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Time-variance in electrochemical impedance spectroscopy: The simple case study of dilution

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Classical analysis of electrochemical impedance spectroscopy (EIS) measurements requires them to be performed on a linear,
time-invariant system. Many electrochemical systems are time-variant (battery under charge/discharge, corroding sample).[1] The effect of time-variance on these systems is not easy to study because there is no reference to which the time-variant results could be compared to.
A simple dilution experiment[2,3] was performed to illustrate the time-variance on EIS measurements performed at a rotating disk electrode (RDE), in an electrolyte containing the classical $K_3Fe(CN)_6/K_4Fe(CN)_6$ redox couple.
Using simulations based on analytical expressions of the Faradaic impedance, experimental parameters are defined. Fitting EIS data using equivalent circuit models (ECM) allows us to qualify the errors made when trying to fit time-variant data with time-invariant impedance expressions.
Repeated impedance measurements and reconstruction of instantaneous impedance graphs via interpolation[4,5] allows to reduce the effect of time-variance and improve the fitting quality.
Finally, another approach is presented, which consists in fitting the time-variant data by an analytical time-dependent expression of the Faradaic impedance where the concentration evolution and its effect are accounted for.[6]

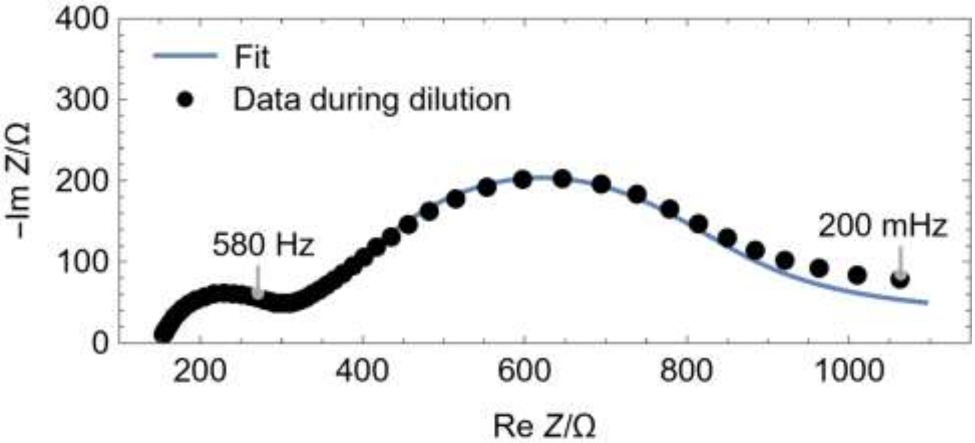

Figure 18. Nyquist diagram of the impedance measured during dilution at an RDE and fitting curve using the time-dependent analytical expression of the Faradaic impedance.

References

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