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Experimental study and modeling of degradation phenomena in HTPEM fuel cell stacks for use in CHP systems

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Abstract: Degradation phenomena in HTPEM fuel cells for use in CHP systems were investigated experimentally and by modeling. It was found that the two main degradation mechanisms in HTPEM fuel cells are carbon corrosion and Pt agglomeration. On basis of this conclusion a mechanistic model, describing the degradation caused by these phenomena, is suggested. Using the proposed model, information about optimum operational temperatures is derived. To investigate how the degradation propagates on stack level, a simplified stack model is developed. The model is 1-dimensional, non-isothermal, and semi-transient (considering degradation with time). The model shows that the degradation in a stack will not progress uniformly, but occurs faster in the hot end of the stack. Furthermore, the model shows that the degradation is very dependent on stack temperature control scheme. Two experiments were conducted; a 500 hours single cell experiment and a long term stack experiment (around 800 hours so far). In the stack experiment two 1kW stacks were operated at temperatures of 150°C and 170°C. Individual stack parameters were monitored during experiments.

Introduction

Fuel cell based combined heat and power production (CHP) systems fuel with natural gas fuel can be configured in several ways. A simplified layout is shown in fig. 1.

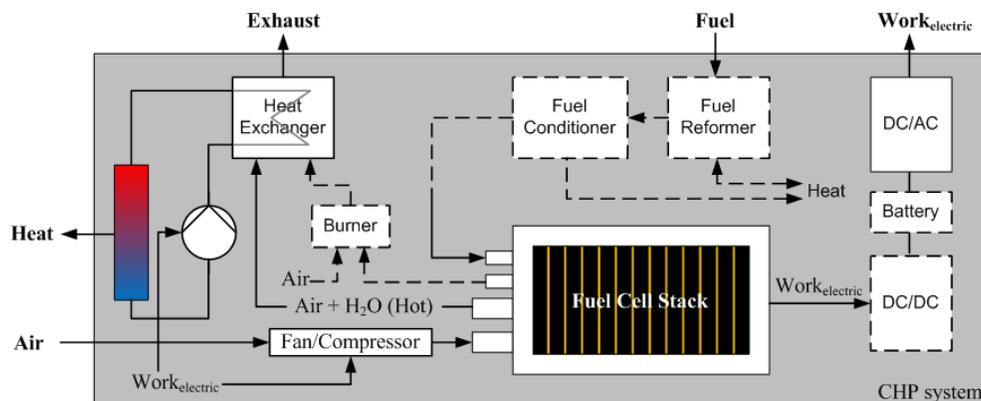


Fig. 1. Simplified layout of a fuel cell based CHP supplied with hydrogen via reforming.

HTPEM fuel cell stacks based on PBI membranes are very interesting candidates for such systems as they can tolerate relatively high concentrations of carbon monoxide compared to conventional PEM fuel cell MEAs based on Nafion due to their higher operational temperature (120-180°C). Furthermore, the excess heat produced by the system is easier to utilize. An extensive description of the performance of HTPEM fuel cells and their application in CHP systems can be found in [1], [2] and [3].

The fuel cell stack is the core component in the system and its performance dictates the operation of the additional components in the fuel cell system. The target set for system lifetime is estimated to be in the order of 40,000 hours of operation for such system to be feasible in competition with other technologies [4]. During its life, the stack degrades, which will affect the operation mode of the remaining system components as the conditions for instance regarding reactant flow and stack cooling will change during life. The stack life is influenced by the nature of the system operation and is a function of parameters such as operational temperature, number of startup cycles and load transients as well as the quality of the anode gas. The lifetime is commonly defined in terms of the initial stack voltage and the final stack voltage [5] as

$$\left| \frac{U_{final} - U_{initial}}{U_{final}} \right| < 10\%$$

In this work, the influence of the abovementioned parameters on stack life is investigated by modeling and experimental work on unit cells and two full scale stack operated on pure hydrogen. The fundamental methodology of the study is outlined in fig. 2.

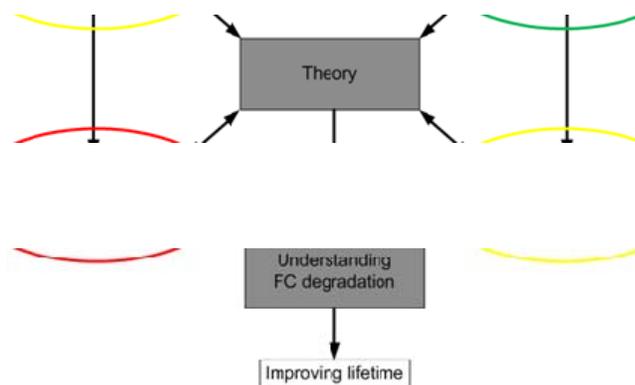


Fig. 2. Methodology of the present stack degradation mechanism study.

