ModuLab®
electrochemistry

Application Guide

EIS cell analysis techniques
Harmonic analysis

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Application Guide: AGML05

Introduction

The Solartron ModuLab system offers a great deal of flexibility for scientists who require to run impedance analysis on batteries, fuel cells, supercapacitors or other types of electrochemical cell.

The system provides the choice of voltage (potentiostatic) or current (galvanostatic) control. Impedance tests on fuel cells are often run under DC current load conditions and therefore current controlled impedance tests are often used. On the other hand, there are a great number of scientific papers where the standard impedance test using potentiostatic mode at 10 mV AC is used.

Then there is the choice of impedance technique using either the standard single sine correlation method (which is recognized throughout the world as being the most accurate and repeatable impedance analysis technique available), or alternatively the multi-sine / Fast Fourier Transform (FFT) method (if high speed impedance analysis is required). Both of these techniques are provided by the ModuLab system and are available to use as appropriate for the speed / quality of impedance data that is required.

This demonstration guide uses the harmonic analysis technique to provide an insight into what is the correct AC level that should be applied to a particular test cell. If the AC level is too low, there will be noise on the results, on the other hand if the level is too high the measurements may be badly affected by distortion (which appears as harmonics of the applied sine wave).

Harmonic analysis is also used by corrosion scientists to gather information that is related to the corrosion rate of the sample under test (several technical papers have been written on this subject).

Key system capabilities used in this demonstration

Harmonic analysis displaying impedance, voltage and current vs. frequency

Equipment required for this demonstration

ModuLab electrochemical test system with FRA option fitted
Sealed lead acid battery - e.g. 6 V or 12 V (for example 2.5 Ah)

Connections

Connect the potentiostat to the battery using the connection diagram shown in the following experiment.

Experiment setup

Select "AGML05 Harmonic Analysis" in the "ModuLab Application Guide" project

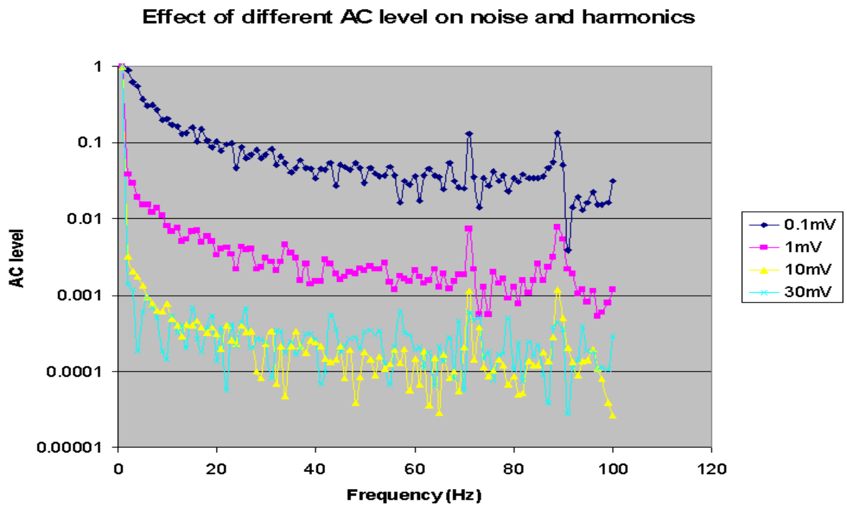
Step #	Purpose
Step 1	Partially discharge a battery until it reaches a particular voltage (more non-linear in this region)
Step 2	Open circuit to allow the cells to settle after discharge
Step 3	Run impedance test (FFT) at 0.1 mV AC 1 Hz base frequency, 2 decades (i.e. to 100 Hz). Custom list of frequencies, only 1st frequency stimulated, measure all frequencies
	Repeat step 3 at different AC levels (1 mV, 10 mV and 50 mV)
Additional test possibilities: Additional AC levels can be tried Battery can be discharged to different levels before running the impedance tests	

Notes on setup

Typically 10 mV AC level is used for a wide range of electrochemical impedance tests. However, this can be a somewhat arbitrary choice which is applied without examining what might be the appropriate level for a particular cell. Harmonic analysis provides a method for choosing the optimum AC level.

Data presentation and analysis

The results below were obtained by applying a 1 Hz single sine wave of different AC voltage levels to a battery (0.1 mV, 1 mV, 10 mV, 50 mV) and measuring the response from the cell at that frequency plus a range of harmonic frequencies (up to 100 Hz) using the ModuLab frequency response analyzer's built-in Fast Fourier Transform (FFT) analysis technique. For this test the current magnitude is calculated and displayed in the ModuLab software. Up to one thousand frequencies can be analyzed if required; for this test one hundred were used so that the results could be seen more clearly.



The battery is a particularly linear system over much of its discharge curve as can easily be seen when using constant current discharge and examining the DC voltage level over a period of time. It is therefore quite difficult to see harmonic distortion on the results (which would appear as harmonic frequencies in, for example, the 50 mV plot). However, there are many cells that are extremely non-linear and repeating this experiment on that type of cell will give a strong harmonic distortion response in the results (for example corrosion cells often respond in this way, hence the use of this technique in corrosion science).

The above results show that measurements were quite noisy when the low signal level (0.1 mV) is used, (the general background noise on all harmonic frequencies was quite high at about 10 % of the main 1 Hz signal level). However, measurements can still be made even at these low signal levels by increasing integration time. As the signal level was increased, the background noise level can be seen to reduce as expected. When the 50 mV signal is applied, there is a suggestion of harmonics appearing out of the general background noise, though a more non-linear test cell would exhibit this more clearly.

Conclusions

Harmonic analysis is another extremely powerful and useful technique that is provided by the ModuLab system. These facilities make it a unique system that may be used for a wide variety of tests in energy storage, corrosion and general electrochemical applications.

Application Guide

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