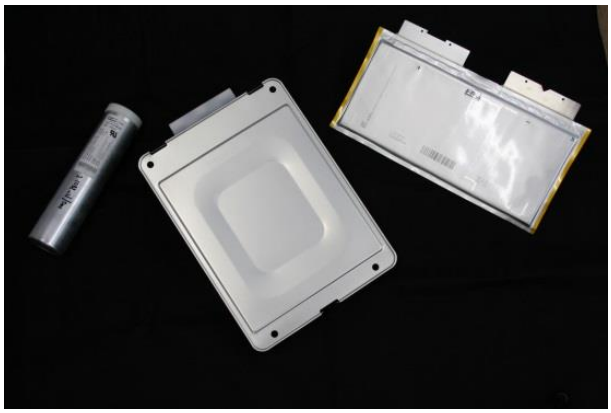
ELIBAMA

EUROPEAN LI-ION BATTERY ADVANCED MANUFACTURING FOR ELECTRIC VEHICLES



Non-Destructive-Testing

Development of a rapid, non-invasive technique, for testing Li-Ion batteries

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Introduction

Assessment of the viability of large Li-ion batteries either as a quality control exercise, or for end of life estimation, is a technology with significant research challenges. Non-destructive-test (NDT) techniques for viability assessment include simple calendar aging for static self-discharge assessment and time consuming capacity assessment through observing Voltage-Current (VI) charging characteristics. The automotive Li-ion cell industry is expected to be a major growth market in the coming decades. Therefore, there is a clear commercial case for the development of a *rapid* NDT to avoid prolonged storage of cells under viability assessment. However, the issues with protecting IP can lead to difficulties in developing a single analysis tool/technique for multiple manufacturing partners. This is especially true if the method requires detailed knowledge of the underlying chemistry or manufacturing process.

For this reason, ELIBAMA partners Newcastle University, Renault, SAFT, and Daimler have collaborated to develop a NDT technique that is intended to be manufacturer non-specific. The commercial partners all have an interest in developing NDT schemes; however, each have isolated production technologies and this presents an interesting research challenge for Newcastle University. After initial consultation, the task was defined as follows:

> *"To define a non-destructive testing technique, initially a prototype for testing on sample cells, but which is applicable and may be configured for multiple, different cell chemistries"*

After further discussion, the following key aspects were defined as important metrics for the test:

- *Based on empirical measurements* – the NDT should be able to determine the viability of a Li-ion cell by external measurements alone. Interference with the cell is not permitted, and special knowledge of the internal chemistry of the cell is not to be used.
- *Pass/Fail result* – a simple viability test is required to ensure sub-standard cells do not leave the production line for use. Importantly, identification of the failure mode of the battery is not necessary at this stage
- *High test accuracy* – regardless of the method used, the technique should correctly determine the viability, or non-viability, of a cell with a good degree of confidence.
- *Test time* – a rapid test is required. Initially, a target test time of less than 1 minute was specified.

To achieve the measurements required industrial partners Renault, SAFT, and Daimler provided sample cells to Newcastle University. These allowed Newcastle University, in collaboration with all industrial partners, to research and develop a robust Non-Destructive Test technique.

Techniques for monitoring Li-Ion batteries

Fully assembled Li-ion batteries have a limited set of measurable properties. In open circuit configuration only the cell open circuit voltage (OCV) and case temperature can be measured. Dynamically, the terminal voltage and any current which is flowing through the cell can be measured over time. With this in mind, following an extensive literature review into the topic, three potential Non-Destructive-Testing techniques were considered.

1. Real-Time monitoring of self-discharge

Excessive self-discharge of cells is a common indication of a cell which is deemed faulty. Therefore, initially a method for measuring self-discharge of cells in a short period was examined. Using a digital data logger (Agilent 34970A) the cell voltages of two sample cells from 'Partner A' were measured over time. The sample time was set to 60 seconds. The self-discharge was measured over 24 hours at three temperatures; 0˚C, 15˚C and 30˚C. Typically, the difference in self-discharge rate was observable within an hour. A normalised self-discharge plot is shown in figure 1; the blue trace is from a known viable cell, whilst the red plot is from a non-viable cell.

