analytical measurement solutions

High frequency, high current impedance spectroscopy: Experimental protocols enabling measurement up to 1MHz at high current densities

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1.0 Introduction

Recent advances in the development of high power electrochemical devices, such as fuel cells, batteries and supercapacitors, have been made possible by an improved understanding of the fundamental electrochemical processes. Electrochemical Impedance Spectroscopy (EIS) stands out amongst all other electrochemical techniques since information regarding ohmic losses, electrochemical kinetics and mass transfer processes can be characterised in a single experiment; in marked contrast with traditional DC techniques.

Until recently the bulk of research using impedance techniques focused on the characterisation of cell membranes and the determination of the electrochemical kinetics. The mid frequency range was therefore of most interest. Scientists and engineers have now realised that the entire frequency response curve yields useful data for example on non-Faradaic mechanisms, such as water management[1], ohmic losses[2] and the ionic conductivity of proton exchange membranes[3]. Therefore impedance is fast becoming a standard analytical tool in high energy, storage device applications.

With the availability of wide bandwidth instrumentation, measurements up to 1MHz are possible. However, due to the bandwidth limitations experienced by potentiostats when they are operating at high DC current levels, valid data acquisition in the high frequency domain is generally limited to below 10kHz. Unfortunately, this has limited the application of EIS to cells with current ratings typically less than 1A. An example of this limitation is the characterisation of solid oxide fuel cells where it is necessary to measure the impedance response at high frequencies c.f. 70kHz. Therefore, engineers have traditionally relied on DC techniques, such as current interrupt, to determine the ohmic losses associated with the stack whilst using the mid to low frequency spectrum from EIS to understand the remaining cell characteristics.

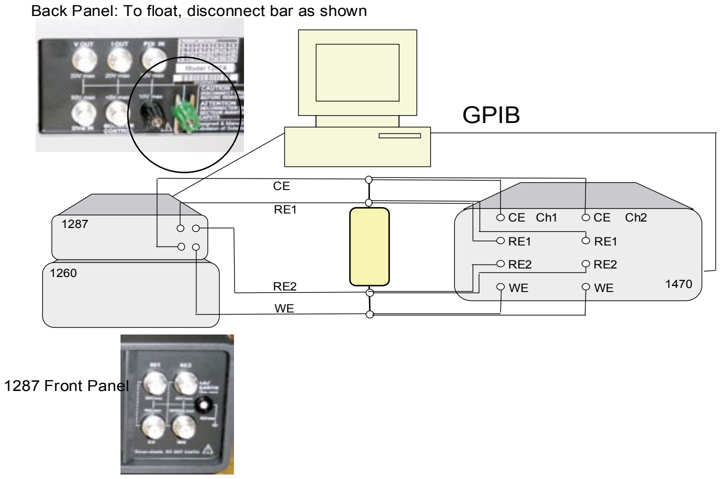
This technical note describes some experimental techniques that overcome the bandwidth limitation at high DC current levels and provide accurate impedance measurements up to 1MHz in potentiostatic mode or 125kHz in galvanostatic mode, thus affording the study of mechanisms that were previously beyond the range of traditional impedance techniques. These techniques apply to the study of high power devices such as fuel cells (SOFC, DMFC and PEMs), supercapacitors and batteries.

Technical Bulletin

2.0 Experimental

In order to take advantage of the full potentiostat bandwidth when measuring cell impedance, the current flowing through the potentiostat must be small and preferably well below its maximum current capability. This is achievable when the impedance of the cell is monitored by the combination of potentiostat and FRA while the DC load current is controlled by a separate potentiostat or electronic load operating in parallel. This ensures that only the AC component of the total current through the cell flows through the potentiostat/FRA. This is maintained typically in the region 10-100mA which allows wide bandwidth performance from the potentiostat. A typical experimental set-up is shown in figure 1.

Figure 1



Experimental set-up enabling high frequency, high current measurements. We recommend that all measurements should be performed with four terminal connections as shown in the diagram as this will minimise any impedance artefacts associated with cable impedance.

