



Mechanical behaviour of membrane electrode assembly (MEA) during cold start of PEM fuel cell from subzero environment temperature

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Abstract

Durability is one of the most critical remaining issues impeding successful commercialization of broad PEM fuel cell transportation energy applications. Automotive fuel cells are likely to operate with neat hydrogen under load-following or load-levelled modes and be expected to withstand variations in environmental conditions, particularly in the context of temperature and atmospheric composition. In addition, they are also required to survive over the course of their expected operational lifetimes i.e., around 5,500 hrs, while undergoing as many as 30,000 startup/shutdown cycles.

Cold start capability and survivability of proton exchange membrane fuel cells (PEM) in a subzero environment temperature remain a challenge for automotive applications. A key component of increasing the durability of PEM fuel cells is studying the behaviour of the membrane electrode assembly (MEA) at the heart of the fuel cell. The present work investigates how the mechanical behaviour of MEA are influenced during cold start of the PEM fuel cell from subzero environment temperatures. Full three-dimensional, non-isothermal computational fluid dynamics model of a PEM fuel cell has been developed to simulate the stresses inside the PEM fuel cell, which are occurring during fuel cell assembly (bolt assembling), and the stresses arise during fuel cell running due to the changes of temperature and relative humidity. The model is shown to be able to understand the many interacting, complex electrochemical, transport phenomena, and stresses distribution that have limited experimental data.

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1. Introduction

Many problems arise when a PEM fuel cell is frozen, most of these are primarily caused by internal ice formation. Internal ice crystallization causes physical tearing of the polymer membrane, clogging of internal fuel passages, dehydration of the membrane, and separation of the Gas Diffusion Layer (GDL) from the Membrane Electrode Assembly (MEA). Automotive fuel cells are likely to operate with neat hydrogen under load-following or load-levelled modes and be expected to withstand variations in environmental conditions, particularly in the context of temperature and atmospheric composition (Figure 1). Prior to the commercialization of the PEM fuel cells, however, successful development of a rapid and reliable cold-start capability from the subzero environment temperature becomes a prerequisite. In order to maintain good proton conductivity, the water content in the membrane must be kept at a certain level to ensure that the membrane remains fully hydrated. However, the water in the pores of the catalyst layer, gas diffusion layer and the membrane may freeze once the cell temperature decreases

below the freezing point. Thus, methods which could enable the fuel cell startup without or with slight performance degradation at subfreezing temperature need to be studied. In addition, repeated freeze/thaw cycles would lead to the irreversible performance decay and device damage. As is well known the densities of water and ice at 0 °C are 999.8 kg/m³ and 916.8 kg/m³, respectively, and there is about a 9% volume expansion when water freezes at this temperature. As a result, water freezing will definitely generate unbalanced stresses in fuel cell and the stress disappears when the volume gets smaller with the melting of ice. The repeated generation and disappearance of the unbalanced stress in the fuel cell with the phase change of ice will cause damage on the structure and performance of the components to some extent. For further investigation, the damage is classified into three parts: impact on membrane, impact on catalyst coated membrane (CL), and impact on gas diffusion layer (GDL).



Figure 1. Toyota PEM fuel cell hydrogen vehicle (FCHV) covered in snow

In order to achieve a high performance, the sulfonated fluoroethylene membrane should be well hydrated. Hence, when the ambient temperature decreases below, the existence of ice may have a significant impact on the membrane. Since the ion conductivity between the membrane and catalyst is low, the interface between the membrane and CL has attracted more and more attention. After a long time of operation, the interfaces will change significantly and the cathode CL will also be dissociated seriously.

The CL of PEM fuelcell generally comprises three components: Pt/C electrocatalyst, PTFE, and polymer resins, such as Nafion[®]. These three components in the CL form three networks, namely, water and proton transport channels, electronic transport channel, and the gas transport channel. Only the gas transport channel composed of PTFE is hydrophobic, and water is present in the networks composed of Pt/C electrocatalyst and Nafion[®] resins. When the water in the CL freezes and expands, the hydrophilic network undoubtedly will be the most directly affected. Since these networks interact with each other, the hydrophobic network will inevitably suffer from the physical effect of the hydrophilic network.