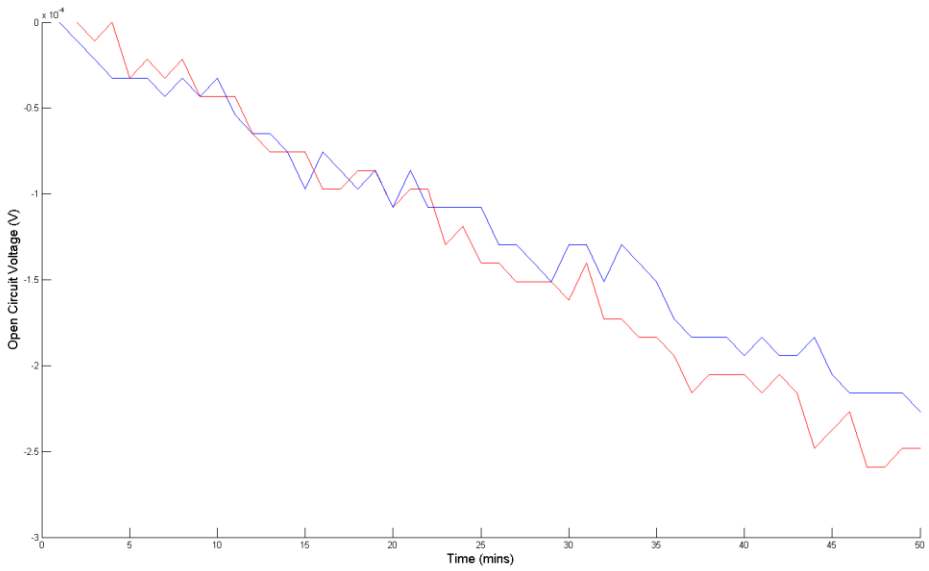

Figure 1 - Normalised self-discharge of 'Partner A' cells at thirty degrees C

Monitoring self-discharge has been shown to be discriminative in the tests. However, the overall test time is still quite significant. It is suggested that the time could be reduced by increasing the sampling frequency. However, the accuracy of most instruments and their ability to reject noise on such measurements is often limited. Therefore, it is expected that the minimum time for such a test would still be in the order of tens of minutes. An advantage of this technique is that it is relatively inexpensive to implement and can measure many cells in parallel. However, because of the more challenging test time target in this project, this technique was pursued no further than for demonstration purposes.

2. Active Perturbation

Active perturbation of the system (cell) allows an active measurement of response. Simple charging and discharging the cell can lead to measurements for capacity and to some degree internal resistance. Such

techniques can be applied for non-destructive testing, however, in the main they are again time consuming and do not meet the test time target for the ELIBAMA project.

3. Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) is a technique which analyses the AC impedance of an electrochemical system. Typically, the data is presented via a Nyquist Plot which displays Real versus Imaginary impedance. Figure 2 shows a typical characteristic plot for a Li-Ion Battery. The impedance spectrum of a Li-ion battery can be used to determine a number of properties of the cell from an electrochemical perspective; however, it can also be used as an electrochemical signature which gives the ability to discriminate between viable and faulty cells. The principal reasons for employing EIS as the measurement technique for the purposes of this task are that it can be achieved relatively quickly – particularly for high frequencies – and also that a large number of data points are produced which helps to reduce potential experimental errors.

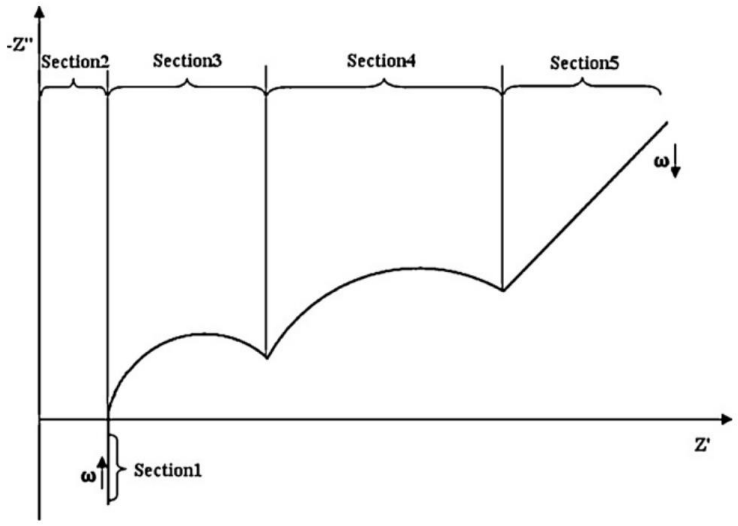

Figure 2 – Typical Nyquist plot for a Li-Ion Cell.

Development of a Non Destructive Technique for Li-Ion Batteries

After a careful review of the aforementioned techniques, Newcastle University chose to research and develop the proposed NDT based upon EIS methods. Theoretically, if cells are manufactured perfectly then they will all have identical impedance spectra. However, physical differences between cells, for example due to contamination, or manufacturing tolerances in the production process, have electrochemical signatures within the impedance spectra. If an "*ideal*" spectrum is known then a test cell can be compared to the known "*ideal*" spectrum and a determination can be made as to whether the test cell's actual impedance response is analogous to the target spectrum. A tolerance band can be envisaged whereby if the test cell's response falls within a certain distance from the target then it is deemed to be viable. For the proposed NDT, a target profile is generated from a mixture of immediate measurements of the test cell (to ascertain cell SOC and temperature) and from a library of lookup table data which is created offline. EIS results can vary significantly with temperature and state of charge (SOC). Therefore, the test cell's temperature and SOC must be known and a library of the target impedance spectrum must be available for the measured temperature and SOC. In order to generate a lookup table a representative set of measurements needs to be made on cells which are known to be viable. These measurements need