Degradation mechanisms

Degradation mechanisms in HTPEM fuel cells have not been widely studied, however a few studies have been made and furthermore some of the mechanisms occurring in phosphoric acid fuel cells (PAFC) can be adopted. In table 1, a survey of the different degradation mechanisms found in the literature is given.

Table 1
 Review of HTPEM degradation modes. The table was expanded based on a similar table in [6]. T: Temperature, p: Partial pressure of water, E: Electrochemical potential, ESA: Electrochemical surface area, MTL: Mass transport losses, IR-loss: Ohmic loss.

Degradation Mode	Effect	Cause
MEMBRANE DEGRADATION		
Pin Hole Formation	H ₂ crossover → Decreased Fuel Efficiency	creep, fibers, f(compression)
Membrane Thinning	H ₂ crossover → Decreased Fuel Efficiency	creep, fibers, f(compression)
Phosphoric Acid Leaching from membrane	Loss in Proton Conductivity → Increased IR-loss	Evaporation, f(T,p)
HO and HO ₂ Radicals Oxidative Degradation	→ H ₂ crossover Loss in Proton Conductivity → Increased IR-loss	
ELECTRODE DEGRADATION		
Pt Particle Agglomeration	Loss in ESA → Decreased Kinetics	Migration, f(T); Dissolution/recrystallization, f(T,E)
Pt Particle Dissolution	Loss in ESA → Decreased Kinetics	Dissolution, f(T,E)
Phosphoric Acid Leaching from catalyst layer	Loss in ESA → Decreased Kinetics	Evaporation, f(T,p)
Carbon Corrosion	→ Increased IR-loss Loss in ESA → Decreased Kinetics Flooding → Increased MTL	Electrochemical oxidation, f(T,E,p), fuel starvation, OCV operation
GDL Corrosion	→ Loss of Structural Integrity → Increased IR-loss Flooding → Increased MTL	Electrochemical oxidation, f(T,E,p)
PTFE Corrosion	Loss in Hydrophobicity, Flooding → Increased MTL	Electrochemical oxidation, f(T,E,p)
Catalyst Poisoning	Loss in ESA → Decreased Kinetics	adsorption, f(T, gas composition)
BIPOLAR PLATE DEGRADATION		
Corrosive Pinhole Formation	Loss of plate material → Fuel and Oxidant Mixing	f(E,T, gas composition)
Micro Pore and Crack Formation	Loss of plate material → Fuel and Oxidant Mixing	Thermal Cycling
Electrocatalyst Poisoning	Loss in ESA → Decreased Kinetics	f(E,T, gas composition)
Passive Layer Formation	Loss of Proton Conductivity → Increased IR-loss	f(E,T, gas composition)
Cracking	→ Fuel and Oxidant Mixing → Loss of Structural Integrity	Mechanical Shock Thermal Cycling

The degradation mechanisms are listed in the table according to their mode, effect and cause. An extensive coverage of the mechanisms regarding membrane degradation and electrode degradation was done by Schmidt et al. [6]. A similar study by the same authors was made on

the effects of catalyst poisoning [7] and in terms of modeling of the poisoning mechanisms of carbon monoxide by [8]. Tawfik et al. described the mechanisms of bipolar plate degradation in [9]. According to these studies, the primary degradation mechanisms are considered to be carbon corrosion (occurring during whole stack life), platinum agglomeration (occurring primarily at the beginning of life) and catalyst layer flooding/failure (late in life and also depends on carbon and PTFE corrosion). The first mentioned mechanism is considered significant at stack temperatures exceeding 150°C [6]. The fine layer of distributed platinum tends to agglomerate above this temperature reducing the active catalytic surface area. Carbon corrosion of the catalyst support material results in similar effects. The path for electro migration can be disrupted if the carbon support corrodes resulting in a reduction of the ESA, yielding increased mass transport and kinetic losses. Usually the carbon corrosion is most extensive at the cathode and is predominantly at higher voltages. The usual recommendation is thus to keep the cell voltage below 0.8V at all times [5]. Phosphoric acid flooding and leaching is reported to be a problem in some cases as described in [6] and [10]. It is however most likely that this problem occurs late in the fuel cell life. Membrane degradation is concluded to be a minor problem in commercial membranes [6]. Some of the degradation data found in literature can be seen in fig. 3.