The DC current level from the test cell can be controlled by an electronic load, potentiostat or a 1470 CellTest system. The 1470 can have all eight channels connected in parallel to provide DC current levels up to 32Amps.

It is highly probable for safety reasons that your cell will be connected to ground. In order to avoid earth loops your potentiostats in the impedance loop and in the DC current loop must all have the ability to float. This is also an important facility when connecting 1470 channels in parallel for high current load applications. All Solartron products have this capability and we recommend the 1287 electrochemical interface or the 1470 for this purpose. The inset picture demonstrates how to enable the 1287 to float by disconnecting the contact pin at the rear panel of the potentiostat.

To summarise,

- **For maximum impedance bandwidth the impedance measurements should be performed by a separate potentiostat, FRA connected in parallel to the DC current loop**
- **All potentiostats in the system must have the ability to float.**
- **All potentiostats must have four terminal connection capability**

3.0 Measurement Techniques

Two impedance techniques are available with Solartron products; galvanostatic and potentiostatic impedance. Each has its advantages and disadvantages and depending upon your application, one of these may be more suitable for your studies than the other.

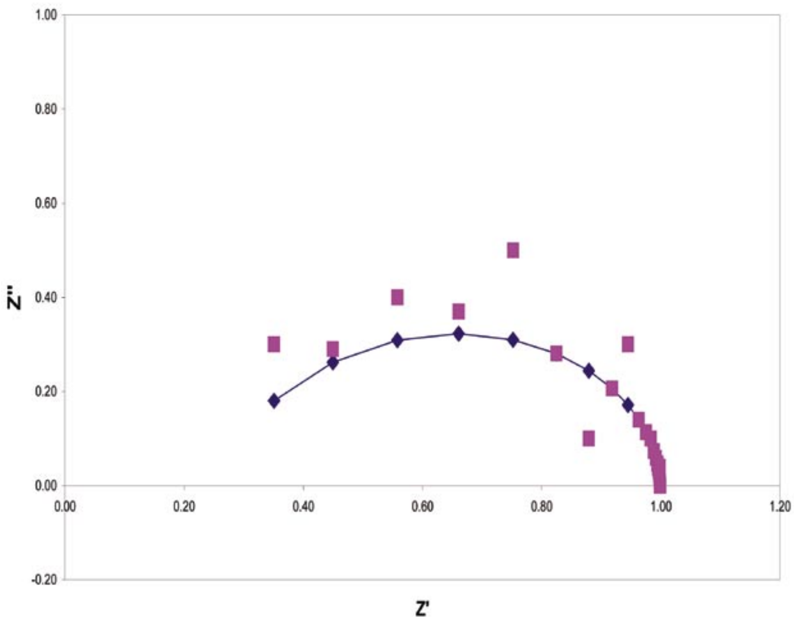
In principle, Potentiostatic impedance permits the use of the full bandwidth offered by the FRA/potentiostat. For example, a 1287 and 1255B FRA connected with a high current load in parallel were shown to yield high quality data up to 500kHz in potentiostatic mode. However, you should proceed with caution when applying this technique to the study of low impedance cells such as fuel cells. In general a small change in potential may result in a large change in current which could overload the cell and the current measurement circuits in the potentiostat. Therefore, it may be necessary to experiment with different AC voltage levels to ensure that the AC current does not exceed the maximum current range afforded by the potentiostat. In addition, the cell impedance changes as the frequency alters during the impedance sweep possibly leading to overloads at high frequency where the cell impedance tends to be lower. Experimentation to find a suitable AC voltage level is therefore required across the frequency range.

Galvanostatic impedance is a more complex mode of operation which, in general, has more limited bandwidth although this is often more than sufficient for most high energy applications. This technique has the advantage that the AC and DC current level is actually selected by the user which avoids the problem of accidentally overloading the cell and potentiostat. Relatively large AC current levels can be used without significantly changing the cell voltage and using galvanostatic mode allows precise control of the current through the cell.