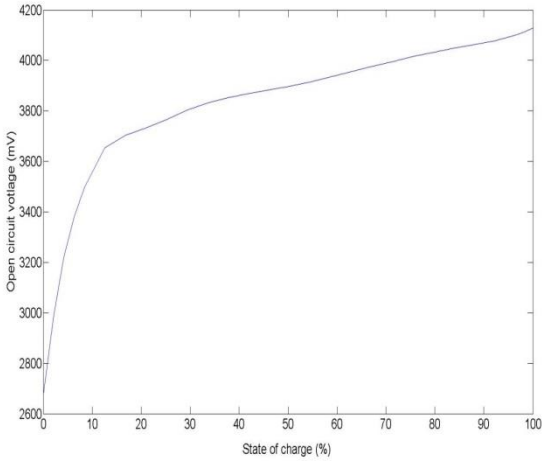

Figure 3 - Open circuit voltage profile of an automotive Li-ion cell

to be completed in such a way as that the test conditions (cell SOC and temperature) form a dataset which encompasses the expected range that a test cell may present at point of test. For the purposes of this task EIS plots were made at seven SOCs; 0, 20, 40, 50, 60, 80 and 100% SOC and at four temperatures; 15, 20, 25 and 30˚C. At rest, a battery's SOC can be calculated by analysis of the SOC vs open circuit voltage (OCV) relationship, an example of which is shown in **Erreur ! Source du renvoi introuvable.**. To avoid mechanical intrusion of the cells the assumption has to be made that the cells are at thermal equilibrium. This may result in the need to thermally rest cells before the test, but this cannot be avoided. A temperature measurement can be taken from the cell exterior to determine a value for temperature. For the purposes of this method the absolute values of temperature and SOC, at which sample impedance spectra are measured and stored in the library, are used. This enables a filtering, normalizing and weighted normalizing approach to the sample data to create a single target spectrum for any SOC/temperature combination within the bounds of the library data. A visual representation of the library structure is shown in **Erreur ! Source du renvoi introuvable.**.

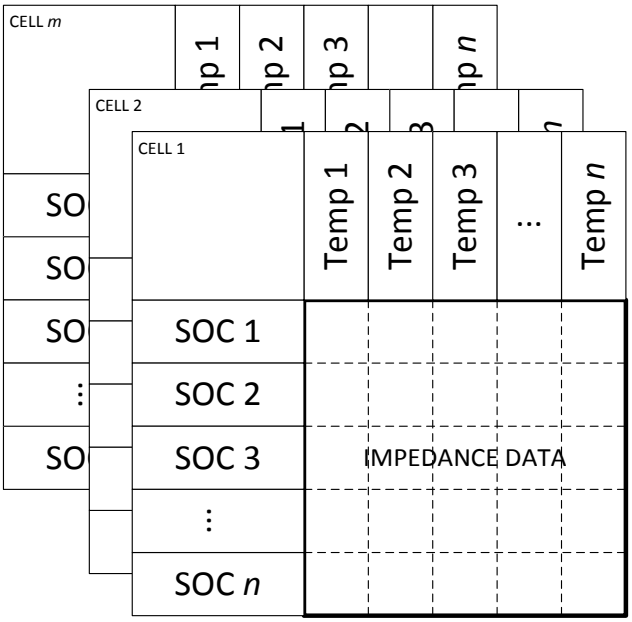

Figure 4 - Representation of sample data library

In order to generate a projected response the library boundary data must be pre-processed and averaged before being interpolated using the weighting factors. Figure shows the raw EIS plots obtained at a specific temperature and SOC from 8 viable cells. The raw data shows good coherence in the shape of the plots; however, there is a discrepancy in the real axis in the range of 1 mΩ. This similarity in shape and

discrepancy in real axis locations represents a dispersion of Ohmic resistance but conservation of reactance response.

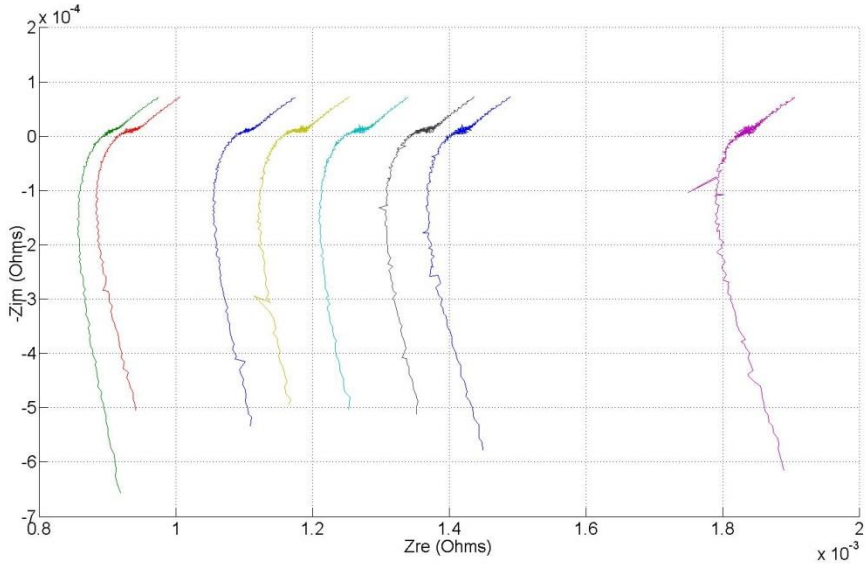

Figure 5 - Unprocessed EIS plots of eight viable cells

In order to process this data meaningfully to provide an averaged response all plots are normalized in respect to the real-axis by subtracting the real component from each response separately using the value of the interpolated real-axis crossing point. This has the effect of shifting each of the plots uniformly in a negative real direction so that they each cross the real-axis at the origin. This processing clearly has no physical meaning; it is simply a mathematical process to enable an averaging of the response to take place. Each response is then filtered to remove noise. The resulting processed profile for the same initial data in Figure , is shown in Figure .

