Characterization and design of HTPEM fuel cells

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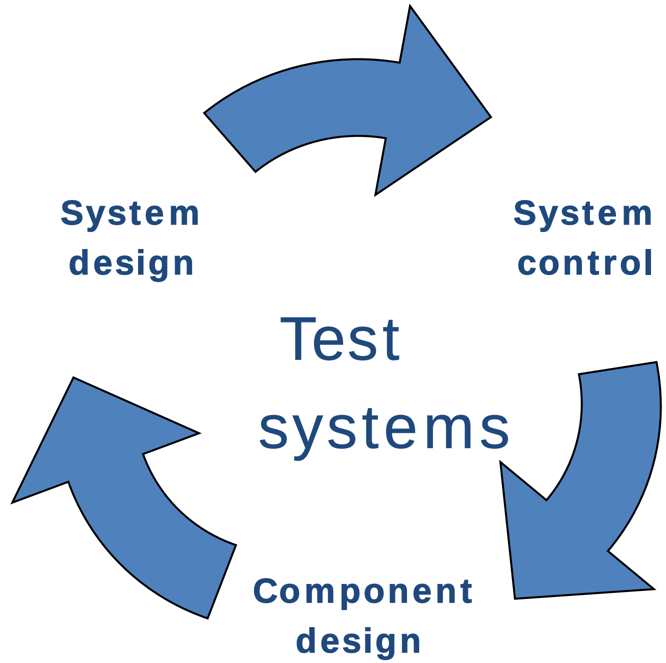
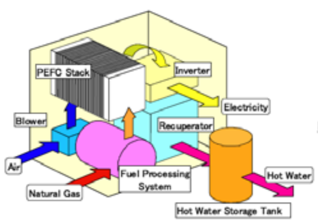
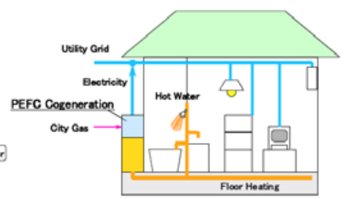
Associate professor Mads Pagh Nielsen
Associate professor Torsten Berning
Assistant professor Benoit Bidoggia
Postdoc Hans-Christian Becker Jensen
Postdoc Samuel S. Araya
Postdoc Vincenzo Liso
PhD student Simon L. Sahlin
PhD student Anders Christian Olesen
PhD student Haftor Örn Sigurdsson
PhD student Jakob Rabjerg Vang
PhD student Xin Gao
PhD student Kristian Kjær Justesen

General activities

- Modeling
  - Ranging from micro scale to macro scale
    - From detailed component design to model based control
- Experimental characterization
  - Component behavior vs. operating conditions
    - Temperature, pressure, load characteristics
- System design, control and testing
  - Micro CHP, Backup power, range extension

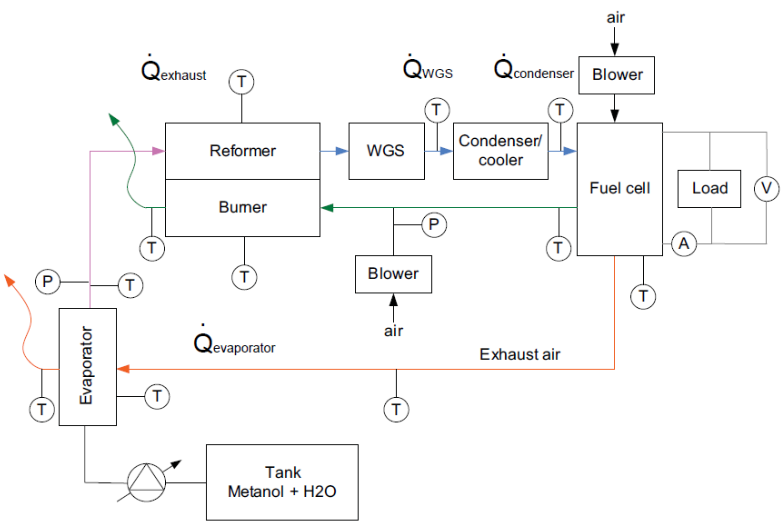


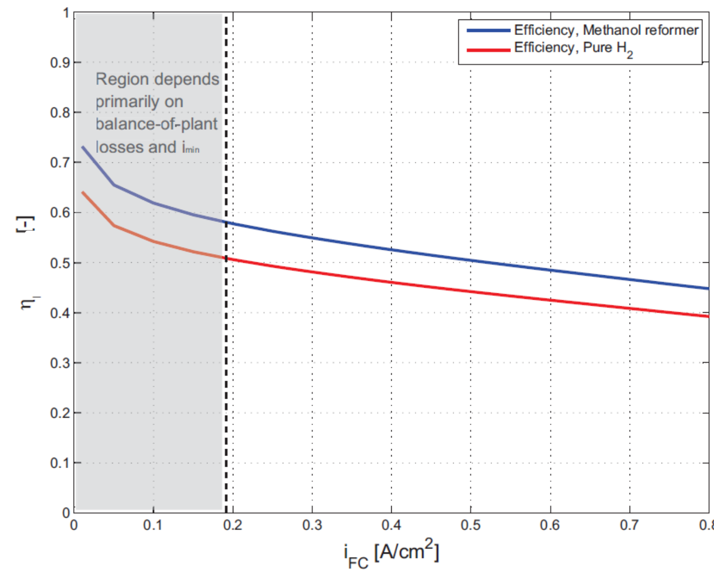




Reformed methanol for HTPEM

- Methanol is an excellent fuel and improve system efficiency compared to **hydrogen** if:
  - We could steam reform it at 160C and S:C=1.0 with no CO formation and no methanol slip!
- These challenges are key to many of our research activities
- *NB: Methanol is available today, it can be produced entirely from renewables and is not constrained by available biomass resources.*





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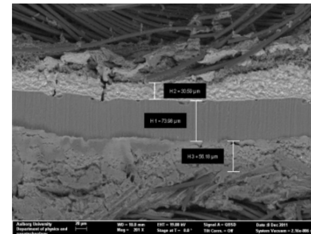
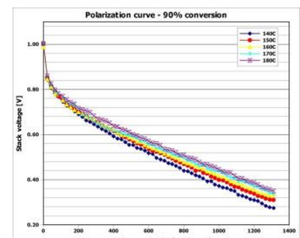
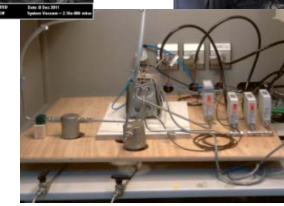
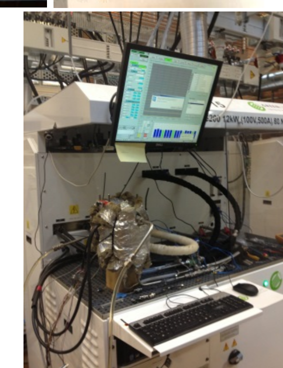
Experimental activities

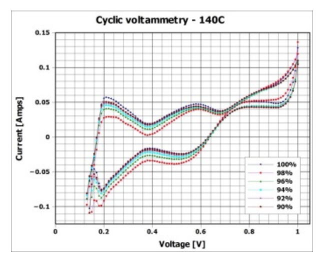
- SEM-EDX analyses of MEAs
  - Structure and elemental composition
- Single cell test facilities 50 cm2 with EIS
  - In-house built H_2/air and reformate setups
  - Performance and degradation rates
    - Start/stop & reformate with methanol slip
  - I,V-curve, EIS and CV
- Methanol reformer tests/mapping
- Stack tests (short stack and 5 kW)

