EIS study of multilayer electrodes

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Due to their potential applications as biological, chemical or electrochemical sensors, polyelectrolyte multilayers have received increasing attention during the last decade [1]. Moreover, the knowledge of the interface between two proton-conducting ionomers is a key factor in proton exchange membrane fuel cell research when the membrane electrode assembly consists of Nafion-containing electrodes in contact with a fluorine-free membrane such as sulfonated polysulfone (SPS) [2].

This work deals with a theoretical description of mass transfer of electroactive species in a fixed bilayer electrode made with Nafion and SPS. It is shown that the layer order drastically influences the electrochemical response of the system, i. e. the impedance diagrams for the Pt | Nafion | SPS electrode and for the Pt | SPS | Nafion electrode are different (Fig. 1 C). The diagrams in Figs. 1 B (monolayer electrodes) and C are plotted using the general expression of the mass-transfer function [3,4] :

$$M(L_1,s)=\frac{\Delta c(L_1,s)}{\Delta J(L_1,s)}=\frac{M(L_2,s)+\dfrac{\tanh\sqrt{\tau\,s}}{m\sqrt{\tau\,s}}}{1+m\sqrt{\tau\,s}\,\tanh\sqrt{\tau\,s}\,M(L_2,s)}$$

where $L = L_2 - L_1$ is the thickness of a layer, $\tau = L^2/D$ is the time constant and $m = D/L$ is the mass transfer rate constant. The other symbols have their usual meanings. The diagram in Fig. 1 A is the classical Warburg diffusion impedance for a bare electrode. Experimental works are now in progress to validate this theoretical approach.

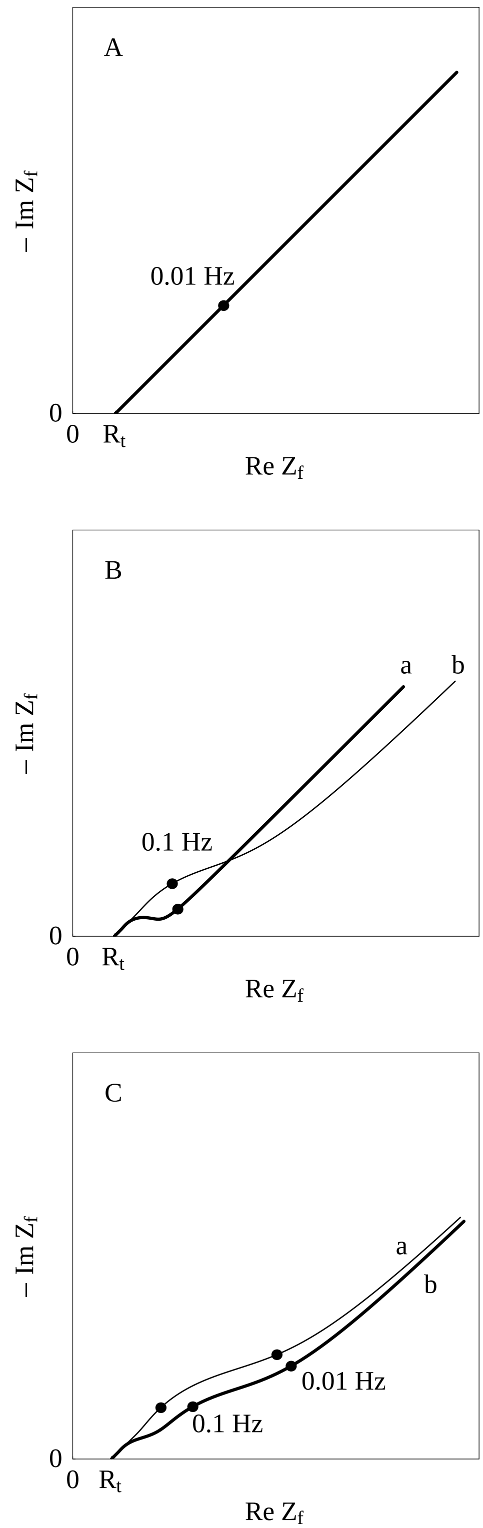

Fig. 1 : Simulated faradaic impedance diagrams for the redox reaction O + e ↔ R on multilayer electrodes for selected values of the physico-chemical parameters. A : bare Pt electrode. B : Pt | SPS (a) and Pt | Nafion (b) electrodes. C : Pt | Nafion | SPS (a) and Pt | SPS | Nafion (b) electrodes.

REFERENCES

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