

Advanced Instrumentation for Solid State Applications

A. J. Hinton and B. Sayers:
Solartron, Victoria Rd., Farnborough, UK

Impedance Analysis is a powerful non-destructive tool for analysing a range of electroceramic materials. The advantages of this technique are that it yields accurate and repeatable results which are unobtainable by other electrical means. The properties of ceramic materials depends on close control of their structure in terms of composition, ceramic texture, and dopants present. Typical examples of such materials are yttria-stabilised zirconia, YSZ, used as an oxide ion conducting membrane in solid oxide fuel cells and oxygen sensors, and Na β - alumina, used as a sodium ion conducting membrane in Na/S batteries.

Electrical analysis allows the complexities of these materials to be discovered by utilising the frequency dependence of the individual components. A variety of solid state parameters can be monitored including, electrical homogeneity, electrode/electrolyte interfaces, surface layers, ferroelectric properties, temperature coefficients related to resistive behaviour and bulk/grain boundary effects. Numerous application areas have benefited from the use of electrical techniques to analyse ceramics these include;

- analysis of conduction mechanisms for ceramics used in fuel cell and battery applications
- development of new component technology, including varistors, transistors, capacitors etc....
- research studies into the properties yttria-stabilised zirconia and other ceramics used as sensing materials
- studies into the ferroelectric/piezoelectric properties of ceramics used in sonar, active car suspensions and non-linear optics
- the study of ferroelectric materials such as novel BaTiO₃ and LiTiO₃ in terms of loss tangent and permittivity

The electronic properties of a system can be defined in terms of its ability to store and transfer charge (i.e. its capacitance and conductance). The use of Electrochemical Impedance Spectroscopy (EIS) records the response of the system to a sinusoidal applied perturbation (i.e. ac signal), over a pre-defined frequency range. The applied ac voltage and the resultant ac current are measured and the impedance calculated ($Z^* = V / I$). The techniques is non-destructive and is particularly sensitive to small changes in the system. To obtain a response electrodes are placed in contact with the system of interest and a sinusoidal voltage applied using a frequency response analyzer (FRA). This produces sample polarisation, the resultant current having the same frequency but different phase and amplitude. By measuring the complex impedance, Z^* , (i.e. the ratio of the applied voltage to the resultant current) and separating the real and imaginary terms, Z' and Z'' (i.e. conductance G and capacitance C) may be calculated.

Complex Impedance

$$Z^* = V / I = V \sin \omega t / I \cdot \sin(\omega t + \theta) \quad \text{where } \omega = 2\pi f$$

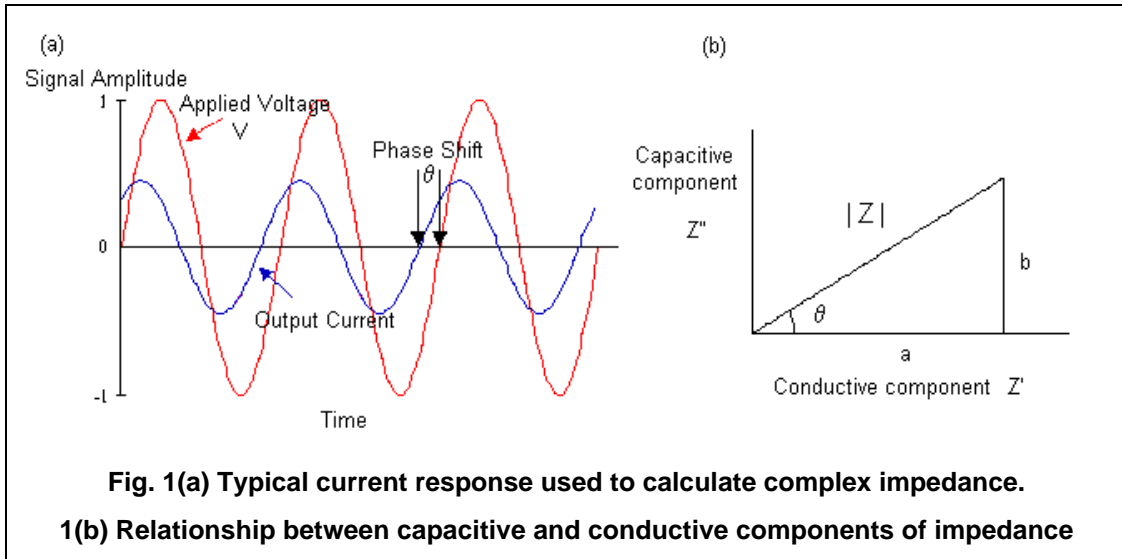
$$Z^* = a \cos \theta + b \sin \theta = Z' + Z''$$

