ModuLab®

electrochemistry

Technical note

EIS analysis techniques

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1. Introduction

The frequency response analyzers developed for the ModuLab electrochemical test system (FRA 1MHz and FRA 300kHz) utilize the latest signal processing technology to provide amazing high-speed impedance measurements while maintaining the accuracy, repeatability and resolution of previous generation Solartron frequency response analyzers.

Solartron's reputation for the design and manufacture of top quality AC measurement instrumentation is built upon the performance of its range of frequency response analyzers (FRAs). Solartron started developing instruments in 1948, initially supplying frequency response test instrumentation into critical, high accuracy aerospace applications. Over the years, the company has diversified into many other applications areas including battery, fuel cell, materials and electrochemical test, but the basic philosophy for producing high quality, accurate and reliable test instrumentation has always remained the same.

This technical note explains why Solartron impedance analysis systems are the worldwide reference standard and by comparison with other (more limited) systems explores some of the reasons why the new product range will be the standard by which all others are judged.

2. Connections to the cell

Impedance analysis is a very popular, non-destructive measurement technique that provides detailed diagnostic information about a wide range of electrochemical phenomena including corrosion mechanisms, state of charge of batteries, electrode material properties, state of health of fuel cells etc.

The technique involves the application of a low level AC waveform to the cell under investigation and measurement of the cell's response to this stimulus. Measurements are taken of the AC voltage across the cell and the AC current through the cell. The impedance of the cell is obtained by taking the ratio of AC voltage / AC current. Since a low level stimulus is used, no damage is caused to the cell. Typically a swept frequency sine waveform or multi-sine waveform is used as the stimulus so that the impedance can be evaluated across the frequency range of interest.

3. Impedance measurement techniques

There are many types of AC measurement instruments on the market including sub-sampling FRAs, lockin amplifiers, frequency response detectors, "soft" FRAs etc. All of these systems exhibit limitations when compared to the latest generation of Solartron frequency response analyzers (FRA).

3.1 Single frequency impedance analysis

The lowest cost, lowest capability implementation is to apply a sinusoidal waveform to a cell at a single fixed frequency and sample the voltage and current at a high enough rate to be able to calculate the impedance from the results. This may be sufficient to get a rough idea of, for example, the equivalent series resistance ESR (ohmic-drop) of a cell if the proper frequency has been chosen. However, systems of this type do not perform a complete impedance vs. frequency measurement, so it is not possible to make a judgement about whether the chosen frequency is suitable. This type of system can produce very large errors on ESR measurement owing to inappropriate selection of frequency and unfortunately this sometimes gives the impedance measurement technique a bad name (which is entirely undeserved). In addition, this type of system gives no diagnostic information about the cell under test.

3.2 Sub-sampling analyzers

Sub-sampling (also known as under-sampling) is a technique that is used to measure at a higher frequency than the actual maximum sample rate of a particular analogue to digital converter (ADC). This is apparent

when the specification of the system indicates a maximum measurement frequency of, for example, 1 MHz while the ADCs are actually measuring at a much lower frequency (maybe tens or hundreds of kHz or even less). The Nyquist sampling theorem requires that to be able to uniquely measure a particular signal frequency, the measurement equipment needs to sample the data at least 2 x that frequency. In some cases however, equipment is deliberately designed to sub-sample the data to utilize reduced cost ADCs, processors and memory. This type of system can be compared to watching car wheels on a movie film, the wheels often appear to rotate in the wrong direction due to the frames of the film being captured at a rate which is too slow compared to the speed of rotation of the wheel. This effect is known as “aliasing”.

