

# “Polymer Electrolyte Membrane and Direct Methanol Fuel Cell Technology”

Edited by Christoph Hartnig (Chemetall GmbH, Germany) and Christina Roth (Institute for Applied Materials – Energy Storage Systems, Karlsruhe Institute of Technology, Germany), Woodhead Publishing Series in Energy, Woodhead Publishing Ltd, Cambridge, UK, 2012; Volume 1: Fundamentals and Performance of Low Temperature Fuel Cells, 436 pages, ISBN: 978-1-84569-773-0, £150.00, €180.00, US\$255.00; Volume 2: *In Situ* Characterization Techniques for Low Temperature Fuel Cells, 524 pages, ISBN: 978-1-84569-774-7, £165.00, €200.00, US\$280.00

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## Reviewed by Bruno G. Pollet

HySA Systems Competence Centre, SAIAMC, University of the Western Cape, Modderdam Road, Private Bag X17, Bellville 7535, Cape Town, South Africa

Email: [bgpollet@hysasystems.org](mailto:bgpollet@hysasystems.org)

## Introduction

This book set covers polymer electrolyte membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs). It is aimed at novice readers as well as experienced fuel cell scientists and engineers in this area. There are 34 contributors in Volume 1 and 30 in Volume 2, predominantly from Germany, with some contributions from the UK, France, Denmark, Italy, Switzerland, the USA and Canada. The editors are well known for their research, work and contributions in the fields of low-temperature fuel cell technology and materials components characterisation. Dr Christoph Hartnig is based at Chemetall GmbH and was formerly Head of Research at both BASF Fuel Cell GmbH and the Centre for Solar Energy and Hydrogen Research (Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg (ZSW)), Germany. Professor Dr Christina Roth is Professor for Renewable Energies at the Technische Universität Darmstadt and Head of a Research Group at the Institute for Applied Materials – Energy Storage Systems, Karlsruhe Institute of Technology (KIT) in Germany.

## Volume 1: “Fundamentals and Performance of Low Temperature Fuel Cells”

Volume 1 consists of two parts. Part I is entitled ‘Fundamentals of Polymer Electrolyte Membrane and Direct Methanol Fuel Cell Technology’, and Part II is entitled ‘Performance Issues in Polymer Electrolyte Membrane and Direct Methanol Fuel Cells’.

## Fuels and Materials

Part I consists of five chapters. Chapter 1: ‘Fuels and Fuel Processing for Low Temperature Fuel Cells’ deals with the effects of fuel type and quality on low-temperature fuel cell performance and degradation. The chapter

gives short overviews of fuel processing, fuel storage methods and alternative sources of hydrogen. An excellent diagram overview of fuel processing for fuel cell systems (Figure 1) by Iain Staffell (Imperial College, London, UK) (1) is given. Chapter 2: 'Membrane Materials and Technology for Low Temperature Fuel Cells' gives a very good overview of the most recent investigations in PEM materials for low-temperature PEMFCs with a section on PEM materials for high-temperature applications. It reviews perfluorosulfonic acid PEMs and non-perfluorinated PEMs including sulfonic acid, phosphonic, heterocycle functionalised and acid doped membrane materials. A short section is specifically dedicated to the morphology and microstructure of ionomer membranes.

### Electrocatalysts

Chapter 3: 'Catalyst and Membrane for Low Temperature Fuel Cells' focuses on fuel cell electrocatalysis and the importance of the type and loading of the cathode catalyst. The current anode and cathode catalyst loadings for low-temperature PEMFCs are ca. 0.2 mg<sub>Pt</sub> cm<sup>-2</sup> and 0.4 mg<sub>Pt</sub> cm<sup>-2</sup>, respectively, with a target for automotive applications of a total catalyst loading of 0.2 mg<sub>Pt</sub> cm<sup>-2</sup> (with anode catalyst loading of 0.05 mg<sub>Pt</sub> cm<sup>-2</sup> and cathode catalyst loading of 0.15 mg<sub>Pt</sub> cm<sup>-2</sup>) for a cell voltage of 0.85 V, assuming a CO-free hydrogen supply. Figure 2 shows the evolution of Pt loading and estimated fuel cell balance of plant from 2006 (2). Both carbonaceous and non-carbonaceous electrocatalyst support materials are mentioned

