High temperature PEM fuel cell activities at Aalborg University

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Current group members:
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Assistant professor Benoit Bidoggia
Postdoc Hans-Christian Becker Jensen
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Postdoc Vincenzo Liso
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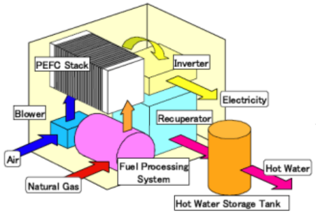
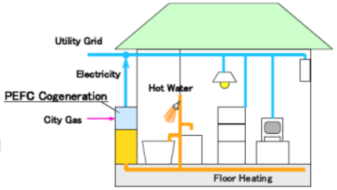
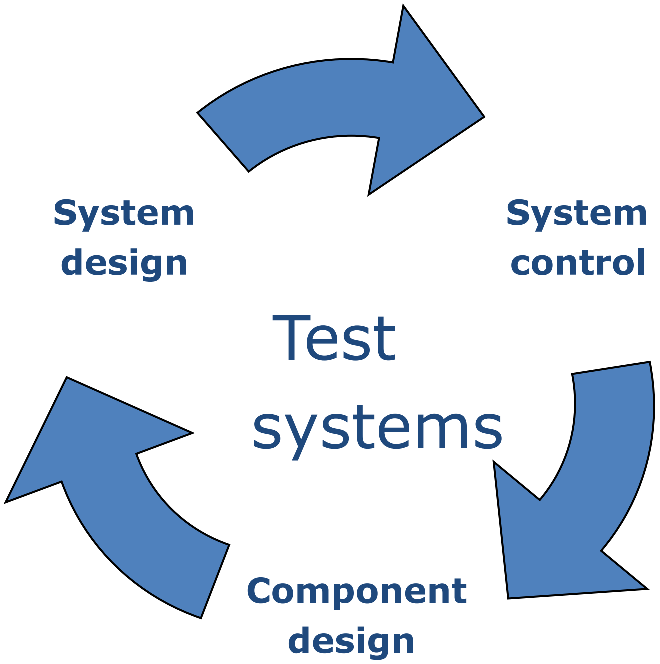
PhD student Anders Christian Olesen
PhD student Haftor Örn Sigurdsson
PhD student Jakob Rabjerg Vang
PhD student Xin Gao
PhD student Kristian Kjær Justesen

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







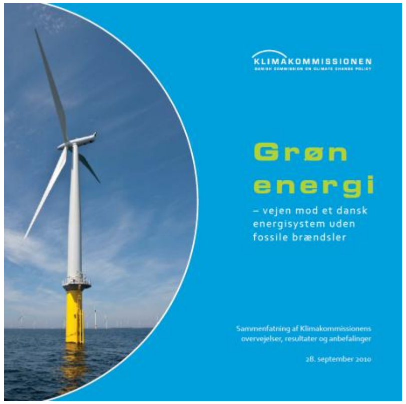
System design

System control

Test systems

Component design

Grid balancing



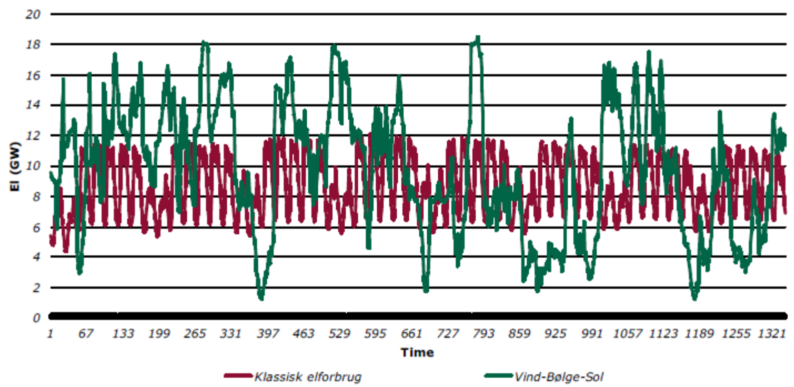
KLIMAKOMMISSIONEN
DANISH COMMISSION ON CLIMATE CHANGE POLICY

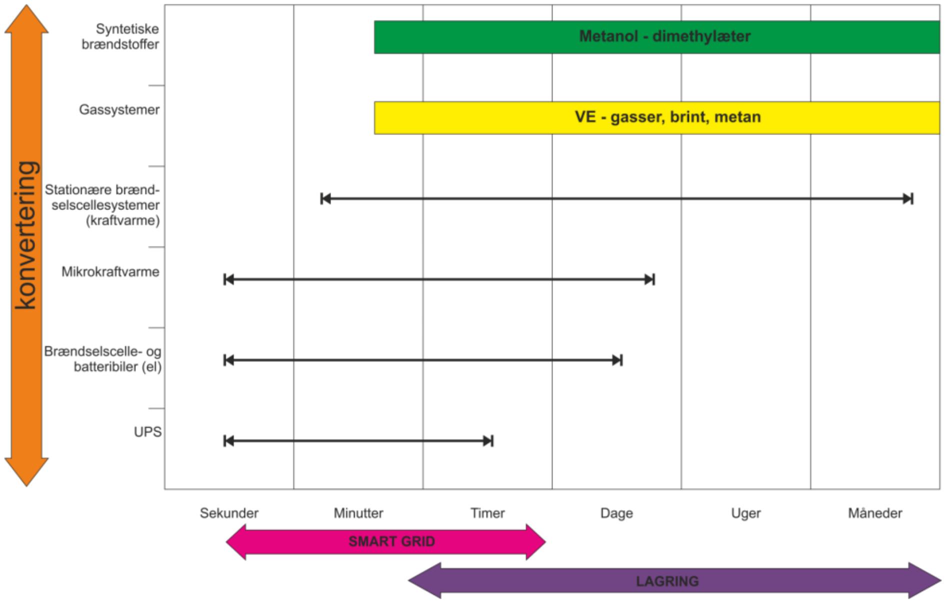
Grøn energi
– vejen mod et dansk energisystem uden fossile brændsler

Sammenfatning af Klimakommissionens overvejelser, resultater og anbefalinger

28. september 2010

ENERGI 2050
VINDSPOR





konvertering

Syntetiske brændstoffer

Gassystemer

Stationære brændselscellesystemer (kraftvarme)