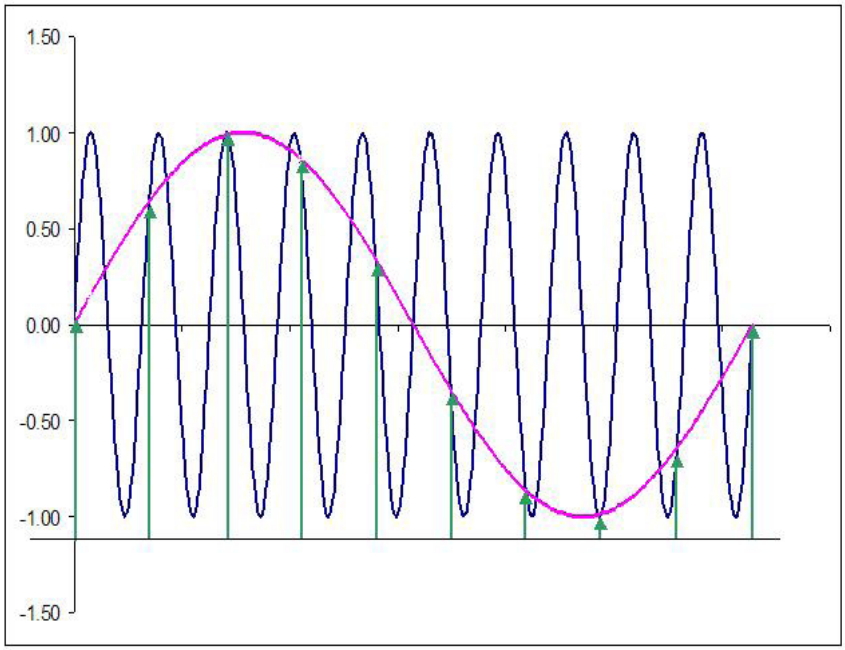


Figure 1: Sub-sampling a sine wave

Figure 1 shows pictorially the effect of sub-sampling a sinusoidal waveform. The higher frequency waveform represents the signal that is to be measured (like the wheel of the car in the film analogy). The arrows indicate the points where the sine wave is actually sampled by the measurement system (these are like the individual frames in the movie film) and the lower frequency curve shows the sub-sampled result waveform. It can be clearly seen from the overlaid lower frequency sine wave, that due to sub-sampling, signals at these two frequencies would both give the same measured response from the system, even though they are at entirely different frequencies (this is the principal by which the sub-sampling system works).

However, in practice there are many additional frequencies that also give the same amplitude levels at the points where the data is sampled and would therefore add into the results. In the above case, to illustrate the technique, the samples are taken at just less than the frequency of the sine wave that is to be analyzed. In practice however, samples are usually taken at a frequency that is at least 10 x or even 100 x less than the maximum frequency that is to be analyzed, so a 1 MHz signal may be actually sampled at around 10 kHz. The higher the ratio of measurement frequency to sub-sampling frequency, the more interference and noise is able to add into the results, and the more ambiguity there is about the signal that is being measured, giving reduced repeatability and reliability of results. The components of a sub-sampling system are lower priced but there is a penalty to pay.

In addition, this type of system does not allow much flexibility since it can only measure one frequency (the stimulated frequency) at a time when measuring at a frequency which is higher than the sample frequency of the ADCs. This leads to restrictions over the frequency range where multi-frequency analysis techniques such as multi-sine / fast fourier transform (FFT) and harmonic analysis can be used. Such systems may offer multi-sine / FFT measurement over a quite restricted frequency range (or not at all). We will return to multi-sine / FFT analysis in section 4 of this paper since this is a useful technique when properly applied with a high sample rate measurement system.

3.3 Lockin-amplifiers - sometimes referred to as frequency response detectors (FRDs)

Some older generation electrochemical impedance measurement systems used analog lockin-amplifiers to make the AC measurements. In this case a sine wave is generated at the analysis frequency that is to be applied to the cell and a lockin-amplifier is used to "lock" to the frequency and make measurements of the AC waveforms that are output from the potentiostat.

One problem generally seen with this type of equipment is that analogue lockin-amplifiers are not able to measure at low frequency (<10 Hz for example) so other techniques must be employed to provide low frequency measurement (which, for example, is required for the measurement of diffusion effects in a cell).

The low frequency analysis is usually obtained from the sample data captured by the DC circuits in the potentiostat which is converted to frequency data by Fast Fourier Transform FFT. This is combined with the high frequency lockin-amplifier data to provide the full analysis of the test cell. However, the two measurement techniques respond quite differently to cell non-linearities and noise, and this results in large steps in the data where the measurement technique is changed. Sometimes the customer is required to perform a system "calibration" to attempt to reduce the size of the data steps.

Another problem with the analogue lockin-amplifier technique is the time that they take to locate and lock to the measurement signal frequency and this can make them relatively slow in operation since this process is required at each frequency in the sweep.