In order to ensure that you collect accurate, noise free data we strongly recommend that you determine an appropriate excitation amplitude for your cell; AC current levels that are too small result in noisy data whilst high current settings may result in harmonic distortion due to the non-linearity of electrochemical systems. The effect of applying a small AC current stimulus is shown in figure 2 and the noise shown in the result is due to the measured AC voltage being too small to be measured accurately. In our experience, AC current levels in the region 10-100mA prove to be adequate for most energy storage devices though experimentation with different AC levels is advised.

Figure 2

Complex plane impedance diagram of a simple resistor-capacitor network. Impedance measurements performed in galvanostatic mode ;
(♦) = 100mA AC current level,
(■) = 1mA AC current level.
Notice the effect of applying a very low AC current.



4.0 Applications

The techniques described in this note apply to many forms of high frequency, high current measurement including:

- High current, low voltage (when the cell voltage lies within the maximum polarisation voltage range of the potentiostat). For instance, individual cells and low voltage stacks.
- High current, high voltage (when the cell voltage exceeds the maximum polarisation voltage range of the potentiostat but is still within its compliance voltage range). This could be on higher voltage fuel cell stacks or multicell batteries or supercapacitors.
- High current, high impedance cell studies (when the impedance of the cell approaches the impedance of the potentiostat or electronic load).

We have limited our studies to galvanostatic impedance only; however, valid measurements up to 500kHz in potentiostatic mode are also possible.

4.1 High current, low voltage

A potentiostat and FRA provide the impedance analysis while a separate potentiostat provides the DC load on the cell. The maximum permissible operating cell voltage is limited by the polarisation potential of the potentiostat e.g. a 1470 is capable of +10V/-3V and therefore the experimental set-up described in figure 1 is suitable for testing devices in this range.

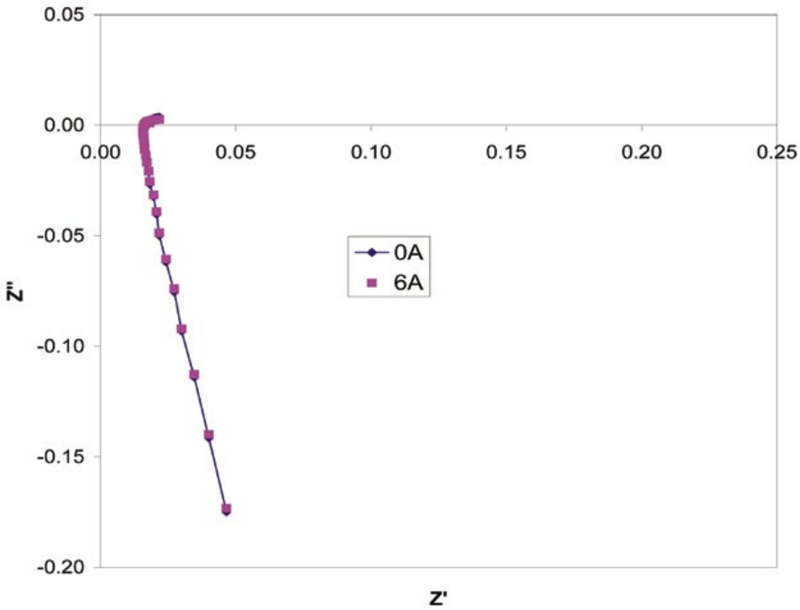
4.1.1 Example

Impedance Spectroscopy of a 6V Lead Acid Battery

The impedance of a standard 6V lead acid battery was monitored at open circuit and at a constant current discharge of 6A using galvanostatic mode from 125kHz to 1Hz using an AC current level of 100mA. In this instance, two channels of the 1470 battery tester were connected in parallel to provide a total DC current load of 6A since each channel is individually only capable of 4A. The results are presented in figure 3.

Figure 3

Complex plane impedance diagrams of a the impedance response of a 6V lead acid battery at open circuit and under a constant load of 6A. Frequency range 125kHz to 1Hz, AC current level = 10mA.

