represented. This stresses the need for standardised durability protocols which would ensure uniformity between these measurements.

Degradation of PEMFC can be caused by a number of factors associated with the design of the cell and its operation. These factors can be classified into two types: catastrophic and ageing. Catastrophic factors are the ones that can cause immediate or early failure in cell performance due to severe mechanical or chemical damage to the cell during operation. The Pinhole formation on the surface of the membrane, for instance, can be very damaging to the cell since it allows reactant gases to cross-over from the anode or the cathode side leading to catalytic combustion and a sudden drop in the cell's power output [43,44]. Membrane perforations or cracks in the cell components may be the result of impaired design/fabrication during preparation process, improper cell assembly, or operation of the cell at extremely high pressures and temperatures. Membrane poisoning is another detrimental factor to the lifetime of PEMFC. High concentration levels of impurities such as carbon monoxide (CO) in the reactant gases results in CO adsorption to the platinum surface of the catalyst which blocks the active hydrogen sites [45,46].

Ageing factors represent the natural cause of degradation due to cell electrochemical reaction. Unlike catastrophic, their effects on depleting cell's performance occur gradually. Three phases of voltage drop were identified in the ageing process representing stable operation, slow decrease in cell voltage and rapid fall in voltage [47]. The degradation rate is a function of the operational

time of the cell and is usually expressed as the drop in microvolt scale per hour of operation (e.g. $\mu V\ hr^{-1}$). This rate is strongly dependant on the deterioration rate of the cell's materials such as the change in the mechanical and chemical properties of the catalyst including the loss in electro-catalyst surface area due to growth in the platinum particle size [48,49], corrosion of platinum-based catalysts [50,51], and corrosion of carbon support catalyst [52]. A comprehensive review of PEMFC components degradation can be found in Ref. [53].

Although deterioration of the material is inevitable, due to the electrochemical nature of the fuel cell reaction, its rate can be minimised. Many attempts were made in the past few years to develop more robust components and operational regimes capable of withstanding harsh fuel cell conditions against degradation. In Ref. [54] the design of membranes was suggested to be made thicker to reduce hydrogen crossover to the cathode. According to Ref. [55], sulfonated polymide membranes exhibit better stability than Nafion under electric load cycling. Refs. [56,57] found Pt stability in the catalyst to be improved against dissolution by using multiwalled carbon nanotubes (CNTs) and by modifying Pt nanoparticles with gold (Au) clusters. Others [58,59] have pointed to the effect of carbon film coating on improving the mechanical and electrical properties of gas diffusion layers. In Ref. [60] the role of homogeneous coating in controlling the diffusion overvoltage from the gas diffusion layers was revealed. Several other studies [61–66] stressed the importance of coating for bipolar plates to prevent surface corrosion. Refs. [67,68] suggested to operate PEMFC under low relative humidity (RH) to minimise the loss of Pt active surface area contrary to Refs, [48,69] which concluded that low RH increases carbon corrosion in the catalyst. Others like Ref. [44] suggested reducing RH, temperature and hydrogen pressure during PEMFC operation to suppress the hydrogen cross-over mechanism. The influence of fuel and oxidant starvation [70], open circuit operation [71], excessive air bleeding [72], humidity cycling [73,74], load-on/off cycling [75], and freeze/thaw cycling [76] on structural changes of the membrane was also demonstrated. A more detailed analysis of the effect of the operating conditions on the PEMFC durability can be found in Ref. [77].

Despite all these investigations, very few studies have highlighted the role of water on the degradation of PEMFC. This review paper attempts to focus on the impact of (a) water production during the electrochemical reaction of the cell, (b) water accumulation in the channels and reaction sites and (c) water transport mechanisms on the electrical, mechanical, thermal and chemical/electrochemical deterioration of the PEMFC components.

2. Water distribution and transport

Good water distribution in PEMFC is a recipe for achieving effective water management and enhanced performance of the cell [218]. The ionic conductivity of Nafion is strongly dependant upon the amount of water available in the membrane [78]. The water which is absorbed by the sulphonic acid groups (HSO3) of the membrane due to its hydrophilic characteristic enables H^+ ions to move freely on weakening the attraction force between H^+ and SO_3^- ions [79]. The more water molecules are present in each SO_3^- chain, the better the conductivity of H^+ becomes. Nevertheless, too much water can block the reaction sites of the neighbouring electrodes preventing the access of reactant gases to the cell. Therefore, the amount of water in these two regions must be kept in optimum balance for cell performance.

New materials and designs were developed to maintain this delicate balance. Appropriate loading of oxygen permeable and hydrophobic dimethyl silicone oil (DSO) [80], hygroscopic γ-alumina particles [81], silicon dioxide particles [82,83] and silica-