

AC and DC cell analysis techniques; Harmonic analysis

Demonstration Expt: DG05

John Harper and Brian Sayers
Solartron Analytical, Farnborough, UK.

Introduction

The Solartron CellTest® 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 (pstat) or current (gstat) 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 pstat 10mV AC level test is used.

Then there is the choice of type of impedance experiment 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 new Solartron CellTest system and are available to use as appropriate for the speed / quality of impedance data that is required.

This demonstration guide explains the use of another very useful technique which provides an insight into what is the correct AC level that should be applied to any particular test cell. If the AC level is too low, there will be a lot of 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 sinewave). Additionally, corrosion scientists are able to gather information from harmonic analysis that is related to the corrosion rate of the sample under test (several technical papers have been written on this subject).

Equipment

- Solartron 1470E multi-channel potentiostat
- one 145x series frequency response analyzer FRA
- one battery demonstration test box with connection leads

Connections

- Connect the coloured cell connection cables from 1470E channel 1 to a battery test box, (red connector on the connection lead to red connector on the battery, blue to blue etc.)
- Connect channel 1 FRA connections on the 1470E to one of the 145x series FRAs (main channel connections).

Software Setup

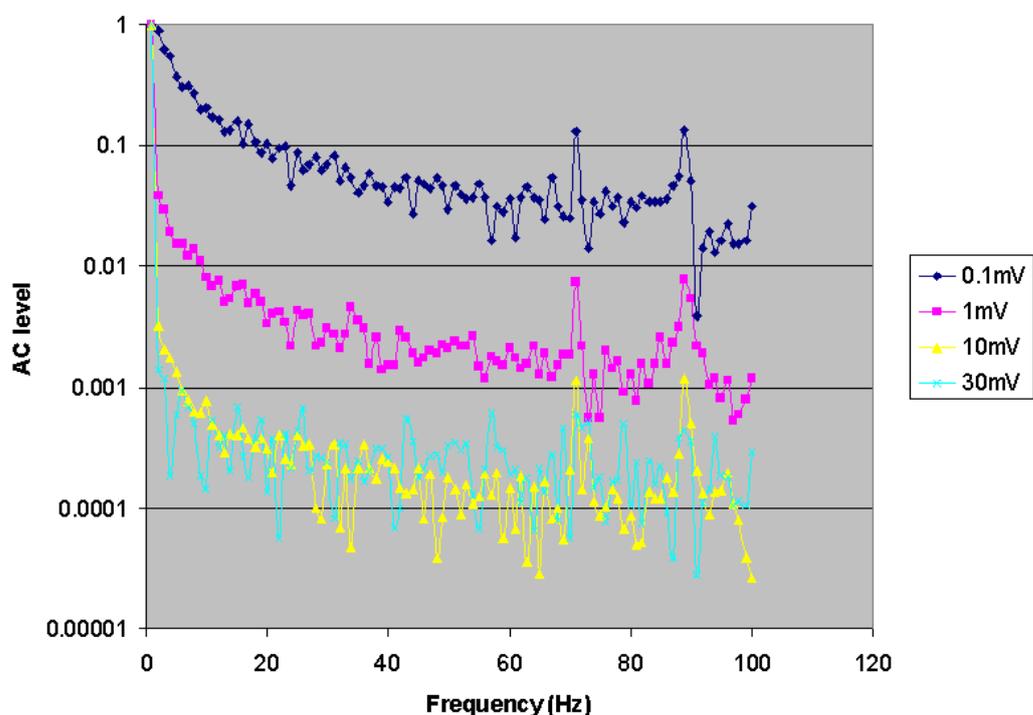
Step	Parameter	Setting	Comment
1 - charge	i) mode ii) start iii) period iv) termination	i) constant current ii) -1 Amp iii) 3 minutes iv) 0.8v	partially discharge the cell for 3 minutes or until the cell reaches 0.8V (AA cell is more non-linear in this region)
2 - rest	i) duration	i) 30 seconds	allow the cells to settle under DC load
3 - impedance	i) mode ii) DC level iii) AC level iv) measurement mode v) multi-sine setup v) AC level	i) voltage control ii) 0 Volts vs previous step iii) 0.1 mV iv) Multi-sine / FFT v) 1Hz base freq, 2 decades vi) 0.1mV	- run the impedance at 0.1mV AC (in order to increase background noise) - 1Hz base frequency, 2 decades (i.e. to 100Hz). - custom list of frequencies, only 1st frequency stimulated, measure all frequencies
repeat steps 2 & 3, but with different AC levels for the impedance test (1mV, 10mV and 50mV)			

Notes on Setup

Typically 10mV AC level is used for a wide range of electrochemical impedance tests. However, this can be a somewhat arbitrary choice which is applied without really examining what might be the appropriate level for a particular cell. In this particular demonstration on an AA cell, different AC voltage levels have been applied and the measured current results have been normalized to the same level at the 1Hz frequency and overlaid for comparison.

Results

Effect of different AC level on noise and harmonics



The above results were obtained by applying a 1Hz single sinewave of different AC voltage levels to an AA cell (0.1mV, 1mV, 10mV, 50mV) and measuring the response from the cell at that frequency plus a range of harmonic frequencies (up to 100Hz) using the 145x series frequency response analyzer's built-in Fast Fourier Transform (FFT) technique. For this special test results are exported to Excel and the measured current magnitude is calculated and displayed in Excel (the spreadsheet that was used for this calculation is provided with the other demonstration files). Up to one thousand frequencies can be analyzed by the 145x series FRAs if required; for this test one hundred were used so that the results could be seen 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. Using a battery, it is quite difficult to see harmonic distortion on the results (which would appear as harmonic frequencies in, for example, the 50mV plot). However, there are many cells that are extremely non-linear and repeating this experiment on that type of cell may 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 (0.1mV) is used, (the general background noise on all harmonic frequencies was quite high at about 10% of the main 1Hz 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 50mV signal is applied, there is a suggestion of some 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 CellTest 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.