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**E-Futures**

# **IMPEDANCE SPECTROSCOPY OF LITHIUM-ION CELLS**

**PRÉCIS OF MINI-PROJECT REPORT**

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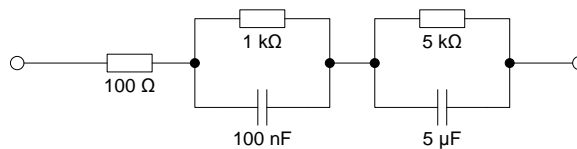


# 1. Introduction

Lithium-ion secondary cells have gained wide acceptance as commercial rechargeable batteries. Consequently, there is a large amount of interest in understanding the mechanisms which affect their capacity and life. One method of study commonly applied to cells to this end is impedance spectroscopy which involves the application of a fixed-frequency alternating voltage to the cell and the measurement of the cell's electrical impedance at that frequency. Analysis of the recorded impedances across a frequency spectrum yields useful information about processes and structures within the cell.

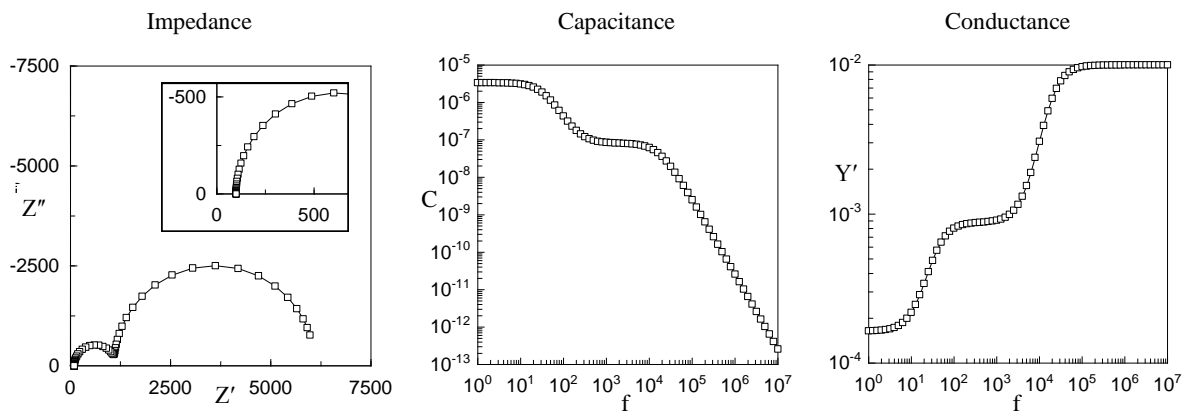
# 2. Impedance spectroscopy

Complex items, such as batteries, contain many areas of resistance and capacitance due to their physical structure and electrochemistry. Impedance spectroscopy is a tool used to characterise the equivalent circuit of the item by measuring its complex impedance across a spectrum of frequencies. It assumes that the item can be described as a network of parallel R-C elements connected in series, such as that as shown in figure 2.1 below.



**Figure 2.1: Equivalent circuit of series-connected parallel R-C elements**

At each frequency, a voltage is applied across the item and the resultant current is measured, both the component in phase with the voltage (the real component,  $Z'$ ) and the component  $90^\circ$  out of phase (imaginary  $Z''$ ). The number of elements and the values (which may be zero for capacitance or infinity for resistance) can be obtained by plotting various combinations of the components.



**Figure 2.2: Impedance, capacitance and conductance plots for simulated circuit**

This is a typical impedance plot and corresponds to the above circuit. It shows two superimposed offset semicircles. Each of these corresponds to an R-C element. The peak of each semicircle occurs when the imaginary part of  $Z$  is at a minimum ( $Z''$  is always negative for capacitive elements). This occurs when  $\omega CR = 1$ , therefore  $Z'' = -j\frac{R}{2}$ . Assuming each semicircle is independent, we can identify the elements to generate the equivalent circuit.

### 3. The Solartron 1250 and 1287

Analysis of many of the batteries was achieved using the Solartron 1250 frequency response analyser (FRA) and the Solartron 1287 electrochemical interface (ECI). The cell we wish to analyse,  $Z(\omega)$ , is connected to terminals on the electrochemical interface. The set up then applies a set frequency and amplitude sinusoidal voltage and, by measuring the voltage across and current through the cell, calculates the complex impedance to generate graphs like those above. A dc bias can also be applied. A computer programme was developed to control the devices and automate the process.

