

Characterization and design of HTPEM fuel cells

Søren Knudsen Kær

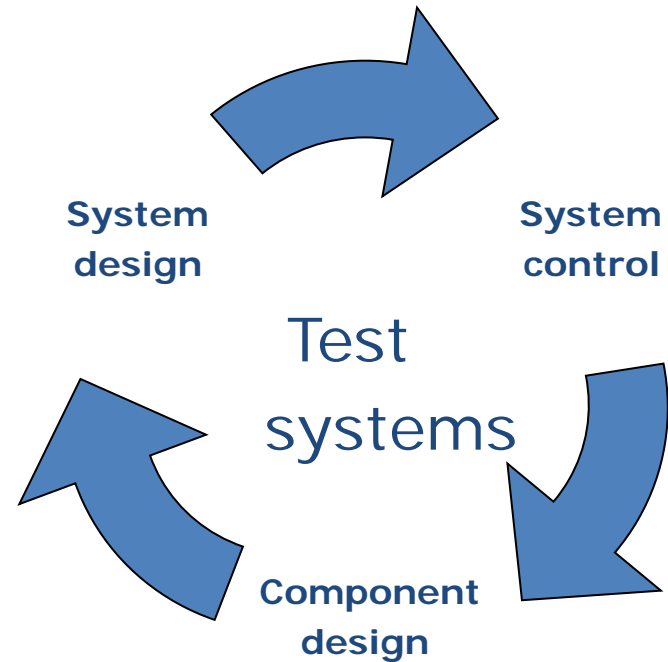
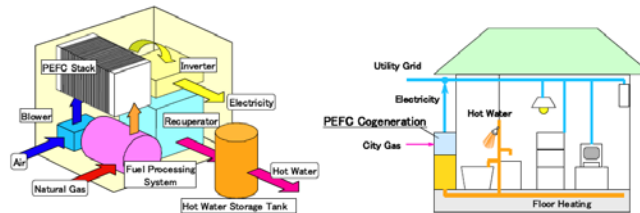
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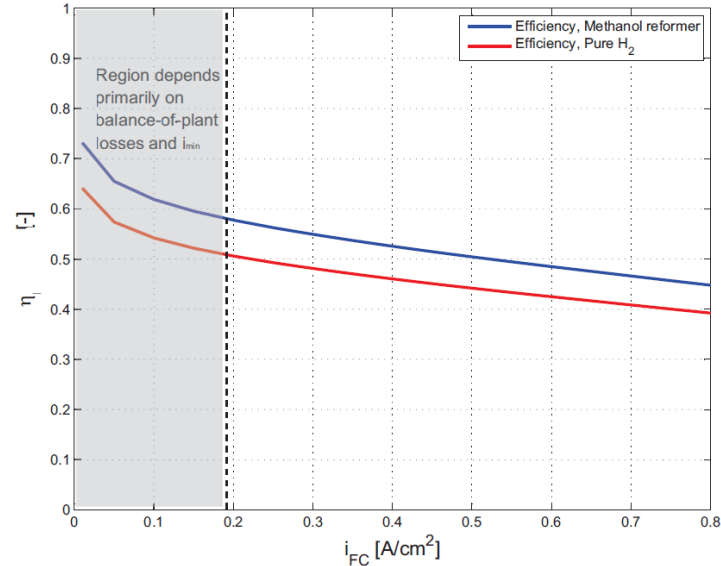
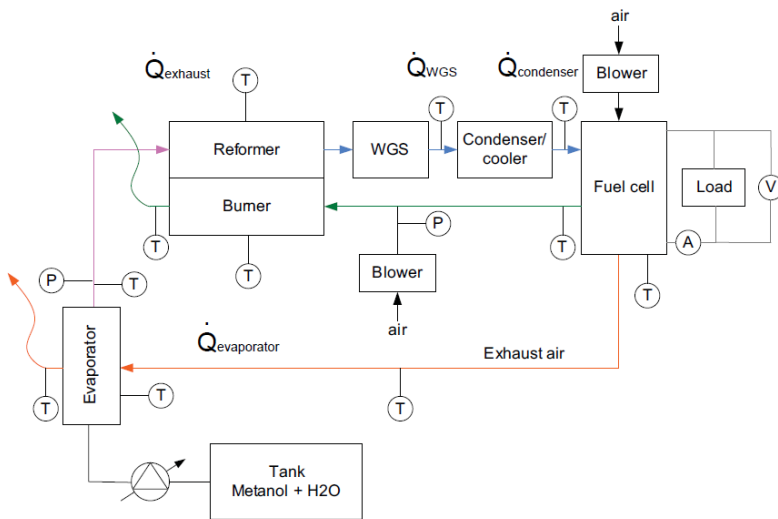
General activities

- 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



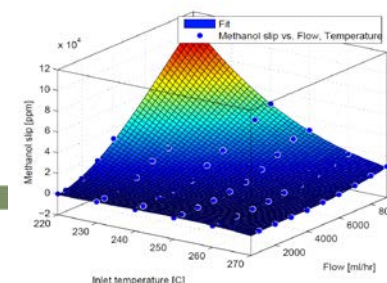
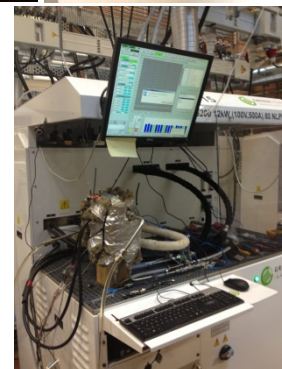
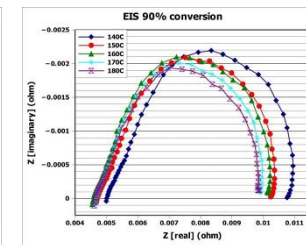
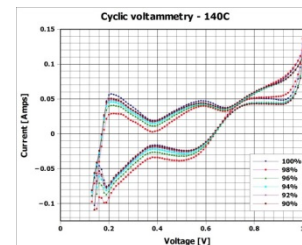
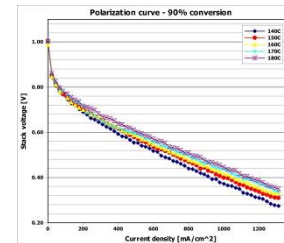
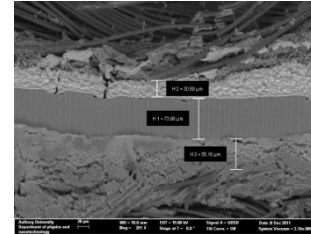
Reformed methanol for HTPEM