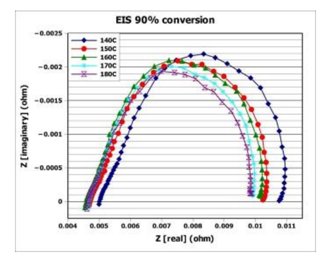


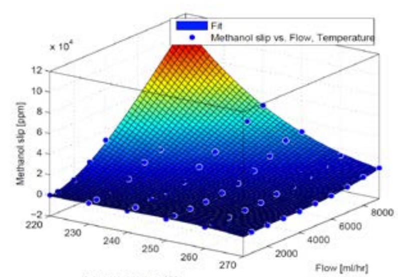












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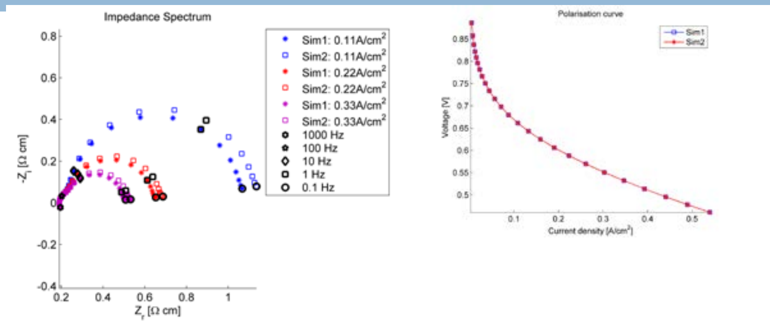
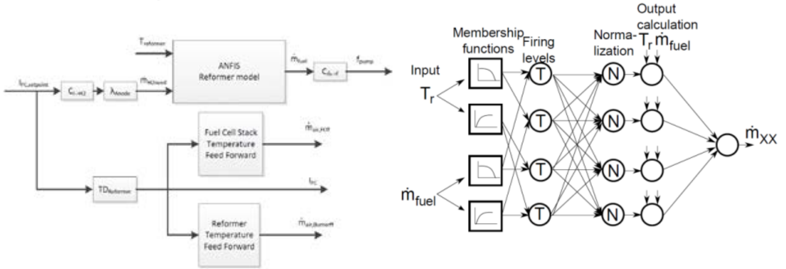
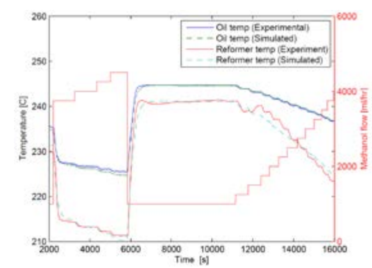
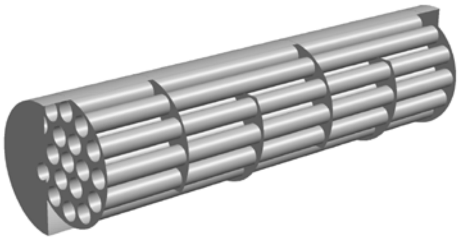
Modelling activities

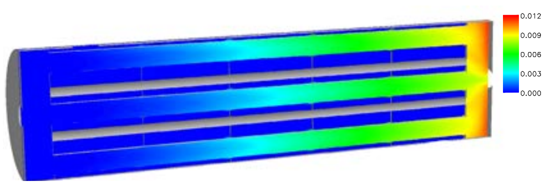
- 1D and 2D electrochemical model
  - Simultaneous EIS and I,V-curve simulation
- System level models
  - BoP design
  - Control concept development
    - Adaptive neuro fuzzy inference system (**ANFIS**)
  - Potential diagnostics capabilities (FDI)
- Computational Fluid Dynamics
  - Reformer reactor analysis
  - Conversion, temperature distribution etc.
  - Assist in design and control development



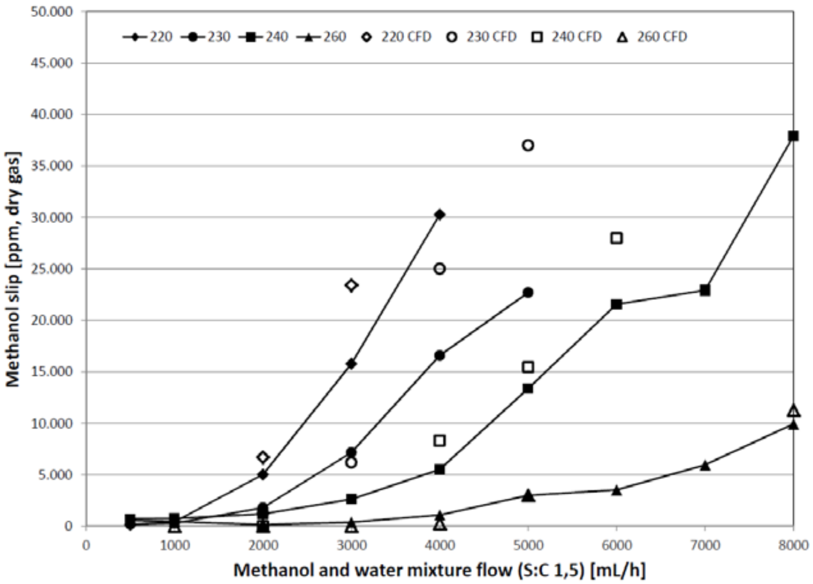


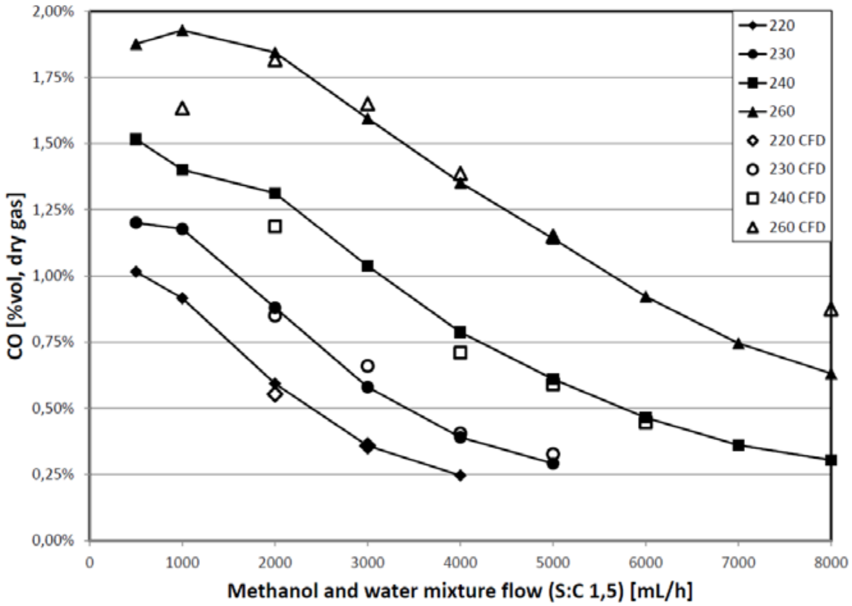




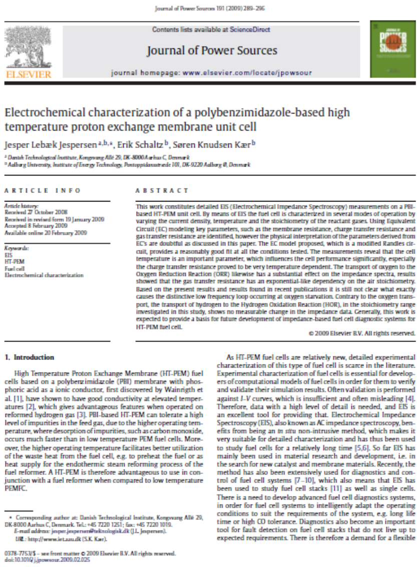


CO and MeOH slip from reformer





EIS based analysis of HTPEMFC



Journal of Power Sources 191 (2009) 289–296

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Electrochemical characterization of a polybenzimidazole-based high temperature proton exchange membrane unit cell

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ARTICLE INFO

Article history:
Received 27 October 2008
Received in revised form 19 January 2009
Accepted 8 February 2009
Available online 20 February 2009

Keywords:
EIS
HT-PEM
Fuel cell
Electrochemical characterization

ABSTRACT

This work constitutes detailed EIS (Electrochemical Impedance Spectroscopy) measurements on a PBI-based HT-PEM unit cell. By means of EIS the fuel cell is characterized in several modes of operation by varying the current density, temperature and the stoichiometry of the reactant gases. Using Equivalent Circuit (EC) modeling key parameters, such as the membrane resistance, charge transfer resistance and gas transfer resistance are identified, however the physical interpretation of the parameters derived from EC's are doubtful as discussed in this paper. The EC model proposed, which is a modified Randles circuit, provides a reasonably good fit at all the conditions tested. The measurements reveal that the cell temperature is an important parameter, which influences the cell performance significantly, especially the charge transfer resistance proved to be very temperature dependent. The transport of oxygen to the Oxygen Reduction Reaction (ORR) likewise has a substantial effect on the impedance spectra, results showed that the gas transfer resistance has an exponential-like dependency on the air stoichiometry. Based on the present results and results found in recent publications it is still not clear what exactly causes the distinctive low frequency loop occurring at oxygen starvation. Contrary to the oxygen transport, the transport of hydrogen to the Hydrogen Oxidation Reaction (HOR), in the stoichiometry range investigated in this study, shows no measurable change in the impedance data. Generally, this work is expected to provide a basis for future development of impedance-based fuel cell diagnostic systems for HT-PEM fuel cell.