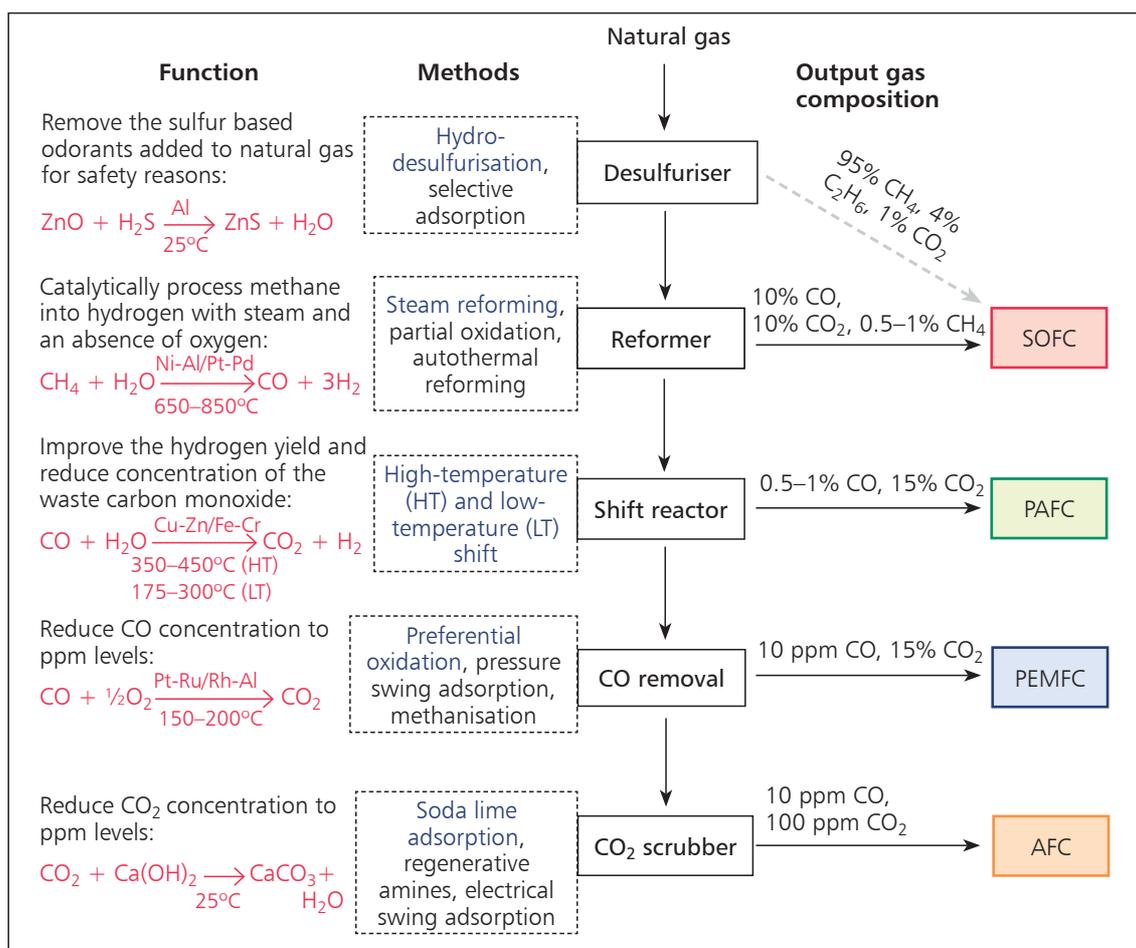


Fig. 1. An overview of fuel processing for fuel cell systems (1) (Courtesy of Iain Staffell, University of Birmingham, UK, and Woodhead Publishing)