A final point about analogue lock-in amplifiers is that they cannot be used to provide multi-frequency data for FFT and harmonic analysis, which reduces their effectiveness in situations where measurements need to be taken quickly, such as for time variant systems (e.g. unstable corrosion processes or fuel cells under high current load and also for measurements in a QA environment where high throughput of tests may be required).

3.4 "Soft" FRAs

There is another category of FRA that is also used. In this case the potentiostat is arranged to sample the data at high frequency, and the sampled data is passed back to the PC where FFT analysis is performed to extract the impedance information. This can be quite time consuming for the PC since it is involved in analysing a great deal of data per measurement frequency. In addition, the fixed sample rate of the ADCs in the potentiostat means that there are often very large gaps between available analysis frequencies (particularly seen at the middle to high frequency end of the analysis), which limits the use of the equipment for detailed research. This type of system often uses sub-sampling techniques resulting in the problems identified in section 3.2.

4. The new concept for impedance measurement

As we have seen, the measurement systems discussed in the previous section all suffer from limitations. In some cases it may be possible to make multi-frequency FFT measurements at low frequency but not at high frequency - or it may be possible to make single sine measurements at high frequency but not at low frequency - or it may not be possible to uniquely measure signals due to the use of sub-sampling techniques. The latest measurement technology from Solartron removes all of these barriers and provides both single sine and multi-sine / FFT analysis over the entire frequency range of the instrumentation. This provides massive advantages in terms of measurement frequency range, speed of analysis and in the consistency of the results.

The ModuLab FRA uses high performance digital signal processing technology to provide the ultimate in impedance measurement performance. The analogue to digital converters (ADCs) and digital to analogue converters (DACs) in the FRA provide sample measurements at an amazing 40 MHz, which means that when the highest frequency of the system (1 MHz) is being analyzed, the ADCs are actually 40 x over-sampling the data. Since the measurements are over-sampled (as opposed to being sub-sampled), it is possible to use any of the impedance techniques, single sine analysis, harmonic analysis or multi-sine / FFT analysis, over the full frequency range of the equipment. This provides accuracy and flexibility that cannot be achieved by any other system.

4.1 Single sine correlation impedance analysis

Single sine correlation is widely used by researchers throughout the world for the accurate impedance characterization of a wide range of electrochemical cells, for example in the fields of corrosion, battery / fuel cell and sensor research. Other techniques have been tried for impedance analysis but none give such good rejection of noise, interference and distortion. The new ModuLab FRAs take this a stage further and provide amazing high-speed performance while maintaining the accuracy, repeatability and resolution of previous analyzers.

4.2 Multi-sine / FFT impedance analysis

The high sample rates that are utilized by the ModuLab FRAs permit multi-sine / FFT analysis to be performed over the entire frequency range of the system, from 10 µHz to 1 MHz. This is a unique feature of Solartron equipment, unlike other analyzers on the market, there are no restrictions where certain techniques can only be used over a particular range of frequency or cannot be applied at all.

The main advantage of multi-sine / FFT analysis is the speed of measurement. Whereas single sine correlation requires a separate measurement at each frequency, (hence the total time taken for the complete analysis is the sum of the individual measurement times), the multi-sine / FFT technique allows multiple frequencies to be analyzed at the same time. The multi-sine / FFT technique can therefore save a lot of time particularly when measuring at low frequency. By comparison, a multi-sine / FFT analysis from 1 mHz to 1 MHz can be performed in less than one quarter of the time taken for an equivalent single sine analysis, which is particularly beneficial for impedance measurements on systems that might be changing with time (for example, some corrosion systems or fuel cells under high load conditions).

4.2.1 Choice of stimulus / analysis frequencies

The multi-sine / FFT technique makes use of waveform generation and Fast Fourier Transform analysis (FFT) techniques. The FFT is a mathematical algorithm that is used to convert time domain data (voltage and current samples collected over a period of time) into frequency domain data (analyzing the frequency content of the signal and presenting impedance vs. frequency result data).

The starting point of this technique is to be able to generate a smooth waveform that contains a number of sine waves at different frequencies that have been added together to produce the composite waveform. Figure 2 shows the result of adding just three sine waves (three frequencies) each starting with the same zero phase offset (i.e. the three individual sine waves each start at the zero amplitude point in the sine wave). The generated waveform contains three frequencies, (the fundamental plus two harmonic frequencies – 1 x, 3 x, 5 x the fundamental frequency). If this waveform were applied to a cell, it would be possible to measure the impedance of the cell at these three frequencies. This particular measurement would be over a quite restricted frequency range due to using only three closely spaced frequencies (for example 10 Hz, 30 Hz and 50 Hz), usually many more frequencies are required and over a much wider frequency range, but this simple waveform shows some of the principles of the technique.