1. Introduction

High Temperature Proton Exchange Membrane (HT-PEM) fuel cells based on a polybenzimidazole (PBI) membrane with phosphoric acid as a ionic conductor, first discovered by Wainrigth et al. [1], have shown to have good conductivity at elevated temperatures [2], which gives advantageous features when operated on reformed hydrogen gas [3]. PBI-based HT-PEM can tolerate a high level of impurities in the feed gas, due to the higher operating temperature, where desorption of impurities, such as carbon monoxide, occurs much faster than in low temperature PEM fuel cells. Moreover, the higher operating temperature facilitates better utilization of the waste heat from the fuel cell, e.g. to preheat the fuel or as heat supply for the endothermic steam reforming process of the fuel reformer. A HT-PEM is therefore advantageous to use in conjunction with a fuel reformer when compared to low temperature PEMFC.

As HT-PEM fuel cells are relatively new, detailed experimental characterization of this type of fuel cell is scarce in the literature. Experimental characterization of fuel cells is essential for developers of computational models of fuel cells in order for them to verify and validate their simulation results. Often validation is performed against I–V curves, which is insufficient and often misleading [4]. Therefore, data with a high level of detail is needed, and EIS is an excellent tool for providing that. Electrochemical Impedance Spectroscopy (EIS), also known as AC impedance spectroscopy, benefits from being an *in situ* non-intrusive method, which makes it very suitable for detailed characterization and has thus been used to study fuel cells for a relatively long time [5,6]. So far EIS has mainly been used in material research and development, i.e. in the search for new catalyst and membrane materials. Recently, the method has also been extensively used for diagnostics and control of fuel cell systems [7–10], which also means that EIS has been used to study fuel cell stacks [11] as well as single cells. There is a need to develop advanced fuel cell diagnostics systems, in order for fuel cell systems to intelligently adapt the operating conditions to suit the requirements of the system, e.g. long life time or high CO tolerance. Diagnostics also become an important tool for fault detection on fuel cell stacks that do not live up to expected requirements. There is therefore a demand for a flexible

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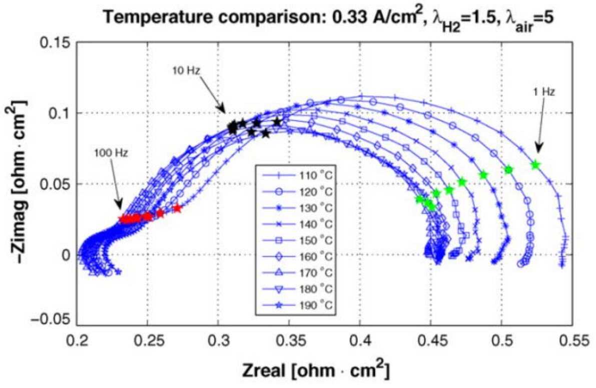
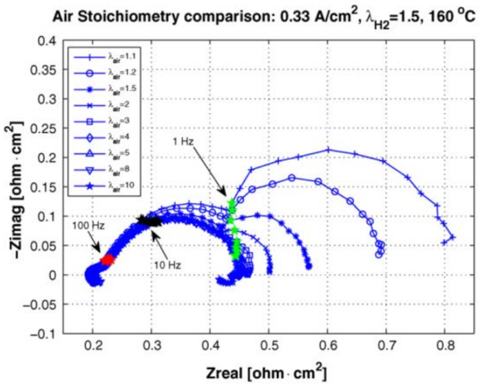
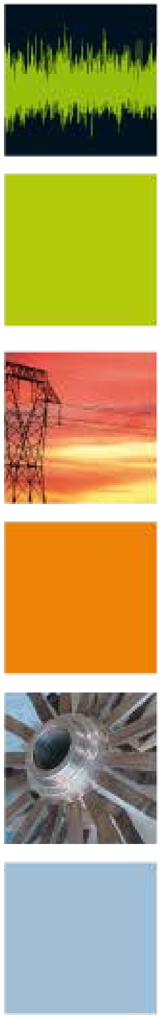
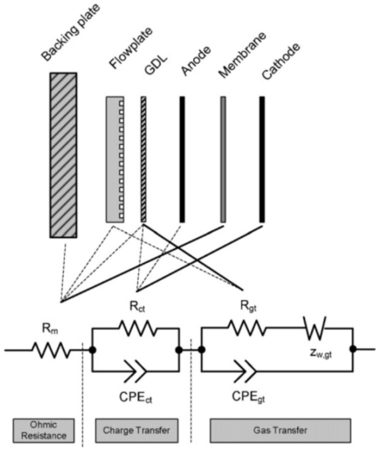
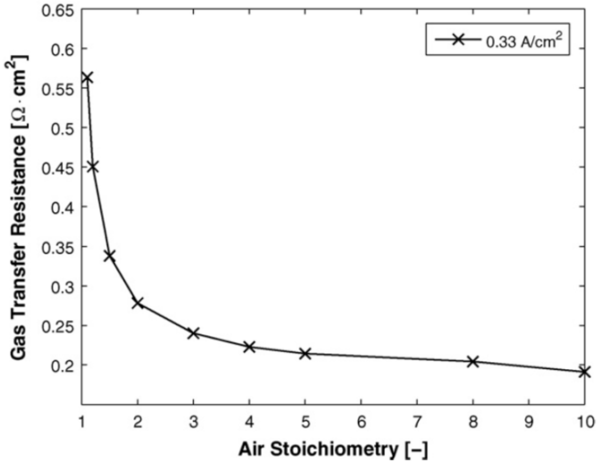
doi:10.1016/j.jpowsour.2009.02.025











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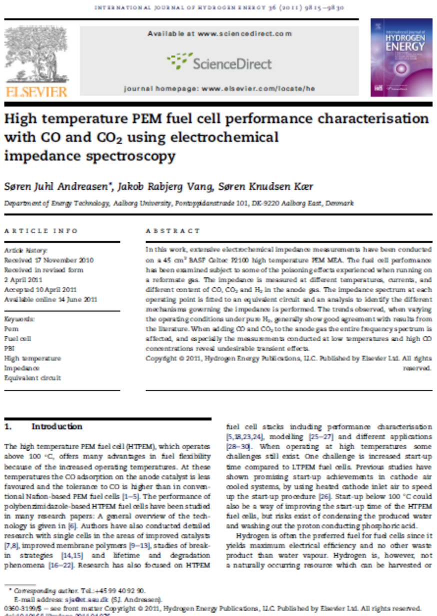
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 36 (2011) 9815–9830

Available at www.sciencedirect.com
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High temperature PEM fuel cell performance characterisation with CO and CO_2 using electrochemical impedance spectroscopy

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ARTICLE INFO

Article history:
Received 17 November 2010
Received in revised form
2 April 2011
Accepted 10 April 2011
Available online 14 June 2011

Keywords:
Pem
Fuel cell
PBI
High temperature
Impedance
Equivalent circuit

ABSTRACT

In this work, extensive electrochemical impedance measurements have been conducted on a 45 cm^2 BASF Celtec P2100 high temperature PEM MEA. The fuel cell performance has been examined subject to some of the poisoning effects experienced when running on a reformate gas. The impedance is measured at different temperatures, currents, and different content of CO, CO_2 and H_2 in the anode gas. The impedance spectrum at each operating point is fitted to an equivalent circuit and an analysis to identify the different mechanisms governing the impedance is performed. The trends observed, when varying the operating conditions under pure H_2, generally show good agreement with results from the literature. When adding CO and CO_2 to the anode gas the entire frequency spectrum is affected, and especially the measurements conducted at low temperatures and high CO concentrations reveal undesirable transient effects.