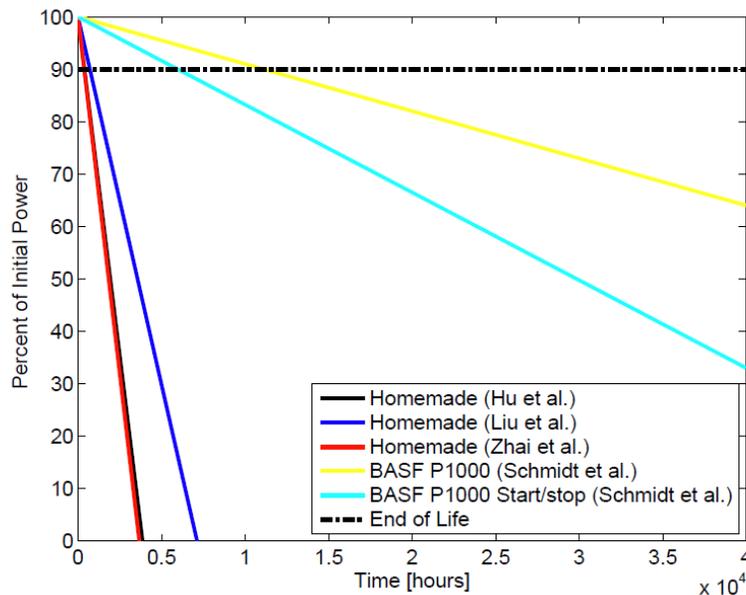


Fig. 3. Degradation data plotted with respect to percent of initial potential at the given set point. It can be concluded that even the best MEAs do not currently meet the lifetime targets for CHP.

Based on this, it is quite important to identify operation conditions minimizing degradation as well as have knowledge about actual degradation designing systems for life time operation.

Modeling

Based on the fuel cell modeling described in [3] and [8] and the results found in the open literature described in the preceding section, a simple degradation model was established enabling a basic theoretical study of the degradation mechanisms in the interaction with poisoning mechanisms. According to [5] Pt agglomeration is proportional to the logarithm of time. Thus it is reasonable to assume that the ESA will be exponentially decaying with time. The carbon corrosion mechanism is also exponentially decaying during life [11]. Considering this, the following equation was formulated for $ESA(t)$.

$$ESA(t) = \left(w_{pa} \cdot e^{-\frac{\alpha_{pa}}{A}t} + w_{cc} \cdot e^{-\frac{\alpha_{cc}}{A}t} \right) \quad \text{where, } w_{pa} + w_{cc} = 1$$

Where α_{pa} [V/h] is the degradation rate due to Pt agglomeration and α_{cc} [V/h] is the degradation rate due to carbon corrosion. w_{pa} and w_{cc} are weights reflecting the impact of the individual phenomena. This correlation was implemented in the model of Korsgaard et al. [8] through a modified time dependent version of the Tafel equation and the model was fitted according to experimental data from single cell experiments. According to [12], the degree of Pt-agglomeration is a linear function of the temperature. In the present theoretical study it has been neglected. In [11] it was concluded that α_{cc} has an Arrhenius like temperature dependence. From the literature data of [6] the pre-exponential factor and activation energy-parameters were found as respectively $4.2122e6$ and $-1.1815e4$. As can be seen in fig. 4, there is a good correlation between the modeling and the experiments of [6] though only few data points were available:

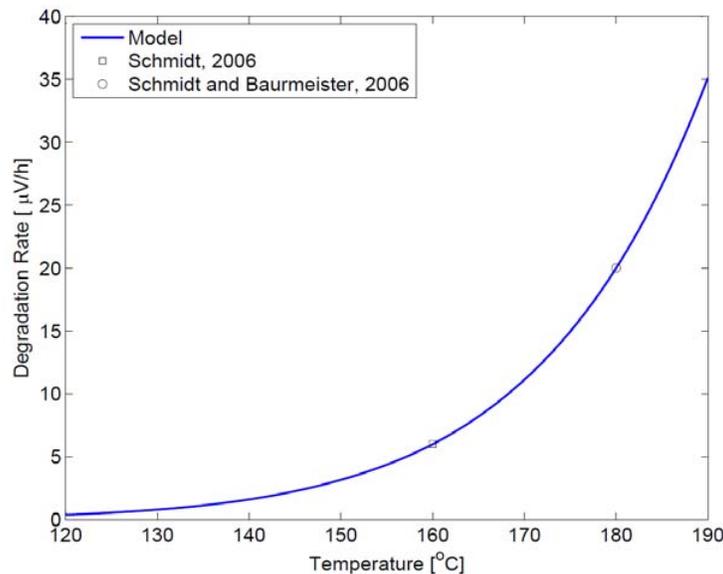


Fig. 4. Comparison between modeled and literature degradation rates - cells are fed with pure H_2 . Note that the degradation rate nearly quadruples increasing the temperature from 160 to 180°C.

In fig. 5 contours are plotted to illustrate the effect of carbon monoxide in the reformate gas over an operational life of 40,000 hours.

Fig. 5. End-of-life cell voltage contours at different temperatures and CO-concentrations.

As would have been expected, optimum cell temperatures can be found depending on the CO-concentration in the reformate gas and the cell temperature due to the counteracting mechanisms of CO-poisoning favoring higher operational temperatures and MEA degradation favoring lower temperature of operation. The interesting conclusion drawn from this analysis is that the optimum operational temperature of the fuel cell stack is increased significantly with higher carbon monoxide content in the reformate gas and furthermore it was found that a CO content of 1% limits the stack temperature to 170°C considering the chosen lifetime criterion.

Based on the cell modeling, a theoretical 2D non-isothermal stack model was derived incorporating overall heat and mass balance of the stack considering individual cell performance. The stack was discretized as shown in fig. 6. The model was implemented in the software EES (Engineering Equation Solver) and was fitted according to measured stack temperatures.

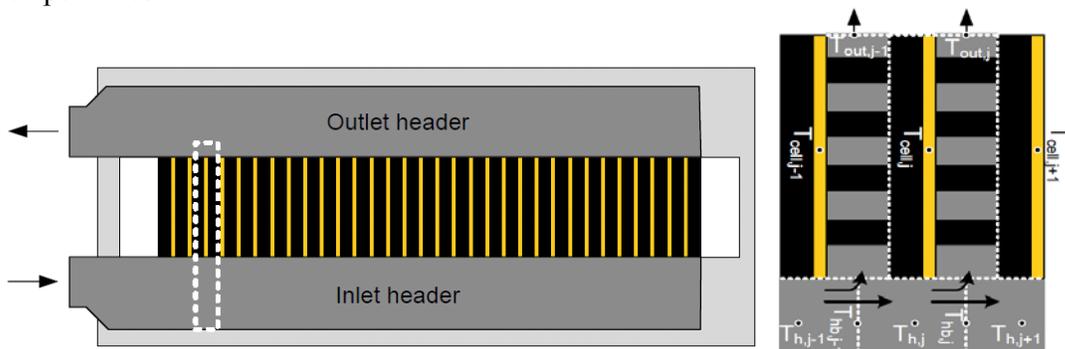


Fig. 6. Discretization of the fuel cell stack (consisting of 65 cells). The figure to the right is sketched along the internal manifold channel, i.e. bipolar plate lands are not shown [13]. The model was used to investigate the impact of different control schemes to stack life. Controlling the stack based on the highest cell temperature in the stack or a middle temperature was considered. Fig. 7 shows the main results of the modeling.

Fig. 7. Extrapolations of experimental results to end-of-life. In (a) and (b) the highest temperature is used as control parameter and in (c) and (d) the midpoint of the stack was used.

For the high temperature control case the degradation is moderate which results in a lifetime exceeding 40,000 hours before one cell fails (disregarding the 10% degradation criterion). The reason for this is that the highest temperature is limited which means that the stack degradation cannot accelerate. The midpoint control scheme allows the temperature of the rear of the stack to increase freely leading to a failure after only 11,000 hours. The average degradation rates (on a cell basis) were found to be respectively $6.4\mu\text{V/h}$ and $18\mu\text{V/h}$ for the two control schemes. The latter is noteworthy small considering that locally part of the stack cells have degradation rates close to $60\mu\text{V/h}$. This is important to consider when performing

long-term testing of fuel cell stacks, since only measuring the total stack potential could indicate a moderate degradation rate, when cells locally are degrading much faster limiting the overall stack life. The highest temperature control mode results in the longest life and is thus the obvious choice from a theoretical point of view but additional thermocouples might have to be mounted on the stacks or an alternative method of estimating the individual cell performance must be used. A single cell failure will have consequences for the entire stack as the cells are both thermally and electrically coupled – a single defect cell performing slightly worse than the other cells can therefore possibly reduce the stack life several hundreds of hours.