One problem is that the generated waveform in figure 2 has quite large peaks which may cause problems for many electrochemical cells since this might start to excite non-linear response from the cell. Ideally the peak values need to be minimized so that any non-linear response from the cell is also minimized.

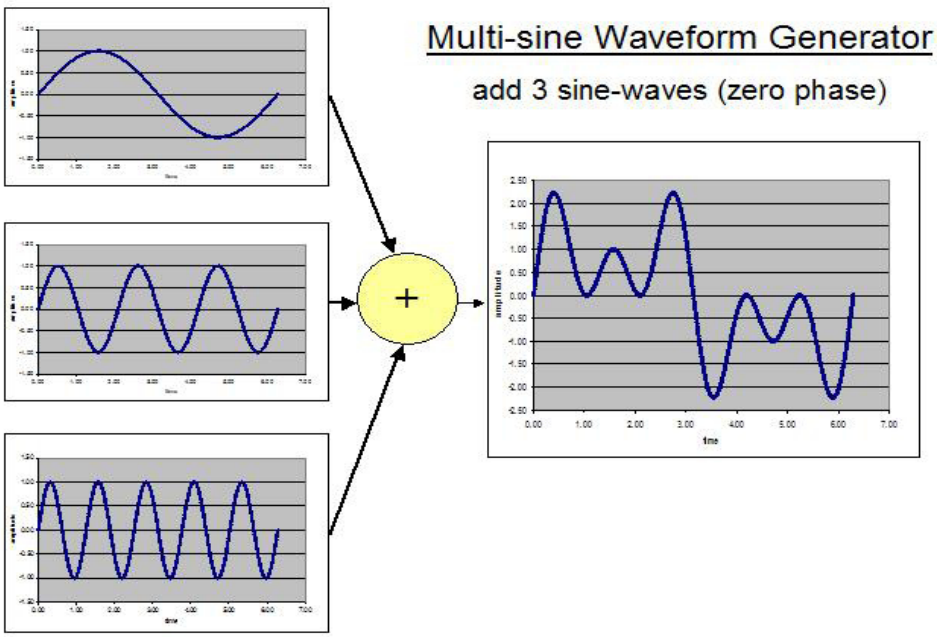


Figure 2: Three harmonically related sine waves with ZERO phase added together

The problem with non-linearities in the cell is that this is usually seen as harmonic distortion which could cause harmonics of the lower frequencies to interfere with measurements at other frequencies. By measuring some of the frequencies that were not stimulated, it would be possible to identify how much distortion the electrochemical cell is producing and make some decisions about whether the amplitude of the applied signal is appropriate (we will return to this idea later). In any case, non-linearity in the measurement needs to be avoided since in the presence of non-linearity, impedance measurements are simply not valid.