Magnitude of the impedance

$$|Z| = (a^2 + b^2)^{0.5}$$

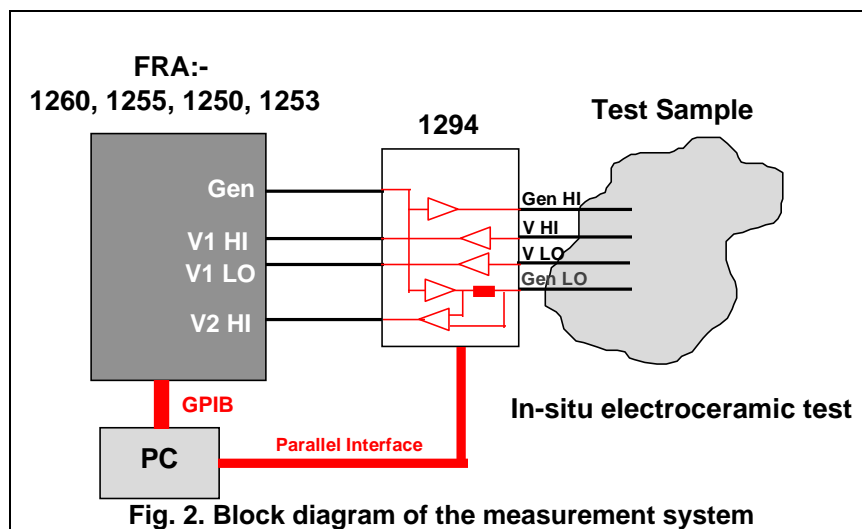
Phase angle

$$\theta = \arctan |Z''| / |Z'| = \arctan(b/a)$$



These results then allow the permittivity (ϵ'), loss factor (ϵ''), tan delta (ϵ'' / ϵ') and ionic mobility ($\sigma = e_0 \omega \epsilon''$) to be calculated. These parameters relate to the dielectric measurement of materials and can give information on molecular structure and dipole alignment.

Previous research has centred on the use of the Solartron 1260 FRA for data collection. It was noted that there is a need to improve this technology specifically for four terminal measurement applications such as the measurement of solid state systems, this led to the development of the Solartron 1294 which extends the analysis capabilities of the 1260 FRA. The specification of the 1294 Impedance Interface is achieved by the use of various techniques including 4-terminal connections to the sample, balanced generator and driven shield voltage measurement connections. In addition, the 1294 makes use of a sensitive multi-range current to voltage converter which allows the measurement of very low current levels which are commonly experienced in high impedance analysis or when using micro-electrodes.



The Solartron 1294 operates in conjunction with a frequency response analyzer (FRA), which provides the AC stimulus signal and correlation analysis of the output signals from the 1294. The use of correlation analysis is very important for the rejection of harmonics which result from non-linearities in the samples being measured.

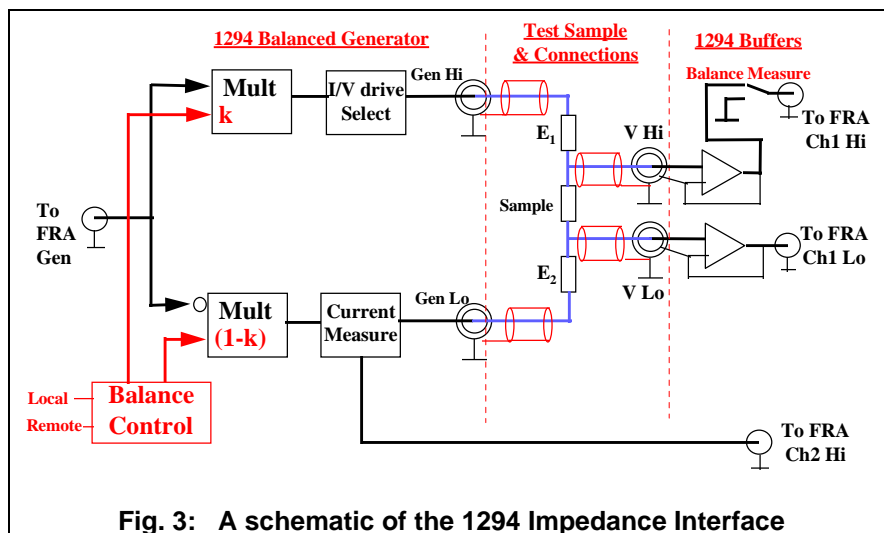
The combination of instruments and associated software provides:-

- Impedance measurement range to >100 Gohm (2-terminal mode), 100Mohm (4-terminal mode)
- Wide frequency range 10 μ Hz to >1MHz
- Increased measurement accuracy by the use of 4-terminal driven shield connections and balanced generator techniques
- Temperature control using external controller (e.g. LakeShore 340 / Oxford Instruments) and cryostat (e.g. Oxford Instruments)
- Flexible PC software allowing the control of complex experiments at a range of frequencies, stimulus levels and temperatures, and the ability to plot results in a wide variety of formats.