The physical structure of GDL may be directly damaged by the formation of ice. Once the water in the hydrophilic porous structure in the diffusion layer freezes, the volume expands. As a result, the hydrophobicity of micro-pores becomes large. After repeated freeze/thaw cycling, the hydrophilic and hydrophobic network structure could possibly be damaged due to the generated stress.

To further understand the fundamental cold-start mechanisms of PEM fuel cells, much research has been expended in this area in recent years [1].

Oszcipok et al. [2] conducted isothermal potentiostatic cold-start measurements of a single cell. It was shown that the product water initially increased the membrane humidity at subfreezing temperatures, and after the membrane humidity reached its maximum, the product water would flood the catalyst layer and the gas diffusion layer (GDL) and became frozen. Ice formation would subsequently lead to strong current density decay and cell degradation. They also carried out a mathematic curve fitting and statistic regression analyses, and showed that dryer membrane and high gas flow rates would benefit the PEM fuel cell cold-start operations.

To obtain direct pictures of ice formation in a PEM fuel cell during cold starts from subfreezing temperatures, Ge and Wang [3] developed a transparent cell with a silver mesh used as the cathode GDL and conducted visualization experiments on liquid water transport and ice formation using this cell. It was concluded that the freezing-point depression of water in the cathode catalyst layer should be less than 2 C and its role in cold-start practice should thus be negligible. They later further narrowed down the value range to -1 ± 0.5 C.

Yan et al. [4] experimentally investigated the effect of subzero temperatures on PEM fuel cell performance and cold-start capability. They cooled down the cell temperature during operation, measured polarization curves at subzero temperatures, and found that when the environmental temperature was -15 C the cell cathode temperature was below zero and cell operation stopped. For the study of cold-start capability, they varied the startup temperature, gas purge process, cell insulation, air stoichiometry, and preheat of the reactant gas and tested whether startup succeeded or failed. In this study, they concluded the preheat of reactant gas also affected the results because the hotter gases could remove more water vapor from the cell. However, it is unlikely because the specific heat of the dry gas is so small. The gas is cooled down to cell temperature as soon as it enters the cell, no matter how much the gas is preheated.

The Membrane-Electrode-Assembly (MEA) is the core component of PEM fuel cell and consists of membrane with the gas-diffusion layers including the catalyst attached to each side. The fuel cell MEA durability plays a vital role in the overall lifetime achieved by a stack in field applications. Within the MEA's electrocatalyst layers are three critical interfaces that must remain properly intermingled for optimum MEA performance: platinum/carbon interface (for electron transport and catalyst support); platinum/Nafion interface (for proton transport); and Nafion/carbon interface (for high-activity catalyst dispersion and structural integrity). The MEA performance shows degradation over operating time, which is dependent upon materials, fabrication and operating conditions [5-8].

Mechanical stresses which limit MEA durability have two origins. Firstly, this is the stresses arising during fuel cell assembly (bolt assembling). The bolts provide the tightness and the electrical conductivity between the contact elements. Secondly, additional mechanical stresses occur during fuel cell running because PEM fuel cell components have different thermal expansion and swelling coefficients. Thermal and humidity gradients in the fuel cell produce dilatations obstructed by tightening of the screw-bolts. Compressive stress increasing with the hygro-thermal loading can exceed the yield strength which causes the plastic deformation. The mechanical behaviour of the membrane depends strongly on hydration and temperature [9]. Due to water management issues, operating conditions need to be carefully chosen in order to properly operate fuel cells. Because of the gas consumption along the feeding channels and water production at the cathode, internal cell humidification is highly inhomogeneous. Consequently, operating fuel cells are very often close to critical operating conditions, such as flooding and drying, at least locally [10].

An operating fuel cell has varying local conditions of temperature, humidity, and power generation (and thereby heat generation) across the active area of the fuel cell in three-dimensions. Nevertheless, except of ref. [9], no models have yet been published to incorporate the effect of hygro-thermal stresses into actual fuel cell models to study the effect of these real conditions on the stresses developed in membrane and gas diffusion layers. In addition, as a result of the architecture of a cell, the transport phenomena in a fuel cell are inherently three-dimensional, but no models have yet been published to address the hygro-thermal stresses in PEM fuel cells with three-dimensional effect. Suvorov et al. [11] reported that the

error introduced due to two-dimensional assumption is about 10%. Therefore, in order to acquire a complete understanding of the mechanical behaviour of the MEA during the cell startup process, mechanical response under transient hygro-thermal stresses should be studied under real cell operating conditions and in real cell geometry (three-dimensional).