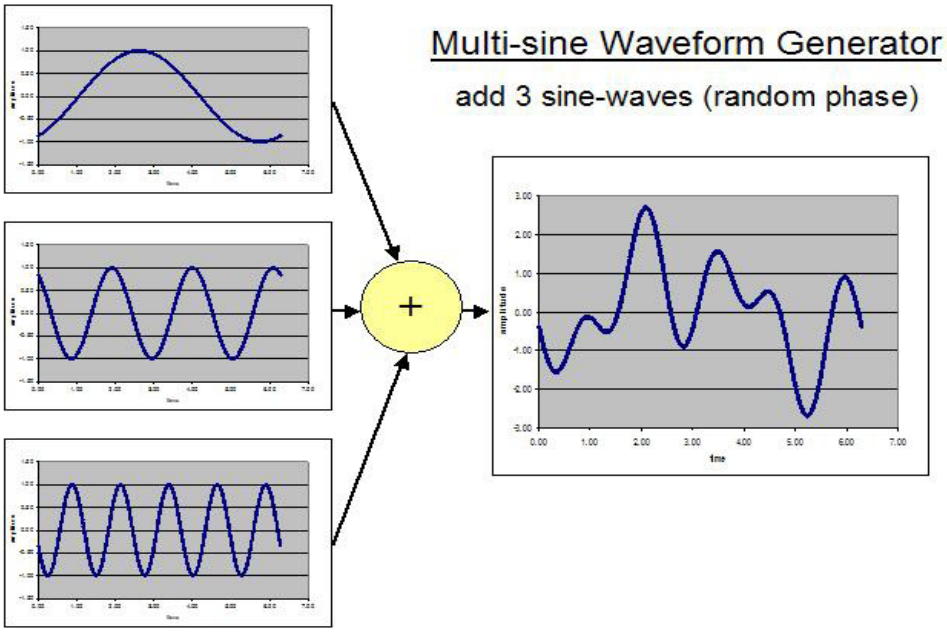


Figure 3: Three harmonically related sine waves with RANDOM phase added together

By randomizing the phase of the three sine waves (the three waveforms now start at non-zero amplitude levels and are now even moving in different directions), a quite different, more random waveform may be produced such as that shown in figure 3. By selecting different random phase values, an infinite variety of waveforms can be produced, some of which look more random in character or have larger peaks or are simply smoother. By suitable phase optimization the peaks on the waveform may be much reduced compared to the original waveform.

The ModuLab FRAs provide complete flexibility and allow the user to select all frequencies if required (though this would give more than one thousand frequencies in the final waveform and would result in very low signal amplitude at each frequency and therefore much noisier results). It is much better in practice to reduce the number of frequencies in the waveform and therefore have a higher signal level at each frequency. In addition, it is usually preferable to use a list of frequencies that are close to being logarithmically spaced since impedance results, when viewed on a logarithmic frequency axis graph, would then appear evenly spaced. The default frequency list provided by the system of thirty-one frequencies logarithmically spread over three frequency decades takes all of these considerations into account and is therefore a good starting point which may be customized if required. This usually provides a smooth impedance curve with minimal noise on the results.

4.2.2. Choice of AC level and non-linearity checks

It may be beneficial to use slightly higher AC level for multi-sine / FFT analysis, since due to the number of frequencies being stimulated by the multi-sine waveform, there is less signal level at each frequency which may tend to give noisier impedance results. However, increasing the signal level should be done with great care making sure that the cell is not being over-driven and is not operating in a non-linear regime.

One way of checking for non-linearity in the results is to apply the multi-sine waveform at the required amplitude and instead of capturing only the stimulated frequencies, capture all frequencies by selecting the “measure non-stimulated frequencies” mode of operation in the ModuLab software. In this case

all frequencies are measured. The results may then be exported into Excel to allow the non-stimulated frequencies to be examined. If the non-stimulated frequencies are relatively low level compared to the stimulated frequencies then the cell is operating in a linear mode, but if the non-stimulated frequencies are of significant level compared to the stimulated frequencies, then the cell is behaving in a non-linear mode and the stimulus level should be reduced. This is a very useful diagnostic test for signal non-linearity. Harmonic analysis is also used in corrosion applications and can provide corrosion rate information.

