A Review of Pinhole Detection Techniques

Grace Amadi[a], Graham Smith[b], Edward Brightman[a]

[a] Department of Chemical and Process Engineering, University of Strathclyde, Glasgow, G1 1XJ, UK
[b] National Physical Laboratory, Hampton Road, Teddington, Middlesex, TW11 0LW, UK
grace.amadi@strath.ac.uk

University of Strathclyde Glasgow

NPL National Physical Laboratory

Introduction

Pinholes in membranes are a key defect that can severely limit the lifetime of PEM fuel cells.[3] Quality control measurements are required to identify these defects during manufacture and thereby improve the reliability, stability and cost-effectiveness of components.[1,2] There is a need to develop detection techniques that can be applied during manufacture, but first the dimension at which pinholes become critical to performance and durability needs to be identified and the growth of pinholes during fuel cell operation better understood.

This poster will discuss the impact of pinholes in catalyst coated membranes (CCMs) and the resolution, limitations, and effectiveness of off-line, in-line and operando techniques that have been used to date to identify and characterise them.

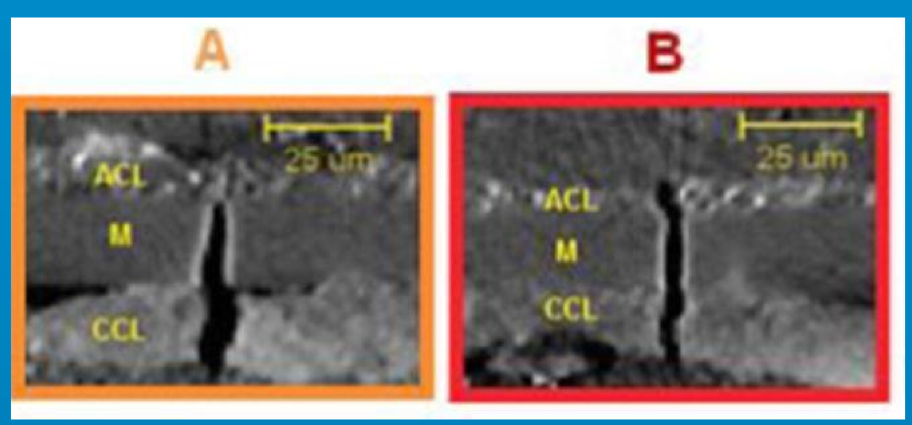

Figure 1. Literature example of XCT Cross-sectional internal images of a crack in a membrane (A) through the cathode catalyst layer and membrane and (B) through both anode and cathode catalyst layers as well as membrane. [5]

Formation & Impact of Pinholes

Pinholes are formed through two main mechanisms:

- Mechanical stress on the membrane leading to thinning and eventual formation of pinholes.[4]
- Chemical (radical) attacks on the membrane, initially causing thinning of the membrane that eventually pinhole formation.[1]

