A new numerical pore-scale model of membrane polarization

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Existing membrane polarisation models

In membrane polarisation models, the motion of ions in the fluid-filled pore space in response to an applied AC voltage is considered. Existing analytic descriptions assume a sequence of active and passive zones, where the counter-ion mobility is reduced in active zones (Marshall and Madden 1959); they partly include some properties of the electrical double layer (EDL) at the matrix-fluid interface as essential source of the IP effect, as well as the finite pore width (most recent Bücker and Hördt 2013a, 2013b). Numerical models based on this conception have also been considered (Blaschek and Hördt 2009, Volkmann and Klitzsch 2010). However, each of these models is either 1-D, or assumes reduced counter-ion mobility in pore throats or close to the pore walls in order to mimic the effect of the EDL, or both, and thus has physical limitations, which are overcome by our model.

Model equations

As in existing models, our set of model equations describing the ions' migration and diffusion, and the associated electric potential, is given by the Nernst-Planck equations and the Poisson equation. The dependent variables are the cation concentration c_p, the anion concentration c_n, and the electric potential φ as functions of spatial position $\underline{x}$. If the spectral response is sought, it is advantageous with respect to computation time to solve the system of equations in frequency domain. A time-harmonic ansatz for the dependent variables is chosen:

$$\begin{cases} c_p\left(\underline{x},t\right) = c_{p0}\left(\underline{x}\right) + c_p'\left(\underline{x}\right)\exp\left(i\omega t\right) \\ c_n\left(\underline{x},t\right) = c_{n0}\left(\underline{x}\right) + c_n'\left(\underline{x}\right)\exp\left(i\omega t\right) \\ \varphi\left(\underline{x},t\right) = \varphi_0\left(\underline{x}\right) + \varphi'\left(\underline{x}\right)\exp\left(i\omega t\right) \end{cases}$$

where i is the imaginary number, ω is the angular frequency of the applied AC voltage, and c_p', c_n', and φ', and thus also c_p, c_n, and φ are complex-valued quantities. The frequency-domain equations are then given by

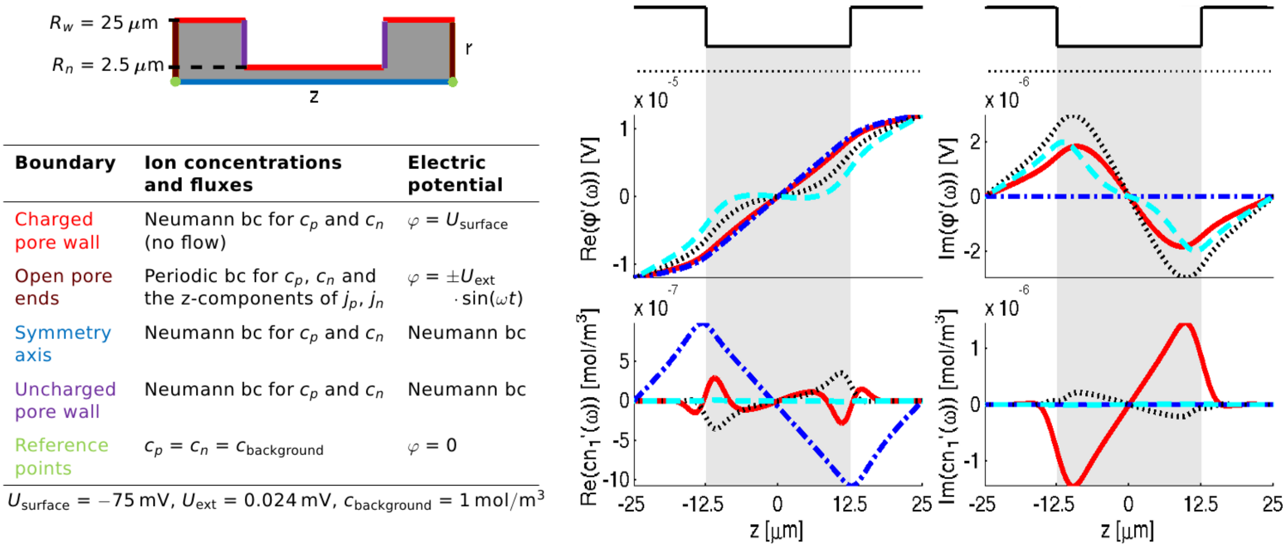
$$\begin{cases} 0 = D_p\Delta c_{p0}\left(\underline{x}\right) + \mu_p\nabla\bullet\left[c_{p0}\left(\underline{x}\right)\nabla\varphi_0\left(\underline{x}\right)\right] \\ 0 = D_n\Delta c_{n0}\left(\underline{x}\right) - \mu_n\nabla\bullet\left[c_{n0}\left(\underline{x}\right)\nabla\varphi_0\left(\underline{x}\right)\right] \\ \Delta\varphi_0\left(\underline{x}\right) = \left(F/\varepsilon\right)\left[c_{n0}\left(\underline{x}\right) - c_{p0}\left(\underline{x}\right)\right] \\ i\omega c_p'\left(\underline{x}\right) = D_p\Delta c_p'\left(\underline{x}\right) + \mu_p\nabla\bullet\left[c_p'\left(\underline{x}\right)\varphi_0\left(\underline{x}\right) + c_{p0}\left(\underline{x}\right)\nabla\varphi'\left(\underline{x}\right)\right] \\ i\omega c_n'\left(\underline{x}\right) = D_n\Delta c_n'\left(\underline{x}\right) - \mu_n\nabla\bullet\left[c_n'\left(\underline{x}\right)\varphi_0\left(\underline{x}\right) + c_{n0}\left(\underline{x}\right)\nabla\varphi'\left(\underline{x}\right)\right] \\ \Delta\varphi'\left(\underline{x}\right) = \left(F/\varepsilon\right)\left[c_n'\left(\underline{x}\right) - c_p'\left(\underline{x}\right)\right] \end{cases}$$

