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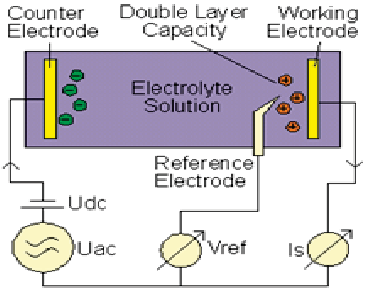
Electrochemical Impedance Spectroscopy (EIS)

In EIS the properties of the polarization layer at a metal to electrolyte or ion conductor interface and the related chemical reactions are of more interest than the bulk sample material which is the opposite to dielectric, conductivity or impedance material spectroscopy where these effects are known as electrode polarization which is unwanted and tried to avoid for example by 4-electrode arrangements.

Figure 1 shows a electrochemical 3-electrode measurement setup.

In addition to the two parallel plate electrodes (denoted as Counter and Working electrode), a third voltage reference electrode is placed close to the polarization layer and measures the voltage difference of the polarization double layer capacity to the working electrode. In contrast to dielectric, conductivity and impedance material spectroscopy where all electrodes are made of inert metal (e.g. gold, stainless steel or platinum) as this applies for the electrochemical cell only for the counter electrode feeding current into the electrolyte.

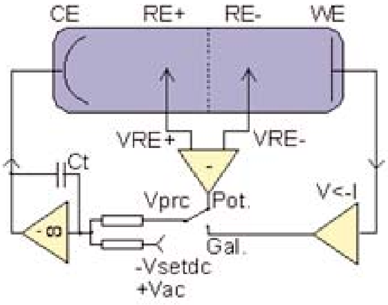
FIGURE 1



The working electrode consists of the metal to be characterized in combination with the electrolyte. The reference electrode is usually an open tipped glass capillary filled with a standard electrolyte coupled to a standard metal in order to create a defined electrochemical potential to the electrolyte.

The total potential drop across the cell is summed up by all contributions of the chemical process like mass transport, chemical and adsorption steps, electron transfer, etc. By measuring the impedance spectrum $V_{Ref}*(\omega)/I_S*(\omega)$ and fitting it with an equivalent circuit model, the several process contributions can be separated from each other. The typical evaluation includes determination of Warburg impedance related to mass transport, electron transfer resistance, electrolyte resistance and double layer capacity.

FIGURE 2



As an electrochemical reaction takes place on the working electrodes, it is necessary to keep the DC potential V_{Ref} at a defined value or alternatively apply a constant DC current to the cell. This can be done by a Potentiostat / Galvanostat DC circuit as shown IN Figure 2.

The voltage amplifier connected to CE electrode compares in potentiostat mode the differential voltage $V_{Prc} = V_{RE+} - V_{RE-}$ of both reference electrodes with the intended voltage V_{setdc}.

The amplifier adjusts its output voltage until V_{Prc} and V_{setdc} matched, resulting in a constant and sample impedance independent reference voltage differential which can be adjusted by V_{setdc}.

In galvanostat mode V_{Prc} is created proportional to the measured cell current by a current to voltage converter (V<-I), resulting in constant sample cell current. In both modes, the variable capacitor C_t adjusts the control loop time constant in order to avoid free high frequency oscillations caused by too high open loop gain.

For impedance measurement an additional small AC voltage VAC is superimposed to V_{setdc} and the AC response is measured in accordance to Figure 2.

The two POT/GAL Test Interfaces for the Alpha-A modular measurement system are optimized for electrochemical impedance measurements of electrolytes with superimposed controlled voltage or current as described above. Alternatively, the NEISYS Electrochemical Impedance System is the latest development for for Electrochemical Impedance Spectroscopy.