Mikrokraftvarme

Brændselscelle- og batteribiler (el)

UPS

Metanol - dimethylæter

VE - gasser, brint, metan

Sekunder

Minutter

Timer

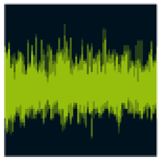
Dage

Uger

Måneder

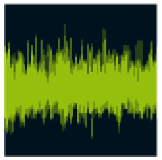
SMART GRID

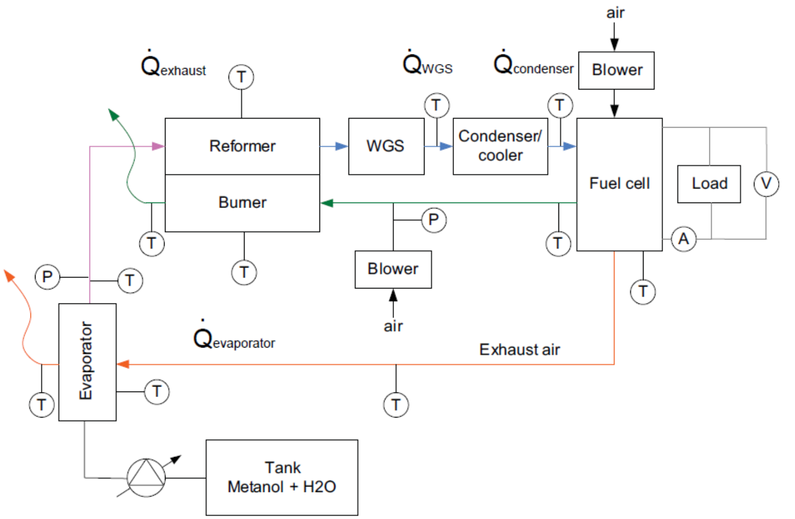
LAGRING

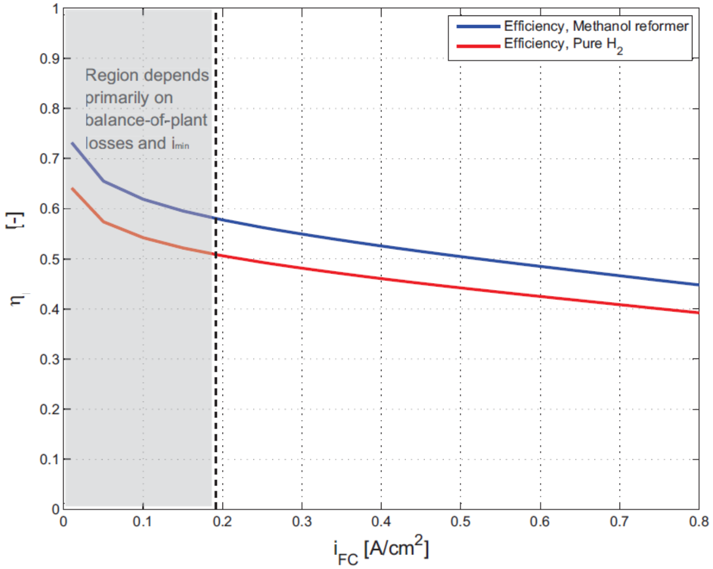


Reformed methanol for HTPEM

- Methanol would be the perfect 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.*







