Simulating Linear Polarization Curves from the Electrochemical Impedance Spectrum

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A few authors have published methods to obtain time-domain polarization response from electrochemical impedance spectra. Most notable among these is the work of Feliu and Feliu[1], who employed equivalent circuit analysis and La Place transformations to simulate the time-domain response of an electrode when subjected to potentiostatic, galvanostatic, and linear polarization stimuli.

In the present work, an algorithm is demonstrated that can be used to create a "simulated polarization curve" from an electrochemical impedance spectrum. The algorithm employs fast Fourier transformations (FFT's) to simulate the time-domain response of an electrode under polarization. Impedance data is used as measured – no equivalent circuit analysis of impedance data is necessary in order to perform the simulations. Simulated polarization curves obtained from this method are strikingly similar to those obtained from linear polarization experiments. The algorithm has direct application in determining corrosion rates and charge transfer resistances from impedance spectra, and provides the possibility for such analysis without the use of equivalent circuits.

The Fourier analysis can be performed on an electrochemical impedance spectrum containing frequencies in the range between 1kHz and 4mHz, and it involves the following steps:

1. Create a curve of potential versus time that describes the experiment to be performed. The mathematical description needs to be one that would allow the experiment to be run many, many times with the same expected result upon each repetition. Linear polarization experiments are normally run as a linear ramp over the potential range ±20mV versus open-circuit potential. An appropriate mathematical description for repetitive linear polarization experiments would include a time delay of several minutes prior to initiating a successive polarization.

2. Perform an FFT on the potential versus time curves from the previous step to obtain a collection of potential sinusoids at different frequencies.

3. For all frequencies except DC, divide the potentials obtained from the FFT by the impedance that corresponds to that frequency. This is the equivalent AC current density at each frequency. For a linear polarization experiment that is centered about the open-circuit potential, enter the DC current as the DC current measured during the impedance experiment. For most open-circuit impedance experiments this value is zero or nearly zero.

4. Perform an inverse FFT on the AC currents calculated in the previous step to obtain the current versus time response.

5. Using the time-domain data only, plot potential versus current to obtain the linear polarization curve.

6. (optional) Determine the polarization resistance in a manner similar to a linear polarization experiment by calculating the slope of the polarization curve in a region of interest.

Simulated linear polarization experiments are shown for materials that exhibit impedance responses composed of single time constants, double time constants, and both active and passive behavior. The striking similarities in electrode response between measured polarizations and impedance-simulated polarizations includes capacitive charging observed during polarization, and multiple linear regions for materials that exhibit multiple time constants in an impedance spectrum. Comparisons are made among R_P values obtained via linear polarization experiments, equivalent circuit analyses, and impedance-simulated polarization experiments, as well as implications on the validity of R_P estimates so obtained.

References:

1 V. Feliu and S. Feliu, J. Electroanal. Chem. **435**, 1 (1997).