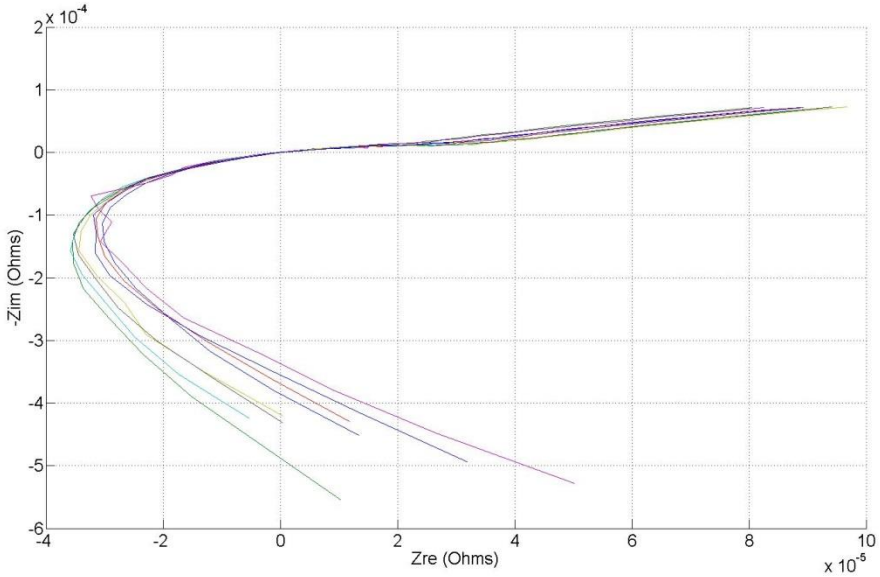

Figure 6 - Normalised and filtered responses

The capacitive region of the plot now shows good correlation between the responses and a mean impedance can be calculated for each frequency point to obtain a single averaged response which will be used as the expected response of a cell at the given SOC and temperature. With this approach the processed results allow for good detection between viable and non-viable cell, as is shown in Figure . Here, we contrast the processed EIS data of 5 viable and 5 non-viable cells with a particular (unidentified) problem. The difference in the characteristic behaviour of good and bad cells is now very noticeable.

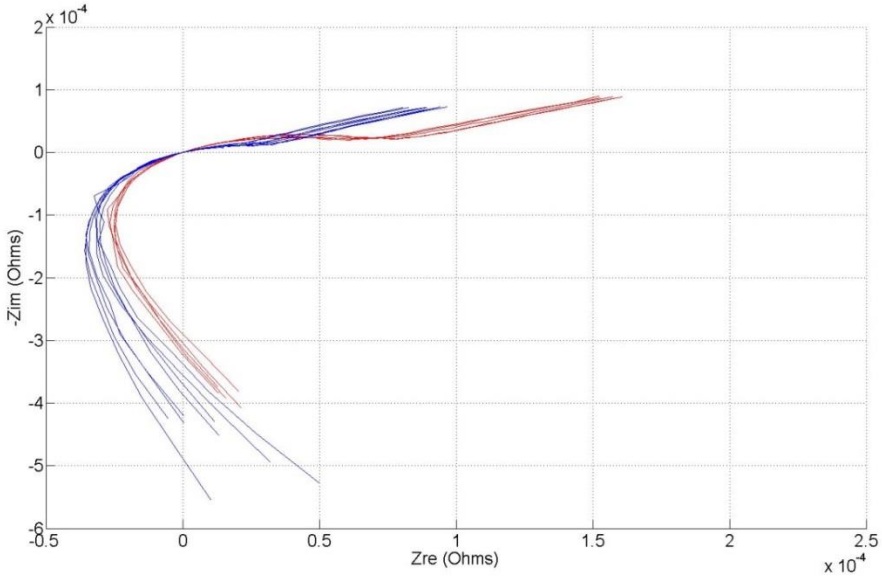

Figure 7 - Normalized and filtered responses of viable (blue) and non-viable cells (red)

In Figure 8, the response of the 5 non-viable cells is compared to the single averaged response of a viable cell; as calculated using the technique previously described. The results clearly show that it is possible to detect a difference between the responses of non-viable cells and the calculated viable cell profile. This demonstrates the feasibility of using EIS measurements to create a background library, data processing to create a benchmark average expected response, and a full EIS sweep in order to differentiate between viable and non-viable cells – this essentially defines the NDT. During actual testing, the SOC and temperature of the test cell must be measured before the known target response can be deduced; this will be a viable cell's expected response, based on the library data, for a given manufacturers test cells. Unfortunately, in practice, the chances of the SOC and temperature measurements matching exactly those used to generate the library profile are very slim; some discrepancy is likely. Dependent upon the situation, it may be possible to simply approximate to the nearest available response in the library. However, recalling that EIS results are very sensitive to temperature and SOC, such a crude approximation may lead to a greater chance of misdiagnosing the viability of the cell. This is highly undesirable, given the initial targets of the NDT. To avoid this problem, there are two potential solutions. Firstly, one can increase the number of profiles available in the library. This helps to reduce approximation errors, but is unlikely to eliminate them. Furthermore, there is an increase in potential development time as additional profiles need to be generated. Secondly, one can consider a solution involving an interpolation and weighting algorithm; based on SOC and temperature variables. Such an algorithm can also take into account the non-linear behaviour of the cell characteristics. Newcastle

University chose to research and develop such an algorithm as overall we found that it significantly improved the fault detection capabilities of the NDT system.