- 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.*



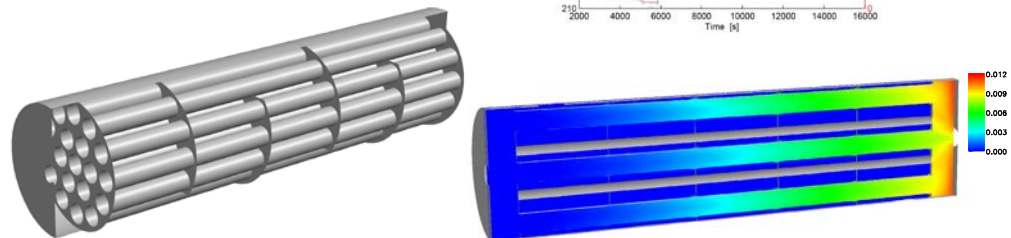
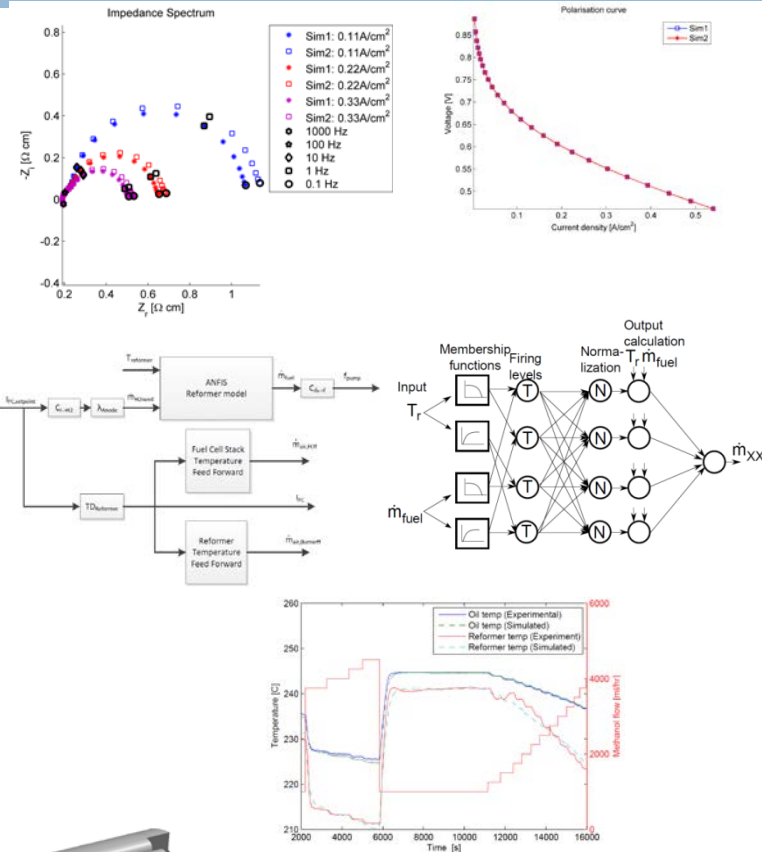
Experimental activities

- SEM-EDX analyses of MEAs
 - Structure and elemental composition
- Single cell test facilities 50 cm² with EIS
 - In-house built H₂/air and reformat setups
 - Performance and degradation rates
 - Start/stop & reformat with methanol slip
 - I,V-curve, EIS and CV
- Methanol reformer tests/mapping
- Stack tests (short stack and 5 kW)

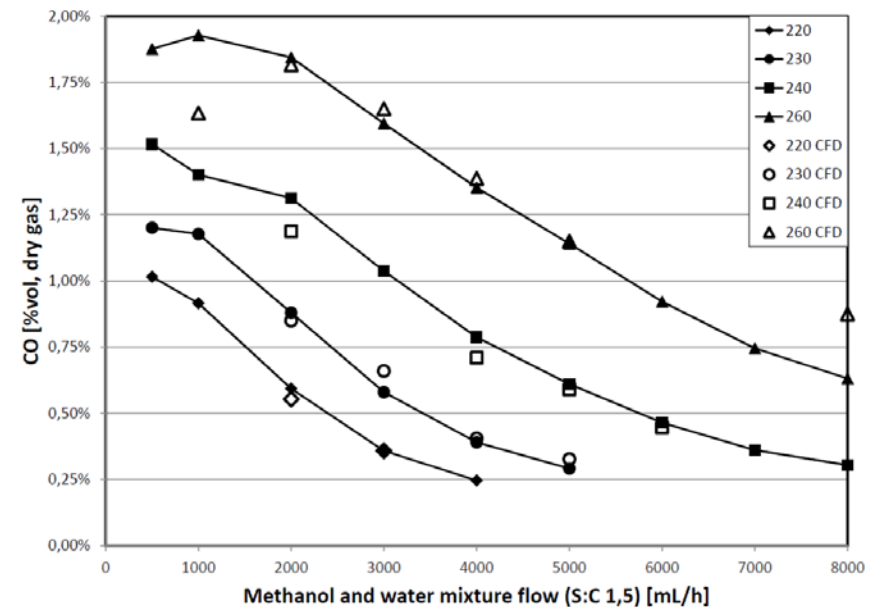
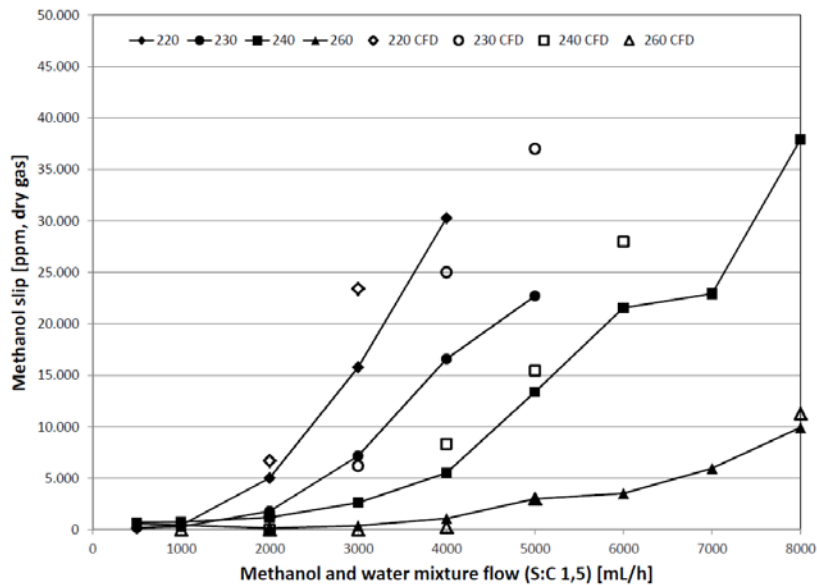


Modelling activities

- 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



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

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ABSTRACT

This work contains detailed Electrochemical Impedance Spectroscopy (EIS) measurements on a PEM-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 ECs are doubtful as discussed in this paper. The EC model proposed, which is a modified Randles circuit, provides a reasonable good fit at all the conditions tested. The measurements reveal that the cell impedance is an important parameter, which characterizes 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) therefore has a substantial effect on the impedance spectra, which shows 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 not clear what exactly causes the distinctive low frequency loop occurring at oxygen starvation. Contrary to the oxygen transport, the transport of hydrogen in 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 cells.

