2D Impedance of a Porous Electrode

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Two-dimensional impedance of an electrode with cylindrical pores (Fig.1) is studied numerically and analytically under assumptions of constant active specific resistivity ρ of electrolyte solution So, purely capacitive behavior of interface In with constant area-specific capacitance c and negligible thickness, constant potential V_M of matrix Ma, and zero thickness of separator Se.

2D Laplace equation for complex potential amplitude V

$$\partial^2 V/\partial x^2 + \partial^2 (rV)/r\partial r^2 = 0 \qquad [1]$$

is considered within the pore with edge conditions

$$V|_{x=0} = \partial V/\partial r|_{r=0} = \partial V/\partial x|_{x=x_0} = 0 \qquad [2]$$

$$\partial V/\rho \partial r\,\big|_{r=r_0} = j\omega c \Delta V \qquad [3]$$

where j is imaginary unit, $\Delta V = V_M - V(x, r_0)$ is a potential drop on In, and ω - an angular frequency.

The first two terms of Eq.2 are zeros due to symmetry, the third - due to inactive Co. Eq.3 expresses current continuity on the border between So and In, the first term being current density in So, the second - in capacitive In.

The pore dimensionless impedance z is defined as

$$z = V_M/IR = V_M x_0 \Big/ j\nu \int_0^{x_0} \Delta V dx \qquad [4]$$

where $R = \rho x_0/\pi r_0^2$ is a total So resistance between planes $x = 0$ and $x = x_0$, I - a total current through In, and a dimensionless frequency ν is

$$\nu = \omega R C = 2\omega c \rho x_0^2/r_0 \qquad [5]$$

where $C = 2c\pi r_0 x_0$ is a total In capacitance of the pore. The total electrode dimensional admittance can be found as a sum of partial pore admittances $1/R_i z_i$.

For numerical solution, Eqs.1-3 have been transformed to a finite-element form corresponding to a rectangular non uniform NxM coordinate mesh (N~M~100). Resulting system of NxM linear equations is solved by modified Gauss method taking advantage of sparse defining matrix that has only five non-zero diagonals. The accuracy better than 0.1 % is easily achieved.

2D analytical solution z_2 of Eqs.1-4 is obtained under assumption of parabolic potential profile $V(r) - V(0) \sim r^2$:

$$z_2(\nu) = a z_1(a\nu);\quad z_1(\nu) = \coth\sqrt{j\nu}/\sqrt{j\nu} \qquad [6]$$

where a =3/2 is a scaling factor and z_1 is the well known 1D solution or transmission line model (TLM).

Computations show that, for narrow pores with aspect ratio $\beta = r_0/x_0 < 0.1$ and not very high frequencies ν < 100, numerical 2D solutions $V(x)$ and $z(\nu)$ practically coincide with corresponding analytical 2D solutions (curves 2 in Figs.1, 2). With increasing β and ν above the pointed limits the difference between numerical and analytical 2D solutions increases and for $\beta = 1$ becomes considerable (cf curves 3, 2 in Figs.1, 2).

As can be seen from Eq.6 and Fig.2, curves z_1 and z_2 are similar to each other on double log scale and can be put in coincidence by shifting along line 1/ν. The difference between them has its maximum value of 50 % for real parts (1/3 and 1/2 accordingly) at $\nu < 1$. It is shown that the scaling factor a depends on the form of the pore cross section (CS). If the pore has a rectangular CS with one side much greater than another, $a = 1/2$. Thus generally accepted TLM may underestimate impedance z for cylindrical pores and overestimate it for slab pores. TLM seems to be most accurate for pores with CS having one dimension several times greater than another.

The developed numerical method can be easily applied to more complex cases of pore geometry, mass and charge transfer in So, and electrochemistry of In, when all analytical methods fail. It can also take into account finite thickness of Se and finite resistance of Ma.

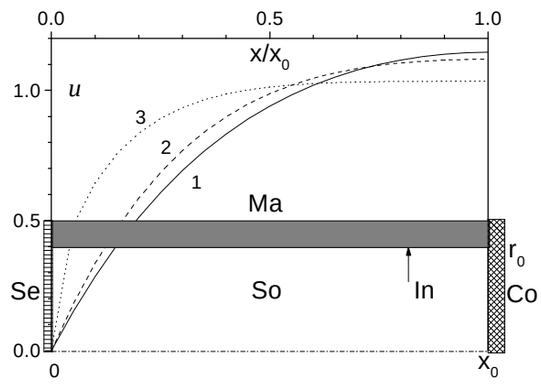

Fig.1. Electrode pore scheme: Co-collector, In-interface, Ma-matrix, Se-separator, So-electrolyte solution, x (x_0) -1st pore coordinate (length), r (r_0)-2nd pore coordinate (radius); and relative potential $u = |V(r_0)/V_M|$ versus x at ν = 10 according to analytical 1D (solid 1) and 2D (dashed 2) models, and 2D numerical computations (dashed 2: β < 0.1; dotted 3: β =1)

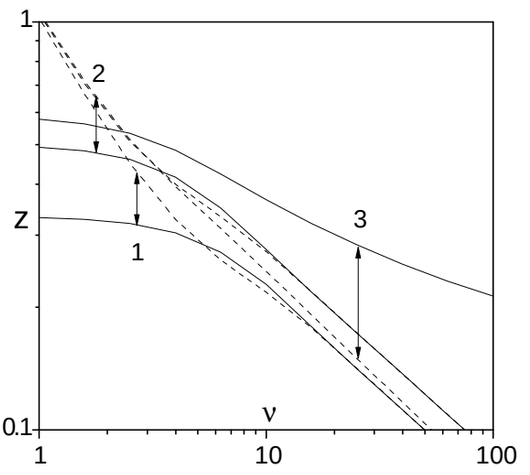

Fig.2. Real (solid) and minus imaginary (dashed) parts of z (Eq.4) versus ν (Eq.5): analytical z_1 (1) and z_2 (2), numerical for aspect ratios β < 0.1 (2) and β =1 (3)