### 4. Lithium-ion secondary cells: results and discussion

Lithium ion cells developed in this project consisted of lithium metal anodes, lithium cobalt oxide cathodes and 1.0 molar lithium hexafluorophosphate dissolved in propylene carbonate electrolytes. The cells were fabricated in 25 mm aluminium coin holders. Cells were made using just the electrolyte, with two anodes (a symmetric cell) and as a fully functional cell.

#### 4.1. Impedance plots

An electrolyte cell was heated to a range of temperatures and its impedance was analysed, the results of which are in figure 4.1.

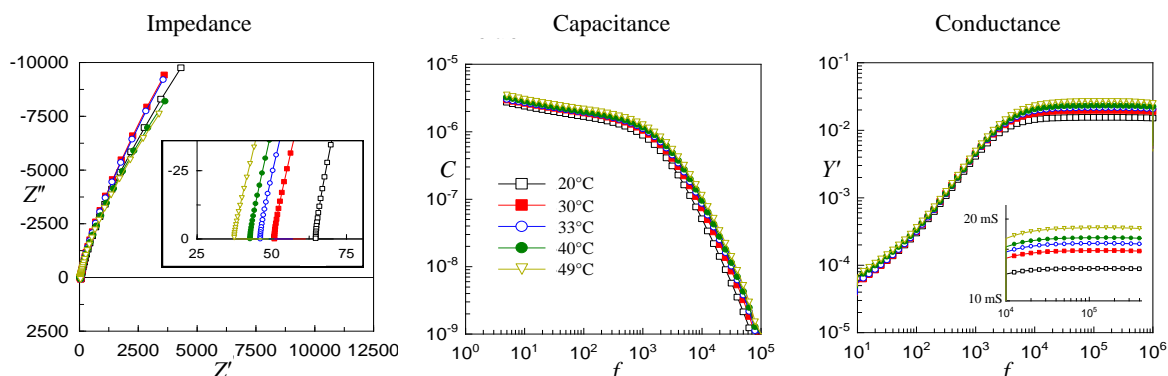
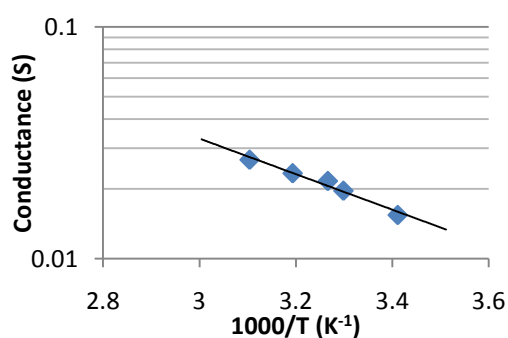


Figure 4.1: Impedance, capacitance and conductance of electrolyte cell at different temperatures



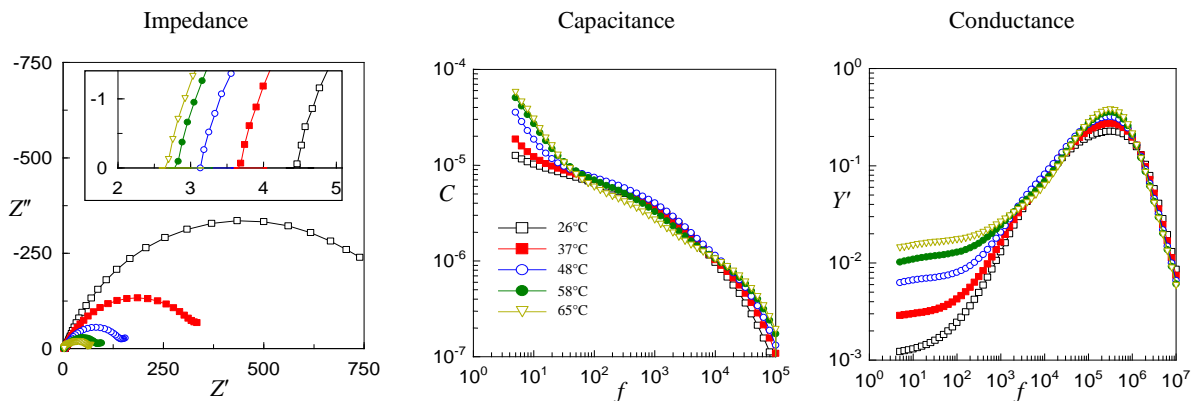
The impedance graph shows the beginning of a semicircle which is too large to be shown up on this scale (which goes down to 5 Hz). There is a temperature-dependent series resistance (see impedance inset and conductance plateau). The temperature dependency seen indicates this is likely to be the activation energy of the electrolyte and therefore the resistance relates to the electrolyte's resistance to ionic current. This value can be confirmed by an Arrhenius plot (left).