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1. Introduction

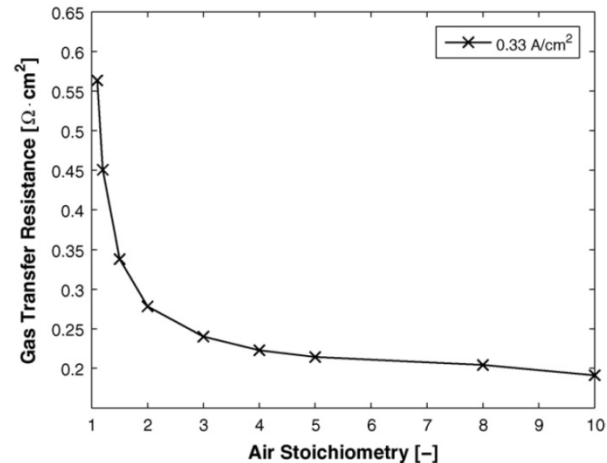
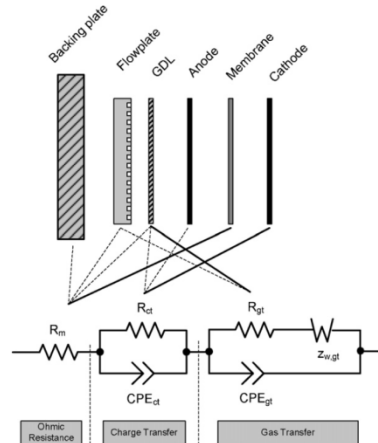
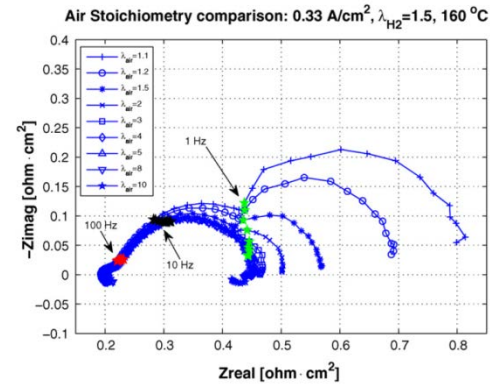
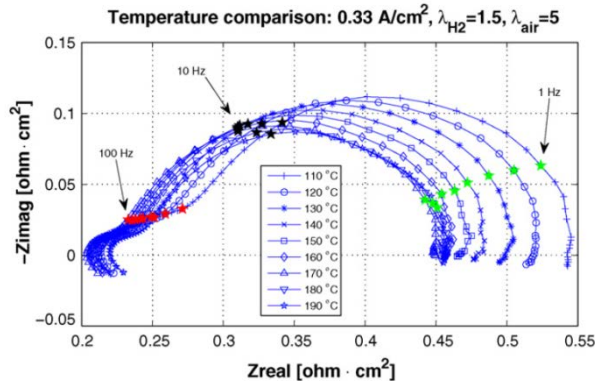
High Temperature Proton Exchange Membrane (HT-PEM) fuel cells based on a polybenzimidazole (PBI) membrane with phosphoric acid as an ionic conductor, first discovered by Wainright et al. [1], have shown to have good conductivity at elevated temperatures [2], which gives advantages features when operated 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 development 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 on in situ non-destructive 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 diagnostic 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



High temperature PEM fuel cell performance characterisation with CO and CO₂ using electrochemical impedance spectroscopy

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ABSTRACT

In this work, extensive electrochemical impedance measurements have been conducted on a 45 cm² ASEP G400 9200 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, CO₂, and H₂ in the anode gas. The impedance spectra at each operating point is fitted to an equivalent circuit and an analysis is used to identify the different mechanisms governing the impedance is performed. The trends observed, when varying the operating conditions under pure H₂, generally show good agreement with results from the literature. When adding CO and CO₂ 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.

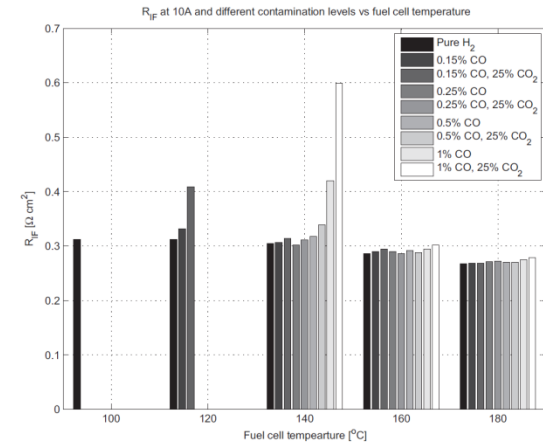
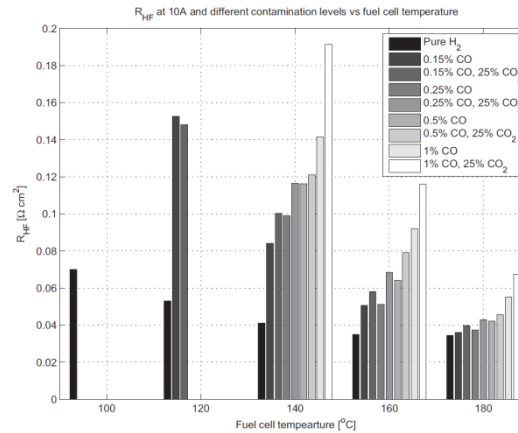
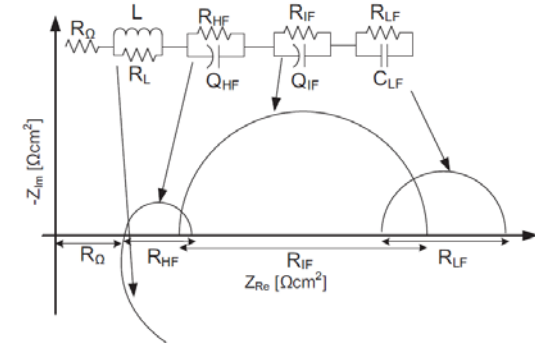
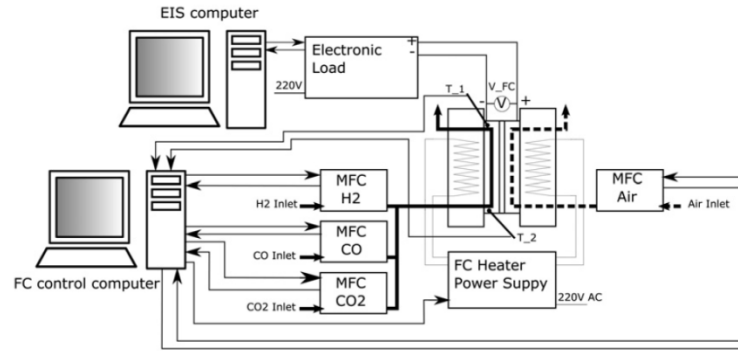
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1. Introduction