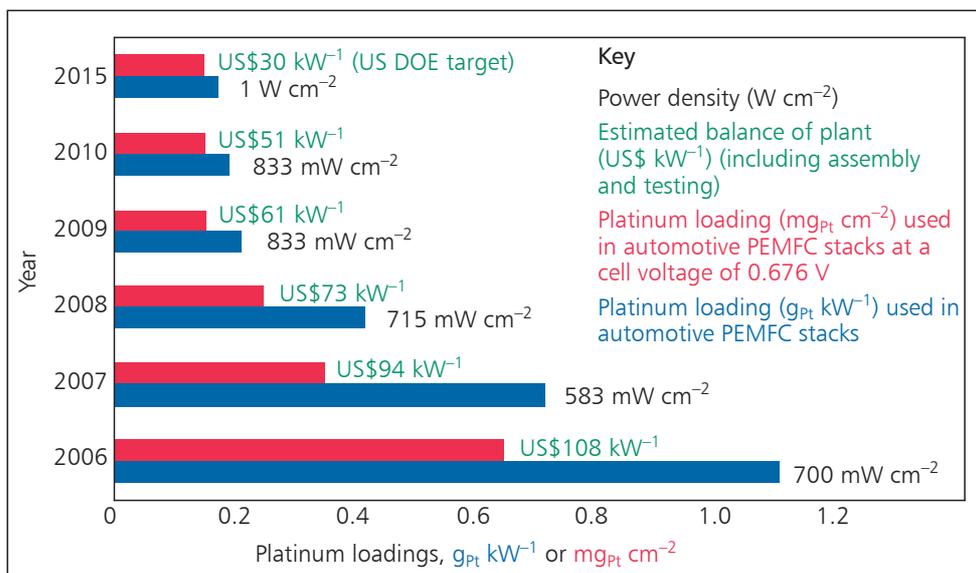


Fig. 2. Evolution of platinum loadings and estimated balance of plant fuel cell (Reproduced from (2) by permission of Elsevier)

(including, for example, metal oxides (3)) for both PEMFCs and direct methanol fuel cells (DMFCs).

The chapter also highlights some of the most recent developments in anode and cathode catalysts (including ultra-low Pt) used in low-temperature fuel cells. These include core-shell and binary and ternary alloy electrocatalysts – platinum alloyed with cobalt, copper, iron, molybdenum, nickel and/or ruthenium. The chapter also discusses new approaches in fuel cell electrocatalysis research and development, for example the reduction of the Pt content and the investigation of Pt-free compounds (for example Co and Fe incorporated in nitrogen macrocycle structures) based upon either non-precious metals or alloyed transition metals. However, the chapter does not touch on advanced cathode catalysts such as the famous 3M platinum nano-structured thin film (NSTF) (4), which is a bit of a disappointment. For those who are interested in learning further about fuel cell electrocatalysis, there are a number of additional books which I would strongly recommend (4–6).

### Gas Diffusion Media

Chapter 4: ‘Gas Diffusion Media, Flow Fields and System Aspects in Low Temperature Fuel Cells’ covers the role and importance of gas diffusion media (teflonated/unteflonated woven and non-woven), flow field plate designs on performance and degradation and system design criteria for low-temperature applications. The chapter briefly states characterisation methods for gas diffusion layers, although it does not

highlight other *ex situ* characterisation methods for bulk or contact resistance, surface morphology or fibre structure and mechanical strength measurements (7). There is also little information on the possible thermal conductivity effect of the microporous layer on cell performance.

The chapter then broadly discusses the role of flow field design for both low-temperature PEMFC and DMFC with some brief discussions around the importance of flow field plate material, especially its interaction with the gas diffusion layer material under various operating conditions and applications (7, 8). Perhaps for completeness the authors could have added a short section on *ex situ* characterisation and accelerated ageing/accelerated stress tests for flow field plate materials. This chapter also discusses the importance of the system layouts of the two low-temperature fuel cells, i.e. balance of plant, including reactant supplies and thermal management. For Chapter 4, perhaps the section on system aspects of low-temperature fuel cells could have been a separate chapter in the book emphasising the correlation between the flow field plate design and material, the gas diffusion layer material and the overall system design and layout.

### Environmental Aspects

Chapter 5: ‘Recycling and Life Cycle Assessment of Fuel Cell Materials’ focuses on the environmental aspects of fuel, fuel cell components and fuel cell stacks as well as recycling. The chapter highlights the fact that pgms such as Pt, Pd and Rh are successfully

recycled from today's vehicles (principally from catalytic converters – modern vehicles may contain around 1 g of Pt for petrol and around 8 g of Pt for diesel (2)) and the technologies can be adopted to recycle Pt from fuel cell systems. This chapter is very interesting and well-written as recycling of fuel cell components and systems and their impact on the environment is often neglected, and a 'zero-to-landfill' approach is required in order to lead to long-term cost savings. It also highlights that recycling in the fuel cell manufacturing industry will become paramount for mass-produced systems in which environmental considerations will have to be taken into account (for example, collection/separation systems, recycling processes, component reuse, remanufacturability and energy recovery). Life cycle assessment models of fuels and fuel cell components are discussed in detail and the standardised life cycle assessment protocol (International Organization for Standardisation – ISO 14040 series) is briefly mentioned.