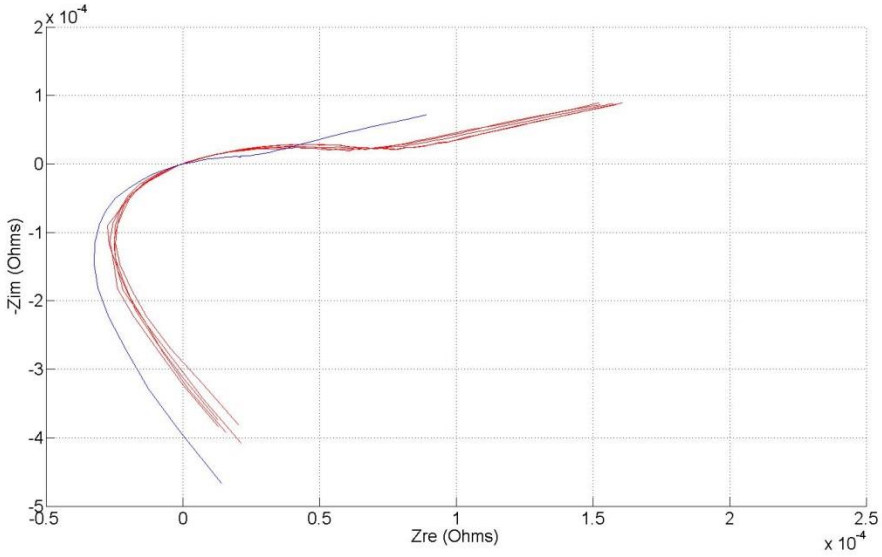

Figure 8 - Measured response of five non-viable cells (red) and calculated response of viable cells based on empirical library

NDT System Refinement and Improvement

The frequency range of the plots shown so far is from 1 kHz to 100 mHz. The measurements which are made to create the library database are made within this bandwidth logarithmically spaced with 100 points per decade. The filtering process includes a decimation step which, for the case of all normalised plots shown is a factor of eight. In total, the amount of time to measure all 400 data points (a single sweep) and to process the results to get the normalised response is around 570 seconds. It is clearly desirable to reduce this time significantly – the target test time for this work is less than 60 seconds. However, during the research it was found that this test time target was the most challenging criteria to achieve without impairing the accuracy and reliability of the test. Obviously, compromising on accuracy and reliability was not permissible in this work, a high confidence NDT was essential.

Ultimately, a method to reduce the number of required measurement points was required to shorten the test time. In the case of the measurements presented so far in this paper, a series of non-viable cells is assumed to have the same failure mode. This being the case, the responses of the non-viable cells are shown to be similar (as initially shown in Figure). Therefore, the response of the non-viable cells can also be stored in an identical library to the viable cells and processed to produce a normalised, averaged response of non-viable cells using the same method previously described. By doing this, two averaged expected responses can be produced, as shown in figure 9. The upper frequency limit is chosen to be definitely within the positive imaginary plane of the response. This ensures that the real-axis intersection point is not omitted from the spectra. Although the lower limit chosen is relatively high for EIS experiments on such cells; the actual value selected is strongly influenced by the strict NDT time limit imposed upon it.

