Electronic Supplementary Material (ESI) for Soft Matter

Supporting information

Information on EIS

Representative Bode and Nyquist impedance plots for the aluminium alloy substrates coated with unmodified and modified coatings are shown in **fig.S1**.

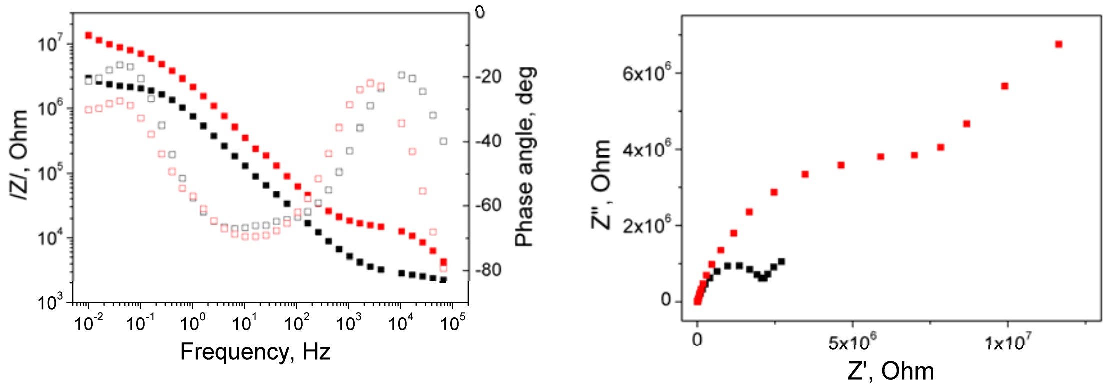

Fig. S1. Experimental Nyquist and Bode plots for the aluminium alloy substrates coated with unmodified (black) and modified (red) coatings.

For the interpretation of the impedance spectra an appropriate equivalent circuit should be chosen. Further, the parameters of the equivalent circuit elements can be determined by fitting of the experimental spectra to the chosen system.

An impedance model[25] of a defect free organic coating on a metal surface in contact with electrolyte is shown in **fig.S2.**

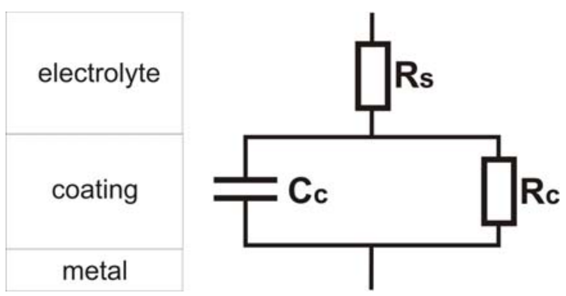

Fig. S2. Simplified Randles circuit in which there is no diffusion limitation.

This model is commonly referred as Randles circuit; it assumes pure charge transfer control and no diffusion limitations or competing processes. Appearance of the defects in the coating as well as coexistence of layers with different resistivity/capacitance leads to the situation, when the obtained impedance spectra can not be fitted with the simple equivalent circuit. Introduction of additional circuit elements to represent the capacitive effect of the coating, the pore resistance and the diffusion limitation phenomena is necessary. It is obvious that the equivalent circuit containing more elements would probably more perfectly fit any experimental spectra. However, implementation of more and more elements would complicate the interpretation of the physical meaning of the additional elements. The final task is, therefore, to choose an equivalent circuit that contains a minimum number of elements, each of them having an appropriate physical meaning, and fit the experimental data in a reasonable way.

The most widely accepted[27] equivalent circuit representing the polymer/metal interface system containing defects is shown in **fig.S3.**

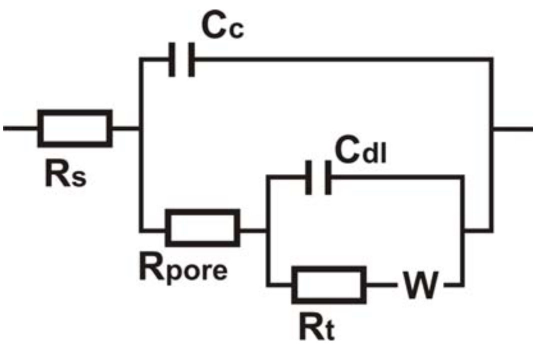

Fig. S3. Equivalent circuit representation for a metal coated with polymer layer. R_s is the solution resistance, R_t – charge transfer resistance, R_{pore} – pore resistance of the coating, W – Warburg impedance (contains mass transport limitations), C_c – coating capacitance and C_{dl} – double layer capacitance. For the reference see Ray Taylor, 1989.