### Operation and Ageing

Part II in Volume 1 consists of seven chapters: Chapter 6: 'Operation and Durability of Low Temperature Fuel Cells' gives an excellent overview of the effects of low-temperature PEMFC operating conditions (thermal, water and reactant management, contamination types and levels and duty cycling) on performance and durability (which is also correlated to component material properties, their designs and cycling abilities). The chapter highlights the major degradation processes occurring in the pgm-based cathode catalyst layer and PEM regions present for

all operating conditions and briefly describes how that degradation can be minimised, in turn increasing performance and durability, by improving the overall stack design at component material and operational levels.

Chapter 7: 'Catalyst Ageing and Degradation in Polymer Electrolyte Membrane Fuel Cells' focuses on performance degradation of electrocatalysts affected by the relatively harsh operating conditions within low-temperature fuel cells and discusses catalyst ageing mechanisms. For example, it explains the three principal mechanisms attributed to the loss of electrochemical surface area for pure Pt and Pt alloys supported on carbon, i.e. dissolution (leading to Pt redeposition or Pt precipitation), migration with concomitant coalescence and detachment of Pt nanoparticles from the carbonaceous support as well as complete or incomplete carbon corrosion of the support material. The discussion then focuses on the main effects causing such mechanisms: temperature, pH, anion types, water partial pressure, Pt particle size and electrode potential variations and for Pt alloy electrocatalysts, dealloying of the non-precious metal (mainly transition metals as they are not stable in acidic environments – for example Pt-Co catalysts are known to exhibit poor performance under intense cycling conditions). The chapter also briefly reviews *ex situ* and *in situ* catalyst degradation characterisation methods with an emphasis on a very useful, powerful and newly developed technique – identical location transmission electron microscopy (IL-TEM) – that was originally developed by the chapter's authors (Figure 3). The technique provides

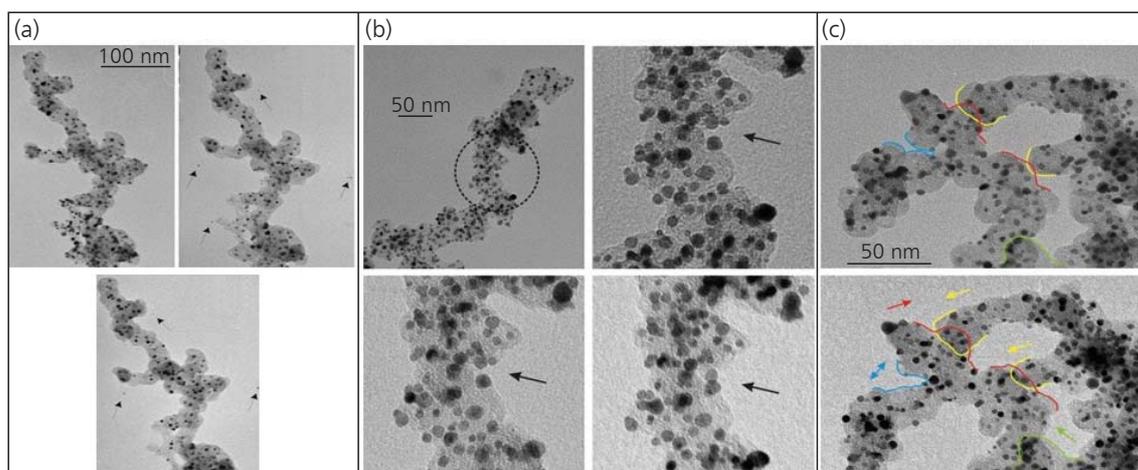


Fig. 3. Series of IL-TEM micrographs of platinum particles on a carbon support, showing: (a) Particle detachment; (b) Particle movement and agglomeration; and (c) Displacement of the carbon support under various harsh potential cycling conditions (Reproduced by permission of Woodhead Publishing)

insights into electrocatalyst stability on the nanoscale level under various regimes and thus allows a direct (visual) observation of the effect of electrochemical treatments on carbon-supported high surface area electrocatalysts (9).

### Durability Tests

Chapter 8: 'Degradation and Durability Testing of Low Temperature Fuel Cell Components' is well-written and well-structured. It discusses accelerated durability test protocols (*ex situ* and *in situ*) mainly for the critical low-temperature PEMFC components which are the PEM, the electrocatalyst and the electrocatalyst carbonaceous support materials. The chapter also briefly covers the effect of fuel contaminants on durability. Chapter 8 nicely highlights the main publications dealing with degradation and durability studies and protocols for the membrane electrode assembly (MEA) and its subcomponents.