Experimental work

A single commercial BASF P2000 MEA was investigated experimentally in a single test facility over 500h of continuous operation. These measurements gave a basis for the stack degradation experiments and furthermore it was attempted to validate the degradation mechanisms using impedance spectroscopy. The latter proved to be useful to calculate the internal resistance of the MEA but it was not possible to fit the achieved spectra's with any theoretically sound circuit. In general it must be concluded that impedance spectroscopy is not currently a useful tool for finding the internal properties of PBI-based MEAs. The single cell facility is shown in fig. 8.



Fig. 8. Single cell test facility at Aalborg University, Department of Energy Technology.

At stack level, two commercial HTPEM stacks manufactured by Serenergy A/S in Denmark were tested. The stacks were operated on pure hydrogen continuously at stack temperatures at respectively 150°C and 170°C. A Labview-based control and data acquisition system supplied by Serenergy was used to perform measurements and uninterruptible power supplies were implemented in the system to be able to handle up to 15 min. power outages.

The hydrogen supply consisted of two hydrogen storage batteries of each ten compressed 50 liter hydrogen storage containers. The system is able to automatically shift between the two batteries when one is empty enabling the possibility of a continuous day-to-day replacement of the batteries. The system is shown on the picture in fig. 9 (one battery lasts approximately 5 days).



Fig. 9. Outdoor stack testing facilities designed for unattended continuous operation.

During operation there were some unintended disturbances affecting the measurement results due to defective data connections. Nonetheless, after the initial problems the system operated more or less continuously for about 800 h. The degradation rates were in general similar to those publicized previously in for instance the works of [6] and [7]. The stack level investigation however revealed interesting findings. As mentioned in the modeling section, an anomaly or failure in one cell can affect the stack life time quite significantly. Fig. 10 shows the initial cell voltages of the two stacks at the operational load point considered.

Fig. 10. Initial cell voltages of the two tested fuel cell stacks.

It is seen that some cells are not performing as well as the majority. The impact of these anomalies over the stack operation recorded is seen in fig. 11.