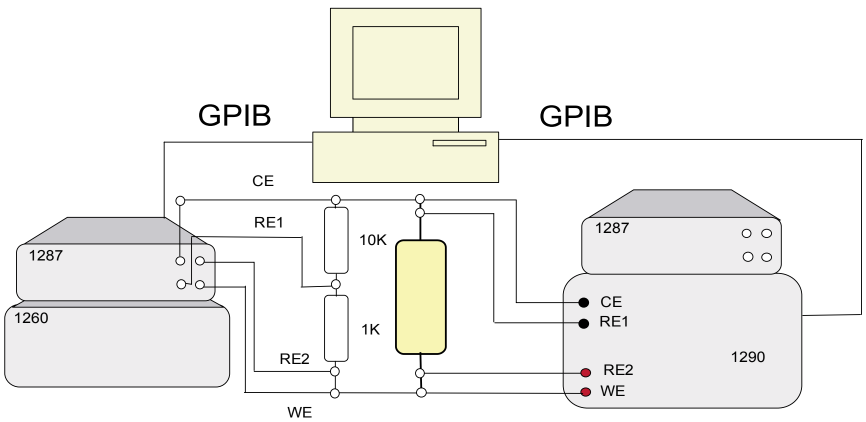


Whilst such high frequency measurements are not usually necessary for this system, the results do however validate the experimental technique. At frequencies in excess of 2kHz we note inductance and this is simply related to the physical properties of the cell (in general the inductance of a wire is 1nH per mm). This artefact should be independent of the load placed upon the cell i.e. all plots should be the same from 2kHz to 125kHz and this is clearly demonstrated in figure 3. Indeed the only discernable difference between the plots is the impedance at low frequencies and this is consistent with the dependency of the rate of the electrochemical process as a function of cell polarisation.

4.2 High current, high voltage

As the open circuit cell voltage approaches the maximum polarisation voltage afforded by the potentiostat it becomes necessary to attenuate the voltage. This is commonly the case when testing larger battery and fuel cell stacks. The potential divider shown in figure 4 attenuates the voltage.

Figure 4



Modification of figure 1 including potential divider circuit allowing impedance studies of high voltage cells. A 1287 in conjunction with a 1290 power booster can also provide the load offering a maximum capability of 25Amps, 50V, though the compliance range of the 1287 would limit this to 30V maximum.

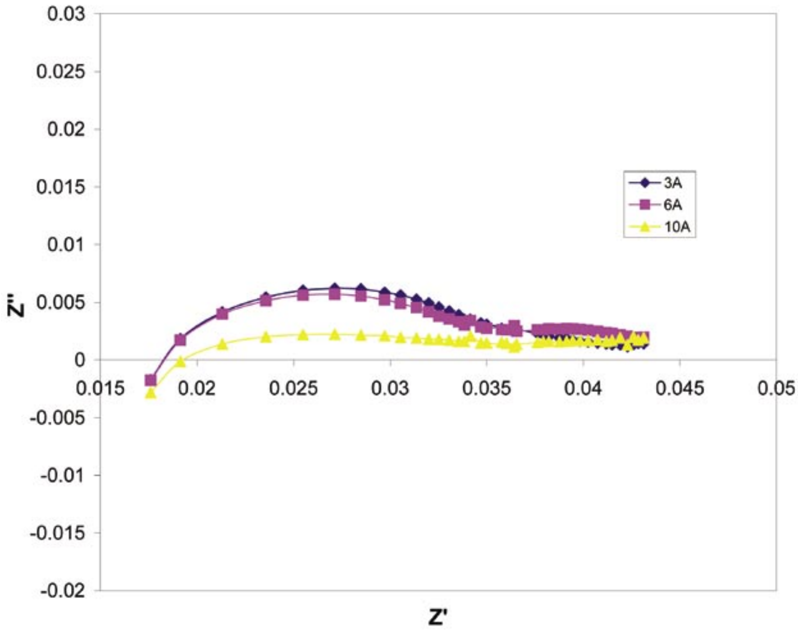
4.2.1 Example

Impedance Spectroscopy of a 12V Lead Acid Battery (figure 5)

In this example we used a 1287 and 1290 power booster which increased the maximum current capability of the DC current loop to 25A. Although the open circuit voltage of the battery was less than the maximum polarisation voltage of the 1287 potentiostat (±14.5V), this example does however validate the experimental technique. The application of this technique to impedance measurements of cells with open circuit potentials greater than that of the 1287 polarisation range is discussed in the next example.