2. Model description

Three-dimensional CFD model of a PEM fuel cell was used with stress model has been developed, validated, and discussed in detail by the current author in his previous paper [9]. This model is modified for transient PEM fuel cell simulations. In brief, the model is based on the computational fluid dynamics method and considers multi-phase, multi-component flow inside the gas flow channels and the porous media of a PEM fuel cell with straight flow channels. The full computational domain consists of cathode and anode gas flow channels, and the membrane electrode assembly as shown in Figure 1. The model includes the transport of gaseous species, liquid water, protons, energy, and water dissolved in the ion-conducting polymer. Water transport inside the porous gas diffusion layer and catalyst layer is described by two physical mechanisms: viscous drag and capillary pressure forces, and is described by advection within the gas channels. Water transport across the membrane is also described by two physical mechanisms: electro-osmotic drag and diffusion. Water is assumed to be exchanged among three phases; liquid, vapour, and dissolved, and equilibrium among these phases is assumed. This model takes into account convection and diffusion of different species in the channels as well as in the porous gas diffusion layer, heat transfer in the solids as well as in the gases, and electrochemical reactions. The model reflects the influence of the operating parameters on fuel cell performance to investigate the in situ total displacement and degree of the deformation of the polymer membrane of PEM fuel cells. A unique feature of the model is to incorporate the effect of hygro and thermal stresses into actual three-dimensional fuel cell model. In addition, the temperature and humidity dependent material properties are utilized in the simulation for the membrane.

3. Results and discussion

Results for a sixty seconds from the start of operation of a PEM fuel cell operates from subzero startup temperature (-20 C) are discussed in this section. The cell operates at nominal current density of (1.2 A/cm²), inlet gas temperature and initial cell temperature of (-20 C), surrounding temperature of (-20 C), cathode and anode pressure of (3 atm), and air and fuel stoichiometric flow ratio of (2). The geometrical and operational parameters, electrode and membrane parameters, and the material properties for the fuel cell components used in this model are taken from ref. [9].

The temperature distribution inside the fuel cell has important effects on nearly all transport phenomena, and knowledge of the magnitude of temperature increases due to irreversibilities might help preventing membrane failure.

The transient distributions of the cell temperature during the cold-start process are presented in Figure 3. The cell temperature continuously increases with time because of waste heat released during a cold-start from -20 C. In general, the temperature at the cathode side is higher than at the anode side, due to the reversible and irreversible entropy production. Naturally, the maximum temperature occurs, where the electrochemical activity is highest, which is near the cathode side inlet area. The temperature peak appears in the cathode catalyst layer, implying that major heat generation takes place in this region.

The temperature distribution profile remains similar at each operating instant, although the overall cell temperature is increasing as the operation time progresses. These results indicate that a similarity solution for the temperature distribution could be assumed during the transient fuel cell startup process.

The durability of proton exchange membranes used in fuel cells is a major factor in the operating lifetime of fuel cell systems. Figure 4 shows stress distribution (contour plots) and total displacement (deformed shape plot, scale enlarged 140 times) inside the cell on the y-z plane at x=10 mm during the cold-start process. The figure illustrates the effect of stresses on the cell MEA. Because of the different thermal expansion and swelling coefficients between gas diffusion layers and membrane materials with non-uniform temperature distributions in the cell during operation, hygro-thermal stresses and deformation are introduced. The non-uniform distribution of stress, caused by the temperature gradient in cell MEA, induces localized bending stresses, which can contribute to delaminating between the membrane and the gas diffusion layers. It can be seen that the total displacement and the degree of the deformation in MEA are directly related to the temperature, where the temperature is highest in the centre of the channel and coincide with the highest reactant concentrations. In addition, the deformation that occurs in MEA under

the land areas is much smaller than under the channel areas due to the clamping force effect. This result may explain the occurrence of cracks and pinholes in the membrane during cell startup and shutdown cycles, especially at high load conditions and subzero environment temperatures.