The schematic (Fig. 3) shows some of the features which have been incorporated to provide accurate and reliable measurement of electrical impedance. The sample is positioned between V Hi and V Lo, either side are electrode impedances represented by E_1 , E_2 . These impedances are due to the sample connections which are present in many solid state applications. There are also other stray impedances due to connections which may introduce imbalance in the electrode impedances which need to be considered and compensated.

The features included in the 1294 are:-

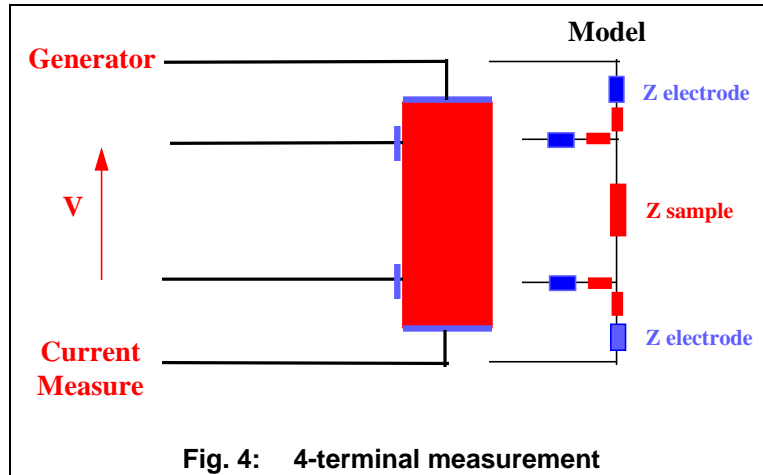
- low capacitance voltage measurement inputs using driven shields
- balanced generator for better common mode rejection
- built in attenuator for low voltage / current outputs
- accurate and sensitive current to voltage converter



Measurement techniques (4-terminal connections)

For solid state measurements, the electrodes which connect the instrumentation to the sample may be high impedance compared to the impedance of the sample itself. If conventional 2-terminal measurement techniques are used, there is no way to measure the impedance of the sample without including the impedance of the electrodes. This can lead to inaccuracies in the measurements, additional “features” on the impedance plots and to problems interpreting the data.

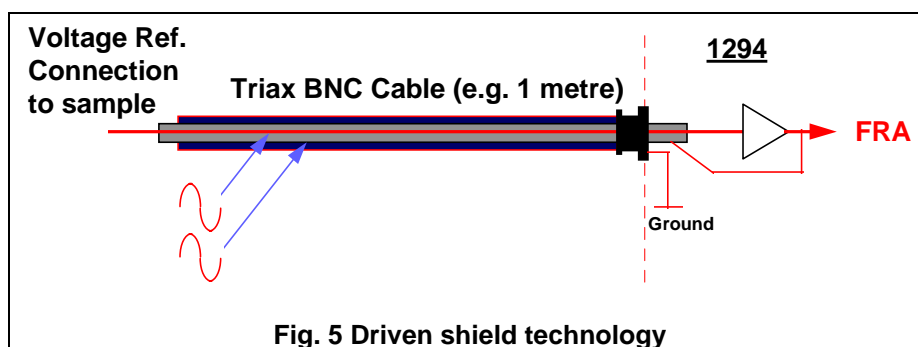
The four electrode connection technique (Fig. 4) uses separate electrodes for current stimulus and voltage measurement. This allows measurements of the sample on its own and minimises errors which would otherwise be introduced by the impedance of the current carrying electrodes. If 4-terminal techniques are employed, no current flows through the voltage measurement electrodes, which means that no voltage is dropped across these electrodes, leading to more accurate voltage measurements across the sample.



In addition, there may be localised disturbances where the current is injected into the sample (GenHi and GenLo). Four terminal techniques allow the voltage measurement electrodes to be placed well away from these disturbances in a region of linear electric field giving increased measurement accuracy.

