Supporting Information

High Resistivity Lipid Bilayers Assembled on Polyelectrolyte Multilayer Cushions: An Impedance Study.

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1. Electrochemical impedance experiments

Impedance spectroscopy was used to analyze the electrical properties of the polyelectrolyte (PE) multilayer/lipid bilayer composites over a wide frequency range. An IM6 electrochemical workstation (Zahner Elektrik) was used to apply an AC-voltage perturbation signal of variable frequency to the electrodes. The current response of the system was analyzed in terms of the modulus of the complex impedance $|Z|$ and the phase shift Φ (Bode plots). Impedance spectra were typically measured in the 3 mHz – 50 kHz frequency range with a voltage amplitude of 10 mV. All experiments were carried out at the open circuit potential. At this potential gold substrates modified with the PE films and in contact with a KCl electrolyte behave as a polarizable electrode and no electron transfer occurs at the gold/PE interface.

The experimental impedance of the bilayer membranes supported on the solid substrate (the working electrode), was modeled by fitting measured data to a theoretical model using complex non-linear least squares (CNLS) derivation of the parameters present in the equation. As usual, the so-called equivalent circuit approach was used. An equivalent circuit is an electric analog in the form of a circuit that contains passive elements such as resistors and capacitors. The equivalent circuit exhibits a specific frequency response of the impedance Z, which represents our model. The equivalent circuit was devised so that the response of the electrochemical system matched the spectral features of the model. Estimates of the parameter values were then used for the system characterization.

The algorithm used for the fitting [S1] yields the least squares estimates of the parameters as well as their uncertainty estimates in percent. The latter calculation serves the purpose of confirming that no parameter may be omitted from the theoretical model. In our fits uncertainty estimates were always lower than 10 %. To warrant uniqueness of a proposed theoretical model and the values of the fit parameters "Identifiability" and "Distinguishability" criteria must be applied additionally, as we proposed in Ref [S2]. However, as already explained, the equivalent circuit approach for the model selection was adopted here instead (see a description in the main text.

2. Control experiments

Figure 1S shows control EIS experiments performed on electrodes modified with polyelectrolyte multilayers comprising 13-Layers (a) and 15-Layers (b) of PAH-PSS films, i.e. the same architectures of the systems in Figure 8 but where the lipid bilayers, in each case, were replaced by polyelectrolyte layers. Experimental impedance data were successfully fitted to the model impedance equation of the equivalent circuit (a) depicted in Figure 6. Fit results are assembled in Table 1S.

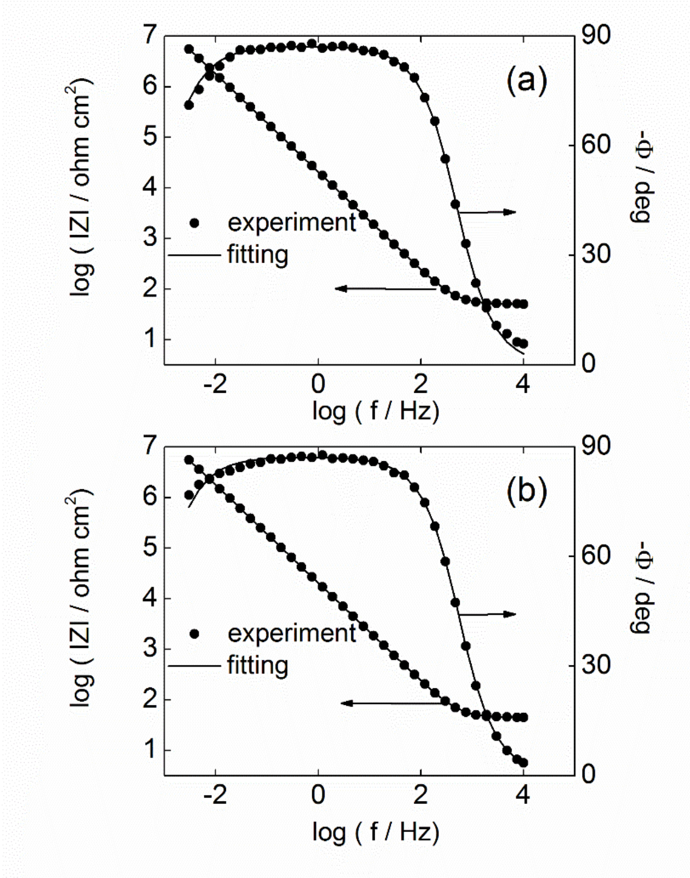

Figure S1. Bode plots for impedance spectra of multilayer cushions on gold electrodes: **(a)** 13-layers of PAH-PSS cushion, **(b)** 15-layers of PAH-PSS cushion. Experimental spectra were fitted to the impedance of the equivalent circuit (a) in Figure 6.

Table S1. Best-fit parameters derived from experimental impedance spectra in Figure S1 and a theoretical impedance according to the equivalent circuit (a) in Figure 6, where Re is the electrolyte resistance, R_f is the resistance of the PE film and the impedance of the constant phase element is $Q_f = (j\omega)^{-n}/Y_O$ with $j = \sqrt{-1}$ and $\omega = 2\pi f$ is the AC signal frequency.

PE cushion	$\mathbf{R_e}$ / Ω cm^2	$\mathbf{Y_O}$ / F cm^{-2} s^{n-1}	**n**	$\mathbf{R_f}$ / Ω cm^2
13 PAH/PSS layers	50.50	8.11 10^{-6}	0.97	2.15 10^{7}
15 PAH/PSS layers	45.00	8.20 10^{-6}	0.97	2.32 10^{7}

These results confirm that, in contrast with electrodes modified with the multilayers with a lipid bilayer on top, the relaxation processes after the application of the AC perturbation signal, are clearly related to a single time constant. Thus, the films in the control experiments behave as a surface capacitor, with increasingly larger impedance values for decreasing frequencies. A discussion of the nature of the large resistance R_f in parallel connection with the capacitor can be found in the main text. These results are different to those shown in Figure 8 where the interaction between the lipid bilayer and the two polyelectrolyte cushions (one on top and one below the lipid bilayer) generates impedance spectra that are related to the relaxation of two processes (two distinguishable time constants) and also to a lower modulus of the impedance.

References

[S1] Boukamp, B., A Nonlinear Least Squares Fit Procedure for Analysis of Immittance Data of Electrochemical Systems, *Solid State Ionics*, **1986,** 20, 31-44.

[S2] Vallejo A. E., Gervasi C.A., On the Use of Impedance Spectroscopy for Studying Bilayer Lipid Membranes, In *Advances in planar lipid bilayers and liposomes*, Volume 3, Chapter 10, H.T. Tien and A. Ottova Eds., Elsevier, Amsterdam, 2006, pp 331-353.