Numerical computation of impedance spectra for the membrane system

In general, the impedance of a system may be determined from the linear response of the system to small perturbations from the steady state. The meaning of the phrase "*the linear response*" means that if, for example, the system perturbed by currents I_1 and I_2 produces potential response $V_1 = V_1(t)$ and $V_2 = V_2(t)$, then the response to the perturbation $I_1 + I_2$ will be $V_1 + V_2$.

The response function (in the case of this project it will be the time dependent potential of a membrane) contains useful information, but to retrieve it in a convenient way we calculate the so called impedance of the system, which is independent on the nature of the perturbation as long as the perturbation is small enough to keep the regime of linearity mentioned above.

The impedance may be calculated by means of the adapted Fourier transform as follows. Let us denote a current perturbation of the system which is in a steady state by $I(t)$. In what follows we recommend the use of the step function, i.e.

$$I(t) = \begin{cases} I_0 & \text{for } t \ge 0, \\ 0 & \text{for } t < 0. \end{cases} \tag{1}$$

The membrane potential will vary in time and we denote it by $V(t)$. Of course the potential will eventually reach another steady state, so formally we can write

$$\lim_{t\to\infty} V(t) = V_\infty . \tag{2}$$

The complex impedance is a complex value defined as

$$Z^*(\omega) = -\frac{V^*(\omega)}{I^*(\omega)}, \tag{3}$$

where

$$\begin{aligned} Z^*(\omega) &= Z'(\omega) + \mathrm{i}Z''(\omega), \\ V^*(\omega) &= V'(\omega) + \mathrm{i}V''(\omega), \\ I^*(\omega) &= I'(\omega) + \mathrm{i}I''(\omega). \end{aligned} \tag{4}$$

Thus the single prime $(')$ and double prime indicate the real and imaginary part in the complex plane $\mathbb{C}$, respectively. The real and imaginary parts of the transform of the potential-time function $V(t)$ are given by

$$\begin{aligned} V'(\omega) &= \int_0^\infty \left(V(t) - V_\infty\right)\cos(\omega t)dt, \\ V''(\omega) &= \int_0^\infty \left(V(t) - V_\infty\right)\sin(\omega t)dt + V_\infty/\omega, \end{aligned} \tag{5}$$

where parameter $\omega \in (0, \infty)$ is called the frequency.

For the current step perturbation (1) the real and imaginary parts of the transform are given by

$$I'(\omega) = 0, \qquad I''(\omega) = -I_0 / \omega. \tag{6}$$

Combining (3), (5), and (6) we have

$$Z^*(\omega) = -\frac{V^*(\omega)}{I^*(\omega)} = -\frac{V'(\omega) + \mathrm{i}V''(\omega)}{I'(\omega) + \mathrm{i}I''(\omega)} = -\frac{V'(\omega) + \mathrm{i}V''(\omega)}{\mathrm{i}\dfrac{-I_0}{\omega}} =$$

$$= -\frac{V'(\omega)}{\mathrm{i}\dfrac{-I_0}{\omega}} - \frac{\mathrm{i}V''(\omega)}{\mathrm{i}\dfrac{-I_0}{\omega}} = \frac{V'(\omega)\cdot\omega}{\mathrm{i}I_0} + \frac{V''(\omega)\cdot\omega}{I_0} = V''(\omega)\cdot\omega / I_0 \; - \; \mathrm{i}V'(\omega)\cdot\omega / I_0,$$

where we used the identity $\frac{1}{i} = -i.$ Thus the expressions for real and imaginary part of the impedance $Z^*(\omega)$ are the following

$$Z'(\omega) = -V''(\omega)\cdot\omega / I_0, \qquad Z''(\omega) = +V'(\omega)\cdot\omega / I_0. \tag{7}$$

The above expressions may be viewed as parametric description of some curve in the complex plane $\mathbb{C}-$ which geometrically is equivalent to two-dimensional plane $\mathbb{R}^2 -$ where parameter $\omega \in (0, \infty).$ This is conveniently displayed in the impedance plot by drawing points

$$(Z'(\omega), -Z''(\omega)) \in \mathbb{R}^2, \tag{8}$$

for selected values of $\omega \in (0, \infty).$ Usually about 60 values of ω is enough.

Computation of integrals

Once we have obtained the membrane potential as a function of time, $V(t),$ we to compute the integrals (5) for selected values of $\omega > 0$ in order to finally produce the impedance plot via (7) and (8). The integrals can be evaluated basically by any composite quadrature taking into account the values of V in a selected times $0 = t_0 < t_1 < \ldots < t_M$ where time t_M corresponds to the reached steady state (2) after the perturbation (1). Here we adopt a simple device by interpolating $V(t)$ on each interval $[t_k, t_{k+1}].$ The values $V(t_{k+1}), V(t_k)$ is interpolated by a linear function

$$V(t) = \frac{t - t_k}{t_{k+1} - t_k}(V(t_{k+1}) - V(t_k)) + V(t_k) \quad \text{for } t_k \le t \le t_{k+1}, \qquad k = 0, 1, \ldots, M-1, \tag{9}$$

and this approximate potential is inserted into the integrals leading to expressions of the type

$$\int_{t_k}^{t_{k+1}} t\cos(\omega t)dt, \quad \int_{t_k}^{t_{k+1}} t\sin(\omega t)dt, \quad \int_{t_k}^{t_{k+1}} \cos(\omega t)dt, \quad \int_{t_k}^{t_{k+1}} \sin(\omega t)dt, \tag{10}$$