1. Introduction

The high temperature PEM fuel cell (HTPEM), which operates above 100 °C, offers many advantages in fuel flexibility because of the increased operating temperatures. At these temperatures the CO adsorption on the anode catalyst is less favoured and the tolerance to CO is higher than in conventional Nafion-based PEM fuel cells [1–5]. The performance of polybenzimidazole-based HTPEM fuel cells have been studied in many research papers: A general overview of the technology is given in [6]. Authors have also conducted detailed research with single cells in the areas of improved catalysts [7,8], improved membrane polymers [9–13], studies of break-in strategies [14,15] and lifetime and degradation phenomena [16–22]. Research has also focused on HTPEM fuel cell stacks including performance characterisation [5,18,23,24], modelling [25–27] and different applications [28–30]. When operating at high temperatures some challenges still exist. One challenge is increased start-up time compared to LTPEM fuel cells. Previous studies have shown promising start-up achievements in cathode air cooled systems, by using heated cathode inlet air to speed up the start-up procedure [26]. Start-up below 100 °C could also be a way of improving the start-up time of the HTPEM fuel cells, but risks exist of condensing the produced water and washing out the proton conducting phosphoric acid.

Hydrogen is often the preferred fuel for fuel cells since it yields maximum electrical efficiency and no other waste product than water vapour. Hydrogen is, however, not a naturally occurring resource which can be harvested or

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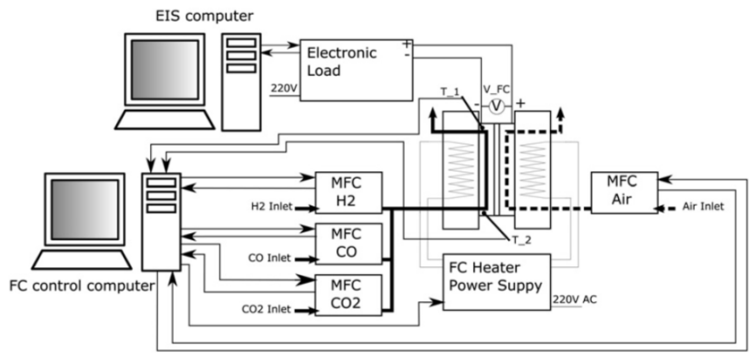
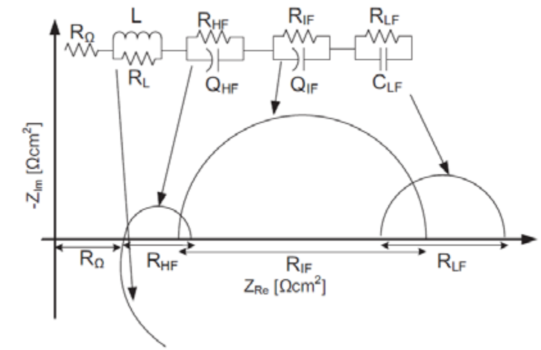
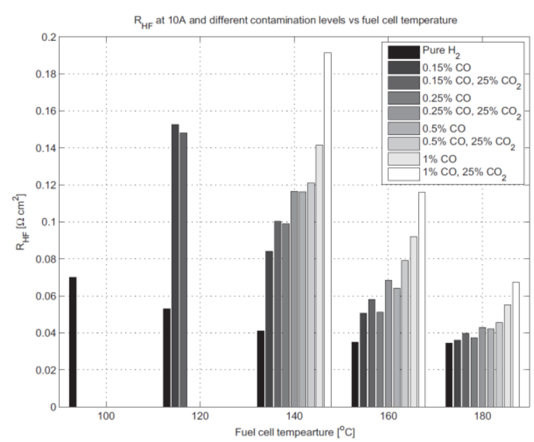
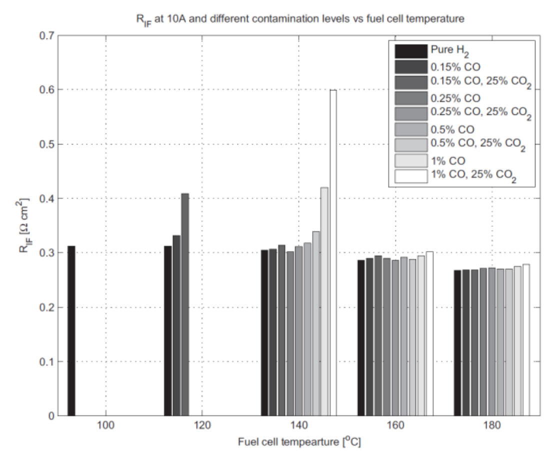
0360-3199/$ – see front matter
doi:10.1016/j.ijhydene.2011.04.076