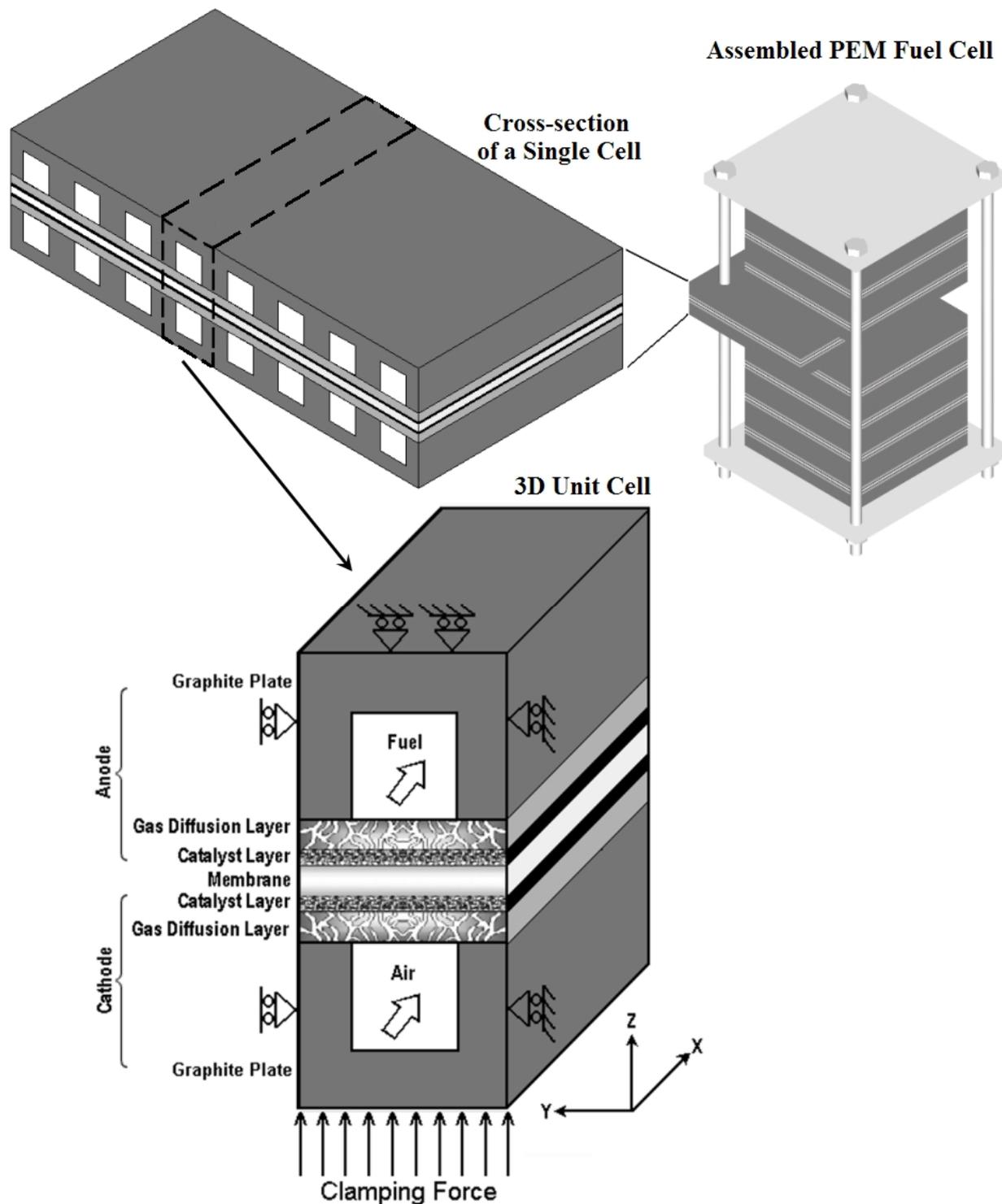


Figure 2. Three-dimensional computational domain

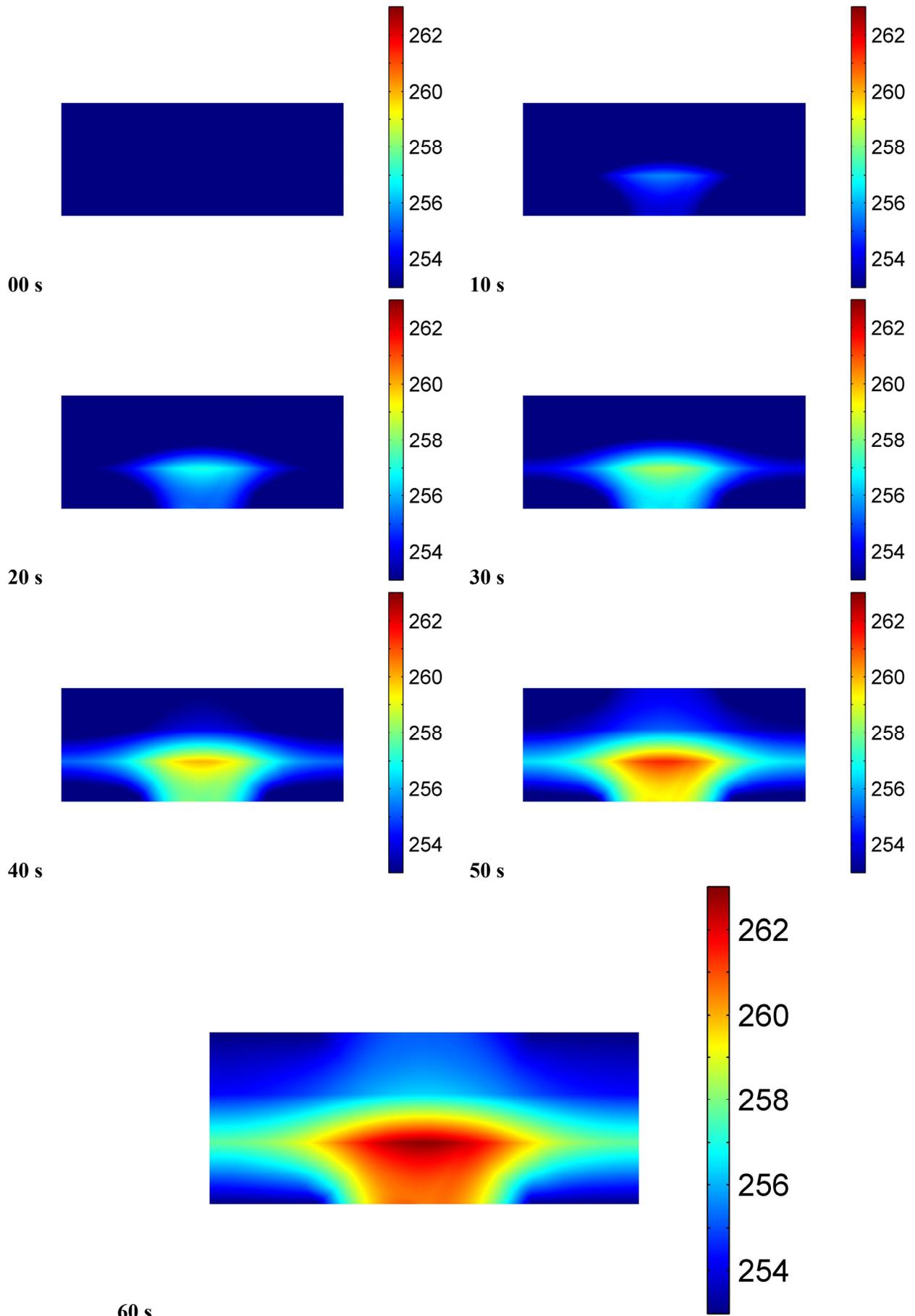


Figure 3. Temperature distribution [K] in MEA on the y-z plane at $x=10$ mm during cold-start of the cell from subzero temperature