Driven shield connections to the sample

Accurate measurements at high frequency are a specific problem due to errors introduced by input and cable capacitance. One technique which has been widely used to reduce the effects of capacitance is to position electrometer buffer amplifiers close to the sample. These buffers are able to drive the cable and input capacitance of the equipment and therefore reduce errors in voltage measurements. However, these external amplifiers require a power supply which usually involves extra cabling. In addition, where the temperature of the sample is to be varied, the accuracy of measurements may be effected since the buffers must be positioned close to the sample and are therefore subject to the same temperature variations.



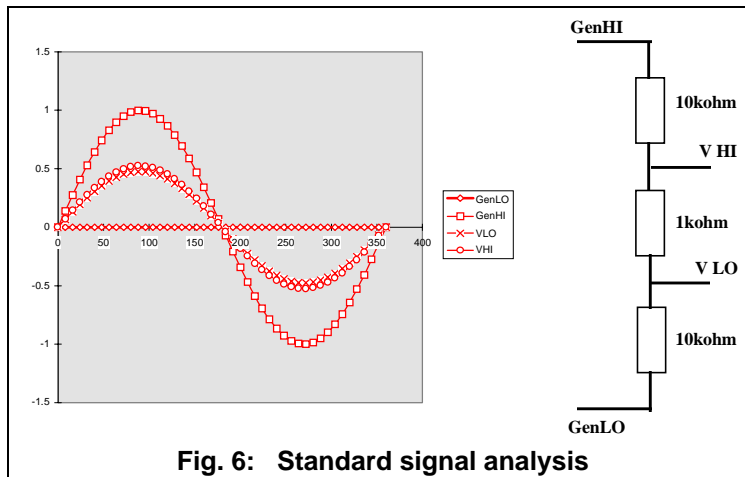
An alternative solution is the use of driven shield cables (Fig. 5). This technique replicates the signal waveform (which appears on the cable inner), onto the cable shield in order to minimise leakage current flow between the cable inner and the shield. Since no current flows between the cable inner and shield, the impedance appears to be very large and therefore the effects of the cable and input capacitance are minimised.

This method allows the high impedance buffers to be kept within the instrument. As an external power supply unit is not required for the electrometers, the cabling is reduced and the sample temperature may be changed without affecting the accuracy of the results.

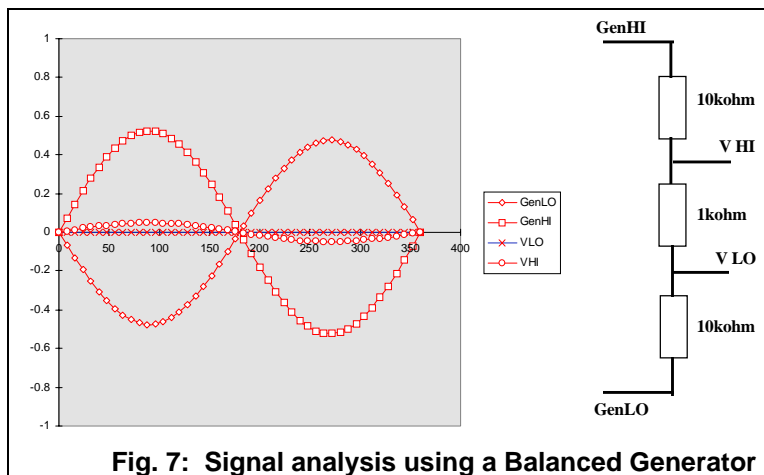
Balanced Generator

One problem associated with four terminal measurements of electroceramics is the requirement to study the impedance of the sample in the presence of relatively high electrode impedances (i.e. to reject the voltages across the electrodes in order to obtain accurate measurements of the voltage across the sample itself).

Figure 6 shows a typical measurement situation where the electrode impedance is ten times higher than the sample impedance which is required to be measured. In the example shown, the sample impedance is simulated by a 1Kohm resistor, and the electrode impedances are simulated by two 10kohm resistors. Using conventional measurement techniques, the AC stimulus voltage is applied to GenHi while GenLo is grounded, and the current through the sample and voltage drop across the sample (between V Hi and V Lo) are measured in order to compute the impedance of the sample.



In this example, the FRA is required to measure a small voltage difference between two relatively high voltage signals which appear at V Hi and V Lo. For example, if 1 volt is applied between GenHi and GenLo, less than 50 mVolts appears across the sample (V Hi - V Lo) whereas the voltage on the V Lo measurement connection is approximately 500mV. The FRA is therefore required to measure a 50 mVolt “difference” signal in the presence of 500 mVolts which leads to errors which are referred to as “common mode” errors. In addition, the relatively high voltage on the V Lo connection causes some current which has passed through the sample impedance to leak to earth via the input / cable capacitance on V Lo instead of being measured by the current measurement circuit.



