Non-linear system analysis:
The application of Electrochemical Impedance Spectroscopy to the study of fuel cells and batteries operated under load

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Introduction

Electrochemical Impedance Spectroscopy (EIS) is routinely used by the energy storage device community for the design, characterization and improvement of cells. Many published studies on electrochemical systems use ac stimulus levels of no more than ±10 mV versus the equilibrium or open circuit potential. In contrast to this, fuel cells and batteries operate under load and therefore information regarding kinetic behaviour far removed from the open circuit potential of the anode or cathode is of great interest. Many scientists new to this technique adhere to two common measurement principles without fully appreciating their significance.

They are;

i) the ac stimulus must never be greater than 10 mV

ii) impedance measurements should only be performed at the open circuit potential of the device.

This application note attempts to demonstrate how impedance measurements can be performed on systems under high DC load from a theoretical standpoint using the concept of non-linear systems analysis. Furthermore, advice and guidance on good measurement practice and analysis to validate the experimental method is presented.

Non linear systems analysis

i) Linear systems

The complex coupling of kinetic, mass transport and convective phenomena in electrochemical systems, results in a high degree of non-linearity upon perturbation of the system with applied overpotential. Indeed, separation and characterization of the processes mentioned above may be impossible using time domain techniques such as voltammetry. It was found that frequency domain techniques could overcome many of the problems of traditional techniques and of these techniques EIS was most widely adopted. Experimentally, many cases of non-linear behaviour are seen. However, if linear equations are known at every point for a steady-state system displaying non-linear behaviour, local linear analysis can be employed. For example, electrochemists use Tafel analysis to determine the electrode kinetics; the derivation of which is from a non-linear relationship between the applied overpotential and the current. However, for sufficiently small overpotentials the Tafel equation is linear. Therefore, EIS is routinely performed using small ac stimulus (usually 10 mV) around the open circuit potential where the linearized form of the Tafel's law applies.

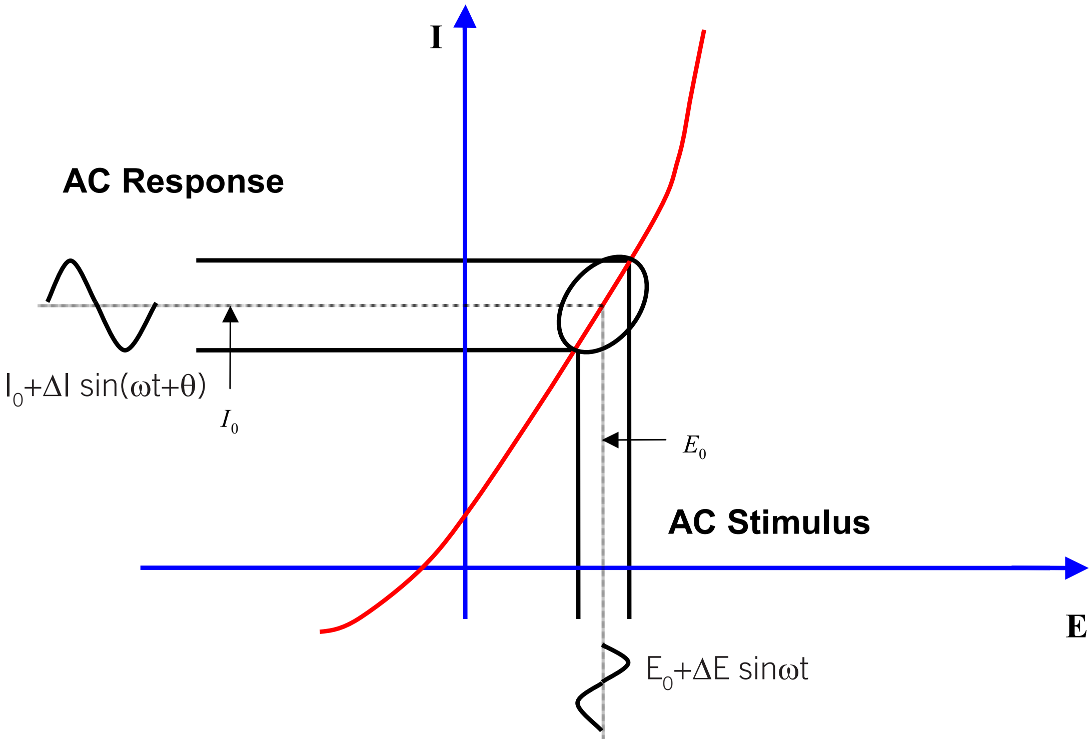

Figure 1. (Taken from Gabrielli, Solartron Analytical Technical note 004). Small signal analysis of an electrochemical non-linear system. Note the non-linearity between current and voltage at potentials beyond $E_0 + \Delta E \sin\omega t$

