

Physical modeling of performance, membrane and catalyst degradation in PEMFC

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Abstract

High cost and performance degradation are still the main issues which hinder the commercialization of low temperature fuel cells on a grand scale [1]. Both of these issues are closely related to the catalyst which accounts for up to 40% of the PEMFC stack cost [2] while the loss of electrochemically active surface area (ECSA) poses a major contribution to the overall performance degradation. Furthermore, chemical membrane degradation is another main issue as membrane thinning and pinhole formation are limiting the lifetime of the cells. Detailed physical models provide a better understanding of the underlying mechanisms leading to these degradation mechanisms and therefore can help in developing strategies to increase the durability of the cells.

Here, we present a two-step approach to achieve this goal. First we develop a transient, two-dimensional single cell model, which includes all relevant mechanisms to describe the cell performance, i.e., electrochemistry, two-phase multi-component transport in the porous layers, charge and heat transport as well as water and gas permeation through the membrane. This model is implemented in our in-house code NEOPARD-X which is based on the open-source framework DuMux [3]. It provides important insights on the local conditions within the cell which are often not accessible in experiments but determine the local degradation rates. In particular we discuss the water management and how simulations of electrochemical impedance spectra (EIS) can be used for process identification.

In the second step we discuss detailed physical models for the degradation mechanisms. A multi-step chemical membrane degradation model is presented which incorporates the formation and decomposition of hydrogen peroxide, iron ion redox cycle, radical formation and degradation via “unzipping” and “side chain scission” mechanism. The model provides insights on the local degradation rates depending on the operating conditions. Strongest degradation is obtained at the anode side during OCV while at higher current densities the degradation is strongly reduced and shifts to the cathode side (left figure). The model is validated with fluoride emission rate (FER) measurements under various operating conditions.

Finally, a catalyst degradation model due to platinum dissolution and particle growth is discussed. Since the dissolution kinetics strongly depends on the platinum oxide coverage, a platinum oxide model has been developed and validated with dedicated CV experiments.

This model is able to describe the experimentally observed logarithmic growth of the oxide coverage. This coverage affects the surface energy of the particles and thus influences the platinum dissolution. Therefore, taking into account the kinetics of the oxide formation is crucial for describing the catalyst degradation under dynamic operating conditions such as fast potential cycling which is typically used as an AST for the catalyst. By coupling the degradation model to the single cell model we investigate the catalyst degradation in AST and long-term degradation tests. The degradation model is validated with experimental data for the ECSA loss during these tests as well as with particle size distributions (PSD) obtained with TEM (right figure). The occurrence of heterogeneities in the catalyst degradation is discussed.

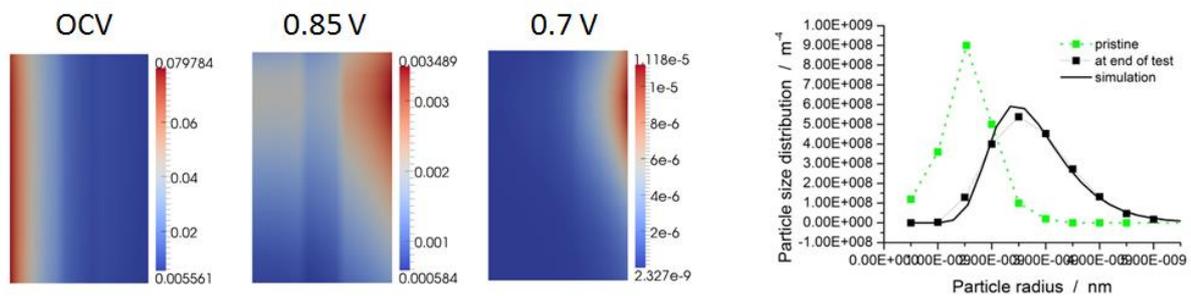


Figure: Simulated local FER ($\text{mol m}^{-3} \text{s}^{-1}$) due to chemical membrane degradation at various cell voltages (left) and comparison between simulated and measured PSD of the catalyst after aging (right).

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- [2] B. D. James et al., "Mass Production Cost Estimation of Direct H₂ PEM Fuel Cell Systems for Transportation Applications: 2016 Update" (2016)
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