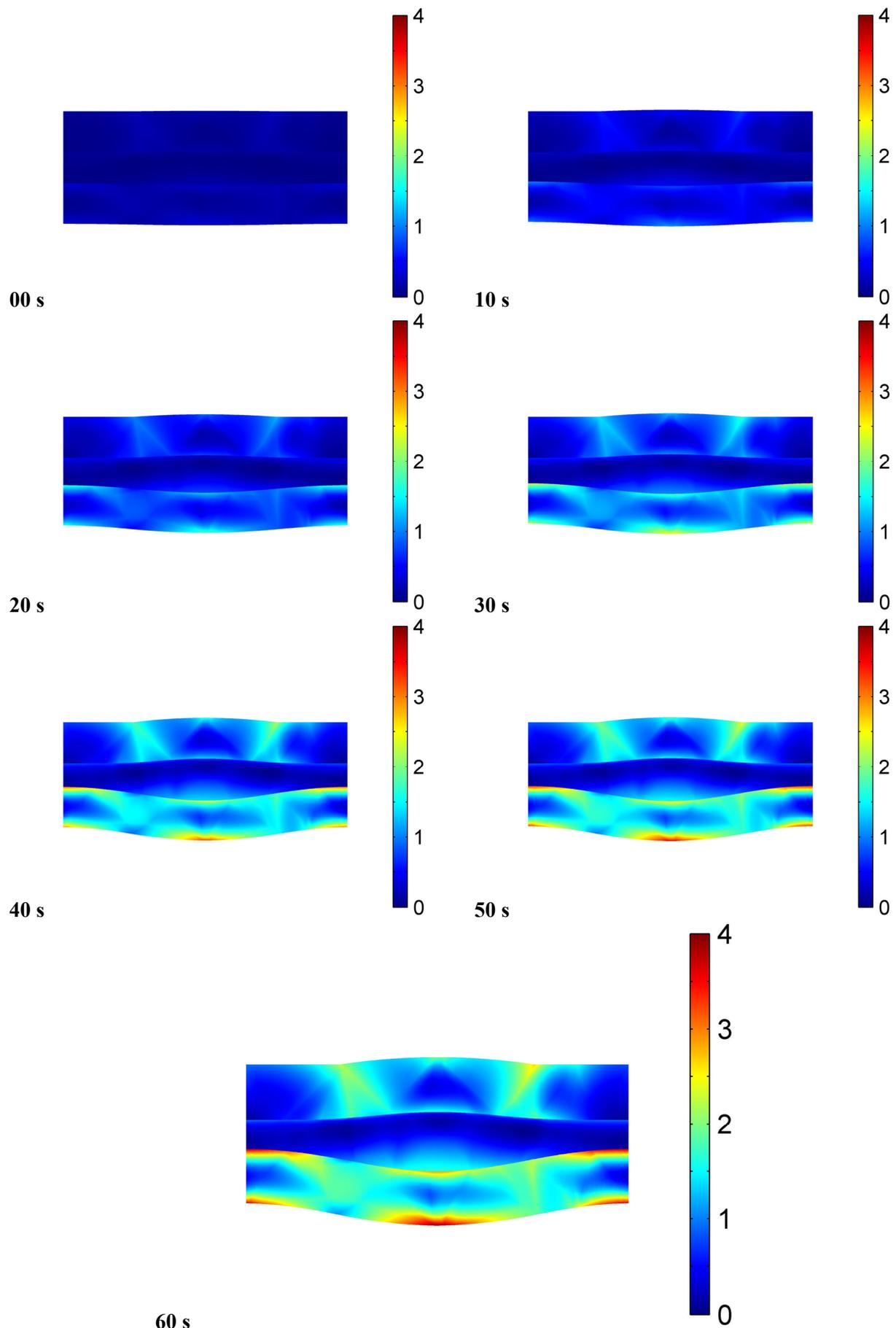


Figure 4. Stresses [MPa] and deformation (deformed shape plot, scale enlarged 140 times) in MEA on the y-z plane at x=10 mm during cold-start of the cell from subzero temperature

4. Conclusion

The behaviour of the cell during operation has been studied and investigated under cold start real operating conditions. The results show that the non-uniform distribution of stresses, caused by the temperature gradient in the cell, induces localized bending stresses, which can contribute to delaminating between the membrane and the gas diffusion layers. These stresses may explain the occurrence of cracks and pinholes in the membrane during cell startup and shutdown cycles over a long period.

In conclusion, the development of physically representative models that allow reliable simulation of the processes under realistic conditions is essential to the development and optimization of fuel cells, improve long-term performance and lifetime, the introduction of cheaper materials and fabrication techniques, and the design and development of novel architectures. In order to achieve the cold startup of PEM fuel cell rapidly without any performance degradation, novel and high performance PEM fuel cell materials, advanced PEM fuel cell system, and appropriate startup strategies are demanded.

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