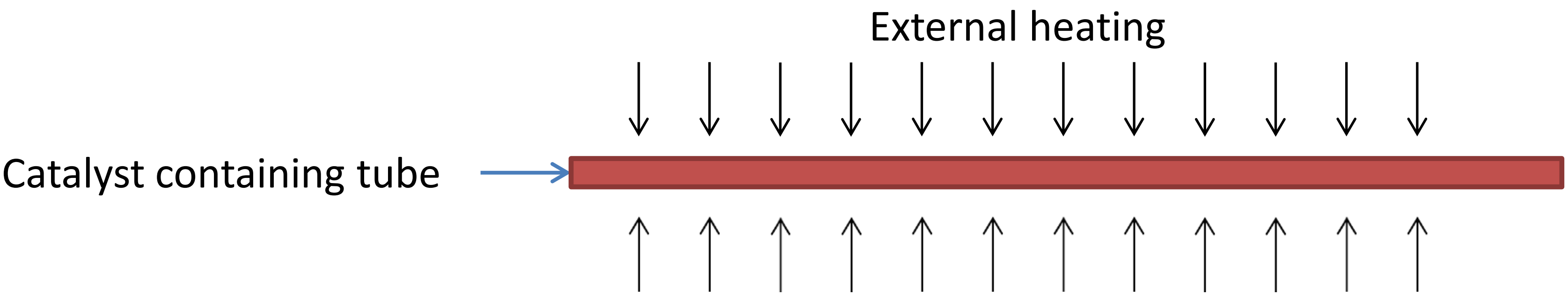
Experimental setup

- Gases analyzed for:
  - H2, CO, CO2 and CH3OH

Reformer reactor

Water and methanol dosing pumps

Reformer model outline



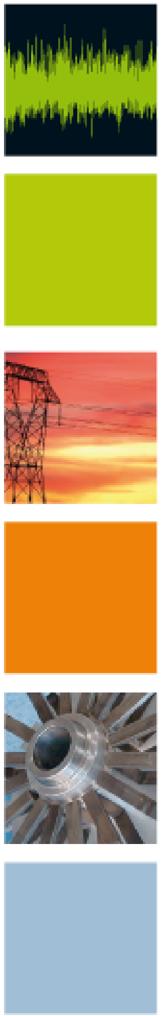
External heating

Catalyst containing tube

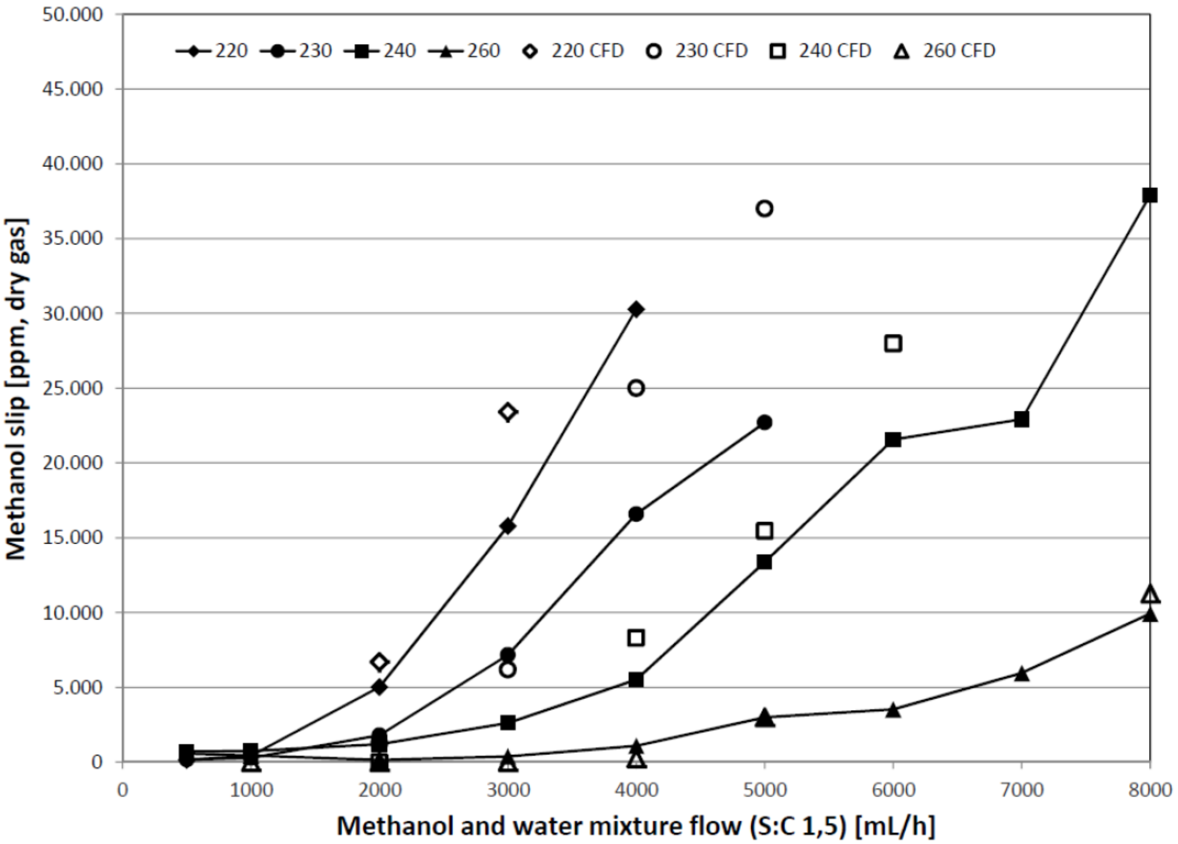
- ANSYS FLUENT v13
  - 3-dimensional flow, heat and mass transfer
  - Catalyst bed modeled as porous media
    - Bed and gas in thermal equilibrium
  - Reaction scheme and rates adapted from Purnama et al. 2004, Applied Catalysis A
  - Tube walls modeled as 1-D conducting elements
  - S:C 1,5 and inlet temperature 200°C
  - Reactions:

$$CH_3OH + H_2O \rightleftarrows 3H_2 + CO_2$$

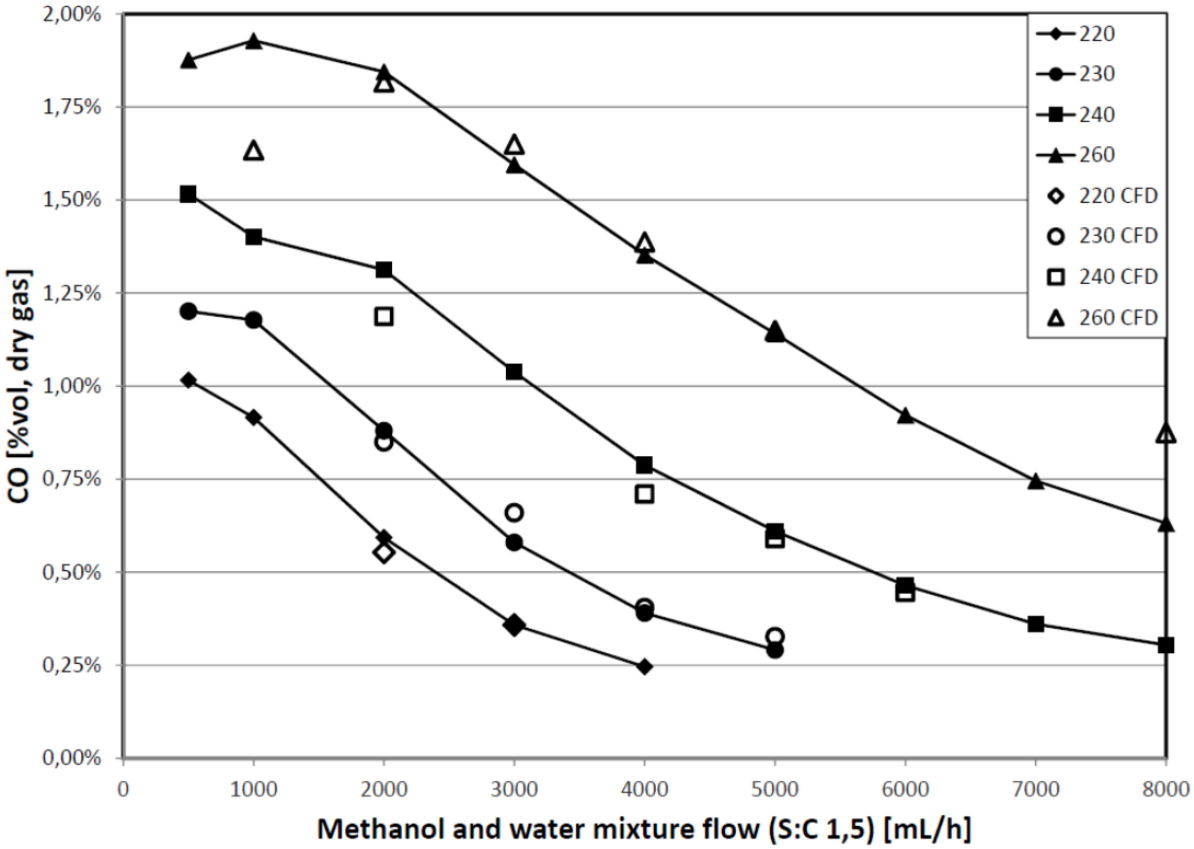
$$CO_2 + H_2 \rightleftarrows H_2O + CO$$