Figure 5

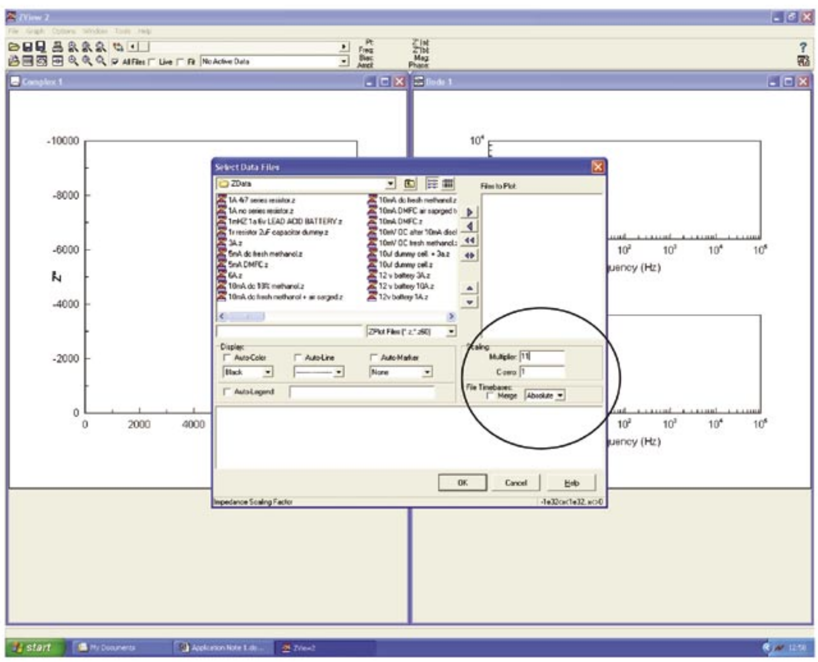
Complex plane impedance diagrams of a 12V lead acid battery using voltage divider circuit shown in figure 4 under various loads up to 10Amps. Note that the values have not been scaled in this instance. The load cell used in this instance was a 1287/1290 combination.



With the addition of the divider network, the voltage across RE2 and RE1 was 1.09V (as opposed to 12V). Remember, the impedance of the cell requires the measurement of both voltage and current and therefore all values need to be scaled to account for the effect of the attenuator. In this particular example all DC voltage and impedance measurements need to be multiplied by a factor of 11. This task is easily performed in ZView PC software. In the 'select data files' window, there is a scaling multiplier box in which you enter the values that are appropriate for your circuit (as shown in figure 6).

Figure 6

Select data files' window showing the multiplier function available in ZView.