with cation and anion mobilities μ_p and μ_n, and diffusion coefficients D_p and D_n, respectively; F is the Faraday constant and ε the electrolyte permittivity. This approach differs from the already published numerical models by assuming a spatial dependence of the static parts of the variables (c_{p0}, c_{n0}, and φ_0).

Model geometries

The model equations are solved for a 3-D cylindrical pore system using the finite-element modelling tool COMSOL Multiphysics. In the model, a fixed surface potential at the pore wall is assumed, causing a dynamic EDL to build up. This means that no mobility contrast needs to be assumed like in previous model approaches, our model instead explicitly considers the (diffuse part of the) EDL. The AC voltage is applied along the cylinder axis. Simulations are run for different frequencies of this voltage in order to assess the spectral behaviour of ion fluxes within the 3-D pore system, and thus to obtain the frequency-dependent impedance of the pore system.

With appropriate boundary conditions, the model can be applied to study a variety of different pore geometries. To have a classical membrane polarisation set-up, the model is in particular solved for a system of alternating wide and narrow pores (Fig.1). A grain-based pore geometry is considered, too.



Boundary	Ion concentrations and fluxes	Electric potential
Charged pore wall	Neumann bc for c_p and c_n (no flow)	$\varphi = U_{\text{surface}}$
Open pore ends	Periodic bc for c_p, c_n and the z-components of j_p, j_n	$\varphi = \pm U_{\text{ext}} \cdot \sin(\omega t)$
Symmetry axis	Neumann bc for c_p and c_n	Neumann bc
Uncharged pore wall	Neumann bc for c_p and c_n	Neumann bc
Reference points	$c_p = c_n = c_{\text{background}}$	$\varphi = 0$

$U_{\text{surface}} = -75\,\text{mV}$, $U_{\text{ext}} = 0.024\,\text{mV}$, $c_{\text{background}} = 1\,\text{mol/m}^3$

Fig. 1. Left: exemplary pore-based model domain with boundary conditions (bc) in time-domain formulation. Right: corresponding simulation results for both real and imaginary components: electric potential and co-ion concentration along the symmetry axis (r=0) at different frequencies (blue: 0.1 mHz, red: 270 Hz, black: 910 Hz, cyan: 3.1 kHz).

Results and future applications

The impedance spectra obtained from time and frequency domain calculations are found to be consistent. The geometry of alternating wide and narrow pores is considered with varying ratios of width and length. The obtained impedance spectra are compared to existing analytic solutions (in case of the grain-based geometry, e.g. with Fixman (1980).

Moreover, the time-dependent and frequency-dependent spatial distributions of the ions as function of position in the pore volume are analysed. For instance, an anti-cyclic oscillation of the counter-ion concentration in the EDL with respect to the counter-ion concentration outside the EDL and the co-ion concentration is found, and an explanation provided. The frequency-dependent spatial distributions of the ions (Fig. 1) are consistent with results of existing numerical studies.

Further analyses are made, for example an evaluation of the electric current through the pore. In the future, the model will be used to study pore-scale SIP signatures of rocks with multiphase pore fillings, such as water-air, water-NAPL (non-aqueous phase liquid), and water-ice, as relevant for hydrogeological, environmental, and cryospheric applications of SIP.

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