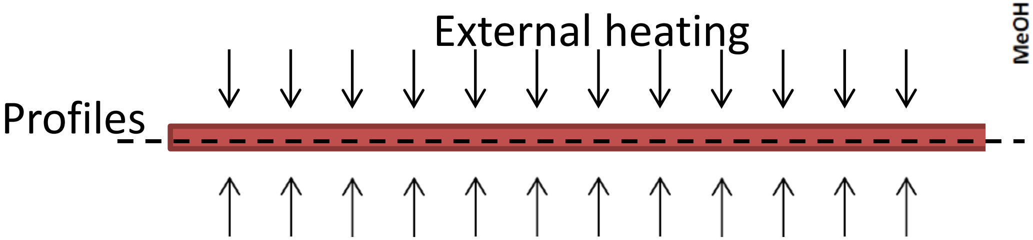
Measured and predicted slip



Measured and predicted CO

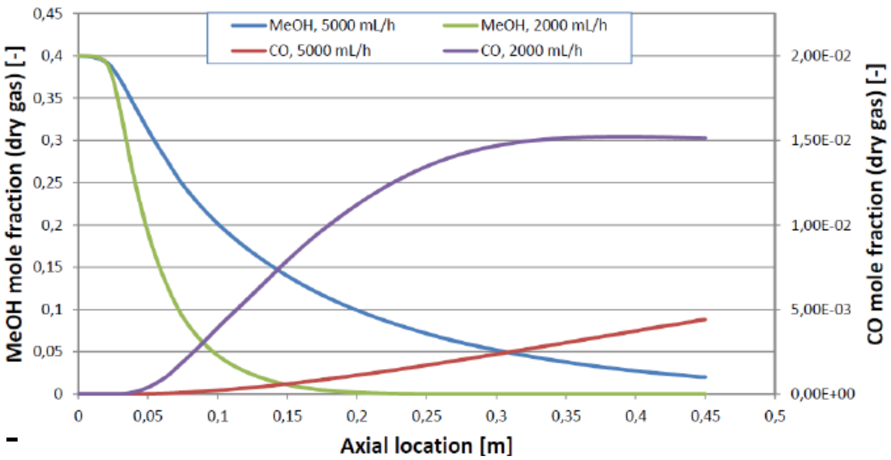


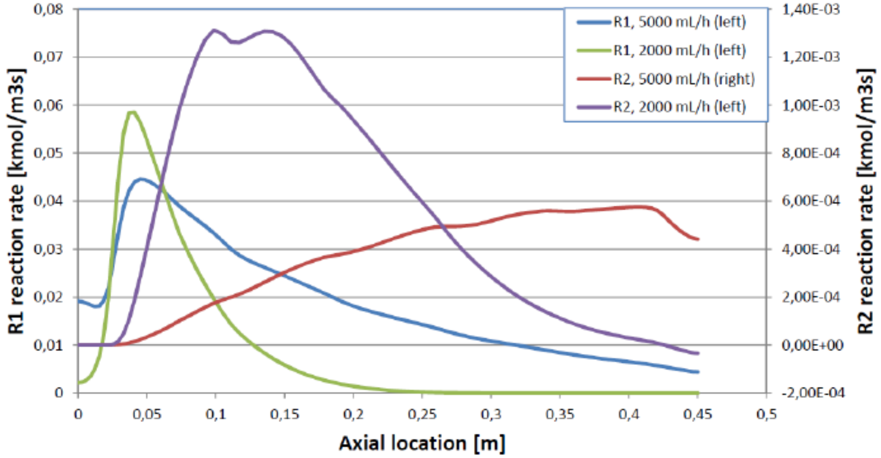
Axial conversion profiles



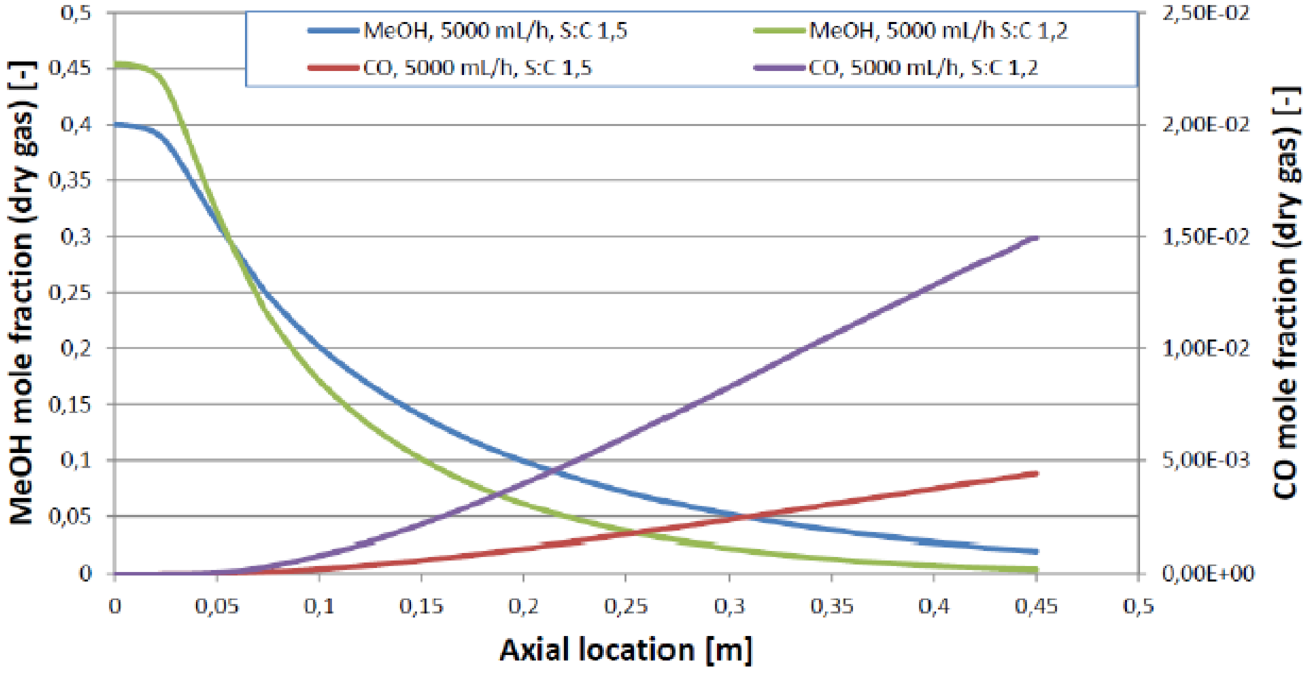
External heating

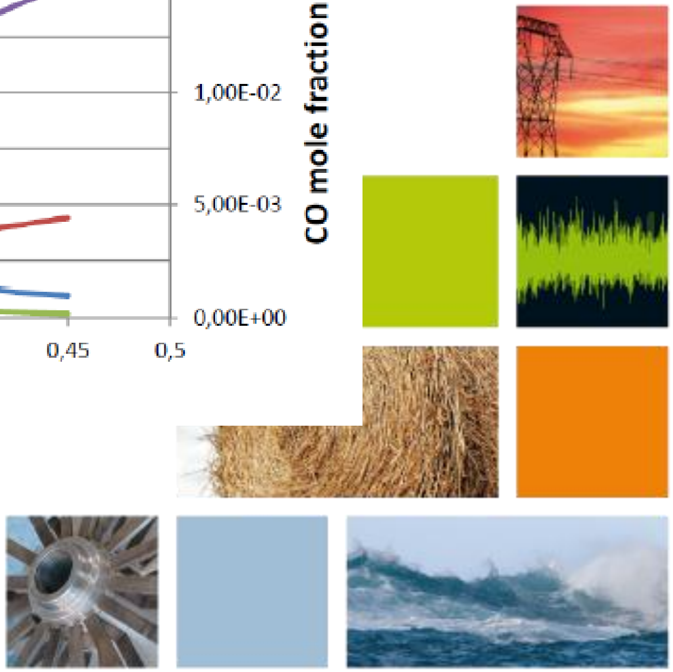
Profiles





Influence from S:C ratio





Test facilities

EIS based analysis of HTPEMFC

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

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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