ii) Non-Linear analysis of fuel Cells and batteries

An understanding of the linearized form of the Tafel equation helps to clarify the rationale behind the selection of the magnitude of the AC stimulus for low impedance devices such as fuel cells and batteries. Under DC load conditions examination of the Tafel equation demonstrates that the system may no longer be linear. An illustration of this point is shown in Figure 1. We must therefore consider how we can measure the impedance of non-linear systems.

As shown in Figure 1, a low amplitude sine wave, $\Delta E \sin \omega t$, is superimposed on the polarisation voltage, E_0. Hence a low amplitude sine wave $\Delta I \sin(\omega t + \theta)$ is observed, superimposed on the dc current. Using Taylor's expansion for the current,

$$\Delta I = \left(\frac{dI}{dE}\right)_{E_0,I_0} \Delta E + \frac{1}{2}\left(\frac{d^2 I}{dE^2}\right)_{E_0,I_0} \Delta E^2 + \ldots\ldots\ldots\ldots \qquad \textbf{(1)}$$

If the magnitude of the AC signal is small, 2nd and higher order terms are negligible compared with the first and therefore small signal analysis can be considered to be in the linear region. This process is often referred to as quasi-linearization. In this instance, the level of AC stimulus must satisfy the conditions in which equation 1 approximates to a linear expression. There is no 'magic' number regarding the size of the AC stimulus level as it depends upon the linearity of the region of the current-voltage curve of interest. However, it is possible to determine the appropriate level using harmonic analysis.

All of the concepts presented assume that the system is at steady-state. This is especially important for devices under load since the cell may not attain steady-state for the duration of the impedance measurement. There are some simple tests that can be used to check for steady-state behaviour including monitoring either the DC current and voltage during the impedance measurement. Any changes in either of these variables suggest that the system is changing and is therefore not steady - state. When such circumstances arise, valid impedance measurements may be difficult or impossible to perform.

Impedance techniques

Of the various impedance techniques available, potentiostatic and galvanostatic are the most widely used. Which one is most applicable to fuel cell and battery research? In order to address this issue we must first understand how the techniques differ.

- potentiostatic impedance superimposes a sinusoidal voltage upon the DC polarisation potential and measures the current. This is perhaps the most familiar technique to the electrochemist in which the AC stimulus level is usually 10 mV (see Figure 1)
- galvanostatic impedance superimposes a sinusoidal current on the DC polarisation current and measures the voltage.

Irrespective of which technique is used, the calculated impedance values will be exactly the same. This can be verified by close inspection of Figure 1 which shows that potential and current techniques are interchangeable (since the current is linear with voltage and vice versa). Because of the limitations imposed by the current measuring component of the potentiostat, it is advisable to use galvanostatic impedance techniques. Consider the current – voltage relationship of a fuel cell or battery. We know that for a relatively small change in the voltage, large DC current will flow. Conversely, large changes in current usually result in small changes in the DC cell voltage (this is particularly true of batteries). Therefore, the application of a small AC signal such as 10 mV as is typical in potentiostatic impedance mode, may result in a DC cell current that exceeds the maximum current range of the potentiostat. Hence, the choice of potentiostatic or galvanostatic methods in this application are not governed by the chemistry of the cell but by the limitations of the potentiostat.

If potentiostatic impedance is not recommended for these devices, then what AC level should one apply in galvanostatic mode? The answer to this question is not straightforward and depends upon the current – voltage characteristics of the cell. As a guide, it is advisable to apply the largest stimulus level possible whilst remaining within the linear region of the current – voltage curve. The instrument is attempting to measure both very small current and voltage and therefore the response may suffer from noise if both signals are beyond the specifications of the instrument. Increasing the AC current stimulus level will improve the accuracy and signal-to-noise ratio. This is demonstrated in Figure 2.