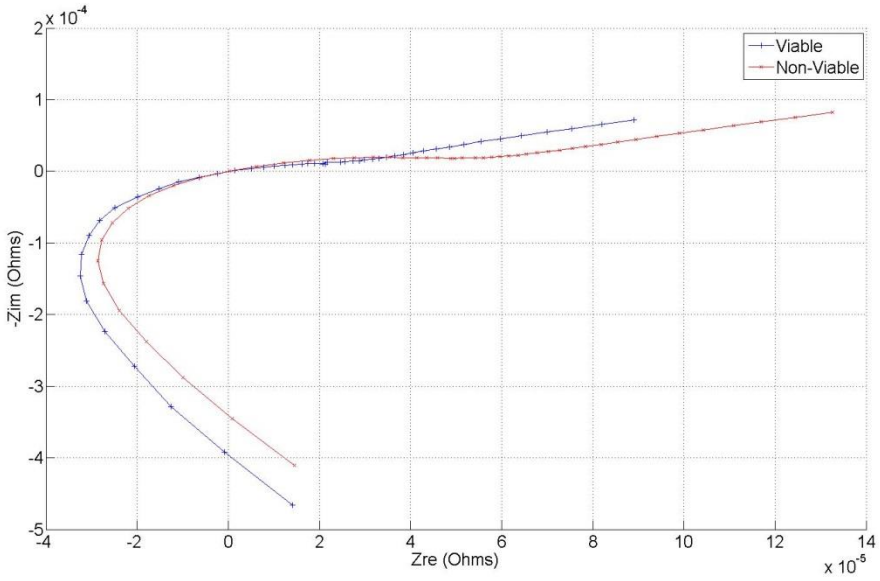

Figure 9 - Normalised and averaged plots of both viable and non-viable cells

In order to gather a range of impedance readings within a short timespan (<1 min) the length of one period of the excitation frequency becomes a limiting factor. At 0.1 Hz the period of one test is 10 s and it is common practice for this test to be repeated at least once. It was decided that a minimum of six readings would be required; meaning that 0.1 Hz is the lowest decade in which six measurements can be recorded in less than one minute. In its basic configuration the potentiostat used is able to make single-sine measurements in frequency bands defined by the experimental parameters. A band selection process is then used by sweeping a window of m frequencies across the entire projected frequency response of both non-viable and viable cells.

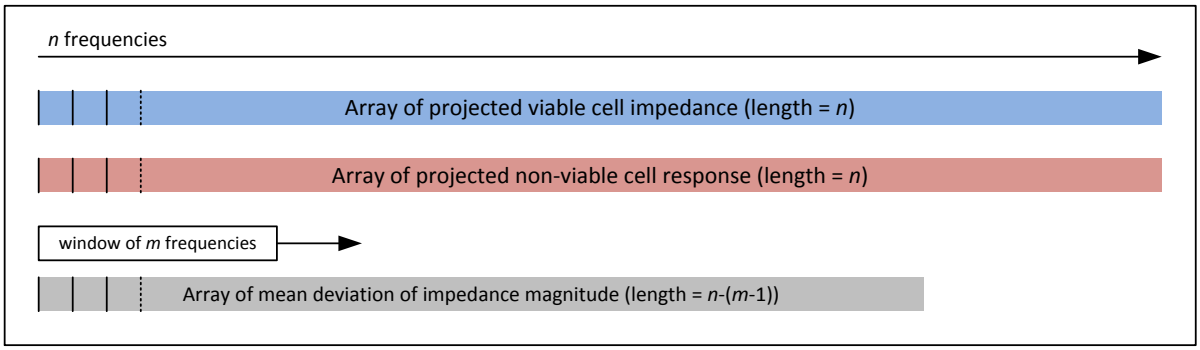

Figure 10 – band selection process

Considering figure 10, a frequency spectrum with n frequency responses from f_0 to f_n, and a frequency window which is m frequencies wide, an array can be constructed to show the mean difference in impedance magnitude between viable and non-viable within the window. This averaged array can then be sorted by magnitude and the window at which the greatest average dispersion of absolute impedance exists in the data set is identified. This window is then used as the frequency target window for use in the online test. The applied frequency range is therefore only m frequencies wide but is targeted at the range

of response at which the deviance is expected to be greatest; this significantly reduces the test time whilst actively searching for the most accurate area of the response. The targeted response of failed and passed cells is shown against the projected response of a viable cell is shown in Figure 11. If the result is inconclusive then a wider window can be attempted or the whole range can be used. This multi-level approach to the testing allows for greater tuning to avoid false results. Should the result of the test be inconclusive then a wider window can be attempted or the whole range can be used. This multi-level approach to the testing allows for greater tuning to avoid false results whilst minimizing the test time.

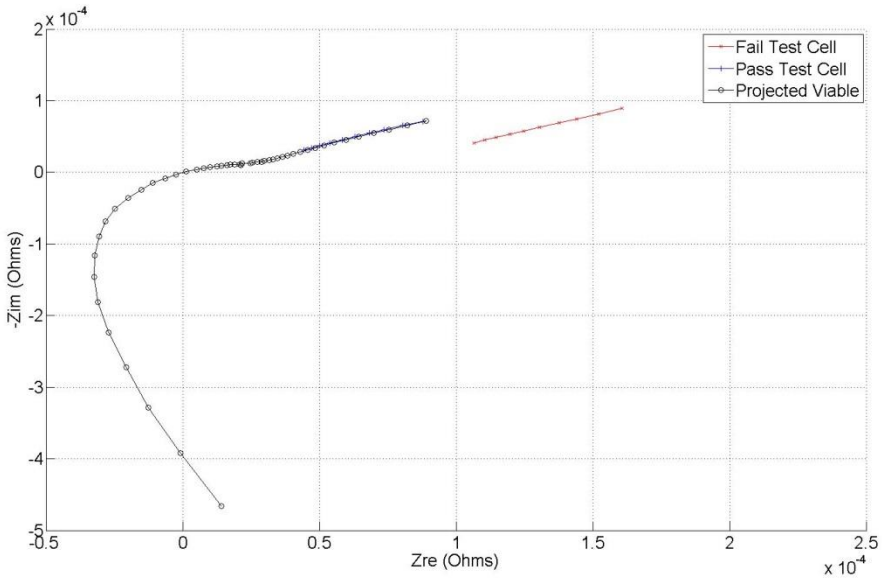

Figure 11 - Frequency targeted response of failed and passed cell compared to full projected response

Practical Implementation of the NDT Prototype

A prototype was constructed and programmed using the above theory to create a practical realisation of the envisaged NDT technique. Most of the hardware used to perform the measurements is readily available from a number of equipment manufacturers. Since this technology readily exists it was not considered appropriate to develop bespoke hardware for this task. Furthermore, readily available hardware and the associated manufacturer support and warranty, was considered a distinct advantage for the longer term industrial uptake of the system. Instead, a larger proportion of the technical innovation exists in the data processing of the library and measured response from the test cell. The prototype therefore consists of a computer, EIS capable potentiostat and the test cell as depicted in **Erreur ! Source du renvoi introuvable.**.