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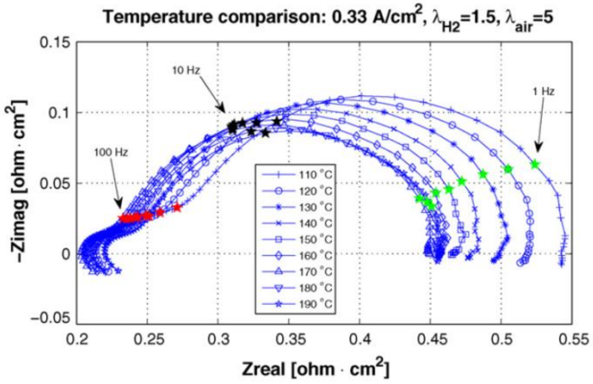
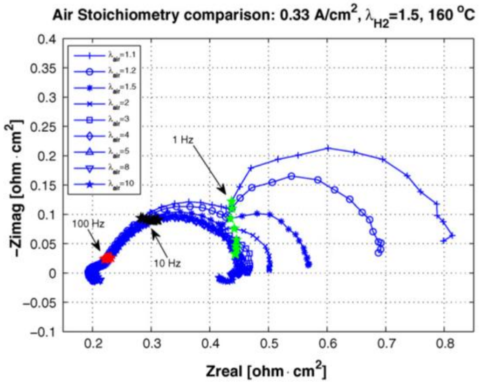
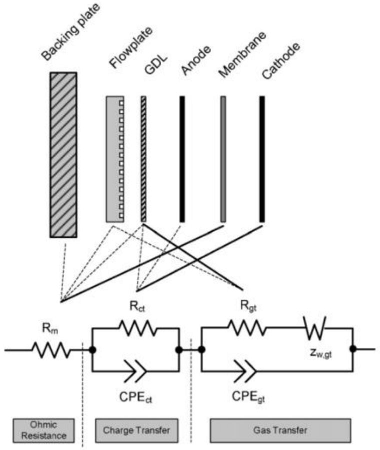
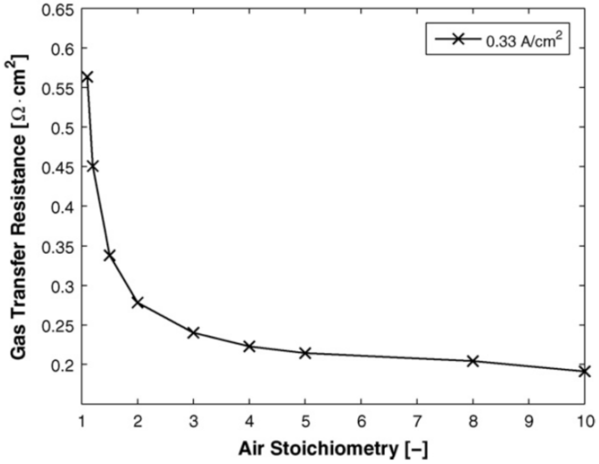
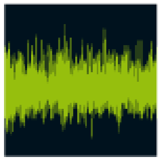


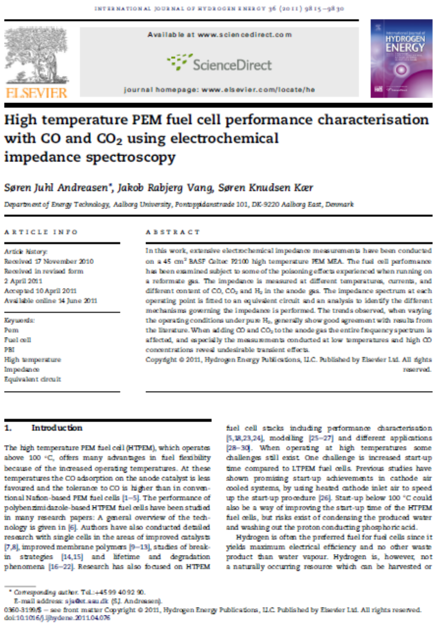








EIS based analyses of HTPEMFC



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High temperature PEM fuel cell performance characterisation with CO and CO_2 using electrochemical impedance spectroscopy