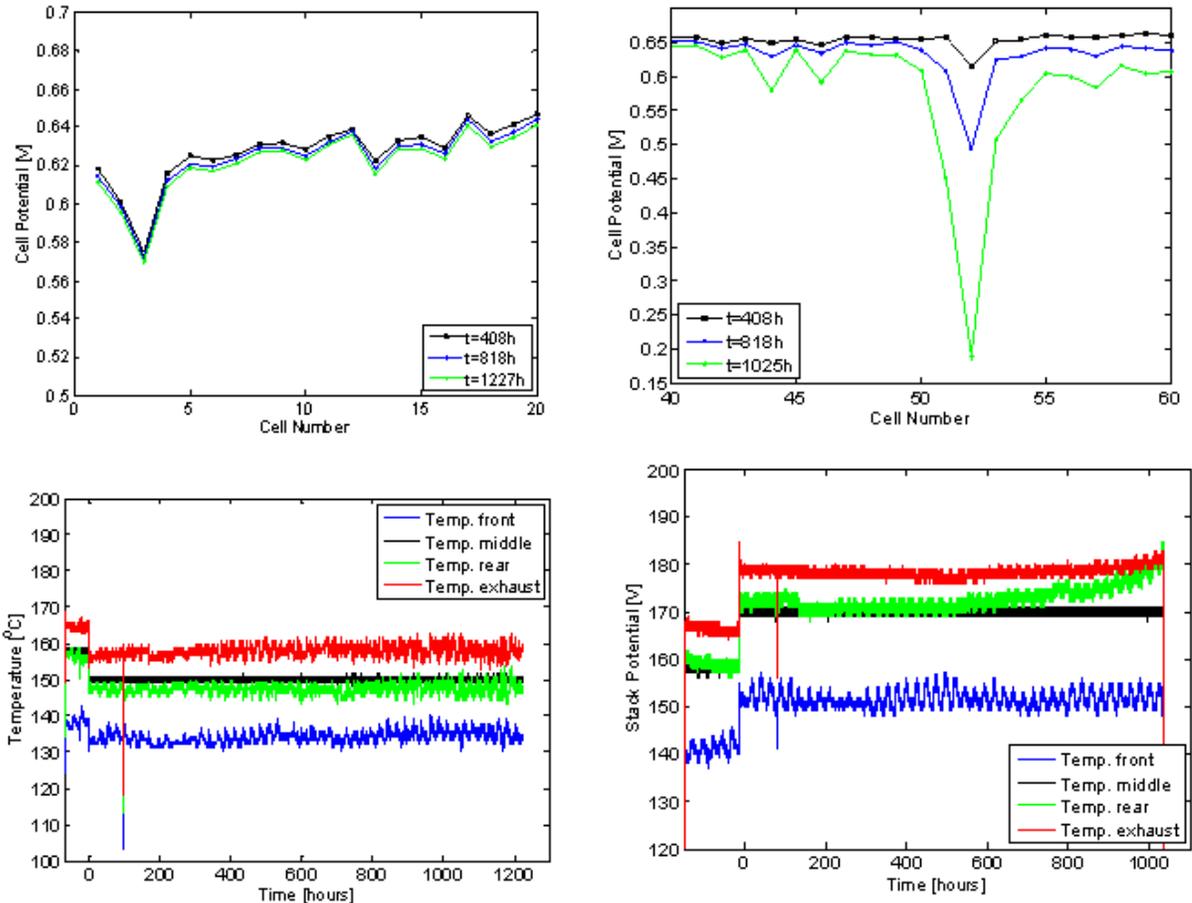


Fig. 11. Effects of single cell anomalies over time.

As can be seen from the figure, the initial anomalies has a quite significant impact on the stack life and to the performance of the neighboring cells which also tend to fail due to increased degradation rates affected by the higher local temperatures. It is thus imperative with an efficient quality control considering the cell production and it is very important to avoid operational situations where there is a risk of failure of the cells. Also making sure that the temperature gradient along the stack is low, is a very important parameter.

Conclusion

Based on the modeling and experimental efforts done in this study, it can be concluded that

- A small temperature gradient over the stack is very important.
- Accurate temperature control is important to get correct feedback.
- Quality control of the MEAs is important to avoid cell anomalies. One anomalous cell can have big impact on stack life time and performance.

- The optimum temperature of operation has been found to be somewhat lower than normally considered for HTPEM-stacks if the stack is to be used in a CHP application.
- The entire system and its components must be designed considering a whole-life-perspective.

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Curriculum Vitae

Peder Lund Rasmussen has a M.Sc. in mechanical engineering specializing in fuel cells and hydrogen technology (HyTec) from Aalborg University and is employed as R&D engineer at Serenergy A/S (<http://serenergy.dk>), Denmark developing commercial PBI based HTPEM fuel cell stacks. During his M.Sc. study he studied one semester at UVic in Canada under the supervision of Professor Ned Djilali. He wrote his M.Sc. thesis on degradation mechanisms in HTPEM fuel cell stacks and this work is the main origin of this work.

Mads Pagh Nielsen is Associate Professor at Department of Energy Technology at Aalborg University, Denmark (<http://www.iet.aau.dk>) with specialization in fuel cell and thermal energy systems. He wrote his Ph.D. dissertation on modeling and optimization of proton exchange membrane fuel cell systems. Besides this he has been involved in several projects concerning development of fuel cell and reforming systems and is the coordinator of the fuel cells and hydrogen technology specialization at Aalborg University. He is a board member of the Danish Simulation Association (<http://dksim.dk>).

Søren Knudsen Kær is Professor at Department of Energy Technology, Aalborg University Denmark (<http://www.iet.aau.dk>) and adjunct research collaborator at Brigham Young University, USA, specializing in fuel cell systems, fluid dynamics and combustion technology and is head of the interdisciplinary fuel cell research group at the department. He is a member of the PEM-strategy group and the transport applications group of the Danish hydrogen and fuel cell platform and is steering committee member and co-founder of the Danish Hydrogen and Fuel Cell Academy (HyFC) doctoral school (<http://www.hyfc.aau.dk>).

Søren Juhl Andreasen is Post Doc. At Department of Energy Technology at Aalborg University, Denmark (<http://www.iet.aau.dk>) and has a background within electromechanical system design. His research is focused upon modeling, control and optimization of HTPEM fuel cell systems based on experimental work and theoretical modeling. He has been involved in several projects on the development of automotive fuel cell systems for hybrid vehicles as well as in the development of fuel cell reforming systems.