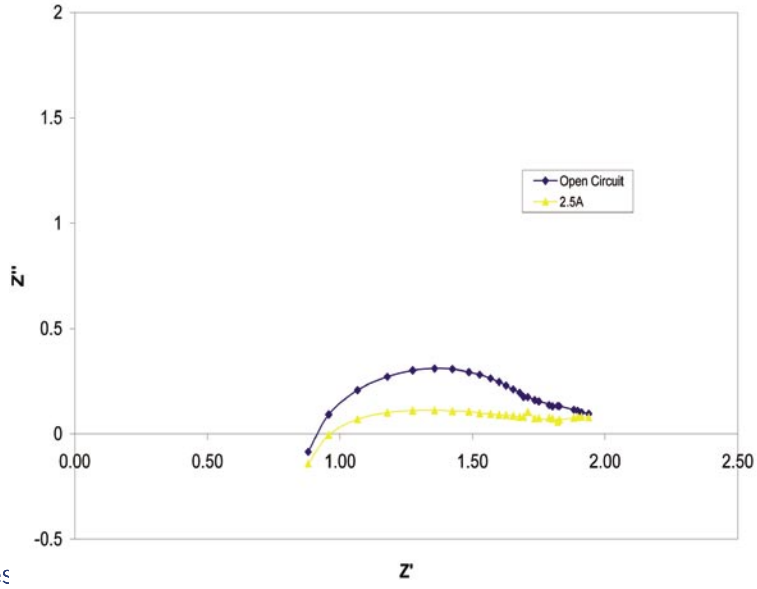
4.2.2 Example

Impedance Spectroscopy of a 16V, 3A Solid Oxide Fuel Cell Stack

In this example we used a 1287 electrochemical interface and a 1260 impedance analyser combination. The main quantity of interest is the calculation of the ohmic loss associated with stack resistance and this value can be found by determining the point of intersection along the real axis on a complex plane impedance plot. It is fairly easy to see that for this cell, the ohmic loss was in the order of 1Ω (see figure 7).

Figure 7

Complex plane impedance diagram of impedance response of a Solid Oxide Fuel Cell measured at open circuit and a constant load of 2.5Amps.

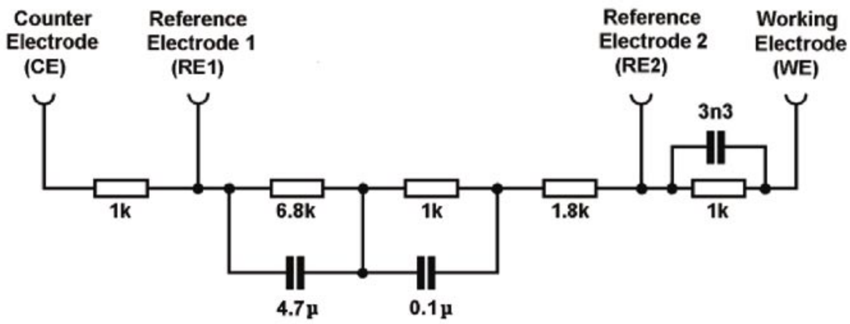


4.3 High current, high impedance cell studies

Thus far we have considered cells with internal resistance in the order of less than 1Ω and demonstrated the application of this novel impedance measuring technique to understanding the underlying electrochemistry at high current. However, if the impedance of the cell approaches the impedance of the load device it is likely that your experiment will produce unwanted high frequency artefacts. This point is demonstrated in figure 8 where the impedance response of a standard Solartron dummy cell was recorded. Note that this is very much a worst case scenario since the dummy cell is very high impedance compared to a typical battery or fuel cell.

Figure 8

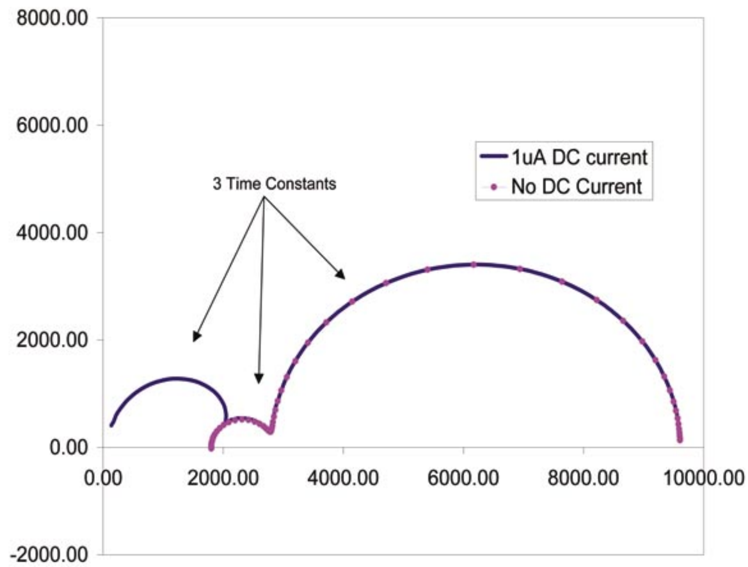
Component Diagram of Solartron Dummy Cell



Firstly, the impedance spectrum was measured using a 1287 and 1260 at open circuit with a 10mA AC current level. Two time constants are clearly shown in figure 9 and the analysis of the curves yielded the correct values. Following this, the experiment was configured as described in the first example and one can clearly see three time constants in the impedance results when presented on a complex plane diagram.

