Electrochemical Investigation of Ion Diffusion through Polymer Membranes in Combination with FEM Modelling

Motivation

What we have:
- Cycled stress test showed
  - Ion diffusion through polyimide
  - Surface degradation

What we want:
- Diffusion Coefficients for the transport of ions, contaminants and corrosion related species.

What we do:
- Electrochemical measurements
- Simulation
- Quantitative analysis

Simulation

Determination of transport parameters by fitting FEM simulation (made in COMSOL Multiphysics®) to the measurement.

- "Transport of diluted species" (Nernst-Planck)
  \[
  f(x, t) = -D_i \frac{\partial C_i(x, t)}{\partial x} - z_i F E(x, t) \]

- "Electrostatics" (Poisson)
  \[
  \frac{\partial E(x, t)}{\partial t} = \frac{\rho(x, t)}{\varepsilon} - \frac{\rho(x, t)}{\varepsilon} = \frac{\rho(x, t)}{\varepsilon} \sum_i z_i C_i(x, t)
  \]

  - Convection and liquid flow are ignored

Concept

Diffusion processes driven by concentration differences are measured with a "Diffusion Cell": Transport parameters are determined by fitting FEM simulation (made in COMSOL Multiphysics®) to the measurement.

Results

Diffusion coefficients for different model membranes (Nafion211 and Self fabricated P84 polyimide).

The values have been extracted from the optimized simulation.

Measurement

The measured voltage is not just influenced by the different concentrations but also by the diffusion voltage over the membrane.

1. Nernst Potentials of the Electrodes
   \[
   \Delta E_{\text{Nernst}}^\text{immediate values} = -0.659 \cdot \lg \left( \frac{c_{\text{H}^+}}{c_{\text{OH}^-}} \right)
   \]

2. Additional Diffusion-Potential
   \[
   \Delta \Psi_{\text{diff}} = \frac{RT}{2F} \ln \left( \frac{c_{\text{H}^+}}{c_{\text{OH}^-}} \right) \cdot \ln \left( \frac{a_{\text{H}^+}}{a_{\text{OH}^-}} \right)
   \]
   (ultra-)fast process!

3. Change of Diffusion- and Nernst-Potential caused by change of concentration:
   \[
   \Delta E = \Delta E_{\text{Nernst}} + \Delta \Psi_{\text{diff}} \rightarrow 0
   \]
   slow process!

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