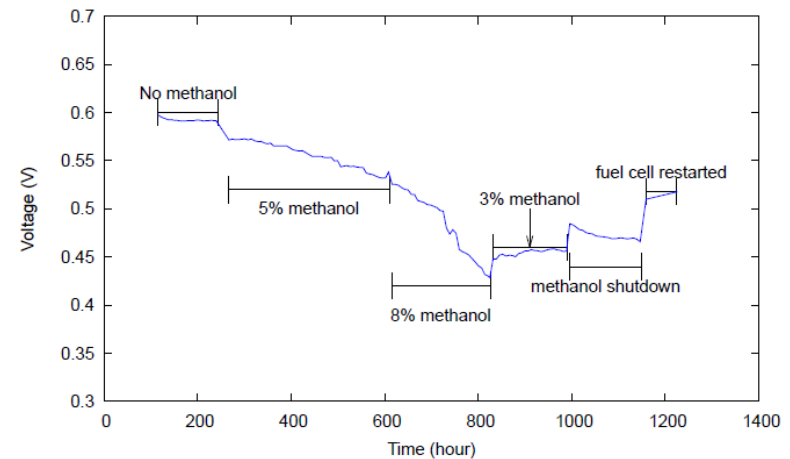
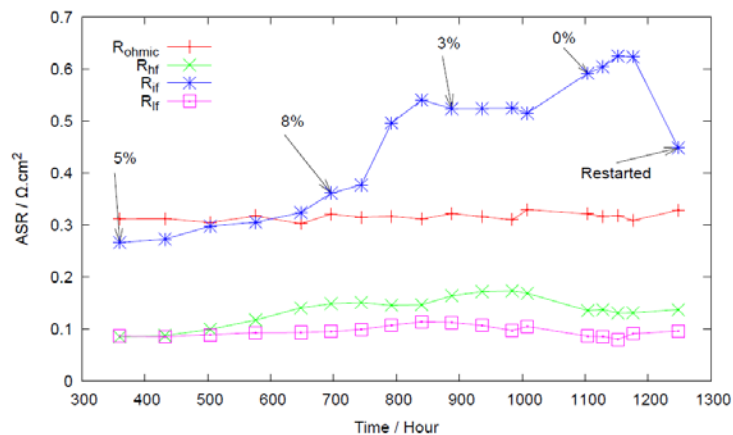
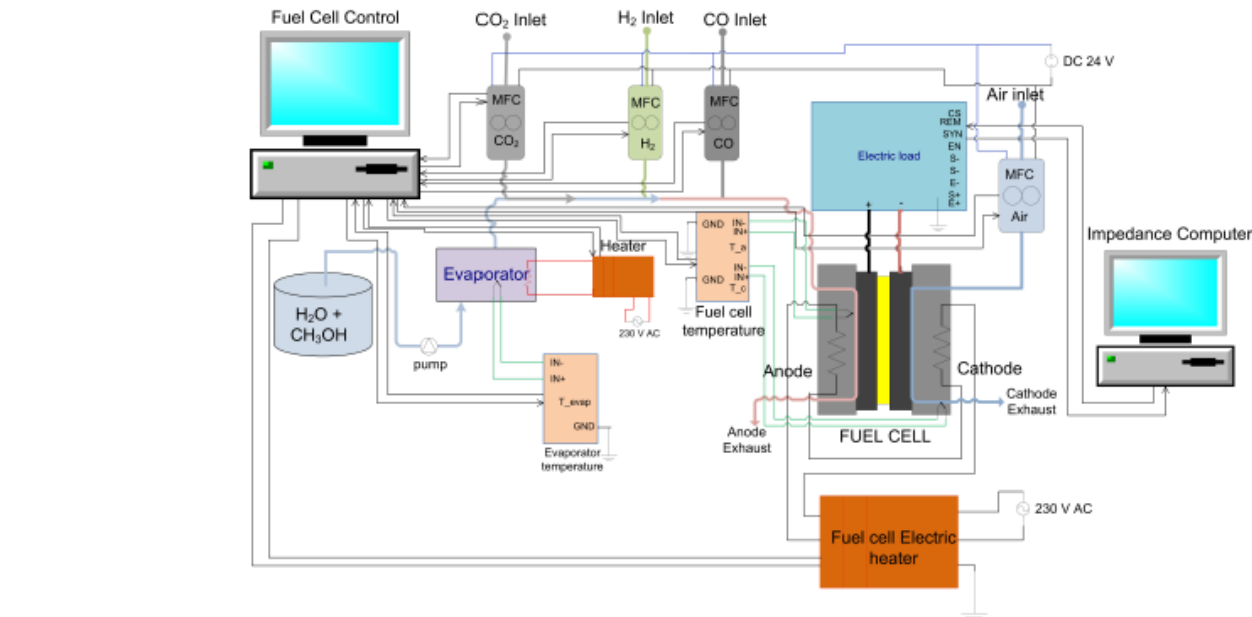
The high temperature PEM fuel cell (HTPEMFC), which operates above 100 °C, offers many advantages in fuel flexibility because of the increased operating temperatures. At these temperatures the CO adsorption on the anode catalyst is less favored and the tolerance to CO is higher than in conventional low-temperature PEM fuel cells [1–4]. The performance of polybenzimidazole-based HTPEM fuel cells have been studied in many research papers. A general overview of the technology is given in [5]. Authors have also conducted detailed research with single cells in the areas of improved catalysts [7,8], improved membrane polymers [9–13], studies of leaks in structures [14,15] and lifetime and degradation phenomena [16–25]. Research has also focused on HTPEM

