Methods for modeling HTPEM fuel cells

Siegel C.[1,2], Bandlamudi G.[1,2], Peinecke V.[1], Heinzel A.[1,2]
Zentrum für BrennstoffzellenTechnik (ZBT) gGmbH (1), Universität University of Duisburg-Essen (2)

***Abstract**. For the past 15 years, a lot of models have been developed to simulate a conventional low temperature PEM fuel cells (LTPEM). However, models related to high-temperature-polymer-electrolyte-membrane (HTPEM) fuel cells (operating at temperatures of 160°C – 180°C) are rather new and still much work needs to be done to realize the same. Based on the LTPEM fuel cells and the phosphoric acid fuel cell (PAFC) modeling equations, the present work shows methods and possibilities for simulating operating and quantities behaviour of HTPEM fuel cells using a PBI/H_3PO_4 (phosphoric acid – PA) based membrane. At higher operating temperatures one does not need to account for two-phase water behaviour within the vital parts of the cell, which strongly simplifies the complexity of the problem. On the other hand, detailed energy conservation should be addressed, e.g. a two-equation system could be introduced to separately account for gaseous and solid phase temperature. Moreover, certain inferences could be drawn from the phosphoric acid fuel cell (PAFC) modeling, more particularly, the catalyst layer related parameters. Further, the PBI/H_3PO_4-membrane conductivity and transport mechanisms should be taken into account, along with the consideration of gas properties. Yet another important modeling related question is the evaluation of cathode side reaction kinetics. Simulative case studies were performed at the University of Duisburg-Essen using a commercial available CFD-software tool.*

1. The HTPEM fuel cell

Fuel cells convert energy stored in a fuel and oxidant into electricity according to the well known anode and cathode half cell reactions. Most problems of the low-temperature (LTPEM) fuel cells using e.g. Nafion® membranes are directly related to the low operating temperature, i.e. presence of liquid water (porous media partial flooding), sluggish cathode electrode kinetics, low carbon monoxide tolerance of the catalyst, difficult water (necessity of gas humidification) and heat management (complex system design) as well as membrane and catalyst ageing phenomena. When using phosphoric acid (H_3PO_4 – PA) doped polybenzimidazole (PBI) membranes, most of the debilitating factors can be avoided. Contrary to the LTPEM membrane, these PBI based membranes do offer relatively high proton conductivity and high mechanical stability for operating temperatures up to 180°C.

2. HTPEM modeling aspects – Combining LTPEM and PAFC governing equations

Based on the principles of conservation, HTPEM modeling especially requires detailed reaction layer and membrane modeling which are supposed to differ from traditional governing equations whereas the computational domain is very similar to the LTPEM (e.g.: 1D; 2D (sandwich and along-the-channel); 3D; coupled dimensions;…).

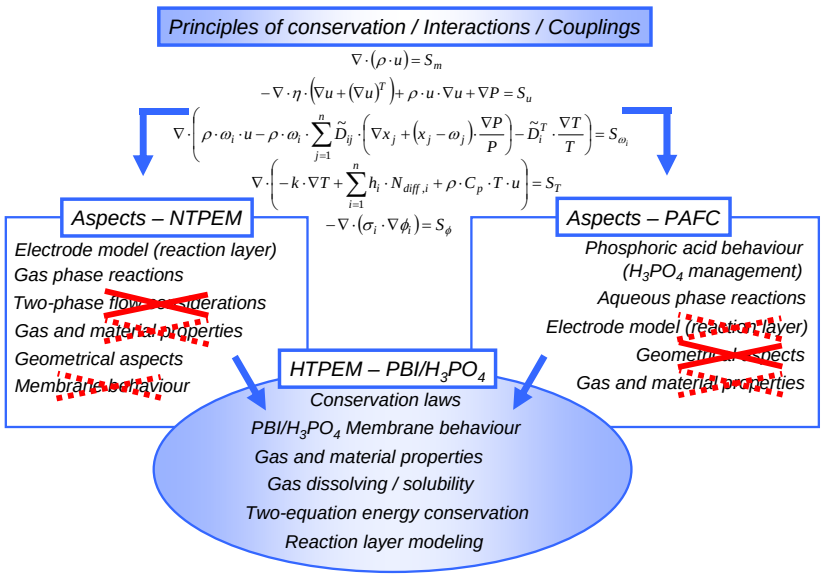

Fig.1. HTPEM modeling aspects regarding LTPEM and PAFC governing equations

2.1 Bipolar-plate and gas channel (flow-field) considerations

ZBT in-house developed high temperature, compound based bipolar-plates

Main modeling aspects:

- Material parameters at elevated temperatures (e.g. thermal, electrical)
- Mechanical aspects (e.g. localized fluid-structural interactions)
- Membrane electrode assembly compression (e.g. clamping pressure distribution, gas diffusion layer deflection) (see case study in Fig.2)

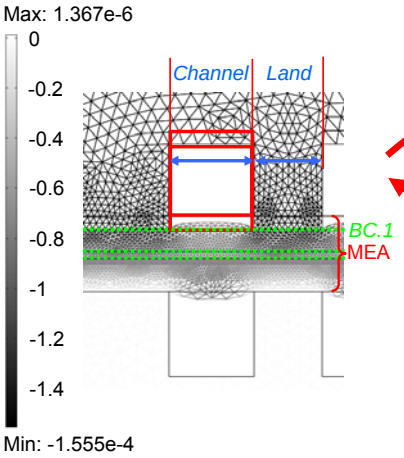

Fig.2. Localized fluid-structural interactions in 2D (e.g. channel-to-land ratio variations)

Flow-field layout → similar LTPEM

Main modeling aspects:

- Channel-to-land ratio
- Pressure loss considerations (e.g. gas properties (Fig.3)
- Separately account for gas-phase temperature as cold gases might entering a hot cell (diffusive heat flux – thermal diffusion coefficients)

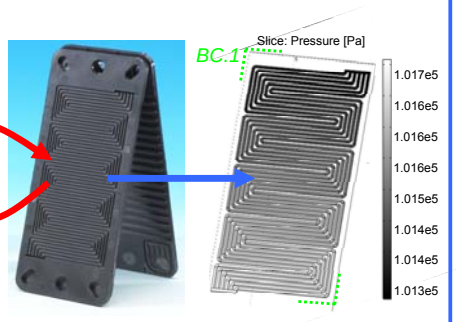

Fig.3. Flow-field design and layout (e.g. inlet pressure 1 [atm])

Outlet B.C.:

$$U_{in}=\frac{\xi}{x_{i,in}}\cdot\frac{\bar{I}}{n_i\cdot F}\cdot\frac{R\cdot T_{in}}{P_{in}}\cdot\frac{a_{MEA}}{a_{ch}}$$

Inlet B.C.:

$$P_{out,i}=P_i$$

2.2 Gas diffusion layer considerations

Gas diffusion layer → similar to LTPEM

Main modeling aspects:

- Two-equation system to separately account for gas and solid phase temperature within the porous media
- Heat exchange between T_s and T_f using a volumetric heat transfer coefficient h_v.

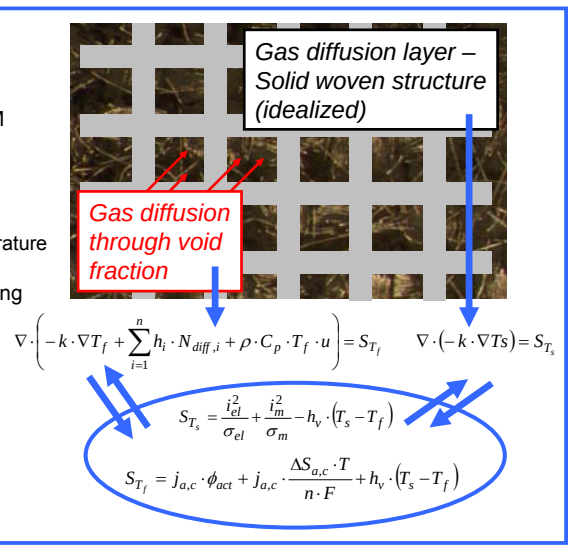

Fig.4. Gas diffusion layer – Energy conservation (two-equation system)

2.4 Reaction layer considerations

Reaction layer modeling → similar LTPEM when assuming gaseous phase reaction (often used)
Reaction layer modeling → similar PAFC when assuming aqueous phase reaction (gas dissolving)

Main modeling aspects:

Gas-phase equals solid-phase temperature (thermal equilibrium)
Evaluation of gaseous to aqueous reaction kinetics
Detailed reaction layer considerations (→ volume fractions)
Concentration of dissolved species (Henry's law)