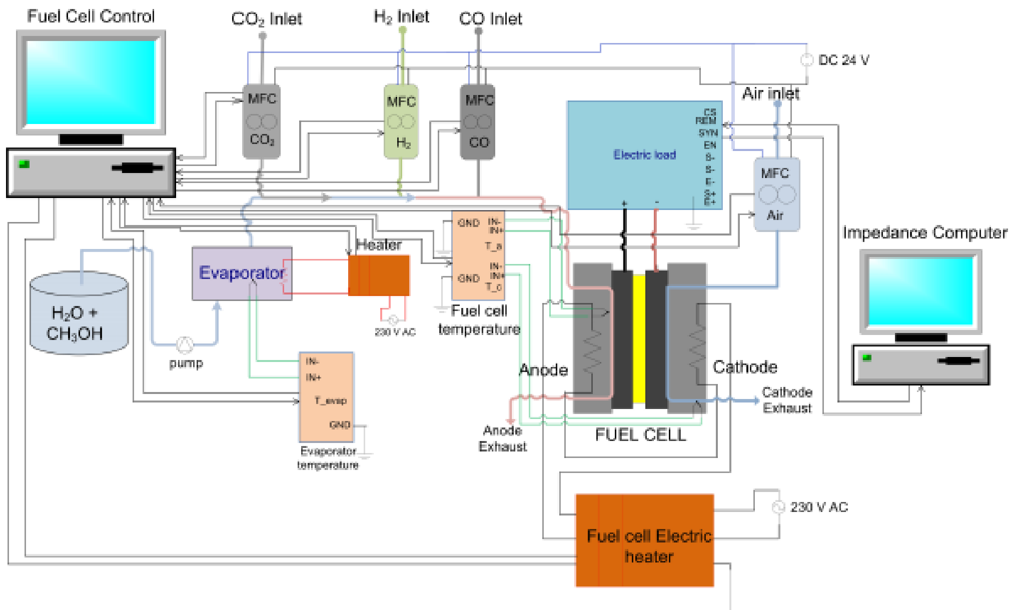


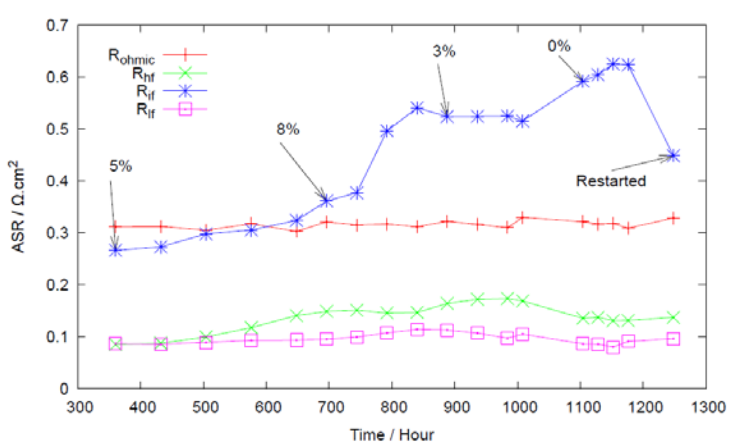


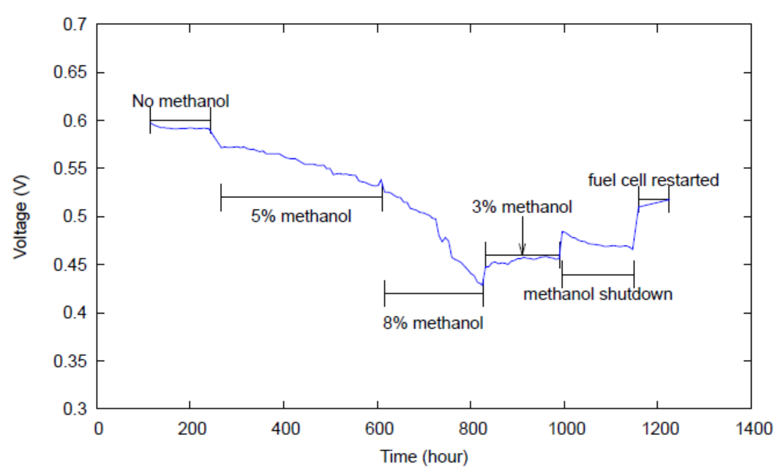




Reformed methanol fuelled HTPEM



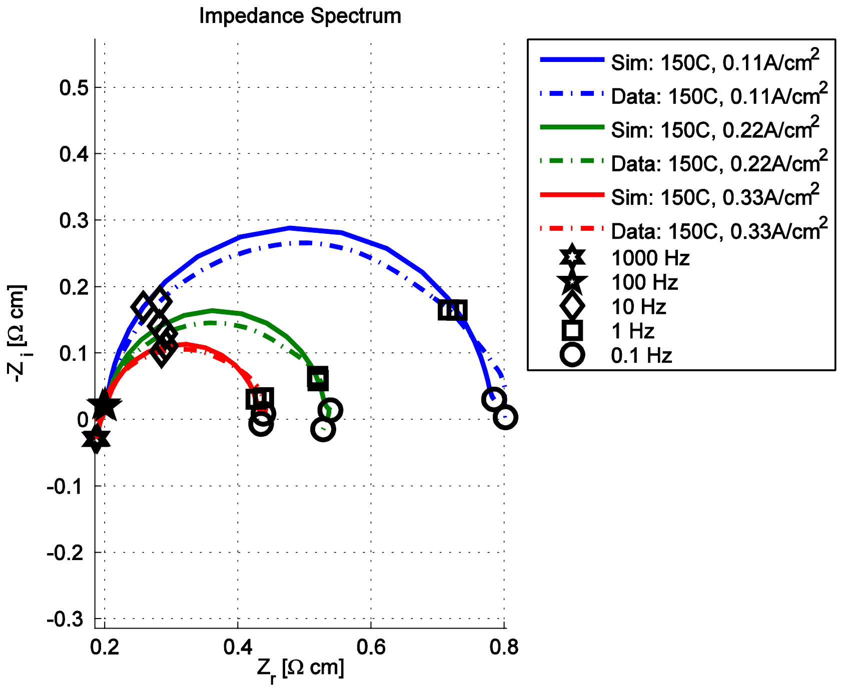


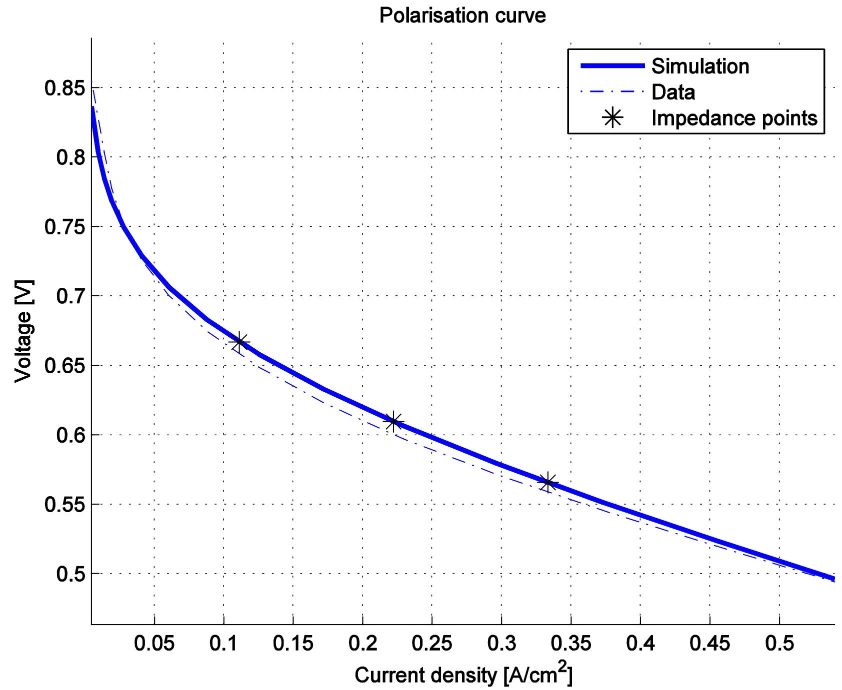


EIS modelling

- Simulate EIS and IV curves
- 1D through the membrane model
- The model at a glance
  - Gas phase transport
  - Transport of O2 in H3PO4
  - Multi step reaction kinetics
  - Ion transport in CL and membrane

Fit to data





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Advanced impedance simulations

A Transient Fuel Cell Model to Simulate HTPEM Fuel Cell Impedance Spectra

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This paper presents a spatially resolved transient fuel cell model applied to the simulation of high temperature PEM fuel cell impedance spectra. The model is developed using a 2D finite volume method approach. The model is resolved along the channel and across the membrane. The model considers diffusion of cathode gas species in gas diffusion layers and catalyst layer, transport of protons in the membrane and the catalyst layers, and double layer capacitive effects in the catalyst layers. The model has been fitted simultaneously to a polarization curve and to an impedance spectrum recorded in the laboratory. A simultaneous fit to both curves is not achieved. In order to investigate the effects of the fitting parameters on the simulation results, a parameter variation study is carried out. It is concluded that some of the fitting parameters assume values which are not realistic. In order to remedy this, phenomena neglected in this version of the model must be incorporated in future versions. [DOI: 10.1115/1.4005609]

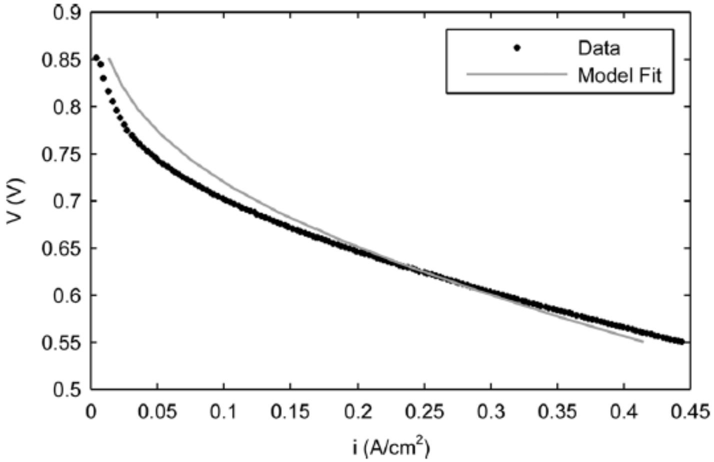
1 Introduction

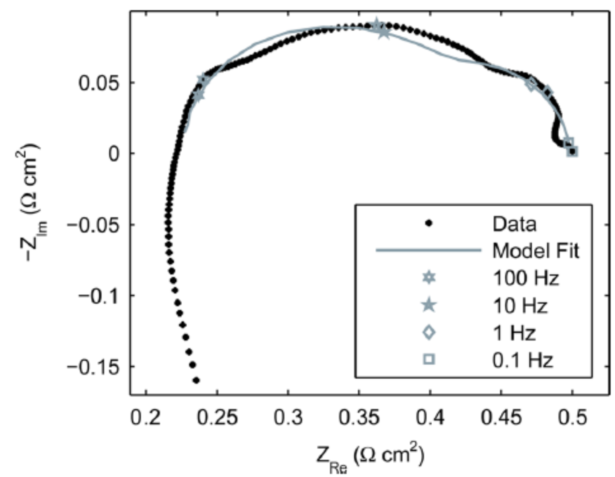
$$Z = \frac{V_{AC}}{i_{AC}}(\cos(\varphi) + j\cdot\sin(\varphi)) \quad (1)$$