fuel cell stacks including performance characterisation [26,27,28], modelling [29–37] and different applications [38–40]. 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 [41]. 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 wetting 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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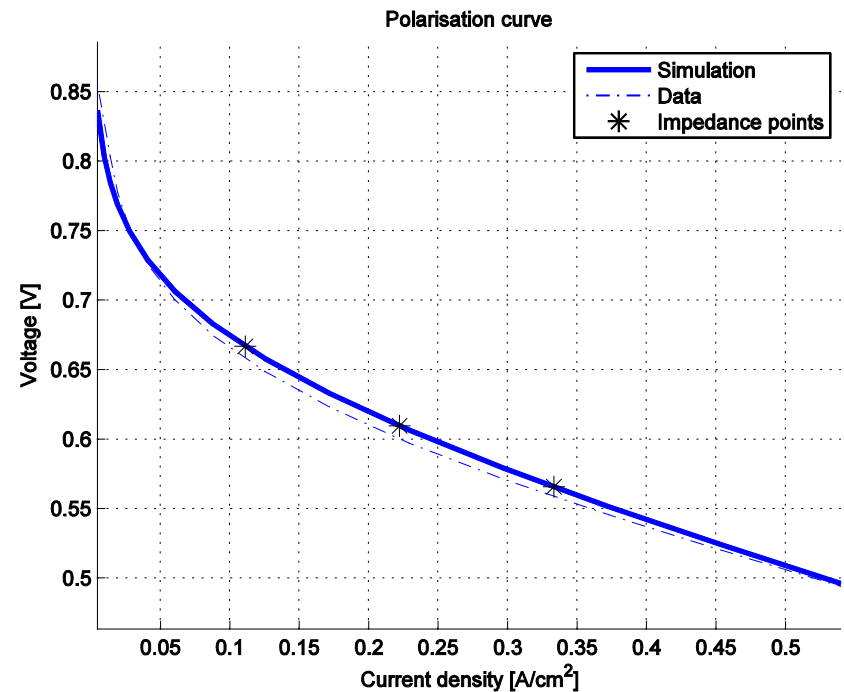
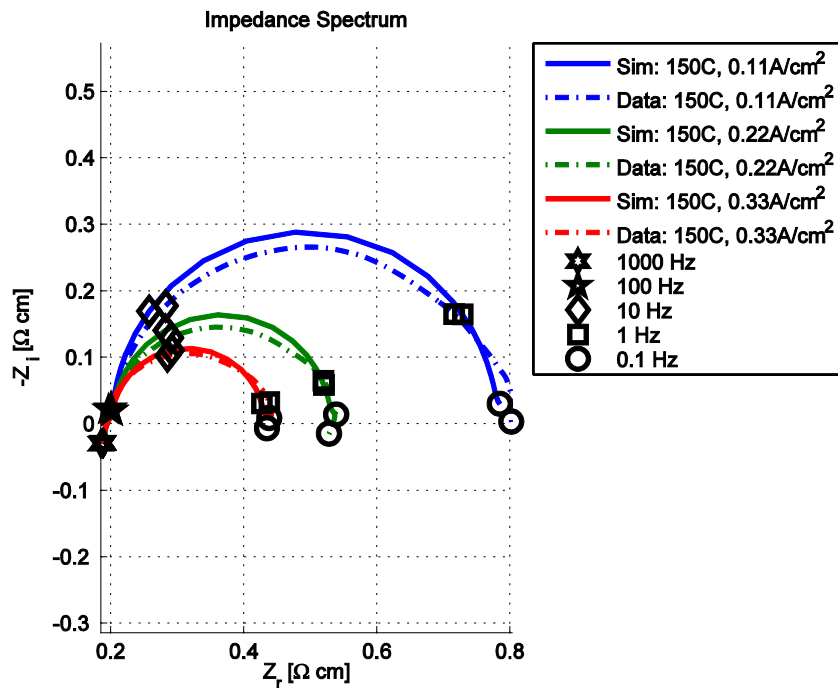
Reformed methanol fuelled HTPEM



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



Advanced impedance simulations

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

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 solved along the channel and across the membrane. The model considers diffusion of substrate gas species in gas diffusion layers and catalyst layers, 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 comparison of the two 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, the parameters in this version of the model must be incorporated in future versions. [DOI: 10.1115/1.4005609]

1 Introduction

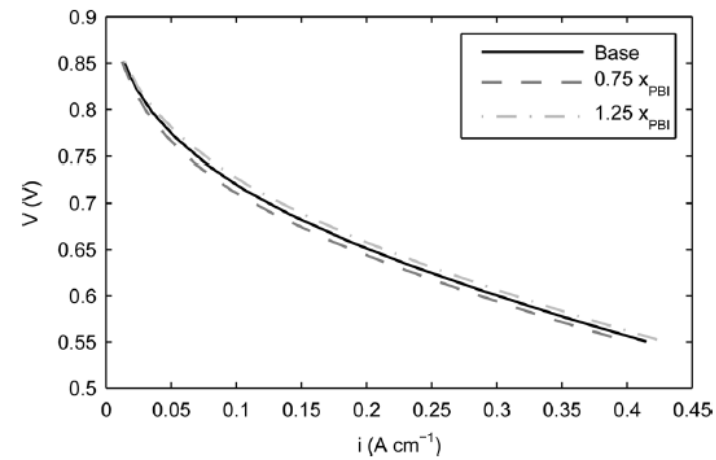
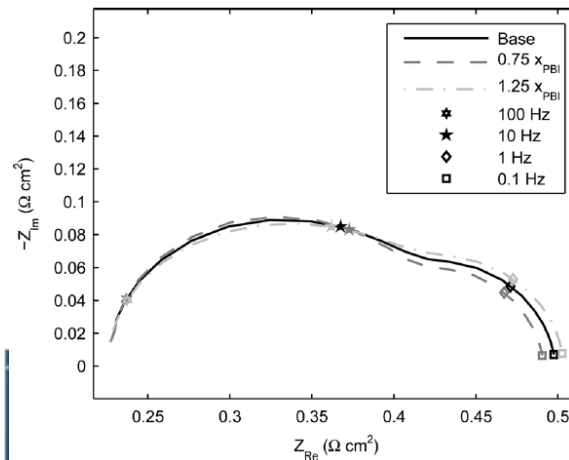
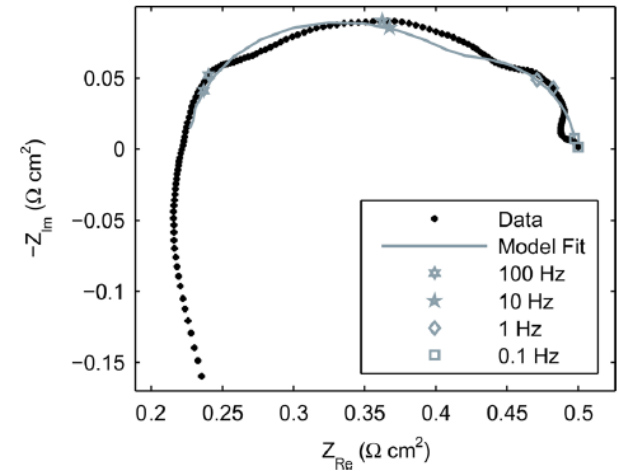
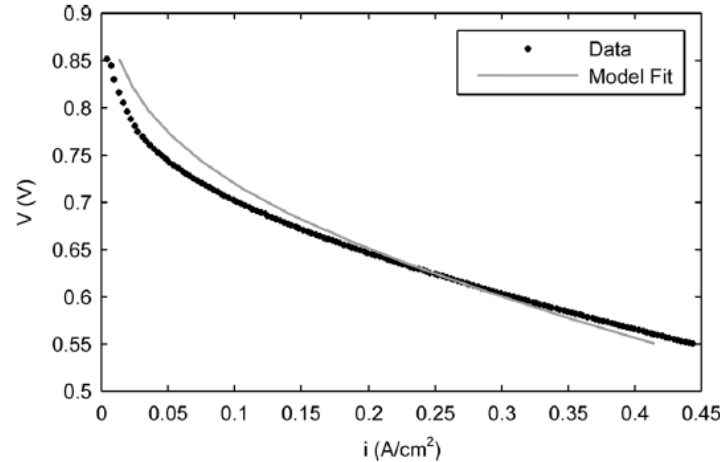
Fuel cells are predicted to get a prominent place in the energy system of the future due to their ability to produce electrical power cleanly, efficiently and silently. Fuel cells can be used in a great variety of applications, since there are several different technologies with different characteristics. In the sub-MW power range most power needs are currently being met by combustion engines, including air pollution and noise levels while improving the efficiency. The low temperature PEM (LTPEM) fuel cell, operating below 100°C, in 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 presence of poisoning during start-up have, however, prevented commercialization. High temperature PEM (HTPEM) fuel cells cannot claim the same level of maturity as LTPEM fuel cells, their many advantages 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 catalyst materials [5], system integration [6,7], studies of durability and degradation [8-12], impedance characterization [13-15] and modeling of 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 (EIS) is a diagnostic tool which has been widely applied in HTPEM fuel cell research. EIS is a non-invasive 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).

$$Z = \frac{V_{oc}}{I_{oc}} (\cos(\phi) + j \sin(\phi)) \quad (1)$$

Here V_{oc} [V] and I_{oc} [A/cm²] 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 [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 [16] and Moeckel et al. [17] used EIS to monitor the development of charge transfer resistance and ohmic resistance during degradation tests. Andersen 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 studying the effect of the reactant and water vapor partial pressure for use in two 3D cathode modeling studies [24,25].

