Electroosmosis in proton exchange membranes : calculation of efficiency of energy conversion

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We give a tentative definition of the efficiency of energy conversion in a proton exchange membrane. The most important application of this type of material is the permselective conduction of ions in fuel cells of the PEMFC type where a chemical potential energy is converted in a proton flux. The PEM acts like an energy converter: but one part of the chemical potential energy is converted in “hydraulic” energy, as water diffuses through the permselective barrier by coupled diffusion (electroosmosis). We compute the conversion-efficiency with the generalized diffusion Nernst-Planck equation and the dusty gas membrane model.

The generalized Nernst-Planck equation

We use here the generalized Nernst - Planck equation with the formalism defined by Schaetzel et al. [1] from the generalized Stefan-Maxwell equation.

$$J_i = -c_i D_i \frac{\nabla \mu_i}{RT} + x_i \sum_{j=1}^{j=n,\, j\neq i} \alpha_{ij} J_j$$

J_i = the average diffusive molar flux of species i,

n = the number of species in the mixture (polymer, water and ions), c_i the molarity of species i,

R = the ideal gas constant,
T = absolute temperature
$\nabla\mu_i$=the gradient of the generalized chemical potential.

D_i = generalized diffusivity of species i in the multicomponent mixture.

α_{ij} is the coupling coefficient between the fluxes J_i and J_j

$$\alpha_{ij} = \frac{D_i}{D_{ij}}$$

D_{ij} is the binary diffusivity.

Definition and calculation of the efficiency of energy conversion

For a proton exchange membrane used in a PEM fuel cell, the total energy input is the generalized thermodynamic force $-\nabla\mu_+$ given to the counter-ion (species +). One part of this energy is used to drive the proton from one side of the membrane to the other side. The other part of the energy is lost energy utilized for the diffusion of water or co-ions. For the counter-ion the generalized Nernst-Planck equation writes in an ideal permselective cation exchange membrane

$$J_+ = -c_+ D_+ \frac{\nabla\mu_+}{RT} + x_+ \alpha_{+w} J_w$$

To get the counter-ion flux J_+ when coupling exist the following generalized force is required:

$$-\nabla\mu_+ = \frac{RT}{c_+ D_+}\left[J_+ - x_+ \sum_{j=2}^{j=n} \alpha_{+w} J_w \right]$$

The utile part of the generalized force, really used to move the counter-ion through the membrane is

$$-\nabla\mu_{+,th} = \frac{RT}{c_+ D_+} J_+$$

So, we propose as a definition of the efficiency of energy conversion in a PEM the following definition:

$$\eta = \frac{\nabla\mu_+}{\nabla\mu_{+,th}}$$

In the case of the membrane with only water-counter-ion flux coupling the efficiency of energy conversion is:

$$\eta = 1 - x_+ x_w \alpha_{+w} \alpha_{w+}$$

Results and discussion

To compute the efficiency of energy conversion we use the mutual diffusivities computed by Schaetzel et al. [2]. This efficiency is shown on Figure 1 in function of the degree of ionization, which is defined as

$$y_+ = \frac{c_{R-}}{c_R + c_R}$$

and the swelling of the membrane characterized here by the volume fraction occupied by the mobile species computed by

$$\Phi = \overline{V_w} c_w + \overline{V_+} c_+$$

In this formula $\overline{V_w}$ and $\overline{V_+}$ are the partial molar volumes. With this example we observe that the efficiency of energy conversion of a membrane is high and dependent on the structure of the membrane.

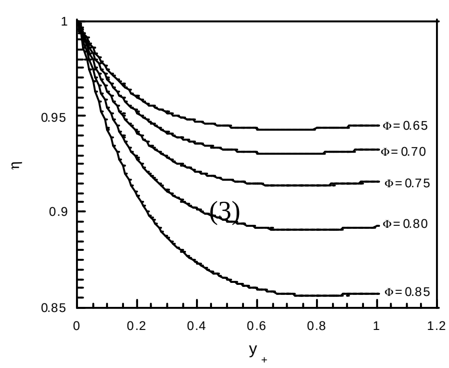

Figure 1. Efficiency of energy conversion in a proton exchange membrane.

The efficiency of energy conversion is growing in function of the exchange capacity. For a realistic membrane, the ionization should be high, to avoid the penetration of the co-ions in the material. On Figure 1 it is obvious that the conversion efficiency is stable for ionization rates larger than 0.6 and than slightly increases. For a given ionization, the efficiency sharply growth when the swelling decreases.

References

1. P. Schaetzel and B. Auclair, Electrochimica Acta, 43(21-22) (1998) 3375-3377
2. P. Schaetzel and B. Auclair, Electrochimica Acta, 38 (1993) 329 – 340.