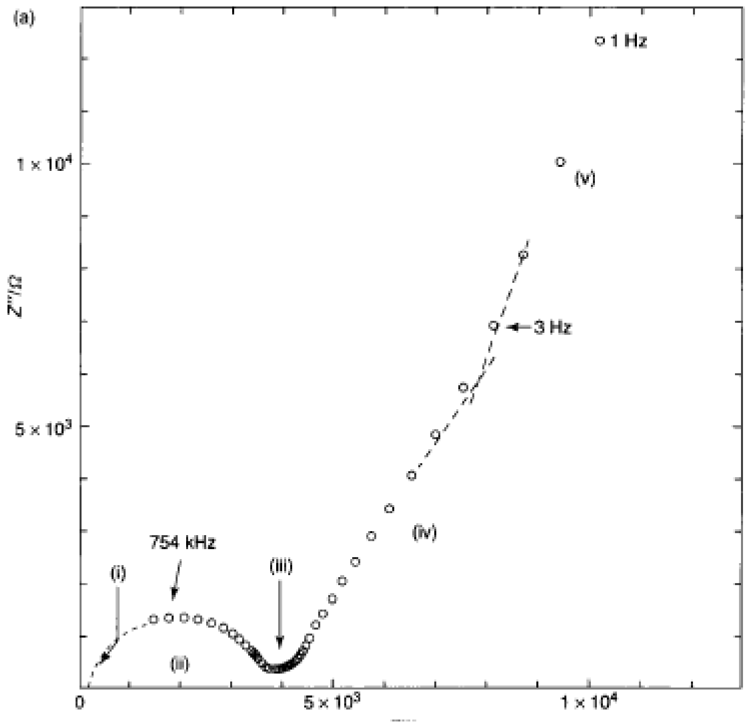
7)CASE STUDY
Impedances of Real Cells: Quantification
Impedance,i.e Warburg diffusion

To summarize the impedance discussion so far: an electrochemical cell is constructed, and its impedance **Z*** determined as a function of frequency.
From these impedance values, the real and imaginary impedances, Z' and **Z",** respectively, are computed and hence a Nyquist plot is drawn.
It is now time to look at the Nyquist impedance plot of a real cell. Figure (a) shows such an impedance plot for the all-solid-state cell,
ITO/$W0_3$/PEO-H_3P0_4/ITO(H) ,t at 8°C.
The two **IT0** layers are needed as transparent electronic conductors



This plot may be taken to consist of five regions, as follows:
(i) A high-frequency intercept arising in the main from ohmic resistances of the electrodes, but which also comprises the resistance of the leads and contacts.
(ii) A semicircular arc representing the polymer electrolyte (PEO-H_3 PO_4) layer.
(iii) Another (less well defined) semicircular arc corresponding to charging of the electrolyte-electrode interface.
(iv) A linear region inclined to an angle of c. **45^0** which indicates that diffusional processes of some kind are involved, e.g. of **H^+**moving through the WO_3.
This feature is termed a **Warburg impedance (Z_ω).**

(v) A steep spike suggesting **blocking** electrode behaviour, as below

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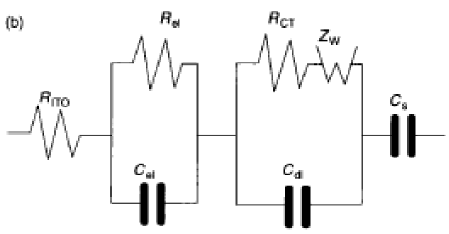
We recall that frequency drops as we go from the left-hand to the right-hand side of the plot. In other words, the impedances nearest to the origin were determined
at high frequencies.

The above features are assigned on the basis of a detailed examination of the experimental data, and by reference to the equivalent circuit for such a call



(a) Nyquist plot obtained for the all-solid-state cell, **ITO/W0$_3$/PEO-H3P04/ ITO** at **8^{0}C,** with the electrolyte being unplasticized. The WO_3 layer was 0.3 pm in thickness (as gauged during vacuum evaporation with a thin-film monitor), while the electrolyte thickness was 0.24 mm (achieved by using 0.3 mm spacers of inert plastic placed between the two **IT0** electrodes). (b) Schematic representation of the equivalent circuit for this cell.

. **We will now discuss each of these regions in turn.**

Region (i). First, we note that there is a slight offset near the origin of the Nyquist plot, as caused by the resistances of the IT0 layers, leads and contacts. We will call this an **ohmic resistance** because we do not know any further details about the features in the gap. Note that it is merely a 'gap' because the frequencies obtainable with the frequency analyser are too low, with the maximum of such an apparatus being usually about **lo6** Hz. Access to higher frequencies would have allowed this gap to be filled.
We will denote this resistance in the equivalent circuit as R_{ITO}.
Region (ii). The next feature to be seen in the Nyquist plot is the first semicircular arc, which falls at frequencies in the range 1 **MHz** > **w** > 50 **kHz,** and represents the polarization of the electrolyte layer.
Region (iii). After the semicircular arc representing the charging of the electrolyte layer, the Nyquist plot in Figure shows a second, much smaller, semicircular arc in the frequency range >50-80 **kHz.** This second arc is sufficiently

small that we merely see here a levelling of the trace between features (ii) and (iii). Accordingly, the apex of the arc is not easily to discern with any accuracy,

but falls at a value of about $\boldsymbol{\omega_{max}}$**~** 100 **Hz.** This feature represents the movement of electrons across the W03 I electrolyte interface.

Region (iv). This region of the Nyquist plot displays a linear portion at an angle of about 45^0 occurring at frequencies in the range 50 > **w** > 15 **Hz.** While the rate-limiting process was the movement of electrons in region (iii), in this region

of the plot, the rate-limiting feature is the movement of ions into and out of the solid layer of WO3.
We recall again that the frequency f decreases when passing from left to right on a Nyquist plot. As f decreases, so the cycle life **t** increases. Longer cycle lives clearly allow the ions a progressively longer time to diffuse into and through the solid layer of WO_3.

Question
Why should the movement of electrons across an interface generate a semicircular arc?
Answer
The double-layer consists *of* ions exposed with the electrode, so it resembles a plate capacitor - we will describe this in terms of its ***double-layer capacitance,*** $\boldsymbol{C_{dl}}$**,**
The movement of the electron is activated, i.e. it requires energy. Stated another way, movement is restricted - there is a resistance. We call this the ***resistance to charge transfer,*** R_{CT}. The latter parameter and ***Cdl*** behave as though being in parallel, and hence the appearance of the semicircular arc in the Nyquist plot.