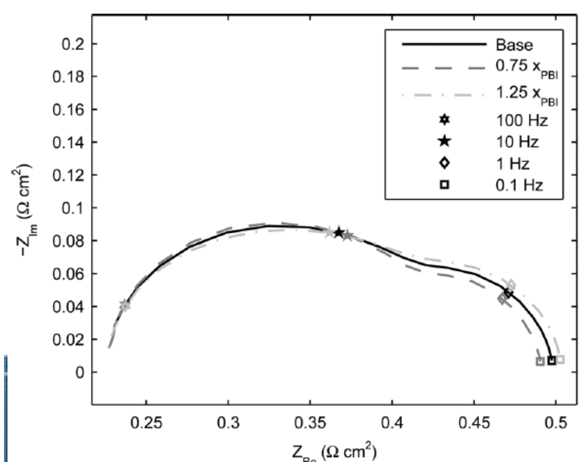
Here V_{AC} [V] and i_{AC} [A cm^{-2}] are the voltage and current density signal amplitudes respectively and φ is the phase shift between the signals. ...

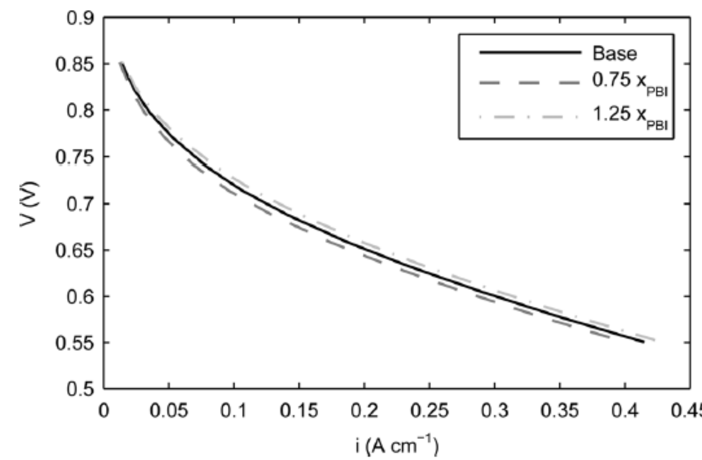
[1]Corresponding author.

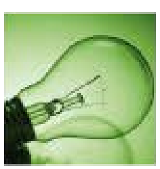
Contributed by the Advanced Energy Systems Division of ASME for publication in the Journal of Fuel Cell Science and Technology. Manuscript received September 2, 2011; final manuscript received October 13, 2011; published online March 7, 2012. Editor: Nigel M. Sammes.











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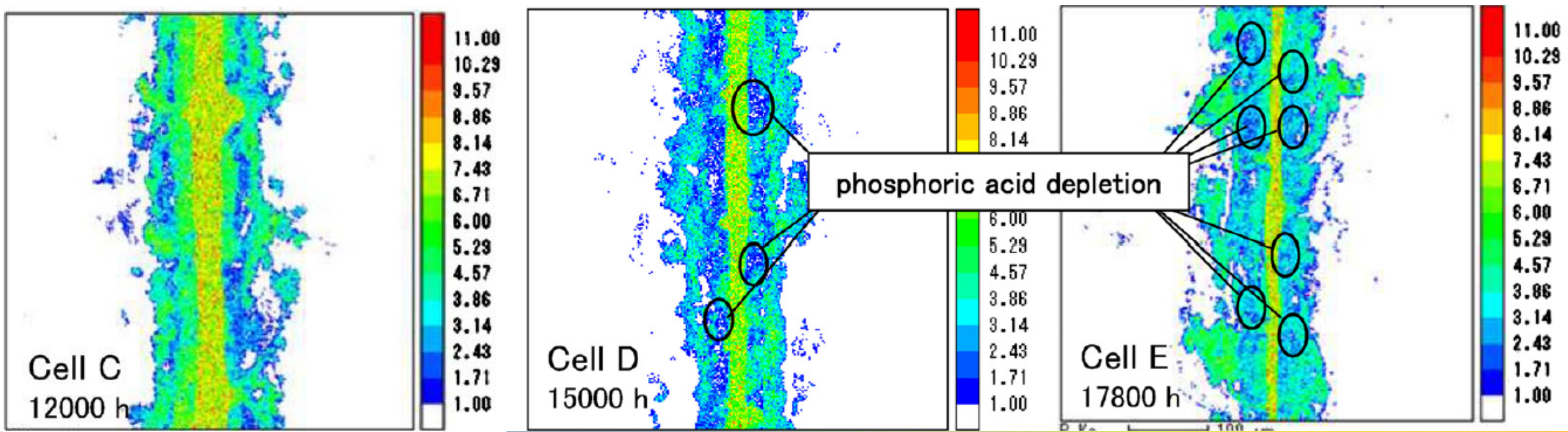
PA distribution & migration

- Effect of long-term operation:
  1. The PA content in the MEA decrease after test, compared with that before cell assembling. Excess PA in MEA may be squeezed out into the flow field by compressing during assembling.
  2. After test, the PA left in the membrane is almost the same (compared with that after assembling); the PA remaining in CL increase with increase in initial amount of PA.
  3. PA distribution in electrodes become more and more nonuniform during long-term test.



In the middle of a test **At the end of a test**

Yuka Oono, Atsuo Sounai, Michio Hori. Long-term cell degradation mechanism in high-temperature proton exchange membrane fuel cells. Journal of Power Sources. 2012, 210: 366 - 373.

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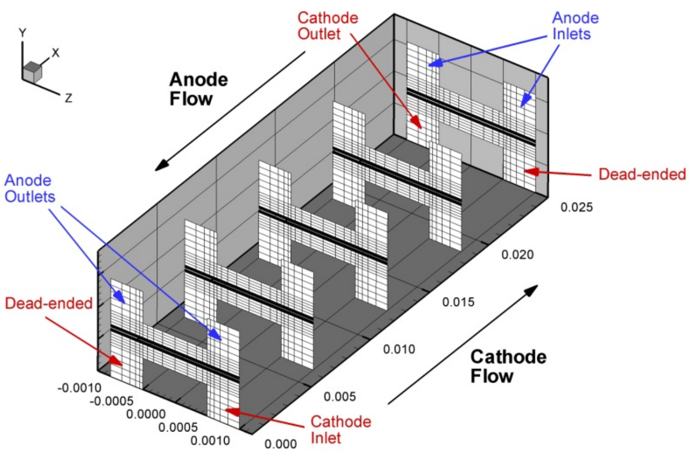
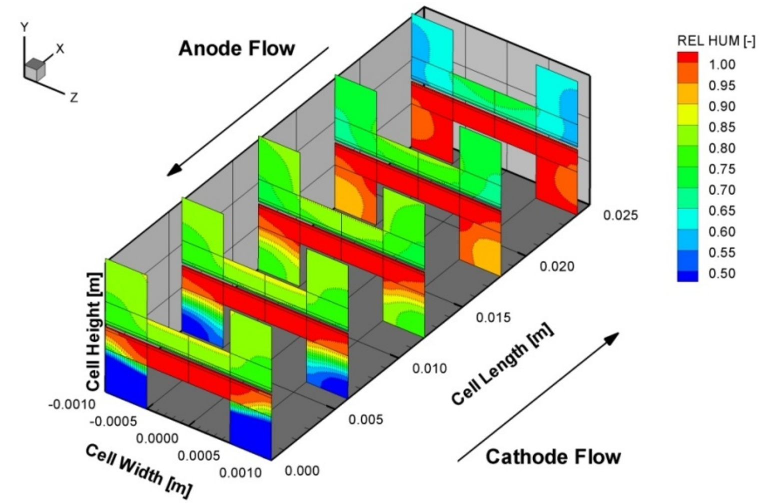
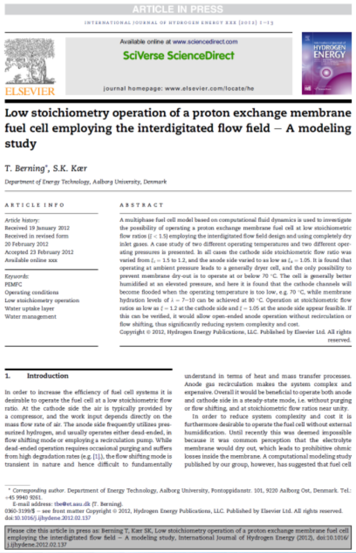
CFD based cell modelling