Many types of models have been developed for HTPEM fuel cells. A simple one-dimensional steady state model was developed by Kongstad et al. [14]. The model was fitted to polarization curves from the commercial GenStor MEA. The model was later expanded to include the influence of CO [17]. Some 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 Chellidurai and Mauer [18] and Pijet et al. [19]. The latter was later expanded to 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 integral and EIS [28,29]. The dynamics of the hydrogen electrode in a symmetrical gas configuration was investigated by Weimer et al. [30,31]. Franco and coworkers published several articles on mechanistic LTPEM impedance models treating detailed modeling of the



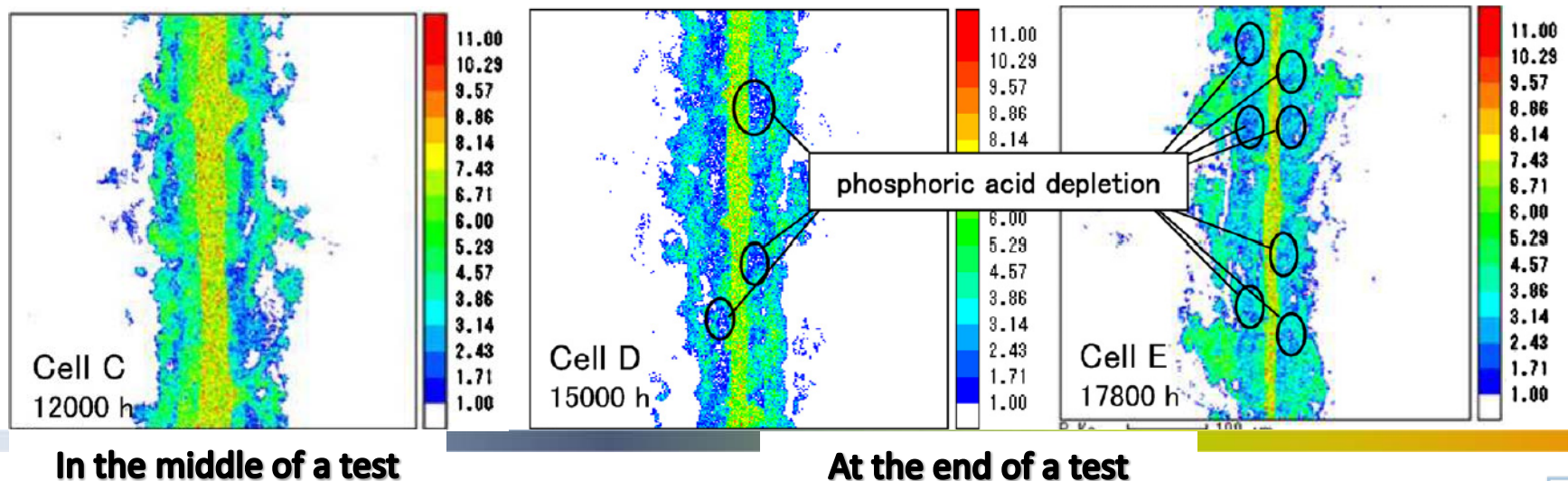
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PA distribution & migration

- 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.



CFD based cell modelling

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



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

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Water management

1. Introduction

In order to increase the efficiency of fuel cell systems it is desirable to operate the fuel cell at a low stoichiometric flow rate. At the cathode side this is typically prevented by a compressor, and the water input depends directly on the mass flow rate of air. The anode side however, can be operated at low stoichiometry, and usually operates either dead-ended, in flow-bypass mode or employing a recirculation pump. While dead-ended operation requires occasional purging and suffers from high degradation rates (e.g. [1]), in-flow-bypass mode is transient in nature and hence difficult to fundamentally

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

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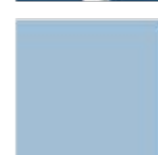
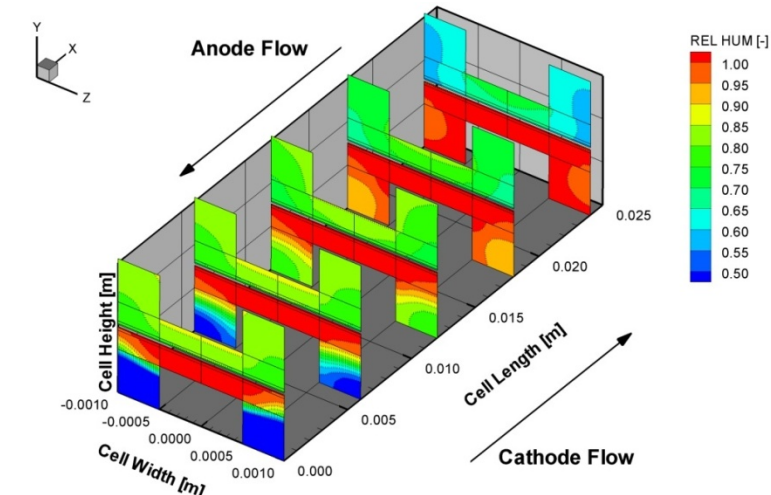
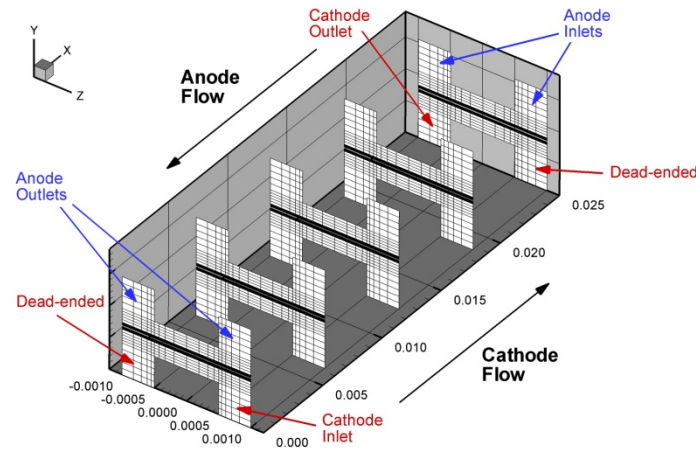
Water management