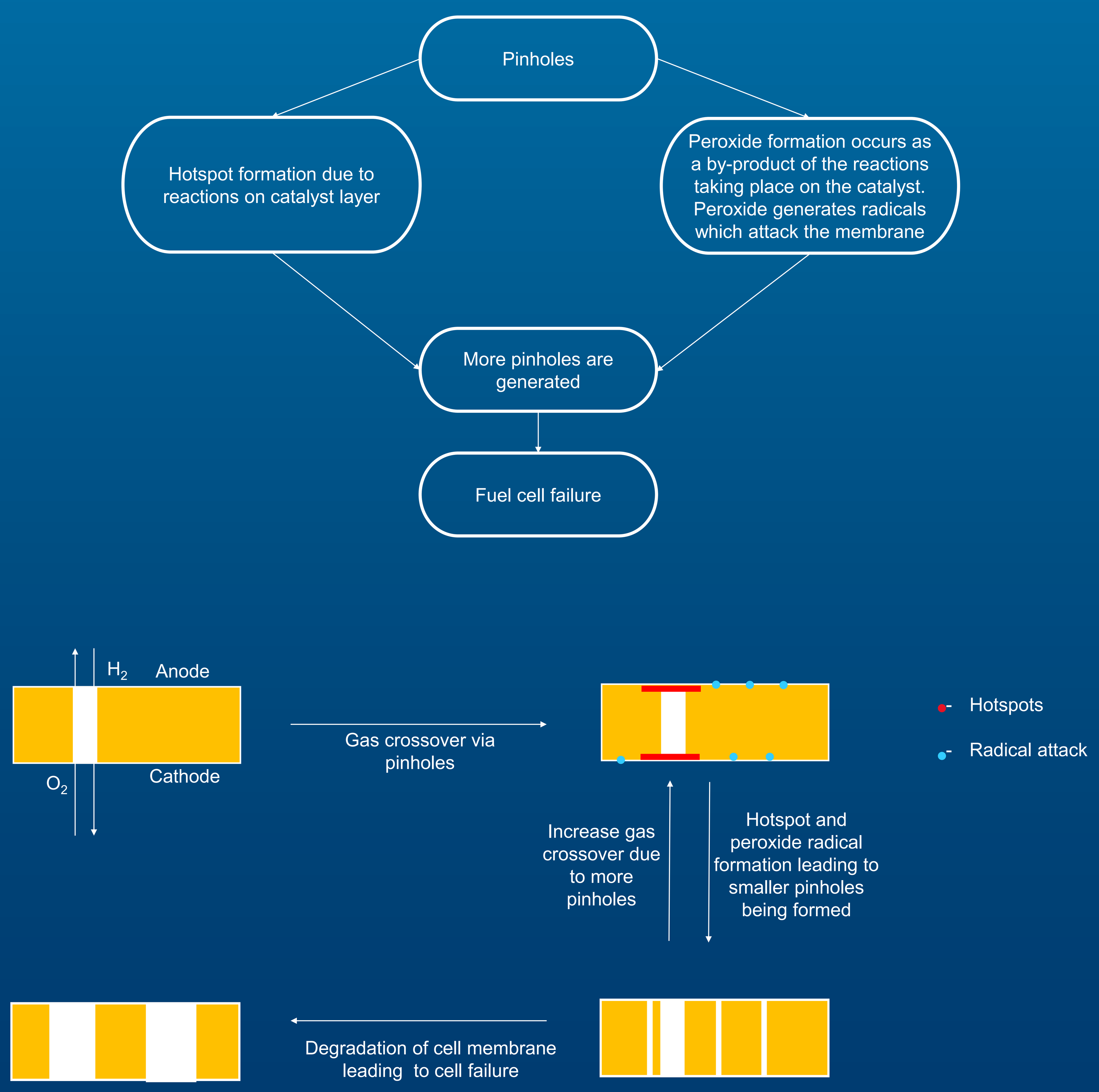

Figure 2. Mechanisms of pinholes inducing degradation of membrane.

Pinhole Characterisation Techniques

Technique	Resolution	Relevant defects	Type	Advantages	Disadvantages	Refs
SEM	10 nm	Catalyst layer morphology and microstructure: cracks, delamination, clusters, clusters, catalyst loss and thickness variations Membrane: pinhole tear and slits	Ex-situ Off-line	High resolution Pinholes can be localised and quantified	Destructive Limited sample size	16–18
Optical Microscopy	250 nm	Catalyst layer: cracks, delamination, scratches, missing catalyst	Ex-situ Off-line	Non-destructive	Lower resolution	19,20
Infrared Thermography	10 µm	Catalyst layer: variations in catalyst layer thickness Membrane: pinholes crack tears thinning	In-situ In-line	Pinholes can be localised and quantified Fast Non-destructive	Resolution low and dependent on operating conditions and cell characteristics.	9–11,21–23
XCT	100 nm	Membrane: cracks and pinholes, bubbles, tears and slits	In-situ Off-line	Pinholes can be localised and quantified Produces 3D images of the defect Non-destructive	Expensive and limited availability	5,6,24–26
Raman Spectroscopy	n/a	Membrane degradation Membrane defects: pinholes	Operando in-situ	Can evaluate the impact of pinholes on fuel cells internal chemistry	No localization and qualification of pinholes	27–34
Leak test	200 µm	Membrane defects: pinholes	Operando	Fast Easily implemented	No localization and qualification of pinholes	9,35
Polarization Curve	N/A	Membrane degradation	Operando	Fast Easily implemented Can evaluate impact on performance & degradation	No localization and qualification/quantification of pinholes	12,13,36
EIS	N/A	Membrane degradation	Operando	Fast Easily implemented Can evaluate impact on performance & degradation	No localization and qualification of pinholes	12,13,37
Hydrogen Crossover	N/A	Membrane defect: pinhole tears slits	Operando	Fast Easily implemented	No localization and qualification of pinholes	9,38

Off-line, In-line & Operando Techniques

Measurement techniques are often suited to complimentary applications:

- Offline testing is when a sample is taken off the production line and analysed in detail. Slow but detailed imaging techniques such as SEM and XCT are well suited to this.
- In-line techniques are performed on the production line, they must be fast. IR thermography has been applied in-line detecting defects > 10 µm.[9-11]
- Operando testing happens during fuel cell operation. The most commonly used operando techniques tend to be electrochemistry based but they are unable to characterise individual defects.

Future Work

- Identify how the size of pinholes influences their impact on fuel cells so that the limits of detection required for online quality control techniques can be specified.
- Develop methods to artificially manufacture membrane pinholes smaller than 3 µm.
- Investigate IR thermography as a possible operando measurement technique

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