Deconvolution of Complex AC Potential Differences in Solution at an Electrode by Application of FFT.

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During localised electrochemical impedance spectroscopy the electrode surface under study is either scanned by a dual probe or by a single vibrating probe. When the electrode is polarised with an AC-perturbation, the scanning probe will pick up a fraction of that perturbation. The signal from the probe is proportional to the local current densities in the solution, at the site of the probe, and to the resistivity of the solution. The signal from the probe can mathematically be described as being proportional to the intensity of local current sources, at the electrode surface, convoluted by a point spread function (PSF). The parameter values for this PSF are determined by the probe height over the electrode surface and by the distance between the two microelectrodes of a dual electrode or by the vibration amplitude of a vibrating probe.

In this work a procedure for deconvolution of complex AC potential differences in solution, at an electrode, by application of the Fast Fourier Transform (FFT), is described and applied to simulated data and to experimental data. The first step of the procedure is to deconvolute the complex AC potential differences in solution so that the local current densities at the electrode surface are obtained. Deconvolution by this PSF does not introduce phase shift and the phase angles of the local complex AC currents are relative to the overall AC-polarisation.
The second step is to determine the local polarisation across the interface. This is achieved by convolution of the local currents that were determined in the first step, by two new point spread functions. One PSF describes the potential at a point in the solution at the electrode surface, as function of all the local currents at the electrode. The other PSF describes the potential at the site of the reference electrode as function of the same currents. Convolution by two different PSF:s is needed because each PSF assumes radial spread of the currents towards infinity and give potentials relative to an infinitely distant zero point.
Having determined both the local currents and the local polarisation relative to the same reference angle, we can determine the true resistive or capacitive nature of the local currents. We can also calculate the local complex admittance as a ratio.
Some aspects of filtering in the frequency plane, to limit the strong amplification of noise during deconvolution, are also discussed.