Chapter 9 is a very good and systematic discussion of the stochastic microstructure techniques for the determination of transport property parameters as well as the study of the effect of porous structure materials upon transport behaviours within the critical PEMFC catalyst layer, gas diffusion layer and microporous layer regions.

### Modelling

Chapter 10: 'Multi-scale Modelling of Two-Phase Transport in Polymer Electrolyte Membrane Fuel Cells' discusses in detail the pore network model and the lattice Boltzmann model for the modelling of two-phase flow in porous PEMFC materials such as gas diffusion layers and catalyst layers. The chapter describes how pore-scale information (for example, microstructure, transport and performance) can be useful for more predictive macroscopic scale-up.

Chapter 11, entitled 'Modelling and Analysis of Degradation Phenomena in Polymer Electrolyte Membrane Fuel Cells', is an excellent review of the various available models describing PEMFC degradation phenomena and mechanisms. The chapter highlights the most important work on the subject in the last 20 years and also briefly introduces pioneering work by, for example, Springer *et al.* (Los Alamos National Laboratory, New Mexico, USA) (10), Bernardi and Verbrugge (General Motors Research and Environmental Staff, USA) (11) and Antoine (Université de Genève, Switzerland) *et al.* (12). This chapter also describes systematically and comprehensively the various modelling approaches

to elucidate ageing mechanisms and their possible predictions. The author also discusses the newly developed transient, multi-scale and multi-physics single cell model MEMEPhys<sup>®</sup> (13) and emphasises the need to generate representative accelerated testing methods in the field.

Finally, Volume 1 ends with Chapter 12 entitled 'Experimental Monitoring Techniques for Polymer Electrolyte Membrane Fuel Cells'. This chapter describes the various techniques and methods employed for on-line and off-line logging, monitoring and diagnosis of important fuel cell parameters (for example, temperature, humidity, current distribution, local pressure distribution and pressure drop) during operation.

### Volume 2: "In Situ Characterization Techniques for Low Temperature Fuel Cells"

Volume 2 consists of three parts: Part I entitled 'Advanced Characterization Techniques for Polymer Electrolyte Membrane and Direct Methanol Fuel Cells', Part II entitled 'Characterization of Water and Fuel Management in Polymer Electrolyte Membrane and Direct Methanol Fuel Cells' and Part III entitled 'Locally Resolved Methods for Polymer Electrolyte Membrane and Direct Methanol Fuel Cell Characterization'. I thoroughly enjoyed reading Volume 2 as it covers comprehensively the important and main (*in situ*) techniques and methods currently employed in characterising in detail MEA and MEA subcomponents (fuel cell electrocatalyst, catalyst layer, membrane and gas diffusion medium) as well as water and fuel management. It would have been very useful to have included a summary table showing the *in situ* and *ex situ* characterisation techniques which help to elucidate the degradation mechanisms for all MEA components and water and fuel management (including extended X-ray absorption fine structure (EXAFS), IL-TEM, three-dimensional (3D)-TEM, *in situ* X-ray tomography (XRT), small angle X-ray scattering (SAXS), X-ray adsorption near edge structure ( $\Delta\mu$  XANES), neutron radiography, neutron tomography, magnetic resonance imaging, synchrotron radiography, Raman spectroscopy, scanning electron microscopy (SEM) and laser optical methods).

### Conclusions

This two-volume set presents a fairly comprehensive and detailed review of low-temperature PEMFCs and DMFCs and their *in situ* characterisation methods by reviewing in detail their fundamentals and

performance as well as advanced *in situ* spectroscopic techniques for their characterisation. I was impressed by the content and breadth of this detailed work. There are of course already books available covering similar areas and there is some duplication between chapters (for example, fuel cell descriptions), but this does not detract from the overall experience. The book set also highlights the key challenges for the commercialisation of PEMFC-based systems, mainly related to life cycle analysis of the overall systems and global research and development efforts on materials development for durability and long term operation.

This is a very informative work, especially with regard to current progress on *in situ* characterisation techniques (Volume 2). Although I was a little disappointed at the lack of high-temperature PEMFC information, I would definitely recommend this book set for readers who are either experienced or new in this exciting field.

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## The Reviewer



Bruno G. Pollet FRSC recently joined Hydrogen South Africa (HySA) Systems Competence Centre at the University of the Western Cape as Director and Professor of Hydrogen and Fuel Cell Technologies. Pollet has extensive expertise in the research fields of PEMFC, fuel cell electrocatalysis and electrochemical engineering. Website: <http://www.hysasystems.org/>