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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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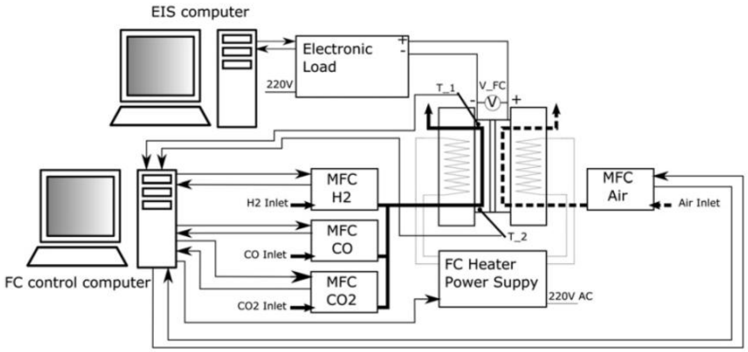
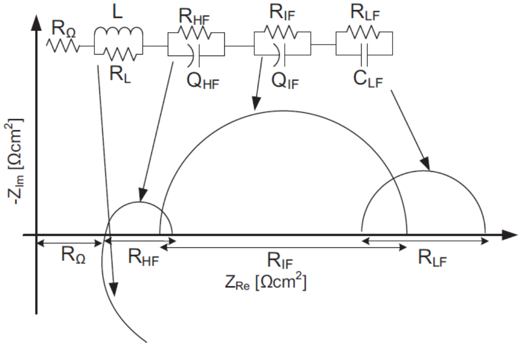
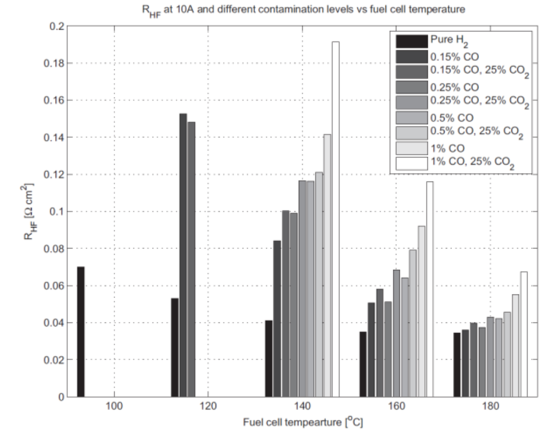
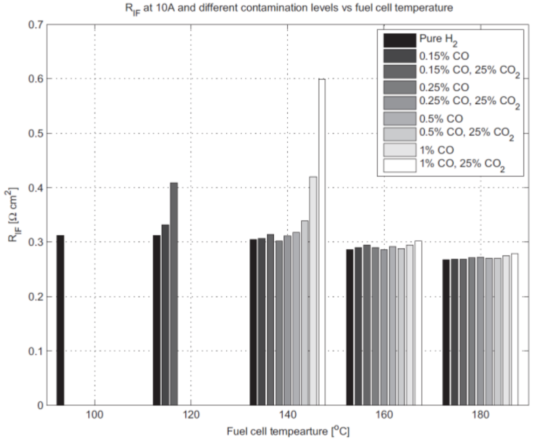
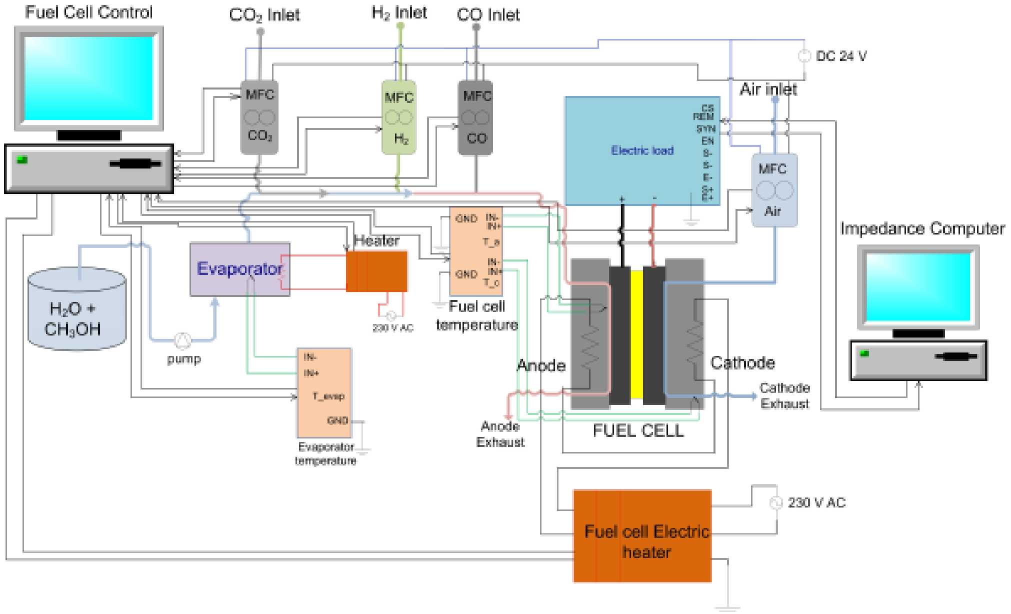