Figure 9

Complex plane impedance diagrams of the impedance response of a Solartron dummy cell at open circuit (purple) and under load (blue).
The three time constants observed when the cell was under load are highlighted with arrows.



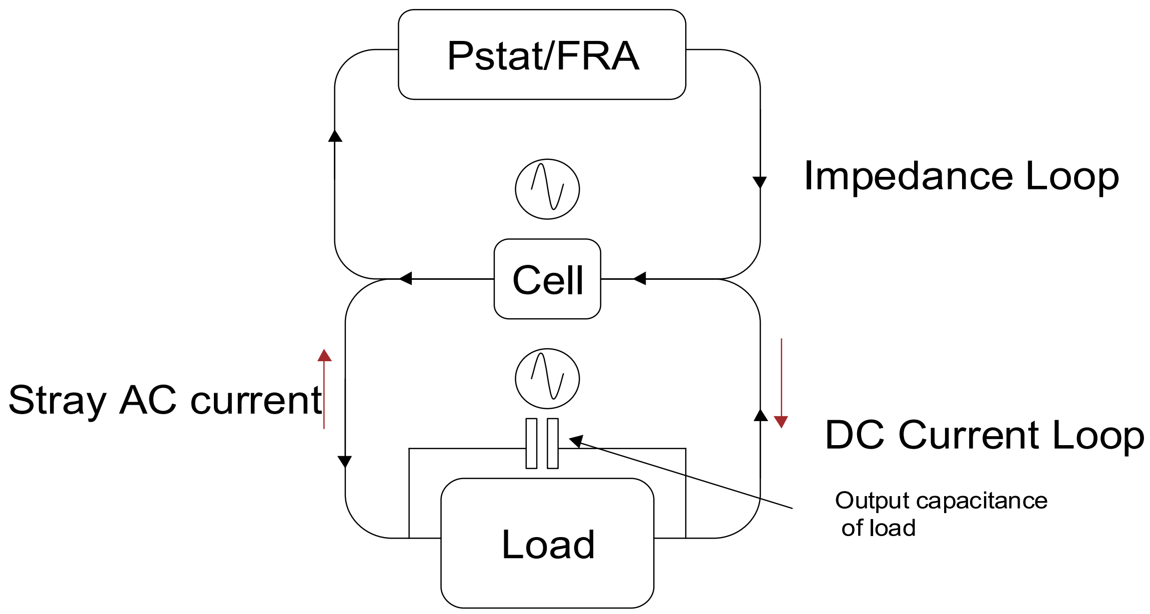
In principle all of the AC measuring current should flow through the cell. However, in practice some of the current is diverted into the DC current loop as illustrated in figure 10. All electronic loads exhibit associated capacitance and it is this that appears as the artefact at high frequencies. According to equation (1), the current flowing through the electronic load is a function of the reactance (X_c) of the capacitance on its outputs (equation 2)

$$i = \frac{E}{X_c} sin(\omega t + \theta) \qquad (1)$$

$$X_c = \frac{1}{\omega C} \qquad (2)$$

where i is the current, E the applied voltage, X_c is the reactance of the capacitor, $\omega = 2\pi f$ and θ is the phase shift.

Figure 10

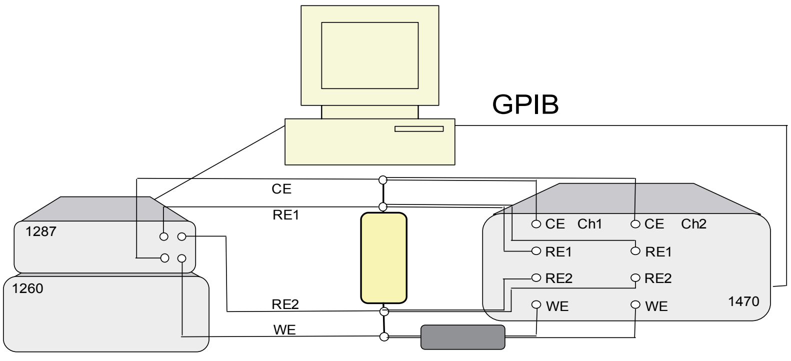


Schematic representation of the current paths that arise when the cell impedance is similar or greater than that of the load device.