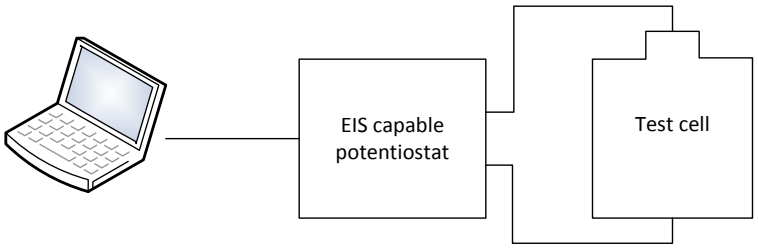

Figure 12 Prototype NDT system

Figure 13 Photograph showing NDT apparatus and environmental chamber

A photograph of the prototype as developed in the laboratory is shown in **Erreur ! Source du renvoi introuvable.**. The interface with the instrument was achieved through use of a LabView virtual instrument program. The function of the LabView program is to provide a usable interface for the operator and to coordinate the communication with the potentiostat. The potentiostat used was a Bio Logic HCP1005. The labView VI coordinates the communication to the instrument using a modified version of the EC-lab development package provided by Bio Logic. Some basic data manipulations are accomplished within the VI however the majority of the data processing is carried out using embedded Mathworks MATLAB functions. A screenshot of the application is shown in Figure .

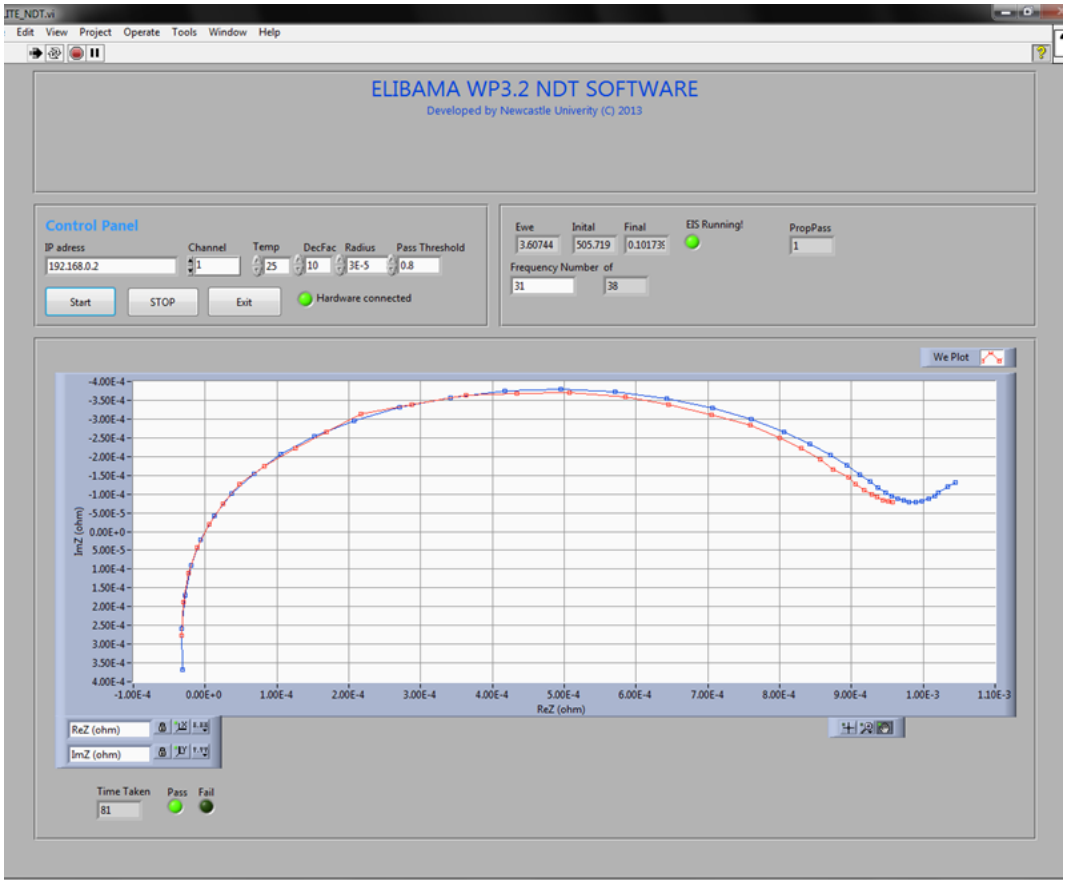

Figure 14 - Screenshot of NDT LabView based application

The user inputs test parameters into the control panel; the IP address of the instrument, the channel number, a decimation factor controls the level of filtering of the library data, temperature is inputted manually, the radius input dictates the tolerance band around the target profile and the pass threshold dictates the percentage of measured points that must fall within the tolerance band for the cell to indicate as passed. The control panel has controls to start and stop the test as well as to exit the application. To the right of the control panel is some information which is being used to indicate the test result. Ewe shows the OCV of the test cell, the frequency range that is being used for the test and the number of points (they are always logarithmically spaced) as well as the current test frequency. The PropPass result shows live the percentage of points which fall within the tolerance band. The Nyquist plot shows the target (blue) and measured (red) profiles in real time. The pass/fail indicators are shown below the chart and there is an indication of the time the test has been running for. The NDT process steps are shown in Figure .

