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Work package: 6 – Degradation Modeling

Deliverable: 6.1 Mathematical model of single HT-PEM MEA, including catalyst degradation and allowing for extraction of kinetic parameters from the experimental results

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Report: Single HT-PEM MEA model

Within the framework of deliverable *D 6.1 Single HT-PEM MEA model* a mathematical modeling concept was developed enabling description of local distribution of mass and charge in the high temperature PEM Fuel Cell (HT-PEM FC) stack, including evaluation of local degradation of the Pt-C based catalyst in the catalyst layer. The developed concept was implemented to develop, at this stage, two-dimensional (2D) isothermal model to verify its ability by means of experimental data obtained by means of single HT PEM MEA fuel cell. It is based on the macrohomogeneous approach. The basic idea is as follows. The working part of the fuel cell stack is heterogeneous and consists of high number of layers of several types (bipolar plates, gas diffusion layers, catalyst layers and membranes). They differ significantly in their physical and structural properties as well as in their function. However, mathematical modeling of the industrial FC stack based on a detail simulation of the individual layers is impossible or inappropriate for practical case studies due to the extremely high computational demands. The macrohomogeneous approach assumes, that for a large stack consisting approximately of 50 to 100 cells the local reaction and transport phenomena occurring on single layer scale or at the interlayer boundary become minor with respect to phenomena occurring on the stack level. In this case the working region of the stack can be assumed continuous characterized by corresponding effective anisotropic reaction-transport parameters. Mass and charge exchange between the individual layers are mathematically realized via source/sink terms in the corresponding balance equations.

As already mentioned, the proposed mathematical model was validated at this stage using the single cell experimental results. An acceptable agreement was obtained. The model provided physically correct results in accordance with theoretical expectation. At the same time it is reasonably demanding regarding the computational power demands. Moreover, an important model input parameters, like kinetic parameter of the electrode reactions, have been identified. For example, Fig. 1 shows local volumetric current of the oxygen reduction reaction, i.e. local rate of oxygen consumption by electrochemical process at the beginning of the FC stack operation at different current loads.

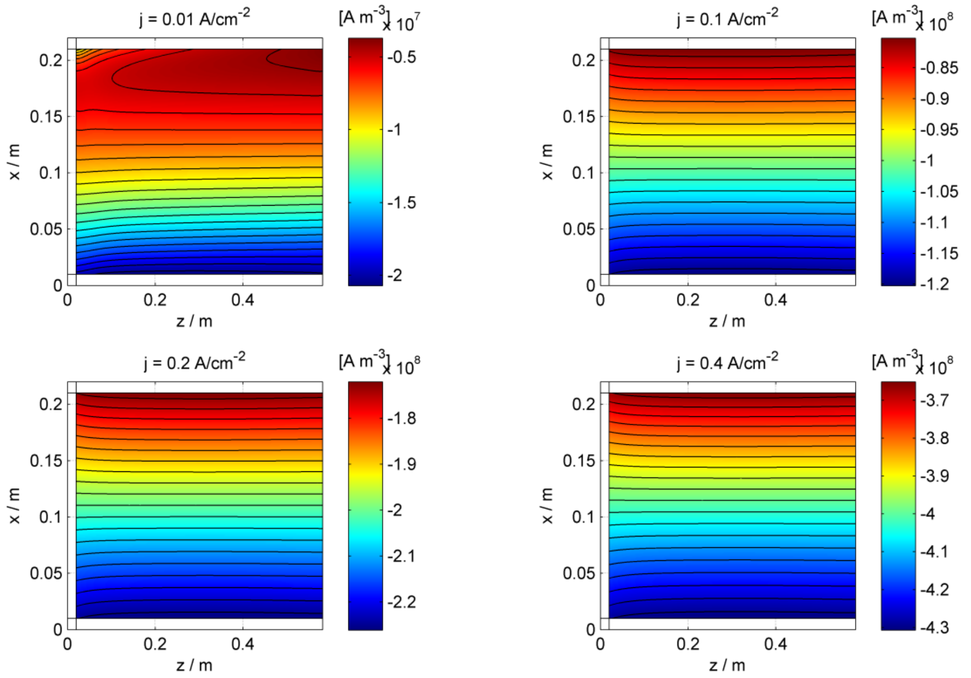

Figure 1: Local volumetric current corresponding to ORR on the TPB (j_{ORR}) at various current loads (in figure title), grey lines – contours.