For example, the reactance of a 4nF capacitor at 100kHz is 398ohms. In this instance, the magnitude of the reactance of the capacitance is approaching that of the impedance of the dummy cell and therefore AC current will flow into the load DC current loop. In effect, one now measures the impedance of two parallel impedances. Furthermore, if the reactance of the load capacitance is significantly smaller than that of the impedance of your cell, most of the AC current from the impedance loop will flow through the DC current loop. This manifests itself as an additional time constant as shown in figure 8.

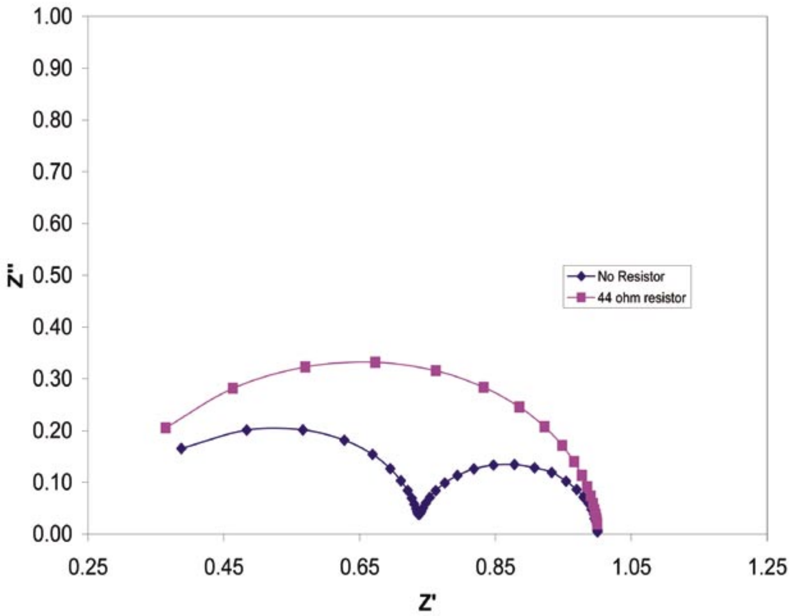
This issue can be overcome if a suitable resistor is placed in series with the DC current loop as shown in figure 11. In essence, since the impedance of the DC current loop is now significantly greater than that of the test cell, most of the AC current will flow through the cell and not the load device. It is important to stress at this point that the choice of resistor depends both upon the impedance of the cell and the reactance of the capacitance associated with the load device. Unfortunately it is not possible to determine the impedance of the load device independently from the test cell and therefore you must rely on trial and error. We overcame this issue by examining the effect of different resistors upon the frequency response of a dummy cell as shown in figure 12. The values of the components were deliberately chosen to represent a real device such as a fuel cell. One can see from the plots that increasing the value of the series resistor decreased the influence of the DC load loop upon the frequency response of the dummy cell until it eventually disappeared. We recommend that you adopt a similar verification process before embarking upon real studies.

Figure 11



The inclusion of the resistor in the DC current loop obviates stray AC current.

Figure 12



The effect of series resistor upon the impedance response of a simple resistor-capacitor network. Experimental conditions, DC load = 3Amps, AC stimulus = 10mA, frequency range = 125kHz to 1Hz in galvanostatic impedance mode.

Summary

The techniques described in this report extend the measurable frequency range from 10kHz to 125kHz in galvanostatic mode or 500kHz in potentiostatic mode while operating a cell under high DC load conditions. These will prove to be invaluable to the researcher who until now has been unable to measure electrochemical processes at high frequency and high current.

References

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