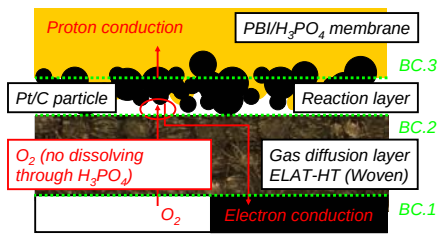

Fig.5. Reaction layer modeling subdomain (gaseous phase reactions)

→ Butler-Volmer reaction kinetics
→ agglomerate approach

Membrane fraction
Pt/C fraction (solid structure fraction)
Void fraction

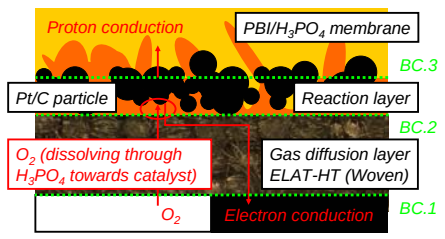

Fig.6. Reaction layer modeling subdomain (aqueous phase reactions)

→ Butler-Volmer reaction kinetics
→ porous electrode theory (macroscopic)
→ agglomerate approach (flooded, electrolyte cylindrical, spherical)
Membrane fraction
Pt/C fraction (solid structure fraction)
H_3PO_4 fraction

2.5 PBI/H_3PO_4 membrane considerations

Main modeling aspects:

- Proton conduction (e.g. Grothuss hopping, contribution of amorphous H_3PO_4)
- Possible water transfer (based on concentration gradients at anode and cathode reaction layer)
- Material fractions (PBI fraction, H_3PO_4 fraction, H_2O fraction)
- Predicting local H_3PO_4 concentrations

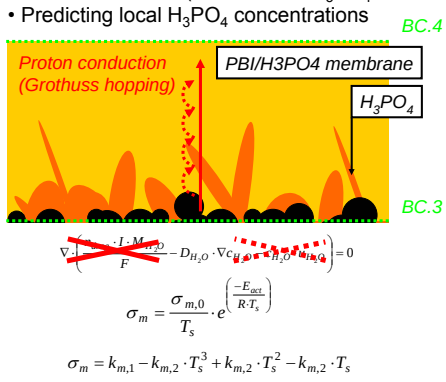

Fig.7. PBI/H_3PO_4 membrane modeling

Fig. 9 shows the membrane conductivity for different gas phase inlet temperatures computed using a 3D modeling domain (case study). The cell operating temperature is 433 [K].

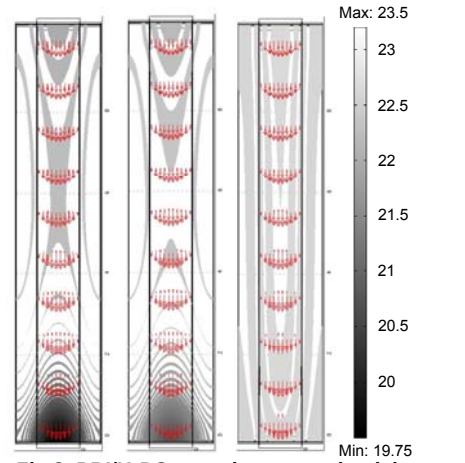

Fig.8. PBI/H_3PO_4 membrane conductivity at different anode and cathode gas inlet temperatures (1. 60°C; 2. 100°C; 3. 160°C) – Counterflow: top = cathode gas channel; bottom = anode gas channel

Conclusion
Several aspects and possibilities for HTPEM modeling using a PBI/H_3PO_4 membrane were presented. All computational domains nearly remain the same for HTPEM as it is the case for LTPEM models. When focusing the different subdomains, one can conclude that especially the reaction layer and the PBI/H3PO4 membrane itself differ from traditions traditional modeling aspects. Volume fractions must be precisely defined. Moreover, free or unbounded phosphoric acid and possible water content may have a major influence on the performance and should be incorporated when modeling HTPEM fuel cells.

***Authors**: Christian Siegel, Zentrum für BrennstoffzellenTechnik (ZBT) gGmbH, Carl-Benz-Straße 201, D-47057 Duisburg, Germany, E-mail: c.siegel@zbt-duisburg.de; George Bandlamudi, E-mail: g.bandlamudi@zbt-duisburg.de; Dr. Volker Peinecke, E-mail: v.peinecke@zbt-duisburg.de; Prof'in. Dr. Angelika Heinzel, E-mail: a.heinzel@zbt-duisburg.de.*

5th Symposium on Fuel Cell Modelling and Experimental Validation, Winterthur (CH) 11.-12.03.2008