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# Degradation modeling of high temperature proton exchange membrane fuel cells using dual time scale simulation

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## HIGHLIGHTS

- Electrochemical effects, thermal effects and degradation effects are described.
- An efficient numerical model for long term simulations is presented.
- A formal dual time scale simulation approach is proposed.
- Analysis of simulation duration and accuracy are performed.

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## ABSTRACT

HT-PEM fuel cells suffer from performance losses due to degradation effects. Therefore, the durability of HT-PEM is currently an important factor of research and development. In this paper a novel approach is presented for an integrated short term and long term simulation of HT-PEM accelerated lifetime testing. The physical phenomena of short term and long term effects are commonly modeled separately due to the different time scales. However, in accelerated lifetime testing, long term degradation effects have a crucial impact on the short term dynamics. Our approach addresses this problem by applying a novel method for dual time scale simulation. A transient system simulation is performed for an open voltage cycle test on a HT-PEM fuel cell for a physical time of 35 days. The analysis describes the system dynamics by numerical electrochemical impedance spectroscopy. Furthermore, a performance assessment is performed in order to demonstrate the efficiency of the approach. The presented approach reduces the simulation time by approximately 73% compared to conventional simulation approach without losing too much accuracy. The approach promises a comprehensive perspective considering short term dynamic behavior and long term degradation effects.

## 1. Introduction

In the joint research project CISTEM a modular system for combined heat and power (CHP) applications based on high temperature proton exchange membrane (HT-PEM) fuel cells and natural gas steam reforming is developed. The system consists of a heat storage, conventional boiler and a CHP part as shown in Fig. 1. In total ten CHP modules of 10 kW electrical power are applied in the system. Within this project a system output of 100 kW electrical power is aspired in order to supply an apartment building or a residential district.

HT-PEM have distinctive characteristics that are suitable for mobile as well as stationary applications. Chandan et al. [1] stated some advantages and disadvantages of HT-PEM in comparison to low temperature PEM technology. The HT-PEM has a better electrode reaction kinetic, a better CO tolerance and the water management is easier to handle. Pasupathi et al. [2] highlighted specifically the temperature range of 140–180 °C, that is ideal for CHP purposes. The disadvantages are the risks of dehydration of conventional membranes above 100 °C and acid losses of acid-base HT membranes, for example phosphoric acid doped PBI type materials [1]. Chandan et al. examined the state of the art developments for the HT-PEM fuel cells. The acidic environment of the fuel cell combined with the humidity level and temperature creates a harsh environment for the components of the fuel cell. The main problems reported in the literature are

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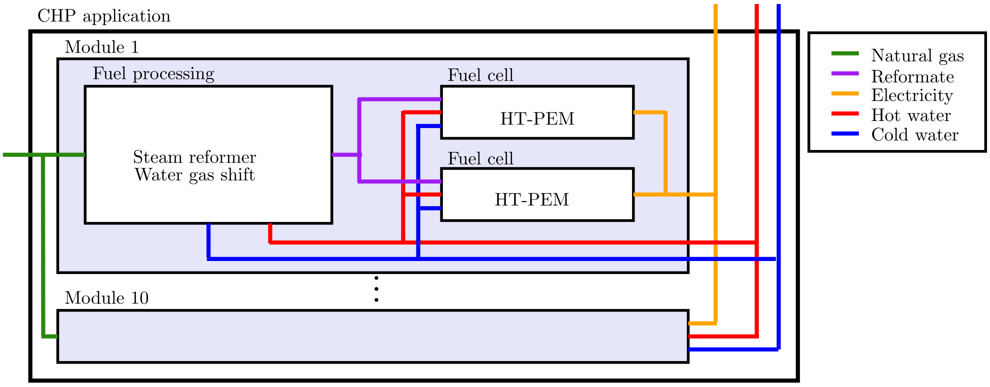

**Fig. 1.** Simplified system setup of the CHP plant. Each module consists of a gas processing unit and two HT-PEM fuel cell units. Each module provides 10 kW electrical power.

- the loss in the catalyst active area due to catalyst agglomeration,
- phosphoric acid loss out from the cell and
- hydrogen crossover.