1. Introduction

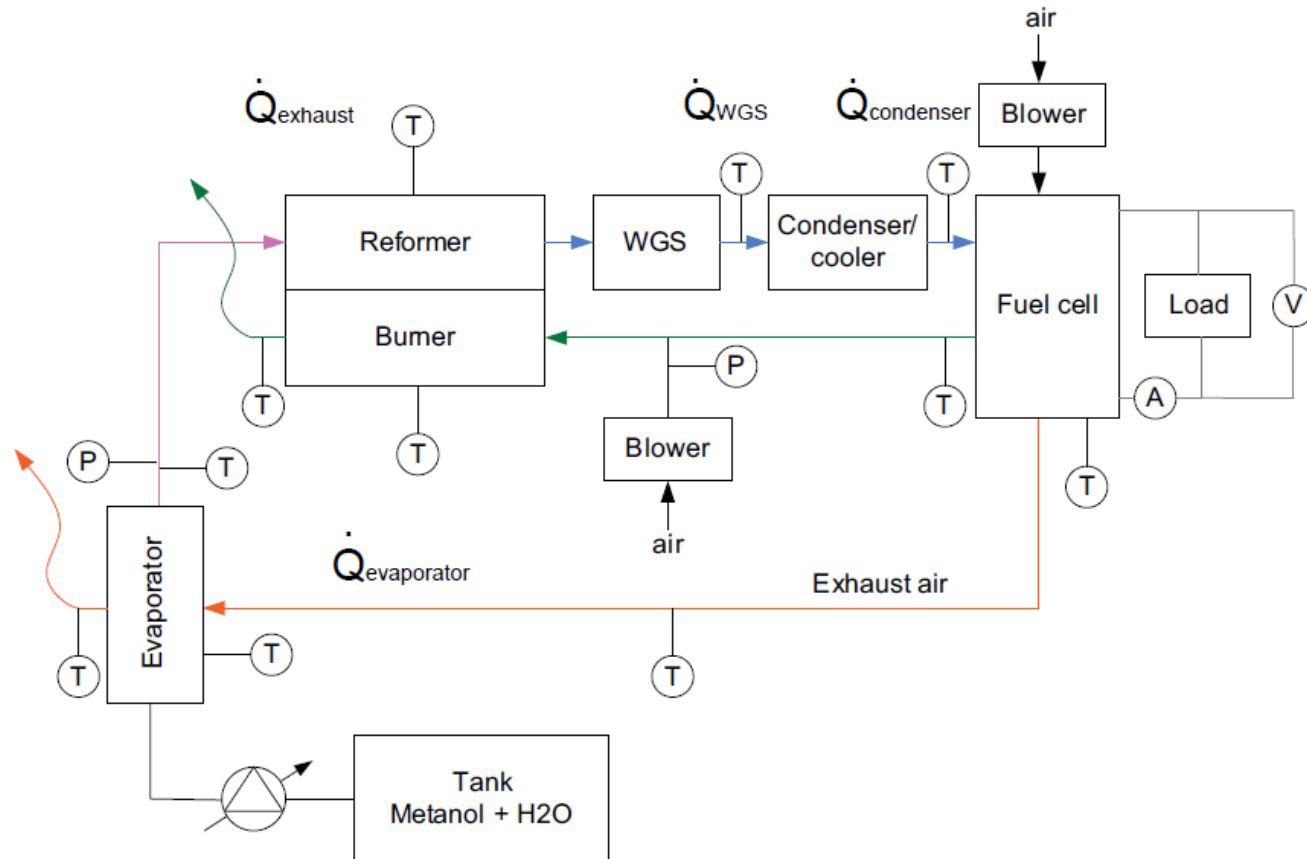
A fundamental understanding of the water balance of a fuel cell during operation is crucial for improving the cell performance and durability. It is well known that an improper water management will lead to excessive flooding of the cathode and presumably to drying out of the anode as water is being dragged from anode to cathode along with the protonic flux through the membrane. A precise estimate of the water balance is essential for the design of a fuel cell system.

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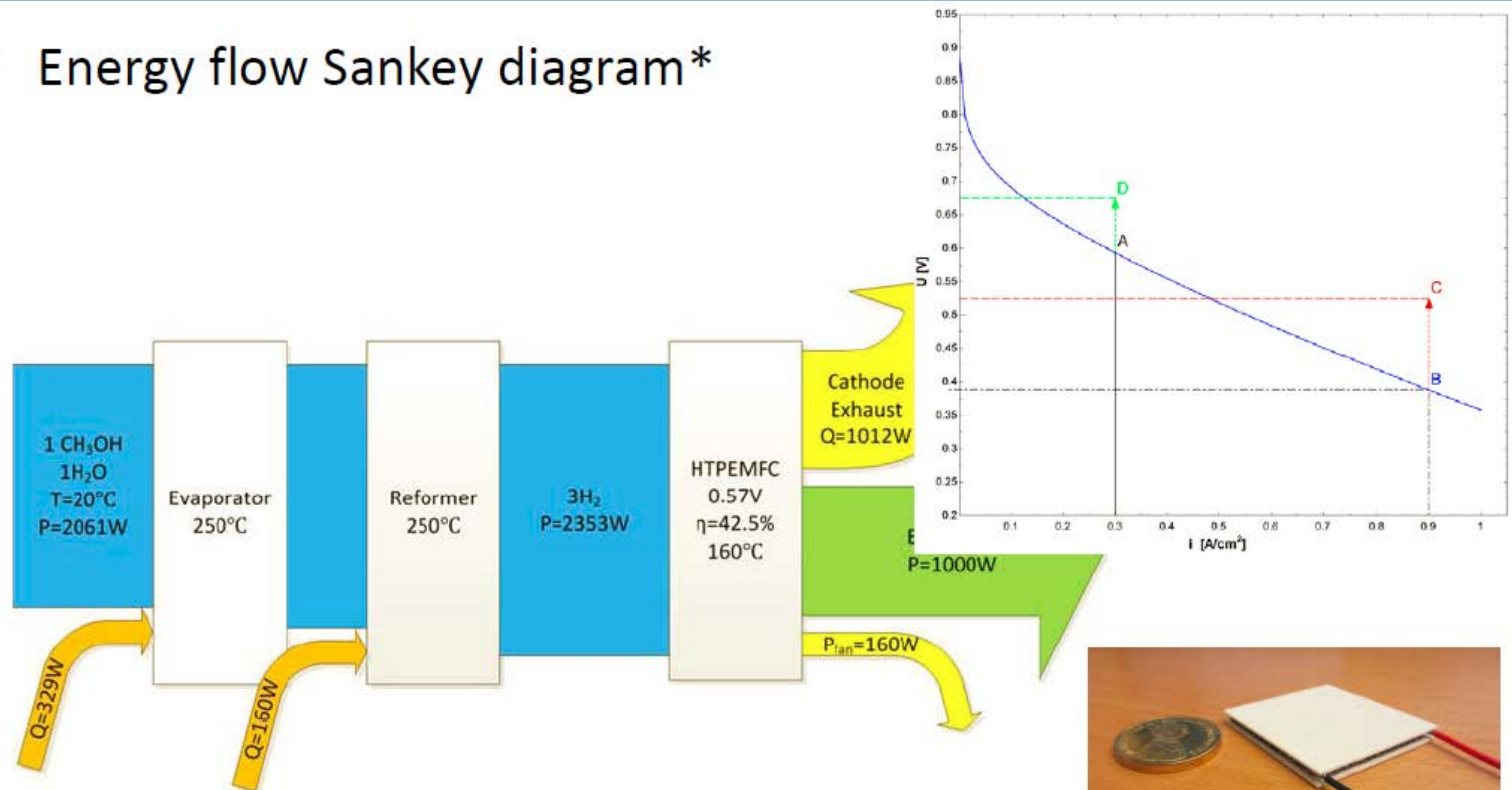