An attempt was made to fit the experimentally obtained impedance spectra with this equivalent circuit (**fig.S4**).

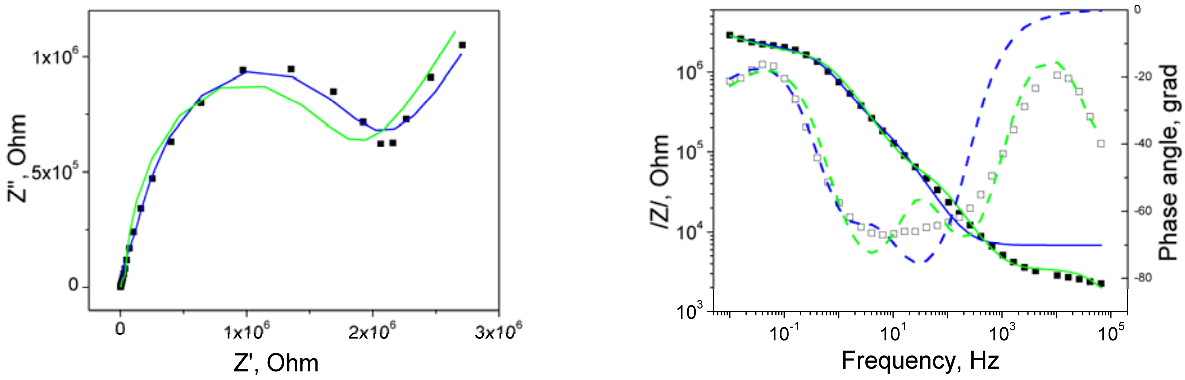

Fig. S4. Fitting of the experimental data for the aluminium alloy substrate coated with unmodified coating by equivalent circuits shown on fig. S3 (blue) and S5 (green).

Though, the Nyquist plot can be easily fitted by the equivalent circuit shown in **fig.S3** , the Bode plot can not be fitted in the whole range of the frequencies (see the frequencies between 10^3-10^5 Hz). To describe the impedance spectra of an aluminium substrate coated with a polymer layer Zheludkevich[26] suggested an advanced equivalent circuit shown in **fig.S5**. Consideration of the oxide layer on the surface of the aluminium alloy allows fitting of both Nyquist and Bode plots in the whole range of the measured frequencies.

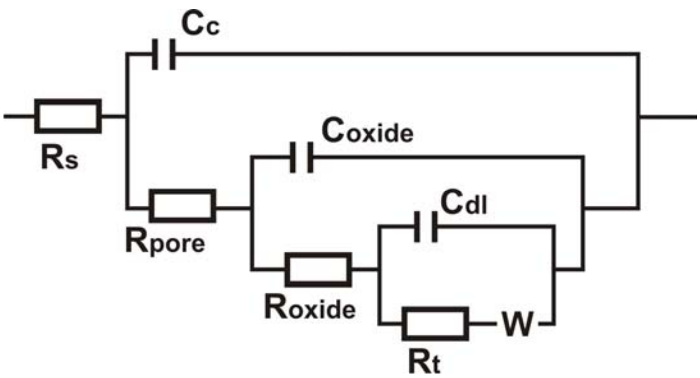

Fig. S5. Equivalent circuit representation for a metal coated with polymer layer. C_{oxide} – capacitance of the oxide layer, R_{oxide} – resistance of the intermediate oxide layer. The other elements are the same as in **fig. S3.** For the reference see Zheludkevich, 2005.

The frequency dependence of the phase angle can not be perfectly fitted by this system (see the appearance of maxima at 30 Hz). Introduction of an additional time constant allows to avoid the appearance of the maxima. Determination of the physical meaning of a system with an additional time constant is, however, not straightforward. Therefore, it was the circuit shown in **fig.S5** that was used for fitting of the experimental data for both modified and unmodified coating. The result of the fitting as well as the table containing the parameters of the fit can be found in the main body of the manuscript.

References

25. G. Grundmeier, W. Schmidt and M. Stratmann, *Electrochimica Acta*, 2000, **45**, 2515-2533.
26. M. L. Zheludkevich, R. Serra, M. F. Montemor, K. A. Yasakau, I. M. M. Salvado and M. G. S. Ferreira, *Electrochimica Acta*, 2005, **51**, 208-217.
27. S. R. Taylor, *Ieee Transactions on Electrical Insulation*, 1989, **24**, 787-806.