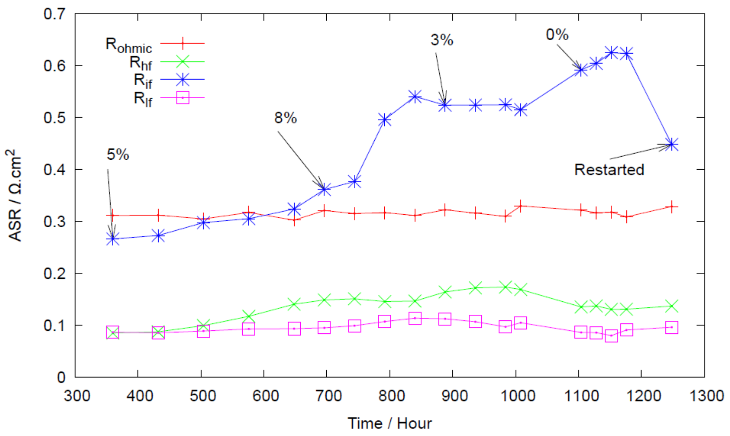


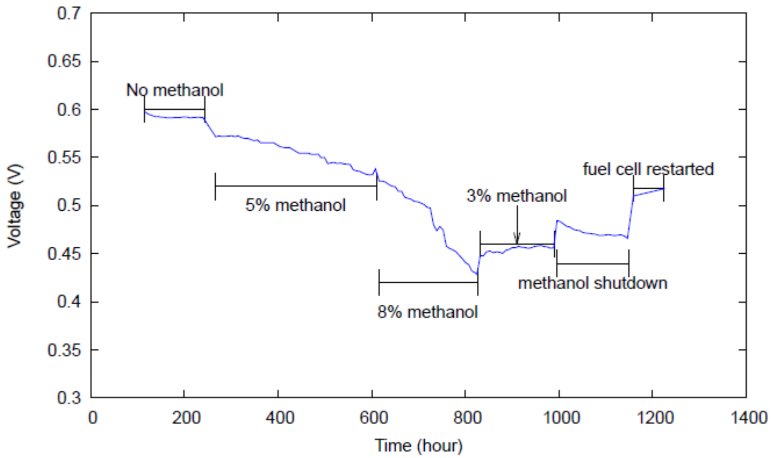




Reformed methanol fuelled HTPEM







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

Fuel cells are predicted to get a prominent place in the energy system of the future due to their ability to produce electrical power cleanly, efficiently and silently. Fuel cells can be used in a great variety of applications, since there are several different technologies with different characteristics. In the sub-MW power range most power needs are currently being serviced by combustion engines or grid power. Proton exchange membrane (PEM) fuel cells can potentially replace most of these combustion engines, reducing air pollution and noise levels while improving the efficiency. The low temperature PEM (LTPEM) fuel cell, operating below 100 °C, is the PEM fuel cell type which has received the most attention from industry and academia alike. LTPEM fuel cells are capable of achieving very high electrical efficiencies and power densities. Problems with water management, high demands on hydrogen purity and the promise of achieving faster electrode kinetics have, however, promoted research into PEM fuel cells working at higher temperatures. While high temperature PEM (HTPEM) fuel cells cannot claim the same level of maturity as LTPEM fuel cells, their many advantageous properties have made them an increasingly popular research topic. Research published on HTPEM fuel cells include investigation of CO poisoning [1–3], testing of different catalyst materials [4], investigation of the influence of different MEA design variables [5], system integration [6,7], studies of durability and degradation [8–12], impedance characterization [13–15] and modeling on cell level [16–20] as well as system level [21,22]. This study focuses on the integration of cell level modeling with electrochemical impedance spectroscopy (EIS).

Electrochemical impedance spectroscopy is diagnostic tool which has been widely applied in HTPEM fuel cell research. EIS is a nonintrusive measurement tool, which can be used for both in situ and ex-situ measurements on fuel cells [23]. EIS measurements are performed by applying a series of sinusoidal current or voltage signals of different frequency to the fuel cell. The phase shift between the current and voltage signals and the ratio of the amplitudes are used to calculate the impedance as in Eq. (1).

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

Here V_{AC} [V] and i_{AC} [Acm^{-2}] are the voltage and current density signal amplitudes respectively and φ is the phase shift between the signals. The frequency response is usually presented in a Nyquist plot. In most cases, the data is fitted to an equivalent circuit model in order to better interpret the data [10, 13–15, 24].

Electrochemical impedance spectroscopy has been used in different kinds of studies for HTPEM fuel cells. The influence of different fuel cell operating parameters on the impedance spectrum has been investigated [14,15]. Hu and coworkers [10] and Mocoteguy et al. [11] used EIS to monitor the development of charge transfer resistance and ohmic resistance during degradation tests. Andreasen et al. constructed an empirical impedance model by fitting impedance spectra recorded at different operating points to an equivalent circuit and performing linear regression of the circuit parameters in the operating range [13]. Hu et al. also used EIS for obtaining the ohmic resistance and cathode exchange current density for use in two 2D cathode modeling studies [24,25].

Many types of models have been developed for HTPEM fuel cells. A simple semiempirical steady state model was developed by Korsgaard et al. [16]. The model was fitted to polarization curves from the commercial Celtec P1000 MEA. The model was later expanded to include the influence of CO [17]. Scott et al. presented a 1D steady state model which was validated against data collected from a home made MEA [26]. Three dimensional steady state models were developed by Cheddie and Munroe [18] and Peng et al. [19]. The latter was later expanded to create a transient model [20].

While many good HTPEM fuel cell models exist the coupling between impedance spectra and mechanistic HTPEM fuel cell models have only been made by Hu et al. [24,25]. Furthermore, mechanistic models capable of predicting the impedance spectra of HTPEM fuel cells have not been presented in the literature. For LTPEM the picture is somewhat different. A significant number of mechanistic fuel cell impedance models have been developed for LTPEM fuel cells. As early as 1996, Springer et al. developed a mechanistic LTPEM impedance model considering the dynamics of oxygen mass transport and double layer capacitive effects [27]. Another modeling study considered models for investigating cathode mass transport limitations using current interrupt and EIS [28,29]. The dynamics of the hydrogen electrode in a symmetrical gas configuration was investigated by Wiezell et al. [30,31]. Franco and coworkers published several articles on mechanistic LTPEM impedance models treating detailed modeling of the