which can be easily calculated analytically. This ultimately leads to the following expressions

$$V'(\omega) = \sum_{k=0}^{M-1} \Delta V_k', \qquad V''(\omega) = \sum_{k=0}^{M-1} \Delta V_k'' + V_\infty / \omega, \tag{11}$$

where

$$\begin{aligned} \Delta V_k' &= (V(t_{k+1}) - V(t_k))(\cos\omega t_{k+1} - \cos\omega t_k)/\omega^2(t_{k+1} - t_k) + \\ &+ \big((V(t_{k+1}) - V_\infty)\sin\omega t_{k+1} - (V(t_k) - V_\infty)\sin\omega t_k\big)/\omega, \end{aligned} \tag{12}$$

$$\begin{aligned} \Delta V_k'' &= (V(t_{k+1}) - V(t_k))(\sin\omega t_{k+1} - \sin\omega t_k)/\omega^2(t_{k+1} - t_k) + \\ &+ \big((V(t_{k+1}) - V_\infty)\cos\omega t_{k+1} - (V(t_k) - V_\infty)\cos\omega t_k\big)/\omega, \end{aligned} \tag{13}$$

for $k = 0, 1, \ldots, M-1$.

Example

The exemplary impedance spectra are presented in Fig. 1. Try the following data: temperature $T = 298.16\ K$, membrane thickness $d = 200\ \mu m$, dielectric permittivity $\varepsilon_r \cdot \varepsilon_0 = 7.08 \cdot 10^{-10}\ J^{-1}C^2m^{-1}$ and diffusion coefficients: $D_1 = 10^{-10}$, $D_2 = D_3 = 10^{-11}\ m^2s^{-1}$. Membrane is not permeable for the anion: $k_{3,Lf} = k_{3,Lb} = k_{3,Rf} = k_{3,Rb} = 0$. For both cations all rate constants vary in the range $k_{i,b} = k_{i,f} = 10^{-6}, \ldots, 10^{-4}\ m\,s^{-1}$.

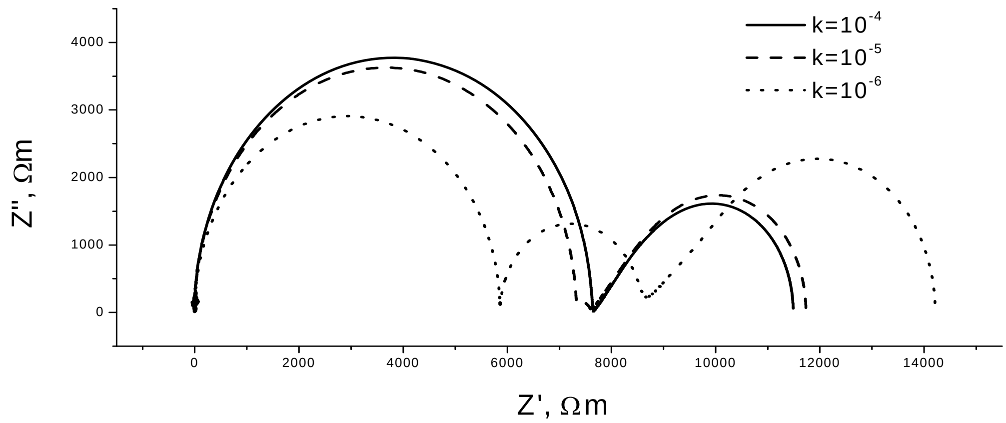

Fig. 1. Complex impedance spectra for different heterogeneous rate constants.

Statement of the Project Assignment

The main task of the project is to produce the impedance spectra for the membrane system. Calculations must be based on the NPP model. This will require modification and expansion of the provided source code *npp, BB.cpp*.

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Notes for the Project, part 3 (Impedance spectra by NPP and Project specification)
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1) The impedance are obtained by transforming the potential response to the perturbed membrane which is in a steady state. It means that the code must be modified in such a way that any initial conditions

$$\begin{cases} c_i(x,0) = c_{i,0}(x), \\ E(x,0) = E_0(x), \end{cases} \tag{14}$$

for $x \in [0, d]$ are possible.

2) The perturbation is achieved by applying small current in the form (1). This current must be included in the displacement current equation, thus the equation

$$\frac{\partial E}{\partial t} = -\lambda \sum_i z_i J_i, \tag{15}$$

should be replaced by

$$\frac{\partial E}{\partial t} = I - \lambda \sum_i z_i J_i, \tag{16}$$

and subsequently the procedure `Function()` from the *main.cpp* changed a bit.

3) The code implementing the formulas (11)-(13) must be provided together with output routine that will store in three columns in a text file the values of ω, $Z'(\omega)$, $Z''(\omega)$, for about 60 values of ω. To draw a plot you can import data $Z'(\omega)$, $Z''(\omega)$ into two columns of Excel sheet and use the scatter chart (in Polish it is called *Punktowy XY*).

As the test membrane system you can choose the standard bi-ionic case: $M^+X^- \mid N^+X^-$ with the following values of parameters

	$c_{i,L}$ $[M]$	$c_{i,M}$ $[M]$	$c_{i,R}$ $[M]$	D_i $[m^2s^{-1}]$	k_i $[ms^{-1}]$
M^+	10^{-3}	10^{-3}	0	10^{-10}	$10^{-6} \div 10^{-4}$
N^+	0	0	10^{-3}	10^{-11}	$10^{-6} \div 10^{-4}$
X^-	0	10^{-3}	0	10^{-11}	0