- State-of-the-art modeling of
  - Flow, heat, electrochemistry
  - Two phase flow, water management
- Cell design improvements
  - Self-humidified cell



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Low stoichiometry operation of a proton exchange membrane fuel cell employing the interdigitated flow field – A modeling study

T. Berning, S.K. Kær


Journal of Power Sources

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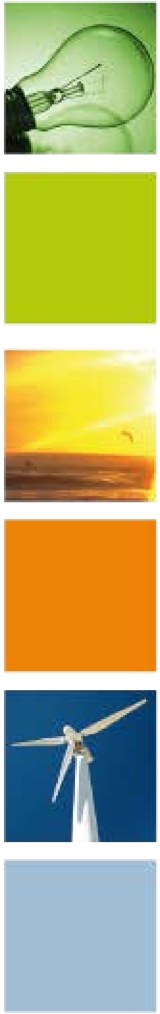
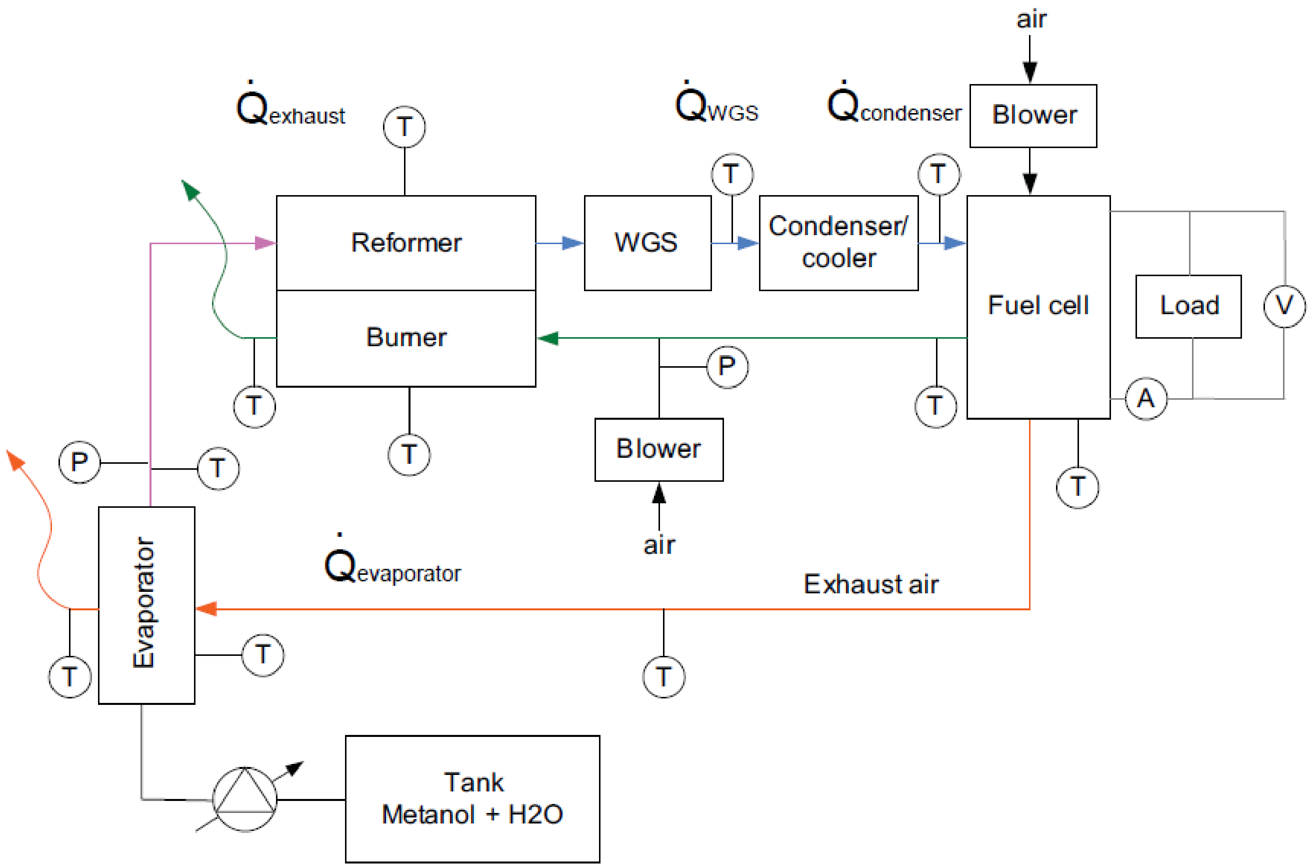
Water balance simulations of a polymer-electrolyte membrane fuel cell using a two-fluid model