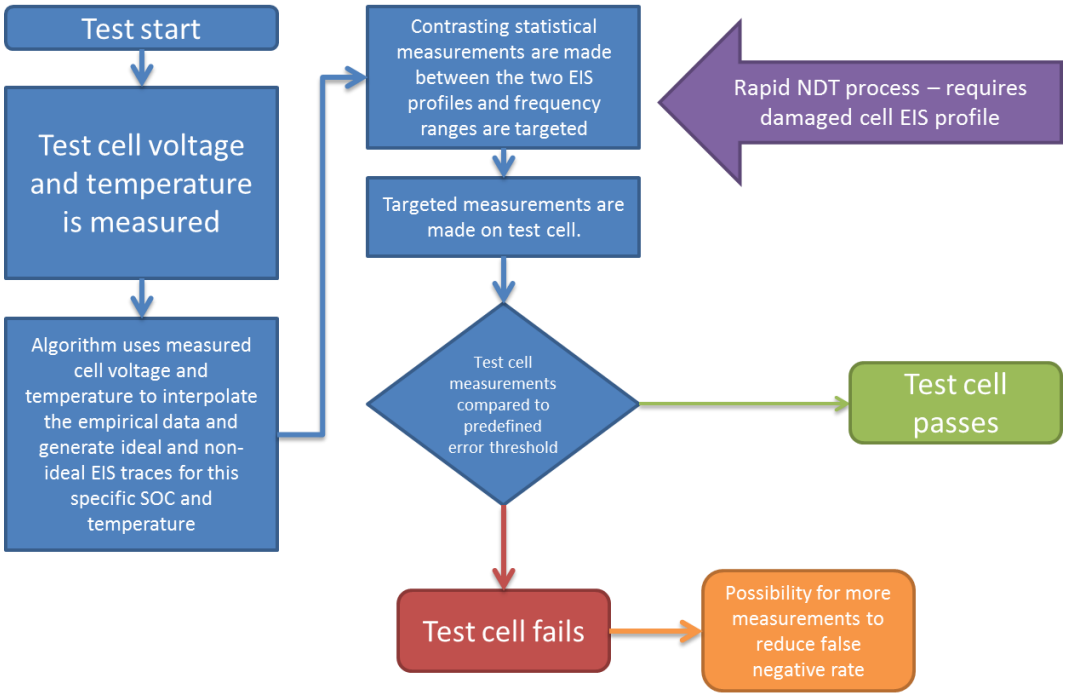

Figure 15 - NDT technique process steps

NDT Prototype performance

The prototype was tested using a number of sample cell sets for validation. In general, the performance experienced was very good. The test is highly accurate on all cell types over test time of up to 180 seconds. The test can be completed in less than 60 seconds by increasing the decimation factor and removing the lowest frequencies from the test; however, under these conditions the technique is significantly more susceptible to discrepancies relating to relaxation time. It was discovered that relaxation state was the primary source for erroneous results whereby the test can be run on the same cell without disconnecting it in the evening and then show a different result the following morning. When care was taken to ensure the relaxation state of the test cell matched that of the sample cell when the library data was captured this error was removed.

The method used for normalisation of the measured spectrum requires that a real axis crossing is measured. For the sample sets received this does not usually coincide with the range of frequencies targeted in the test. Therefore, the test must run all of the higher end frequency measurements down to the lowest required frequency. The test could not be modified to run two separate tests: one at higher frequency and one at the target frequency at the time of writing. This was due to limitations in the commercial software package. However, this is being addressed and a modification should be made possible in a future version. The overall effect of this is to extend the test time. However, the time taken in the higher frequency range only accounts for a small period of the test since lower frequencies necessarily take longer to measure.

Conclusions and Recommendations

The developed technique has been shown to rapidly discern between cells with known electrochemical behaviour discrepancies. The prototype is shown to be accurate with all sample cells provided by the industrial partners in under 180 seconds. The target test time of less than one minute can be achieved by frequency targeting techniques. However, careful attention must be paid to the accuracy of the test when using decimation techniques - the more informative part of the impedance spectrum is at lower frequencies and these take longer to process. The condition of the test cells has been shown to be very important when considering relaxation time. Therefore, it is recommended that the library is created using cells which are precisely in the same condition, in terms of relaxation state, as would be expected in the actual test. The various numbers of sample cells show that the fidelity of the library response is greatly improved through greater sample sizes. The recommended sample size for the library is therefore considerably higher than the numbers used in this work. A sample size in the numbers of tens would be considered to be the minimum for a scaled-up version of the prototype. The range of SOCs and temperatures used to create the library in this work was quite broad. Depending on the final application these ranges could likely be narrowed. A greater resolution in the library could be attained by making the same number of measurements at a smaller range.

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