



Advanced Digital Signal Processing for Electrochemical Systems

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Conventional amperometric and voltammetric sensors are based on steady-state measurement techniques where a constant potential is applied to the sensing electrode and the current response is measured. Steady-state techniques may suffer from interference such as capacitive charging current and Faradaic background currents resulting in decreased signal/noise ratio. These limitations may be overcome by the use of transient techniques.

Electrochemical impedance spectroscopy is a transient technique that implies the application of a small amplitude potential signal of the electrochemical system. Examination of the current response in the frequency domain provides a means of improving sensitivity and selectivity that would not be possible in the conventional time domain ^[1].

A schematic of an electrochemical impedance system is shown in Figure 1. The potentiostat controls the voltage across the working (W) – counter electrode (C) pair in order to maintain the potential difference between the W and the reference (R) electrodes of the electrochemical cell. The frequency response analyzer (FRA) generates sinusoidal perturbations, acquires the response signal and performs signal processing. Current instrumentation for performing electrochemical impedance spectroscopy is essentially analog-based. Its cost is typically comprised in the range of a few 10 k\$ ^[2] and therefore not appropriate for large volume markets and portable applications. This drawback can be overcome by digitizing the signal and analyzing it by digital signal processing (DSP) methods.

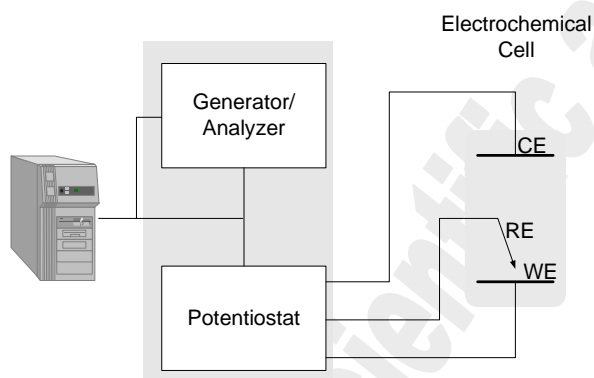


Figure 1
Schematic of the electrochemical impedance platform. The electrochemical cell possesses three electrodes: working (WE), reference (RE), counter (CE).

The goal of this collaborative project between CSEM and IMT is to develop a portable DSP-based electrochemical platform for performing electrochemical impedance.

During the first year of the project, the 10-kHz bandwidth of the existing CSEM's analog minipotentiostat ^[3] was modified to extend the bandwidth up to 100 kHz. A PC based digital FRA system was developed using the Labview™ software. This part includes the generation of a sinusoidal potential signal in the 10 mHz to 100 kHz frequency range having an amplitude that

can be varied from 10 to 100 mV. The digital FRA system also performs current response acquisition and calculates the real (ZRe) and the imaginary (ZIm) parts of the electrochemical cell impedance for every frequency used.

In the second year, the system, that is the modified potentiostat in combination with the digital FRA, was tested. A measured impedance spectrum is shown in Figure 2a, for the model electrical circuit of Figure 2b. The values of resistors and capacitors were determined by regression of the measured impedance spectra. A good agreement between the determined values and the real values of the electrical circuit were obtained validating the system concept and functionality.

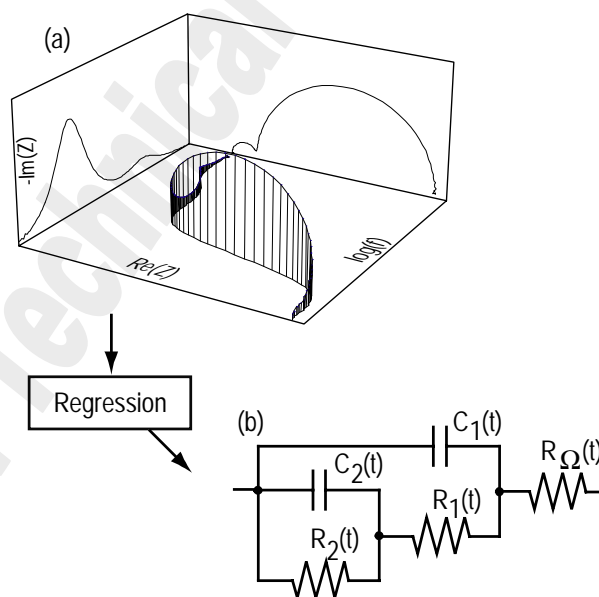


Figure 2
Measurements analysis, (a) typical impedance frequency response of an electrochemical cell. (b) Example of an equivalent electrical circuit that should fit the frequency response after the regression.

The novelty of the present work lies in the conception of the digital FRA allowing for portability and cost reduction. Future work will concentrate on the optimization and the reduction of the size of the complete system.

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 - ^[2] J.R. McDonald, editor, *Impedance Spectroscopy Emphasizing Solid Materials and Analysis*, John Wiley and Sons, New York (1987)
 - ^[3] J. Gobet et. al., "Electrotechnical Platform for Application in Water Quality Control", Scientific and Technical Report, CSEM, (1998) 13