T. Berning, M. Odgaard, S.K. Kær

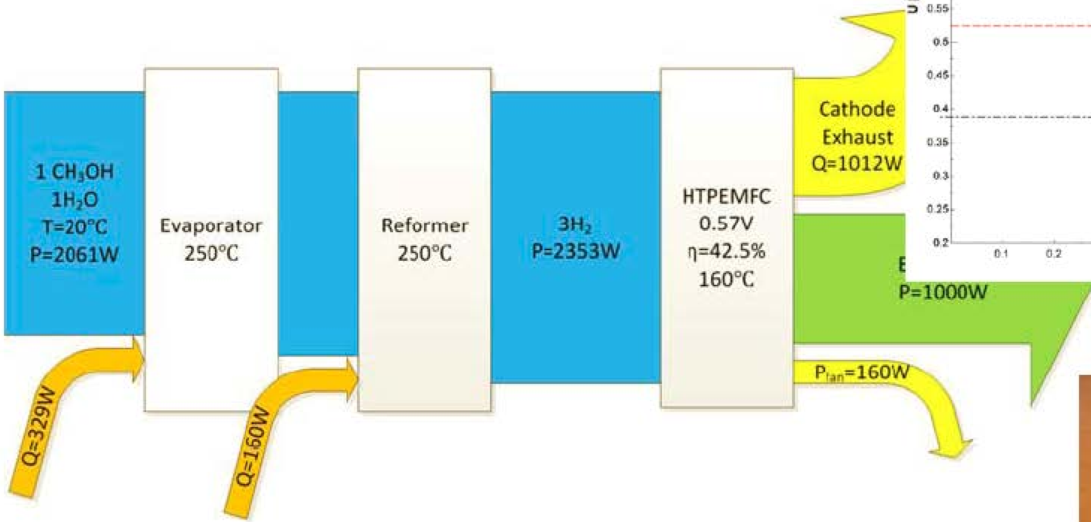


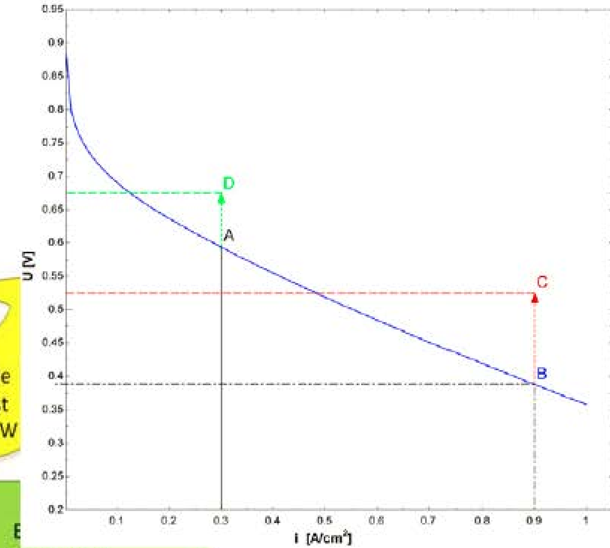
Reformed methanol FC system



Energy harvesting potential

- Energy flow Sankey diagram*

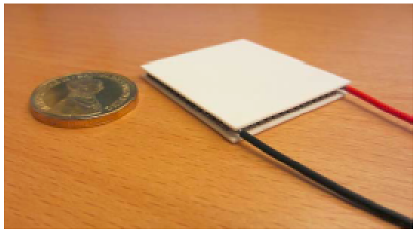


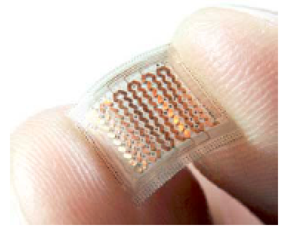


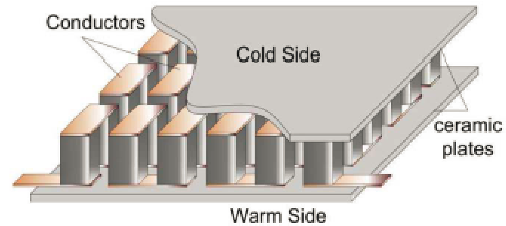
Exhaust heat temperature: ≈160℃; Capacity: 1kW

Thermoelectric elements

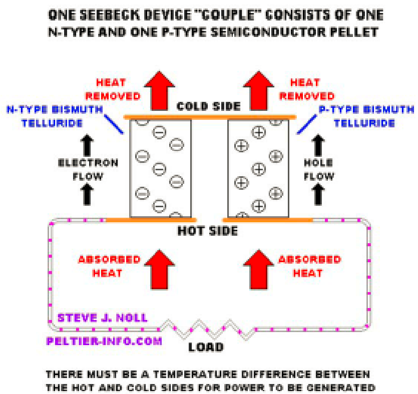
- One TE module

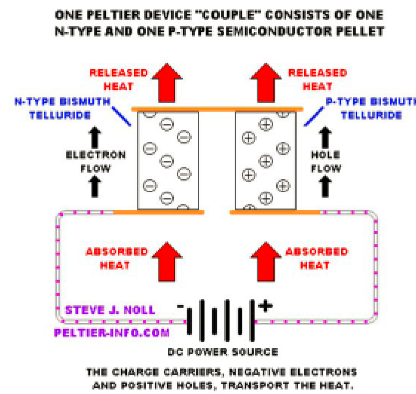






- Two working modes: TEG, TEC



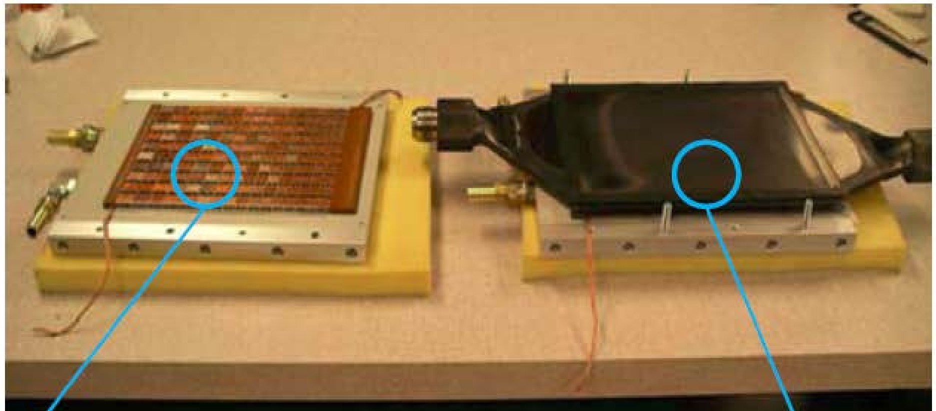


TE generator (TEG), Seebeck effect & TE cooler (TEC), Peltier effect

Pros and Cons: reliable, clean, excellent scalability, but low efficiency/COP

Thermoelectric generator HEX

1. What we need? A TEG heat recovery subsystem, efficient, compact, and low pressure drop.

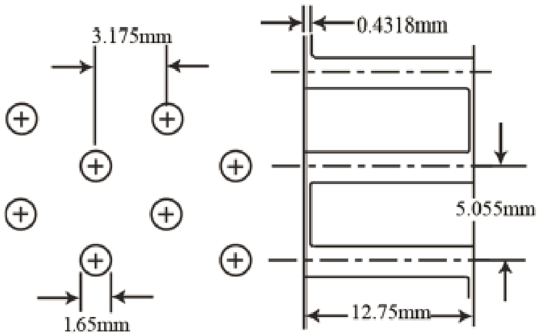


2. Best type of heat exchanger?
3. Right size of the subsystem?

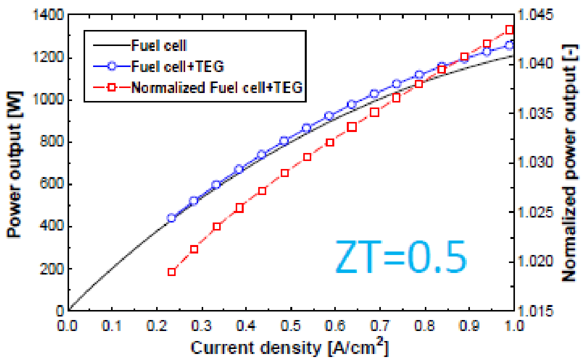
Current and future performance

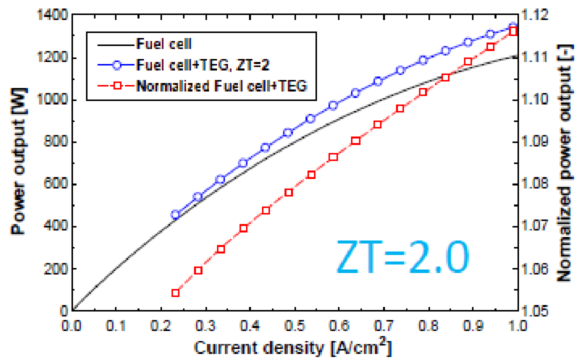
Main conclusions*:

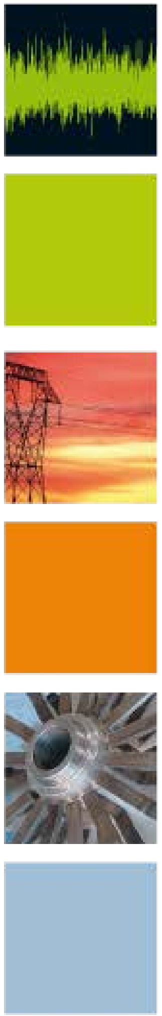
1. The subsystem configuration is optimized, MPPT considered:



2. Its power output:







Conclusions

- Methanol is a promising fuel for HTPEM fuel cell system
  - Excellent system efficiency
  - Support 100% renewable energy production
  - Electricity grid balancing potential
- An optimization potential still exists for methanol reformers to reduce CO production and methanol slip
- More work is needed to understand and reduce the influence from CO and methanol on HTPEM-FC performance and durability

This work was sponsored by:

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