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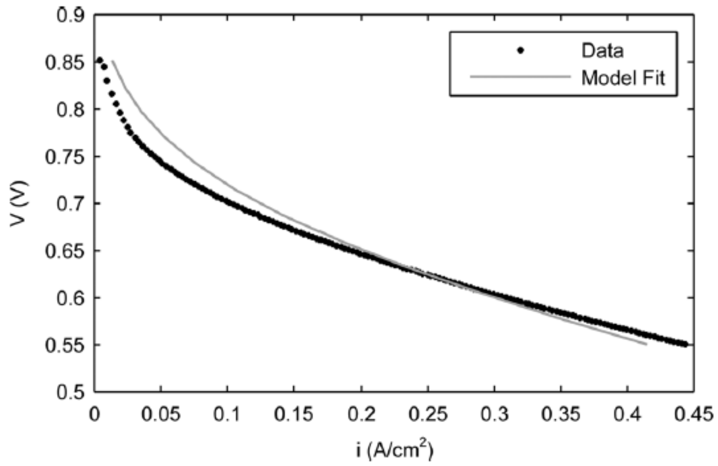
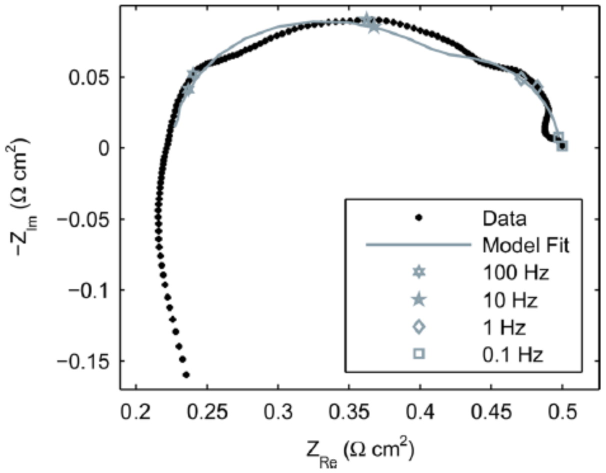
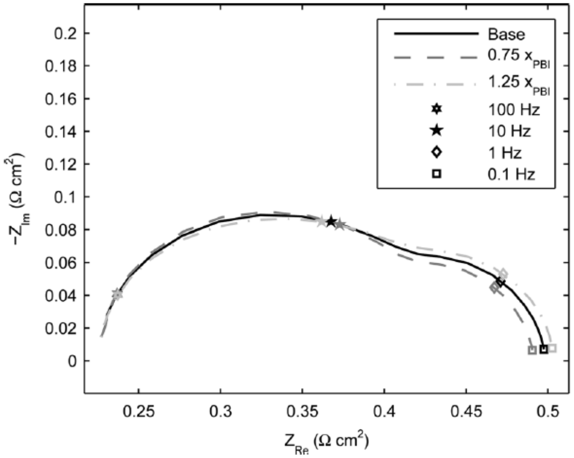
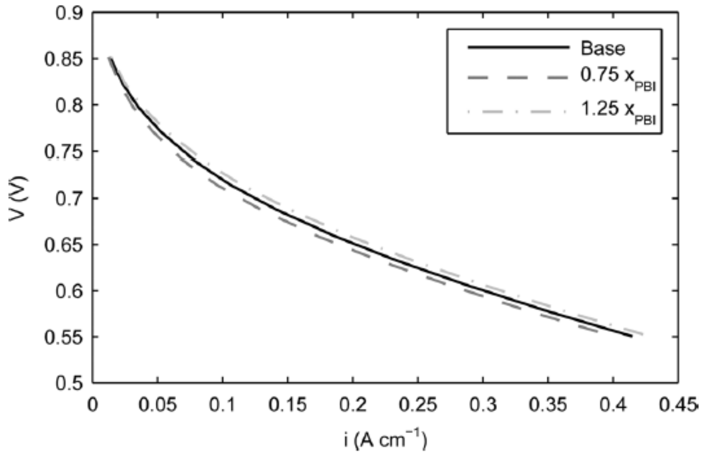
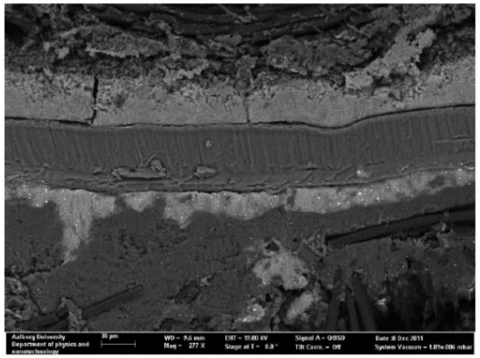








Changes in MEA components



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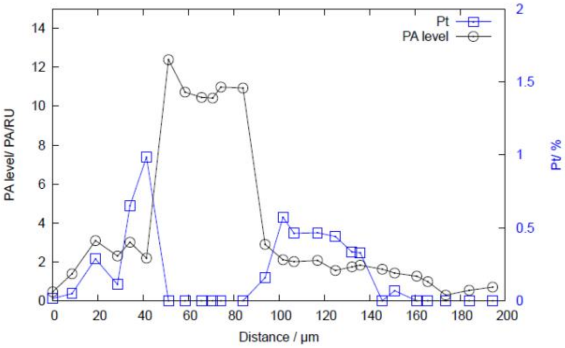

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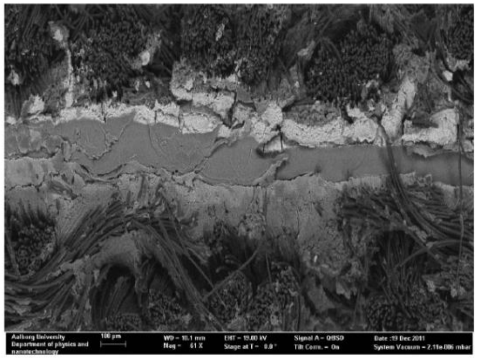

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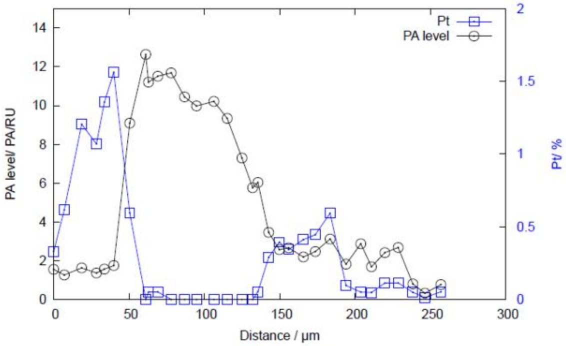

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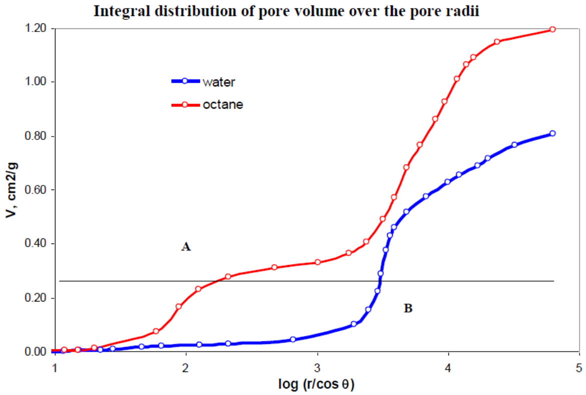



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Conclusions

- 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

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