The use of a balanced generator (see Fig. 7) reduces errors due to common mode voltages and earth leakage allowing more precise measurements of the sample impedance. This is achieved by adjusting the GenHi and GenLo signals in order to provide a balanced stimulus to

the sample which has the effect of making the voltage which appears at V Lo as close as possible to earth voltage, (i.e. zero volts).

The balanced generator can also cope with extremely difficult measurement situations where for instance the electrode impedances are not equal. In this case the signals on GenHi and GenLo are set to different voltage levels in order to again achieve zero volts on the V Lo connection.

Software capabilities

The software developed for use with this system is compatible with Windows 3.1 / 95/ NT4. It contains a variety of functions which allow maximum flexibility in terms of measurement and presentation of results, including:-

- Control of complex experiments involving multiple frequencies, stimulus levels and temperatures
- Presentation of results in a wide variety of formats including impedance, admittance, capacitance; with the ability to plot these as a function of frequency, stimulus level or temperature
- Multiple graph overlays allowing easy comparison of results taken at different frequencies or temperatures; or overlays of previously collected data
- Driver for Oxford Instruments and LakeShore Temperature controllers

The future of solid state measurements

Electrical Impedance Spectroscopy is a non-invasive, non-destructive technique which gives a great deal of information about the properties of the materials under investigation. The new generation of solid state analysis equipment with its advances in measurement technology allows more accurate four terminal measurements of a wide range of ceramics and piezo / ferroelectric materials to be obtained. The adverse effects of stray impedances and electrode impedance are minimised by the use of driven shield and balanced generator techniques.

The technology incorporated into the 1294 Impedance Interface will push the boundaries of measurement capabilities for electroceramic characterisation. This will enabled different ionic and charge transfer processes to be studied leading to a greater understanding of material behaviour, lifetime and failure rates. Materials can now be designed and characterised for specific applications and fabrication processes improved due to the measurement technology available.

Further reading

1. G. Hsieh, S. J. Ford, T. O. Mason, L. R. Pederson, Experimental limitations in impedance spectroscopy: Part I - simulation of reference electrode artifacts in three-point measurements. *Solid State Ionics*, 91, 191 - 201, 1996
2. G. Hsieh, S. J. Ford, T. O. Mason, L. R. Pederson, Experimental limitations in impedance spectroscopy: Part II - electrode artifacts in three-point measurements on Pt/YSZ, *Solid State Ionics*, 91, 203 - 212, 1996
3. G. Hsieh, S. J. Ford, T. O. Mason, L. R. Pederson, Experimental limitations in impedance spectroscopy: Part III - Effect of reference electrode geometry / position, *Solid State Ionics*, 96, 153 - 172, 1996
4. G. Hsieh, S. J. Ford, T. O. Mason, L. R. Pederson, Experimental limitations in impedance spectroscopy: Part IV - Electrode contact effects *Solid State Ionics*, 96, 93 - 104, 1996
5. G. Hsieh, S. J. Ford, T. O. Mason, L. R. Pederson, Experimental limitations in impedance spectroscopy: Part V - Apparatus contributions and corrections, *Solid State Ionics*, 99, 85 - 93, 1996
6. G. Hsieh, S. J. Ford, T. O. Mason, L. R. Pederson, Experimental limitations in impedance spectroscopy: Part VI - Four-point measurements of solid materials systems, *Solid State Ionics*, 91, 191 - 201, 1996
7. J. R. Dygas and M. W. Breitter, Measurements of large impedances in a wide temperature and frequency range, *Electrochimica Acta*, Vol. 41, No 7/8, 993-1001, 1996
8. J. T. S. Irvine, D. C. Sinclair and A. R. West, *Electroceramics: Characterisation by Impedance Spectroscopy*, *Adv. Materials*, No 3, 132 - 138, 1990

For further details

Web: <http://www.solartron.com/lap>

E-mail: lab_info@solartron.com

UK

Victoria Rd., Farnborough
Hampshire GU14 7PW England
Telephone +44 (0) 1252 376666
Fax +44 (0) 1252 544981

USA

964 Marcon Blvd. Suite 200
Allentown, PA 18103, USA
Telephone: +1 610-264-5034
Fax +1 610-246-5329
Toll-free 1-800 CALL SOL

France

37 rue du Saule Trapu
91882 MASSY, Cedex, France
Telephone +33 (0) 1 69 53 63 53
Fax +33 (0) 1 60 13 37 06

China

Beijing Liaison Office
Room 327, Ya Mao Building
No. 16 Bei Tu Chen Xi Road
Beijing 100101
Peoples Republic of China
Tel: +86 10-62381199 ext 2327
Fax: +86 10-62384687