The developed model enables local simulation of the Pt-C catalyst degradation depending on the local operating conditions in the FC stack. The Pt catalyst dissolution mainly leads to the loss of electrochemically active surface area and to the increase in the local overvoltage of the electrode reactions. It can significantly reduce the stack performance or even affect the uniformity of charge and mass distribution inside the device. Due to the latter aspect the degradation process can even be locally accelerated.

The catalyst degradation mechanisms considered are mainly based on the Pt dissolution:

1) electrochemical dissolution of Pt (EDPt, Reaction 1),

2) electrochemical oxidation of Pt to PtO (EOPt, Reaction 2) and

3) chemical dissolution of PtO (ChDPtO, Reaction 3).

The individual degradation processes are implemented in the model (a) by means of source/sink terms in the conservation equations of the platinum based compounds and (b) in the active surface area affecting value of volumetric current of individual reactions shown in Fig. 1.

$$\mathrm{Pt}^{2+} + 2\mathrm{e}^- \leftrightarrow \mathrm{Pt} \tag{1}$$

$$PtO + 2H^+ + \ 2e^- \leftrightarrow Pt + H_2O \tag{2}$$

$$PtO + 2H^+ \leftrightarrow Pt^{2+} + H_2O \tag{3}$$

The corresponding kinetic equations were proposed and required input kinetic parameters were determined experimentally under HT PEM FC conditions. As an example, a kinetic equation of EOPt is shown, see Eq. 4,

$$\begin{aligned} r = k_a exp\left\{-\frac{\omega_a \theta_{PtO}}{RT}\right\}\left(1-\frac{\theta_{PtO}}{2}\right) exp\left\{\frac{\alpha_a\,F}{RT}(E - {}_rE'\ )\right\} - \\ - k_c exp\left\{-\frac{\omega_c \theta_{PtO}}{RT}\right\}\frac{\theta_{PtO}}{2} exp\left\{-\frac{\alpha_c F}{RT}(E - {}_rE'\ )\right\} \end{aligned} \tag{4}$$

where r corresponds to the reaction rate, *k* is rate constant, respectively, θ_{PtO} is surface coverage of Pt crystals by PtO, ω is activation energy type parameter, α is charge transfer coefficient, *E* is electrode potential, ${}_rE'$ is formal reversible electrode potential and subscripts *a* and *c* identify anodic and cathodic reaction, respectively. Fig. 2 shows comparison of the cyclovoltamograms recorded for the Pt sheet electrode determined experimentally with mathematical model based on Eq. 4. The experiment was performed in pure hot (160 °C) phosphoric acid. A good agreement is obtained for various upper vertex potentials. The lower vertex potential was set high enough to eliminate formation of various phosphorus acids representing catalyst poison for Pt.

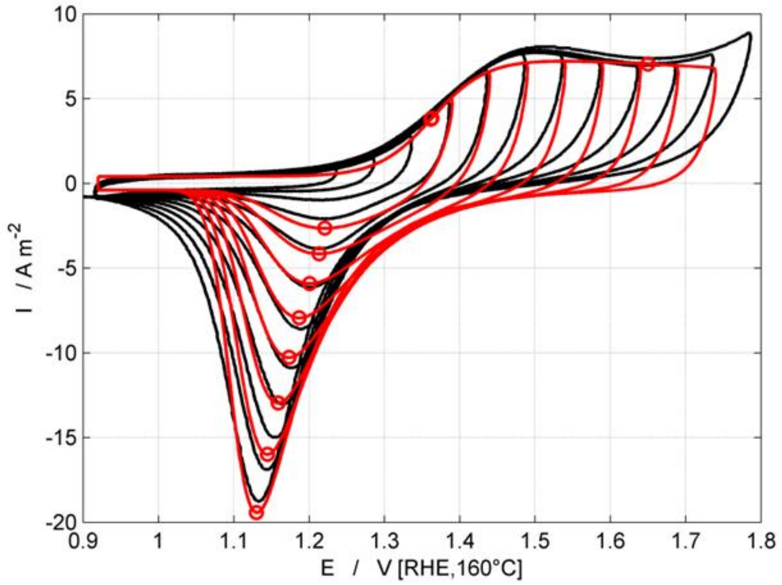

Figure 2: Cycling voltammetry of Pt sheet, black curves – experimental results, red curves – results of mathematical model, temperature 160°C, 99% H_3PO_4, k_a = 9.42 × 10^{-6} mol m^{-2} s^{-1}, k_c = 1.25 × 10^{-4} mol m^{-2} s^{-1}, α_a=1, α_c=0.41, ω_a = 27728 J mol^{-1}, ω_c= 5051 J mol^{-1}, ${}_rE'$ = 1.31 V.