Summary

Traditional EIS studies were developed to measure the properties of the electrode at the open circuit or equilibrium potential. However, fuel cell and battery scientists are often interested in the performance of the device at potentials far away from equilibrium. In this application note we have described the theories that address this is issue.

Non-linear EIS is a powerful tool for the development of the understanding of processes that occur in energy storage devices. With modern instrumentation such as the Solartron ModuLab or CellTest systems, verification of results such that measurement are ‘quasi linear’, is facilitated by employing simple noise and harmonic and are discussed in another Solartron technical note.

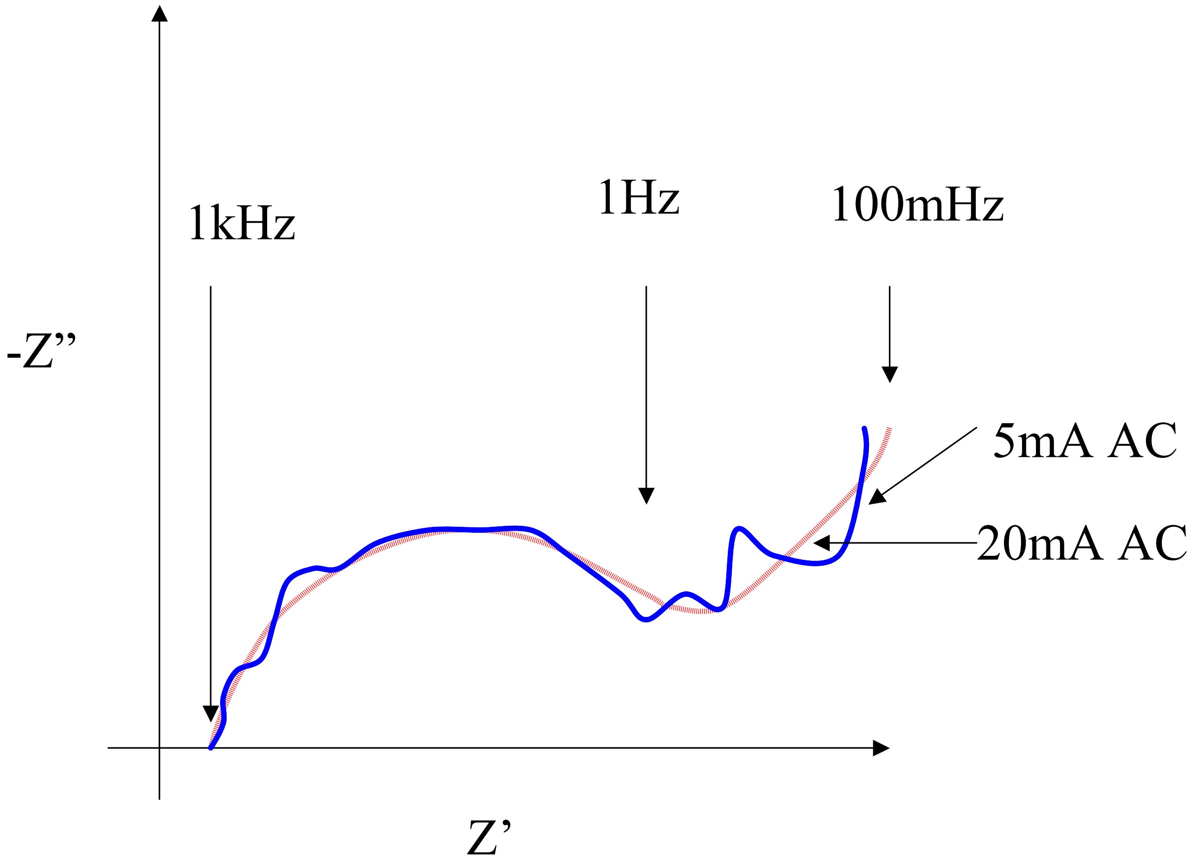

Figure 2. Complex plane diagrams of impedance spectra of a 1.5 V alkaline battery. Note that increasing the ac stimulus level from 5 mA (blue) to 20 mA (red) greatly improved the quality of impedance data.

Recommended Reading

1) Identification of Electrochemical Processes by Frequency Response Analysis, Claude Gabrielli, Solartron Analytical Technical Report Number 4

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