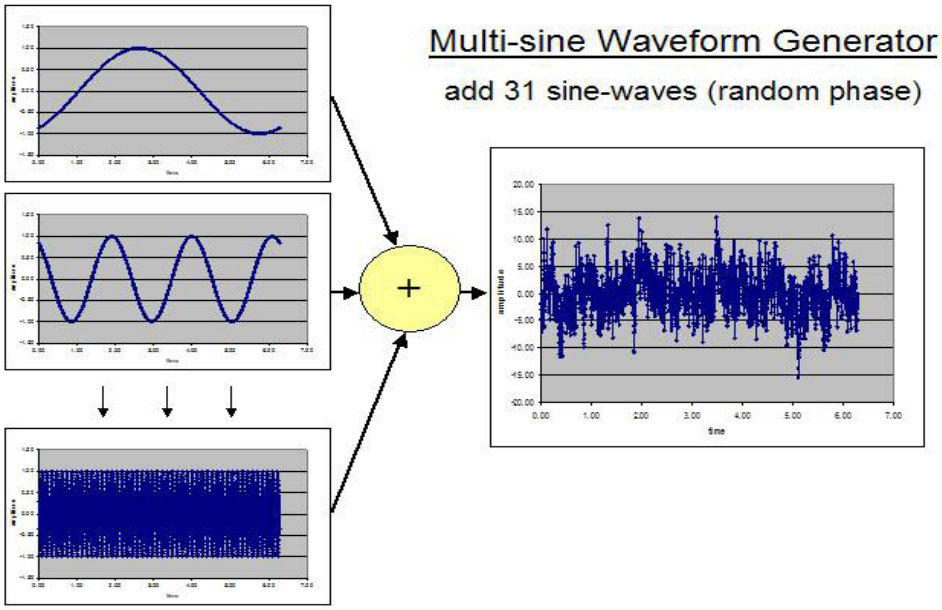


Figure 4: Thirty-one harmonically related sine waves with RANDOM phase added together

The ModuLab FRAs allow the user to select any list of frequencies in the measurement range, but best results are usually obtained by selecting frequencies where harmonics of one frequency interfere as little as possible with other frequencies that have been selected. The ModuLab system assists the user, by providing a default frequency list that may be used if required. By selecting a number of frequencies (for example the default frequency list) it is possible to produce a waveform that looks very much like random noise but in fact still contains only the frequencies that were selected. By optimizing the phases it is possible to produce a waveform that has reasonably low peak amplitude (see figure 4).

4.3 Other important requirements for impedance measurement systems

4.3.1 Smooth continuous applied AC waveform

Whether using single sine or multi-sine / FFT modes of operation, It is important to have a smooth continuous AC waveform applied to the cell. At low frequency, the ModuLab FRAs generate waveforms with over 200,000 points per cycle of the waveform ensuring that the cell sees a pure AC waveform. At high frequencies, the waveforms are produced at least 40 x the maximum measurement frequency and analogue filtering is applied so that these waveforms are also very pure.

4.3.2 DC bias rejection

The ModuLab FRAs have their own built-in automatic bias rejection facilities that remove DC from the signals to be measured (the signal from the potentiostat current to voltage converter representing the AC current through the cell and the buffered signal that represents the AC voltage across the cell). This is especially important if attempting to measure the impedance of a battery or fuel cell while it is under high DC current load conditions. Once the DC bias has been rejected, the FRA can measure on a more sensitive range, reducing result noise and improving accuracy.

4.3.3 Multi-channel capability

In the race to develop better products, whether they are batteries, fuel cells, sensors or corrosion corrosion protection devices, the ability to test more cells in parallel is becoming ever more important.

In addition, measurements taken at the same time offer the possibility to test cells in exactly the same environmental conditions.

Facilities such as auxiliary channel impedance measurement offer the opportunity to test whole cells or electrodes within a cell, or to test cells within a fuel cell stack (other Solartron technical notes are available that give more information on this capability).

4.3.4 Frequency resolution

The ModuLab FRAs have very high frequency resolution due to the use of a purpose designed 26 bit frequency synthesizer. This gives the ability to zoom into any frequency range to obtain detailed results almost without limit. This is ideal for tests on quartz crystal microbalances (QCM) where the resonance frequency gives information about deposition film thickness.

4.3.5 Bandwidth

It is worth remembering that the frequency bandwidth of any impedance measurement system is only as good as its most limited component. Often manufacturers specifications quote the bandwidth of only one element of the system (quite often this is the voltage measurement electrometer, which is usually the component with the widest bandwidth). This can give the false impression that the whole system has very wide bandwidth. Another way that specifications are sometimes presented is to only quote impedance accuracy at one or two particular impedance levels (which happen to be the best impedance levels for that system). It is important to investigate the bandwidth of the test system for the particular impedance levels that are to be measured (for example, it may be less than a few hundred mΩ for batteries or fuel cells and that is often not quoted in specifications).

Another type of impedance specification to watch out for is one that indicates a constant accuracy for all impedance levels and frequencies being measured, this is very unlikely since in all cases electronic amplifiers operate best in the middle of their range and operate less well at very high frequency or at the bottom of their amplitude range (which occurs at extremely high or low impedance levels). Solartron products always give a detailed accuracy specification to allow assessment of whether the equipment is suitable for particular measurements.

5.0 Summary

The new ModuLab system from Solartron, is a major step forward in testing technology which will lead to even faster development of new battery, fuel cell and electrochemical devices.

Technical note

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Solartron Analytical's Quality System is approved to BS EN ISO 9001:1994

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