The activation energy is calculated from the gradient as follows ( $k$  is the Boltzmann constant)

$$E_{act} = -k \frac{\Delta \ln G}{\Delta \frac{1}{T}} = 86.2 \times 10^{-6} \times 552 \times 10^{-6} = 47 \mu\text{eV} = 4.6 \text{ J/mol} \quad 4.1$$

Differences in spectra are noted between cells and are put down to differences of geometry.

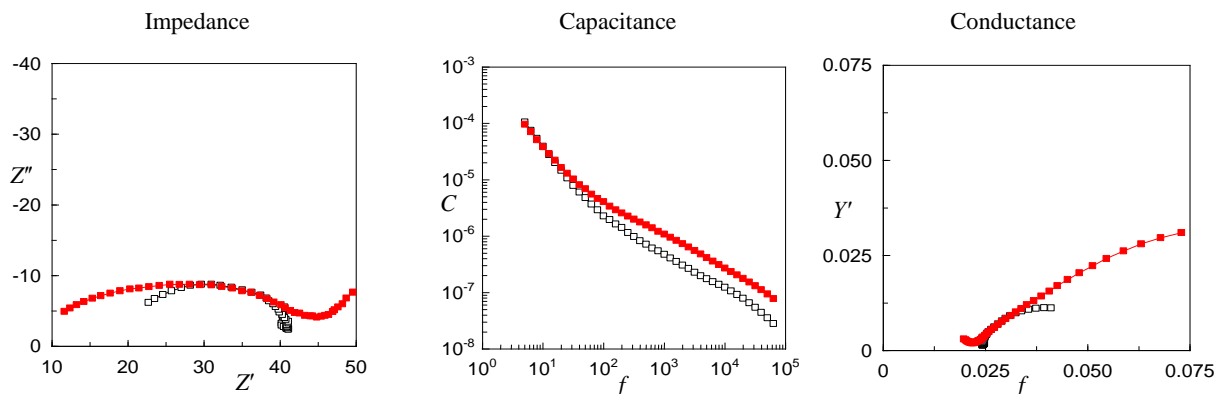
Symmetric cells of two anodes were analysed as shown in figure 4.2.



**Figure 4.2: Impedance spectra for two-anodes symmetric cell at various temperatures**

The cell is very similar to the electrolyte-only insofar as it consists of the same electrolyte between two metal contacts. It differs insofar as the contacts are lithium, not aluminium. The non-perpendicular impedance intercepts indicates that an inhomogeneous double-layer capacitance has formed. It is noted that with time, the double-layer effect increases (therefore the semicircles grown in size over several weeks); this can be removed by applying a temporary dc voltage.

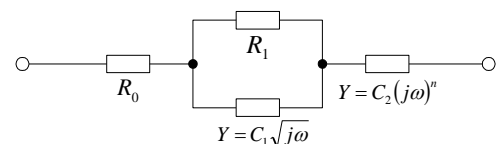
The analysis of the full cell is shown in figure 4.3.



**Figure 4.3: Impedance spectra of full cells**

Given that only two results are available, it is difficult to garner a large amount of information. Both impedance plots show the beginning of a spike at 50  $\Omega$ . This spike is at 45° which suggests it is due to the limited diffusion of ions. It is associated with a high capacitance indicating electrochemical charge storage. A high frequency smaller semicircle is also present and matches the double-layer capacitance observed in the incomplete cells. As with the other cells, the resistance at higher frequency is probably the ionic resistance of the electrolyte.

The equivalent circuit for the cell is to the right. Similar equivalent circuits exist for the electrolyte and anode; however, they do not have the rightmost element.



## 5. Recommendations for further work

Characterisation of all types of cells at a larger range of temperatures would give more data, including high frequency effects (which can be observed at low temperature). Simulating cell charge and discharge would allow ageing to be observed. Finally, the materials used here for anode, cathode and electrolyte could be compared to alternative materials to find the best.