Reformed methanol FC system



Energy harvesting potential

- Energy flow Sankey diagram*

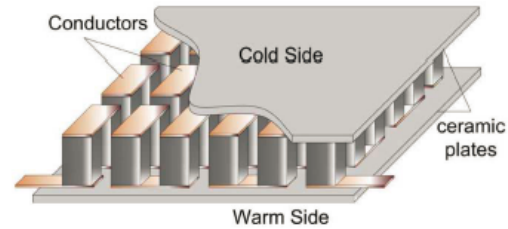
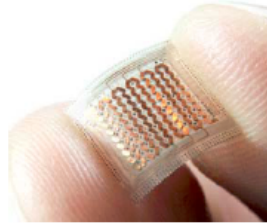
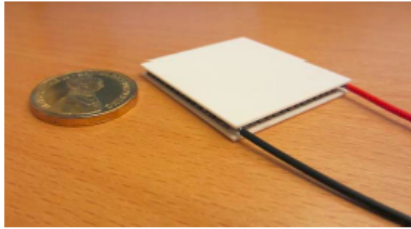


Exhaust heat temperature: $\approx 160^{\circ}\text{C}$; Capacity: 1kW

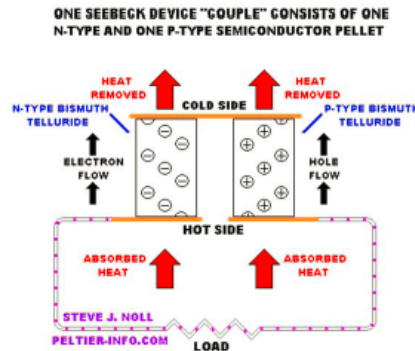


Thermoelectric elements

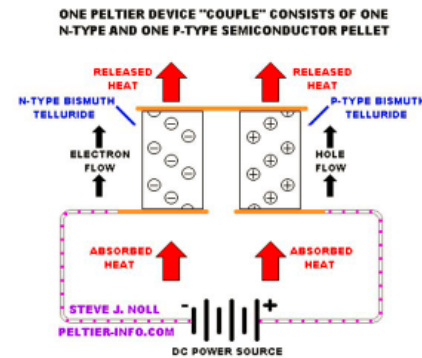
- One TE module



- Two working modes: TEG, TEC



THERE MUST BE A TEMPERATURE DIFFERENCE BETWEEN THE HOT AND COLD SIDES FOR POWER TO BE GENERATED



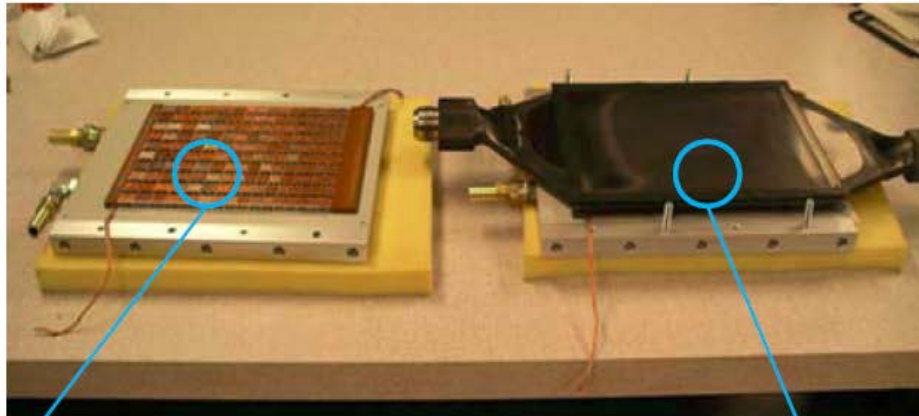
THE CHARGE CARRIERS, NEGATIVE ELECTRONS AND POSITIVE HOLES, TRANSPORT THE HEAT.

TE generator (TEG), Seebeck effect & TE cooler (TEC), Peltier effect
Pros and Cons: reliable, clean, excellent scalability, but low efficiency/COP

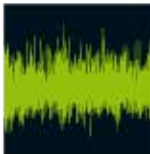


Thermoelectric generator HEX

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



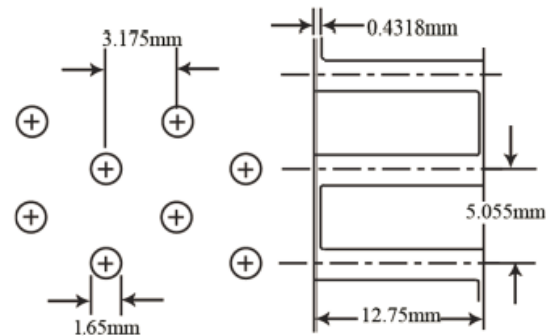
2. Best type of heat exchanger?
3. Right size of the subsystem?



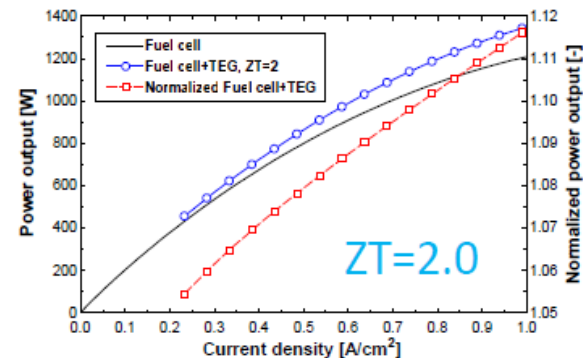
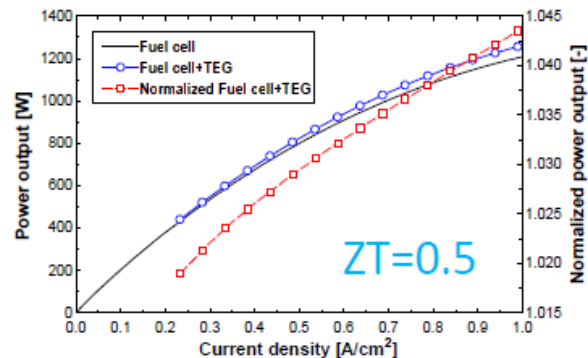
Current and future performance

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

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