To be able to compete with existing technologies, the durability of HT-PEM has to be improved. The fuel cell degradation is often investigated in accelerated lifetime testings. In order to reduce time and costs during development, simulations of the fuel cell performance and degradation are being performed. In simulations, the physical phenomena of short term and long term effects are often modeled separately with different time scales. However, in accelerated lifetime testing, degradation (which is considered as a long term effect), has a crucial impact on the dynamic behavior (short term effect).

The presented work contributes to the development of a key component in the CISTEM project. It describes the transient aging behavior of a fuel cell. Since the fuel cell is a component of a modular CHP application, changes in cell performance have a feedback on fuel processing and heat integration. Therefore, the model must depict the dynamic behavior in short term perspective and the degradation effects in long term perspective.

### 1.1. Short term and long term simulation

Dynamic *short term* system models of fuel cells are often described in sub models for electrochemical processes, mass balance and energy balance based on physical ordinary differential equations (ODE). The system of ODEs is interconnected by constitutive equations. The purpose of these models is to describe the energy balance, thermal and electrochemical behavior and other characteristic effects. Such models are found in e.g. Refs. [3–6]. Depending on the research interest more detailed models are used. Approaches for the modeling of gas crossover are introduced e.g. by Chippar and Ju [7]. Oh et al. simulated thermal stress models [8]. The effect of double layer charge is considered with electrical equivalent circuit models in Refs. [4,9–13].

An overview of degradation mechanism in *long term* models is found in e.g. Refs. [14–21]. For the modeling of long term degradation effects physical and empirical approaches have been developed. For example Bi and Fuller [22] developed a degradation model caused by platinum dissolution and deposition with three reactions using empirical model equations. Fowler et al. [14] described a voltage degradation model considering generalized steady state electrochemical models. Kim et al. [23] described the degradation effect of HT-PEM as a function of phosphoric acid doping level, relative humidity, temperature and time. In conventional models the degradation is often considered as a function of time [14,23,24], but not as a function of the operating conditions.

The behavior of short term and long term effects is very distinctive. The time scales of capacities for electrical ($c_{\mathrm{el}}$), thermal ($c_{\mathrm{th}}$) and degradation effects ($c_{\mathrm{degr}}$) are distributed in a wide range, such that $c_{\mathrm{el}} \ll c_{\mathrm{th}} \ll c_{\mathrm{degr}}$. The model depth depend on the focus of interest, the models are either designed for short term or long term simulation. Models considering both time scales are still not common in fuel cell literature except for a few approaches [25]. However, such models promise a wide perspective for understanding the feedback of long term effects on short term effects. During the system lifetime, the behavior of fuel cells can change significantly. Especially in accelerated lifetime testing these changes are analyzed in detail.

### 1.2. Accelerated lifetime testing and fuel cell diagnosis

Accelerated lifetime testing (ALT) is used to reduce the testing time of a product. So called stressors are applied in order to force the aging process. An overview on classical ALT approaches for fuel cell testing is given by Rodgers et al. [26] or Zhang et al. [27]. The degradation mechanism depends strongly on operating conditions and applied stressors. The open circuit voltage (OCV) test is designed to measure chemical degradation and is analyzed for example by Healy et al. [28] and Teranishi et al. [29]. The humidity cycling test is designed to measure mechanical degradation and is analyzed by Knights et al. [30]. Potential cycling tests and drive cycle tests are described by Bi et al. [31] and Hamrock et al. [32]. Rodgers [26] noted that neither test can be completely separated from other degradation mechanisms.

For the analysis of degradation effects various diagnosis methods exist. The electrochemical impedance spectroscopy (EIS) is a standard in-situ diagnosis method for the characterization of fuel cells. The analysis of the EIS results contain crucial system information that describe the short term electrochemical behavior of fuel cell applications. EIS measures the impedance of a system over a range of frequencies. The analysis includes the energy stored in capacitors and dissipation energy. Adopting an equivalent circuit model, the specific parameters (e.g. capacitive and ohmic resistances) are obtained from EIS results, and the changes of the values are compared with the performance loss of individual membrane electrode assemblies [33,34]. Comparing the results of the EIS in time intervals allows an insight of the changes of the fuel cell performance and losses over the time.

### 1.3. Objective

In this paper the degradation is modeled depending on the working condition of the HT-PEM fuel cell. In conventional approaches, separated models for different time scales are set up. The