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A fully automated four-probe d.c. conductivity technique for investigating solid electrolytes

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A fully automated four-probe d.c. conductivity technique has been described for investigating the conductivity of solid electrolytes as a function of temperature and time. The technique is equally applicable to semiconducting and superconducting materials. With full automation, the time for data acquisition is very short and the reproducibility is high. Several uncertainties associated with manual recording of data are reduced. Some applications of the technique have been described. Various sources of error associated with collection of data have been considered and limitations and advantages of the techniques have been discussed.

1. Introduction

Several techniques are available for measuring the conductivity of ionic and electronic materials. Two probe d.c. conductivity measurements can be made with simple equipment but it is one of the most error prone techniques and the measured resistance in addition to the material resistance includes contributions from both lead wires and contact resistance between probes and the material under study. In solid electrolyte cells, electrode resistance also makes a major contribution. In principle, most of the sources of error could be avoided with the use of a four-probe d.c. technique in which the current is passed through the two outer probes and the voltage drop is measured across the other two. All the probes must be physically separated and in the case of ionic conductors must also be reversible to the charge carrying species within the material. The two or four-probe a.c. techniques in which measurements are made at a constant frequency are also less accurate for measuring the conductivity of ionic conductors as the contribution of various processes in a solid electrolyte cell at a constant frequency varies as a function of temperature, the electrode (type and morphology) and how the electrolyte is processed. Impedance spectroscopy where measurements are made over a wide frequency range is a particularly useful technique for measuring the conductivity of ionic conductors as contributions of various processes such as grain boundary and lattice resistivities can be separated in the frequency domain. Despite its versatility, this technique is slow, provides information over a limited temperature range and is useful only for systems which are sufficiently stable over a period of time to allow accurate measurements to be made.

In this paper we describe a fully automated four-probe d.c. conductivity technique. The four-probe d.c. method, although limited in that it can provide information only about the total resistivity (grain boundary and lattice), is more accurate, fast and therefore less prone to minor temperature fluctuations and can be used over a much wider temperature range. The technique is also ideally suited for studying ageing phenomena in solid electrolytes at a constant temperature.

2. Four-probe d.c. technique

A block diagram of the technique is shown in Fig. 1. The electronic equipment consists of a constant current source, digital voltmeters, IBM compatible desk-top computer and a programmable temperature controller. The computer software has been written to control all the main instrument functions and for data acquisition and manipulation. The constant current source is a Keithley model 224 capable of delivering full range current of 20 μA to 101 mA. The smallest step of current output is 5 nA. The maximum compliance voltage is 105 V and can be programmed in 1 V steps. The current and the compliance voltage can be controlled remotely through an IEEE 488 interface. All the current settings used for conductivity measurements are precalibrated and the values corresponding to a given setting are read from the calibration table within the computer program. These values are only slightly different (within $\pm 0.1\%$) from those on the settings in the constant current source. The voltage drop across the potential probes is measured with either a Keithley model 617 programmable electrometer with an input impedance of $> 10^{14}\,\Omega$ and 10 μV resolution on the lowest voltage measurement range

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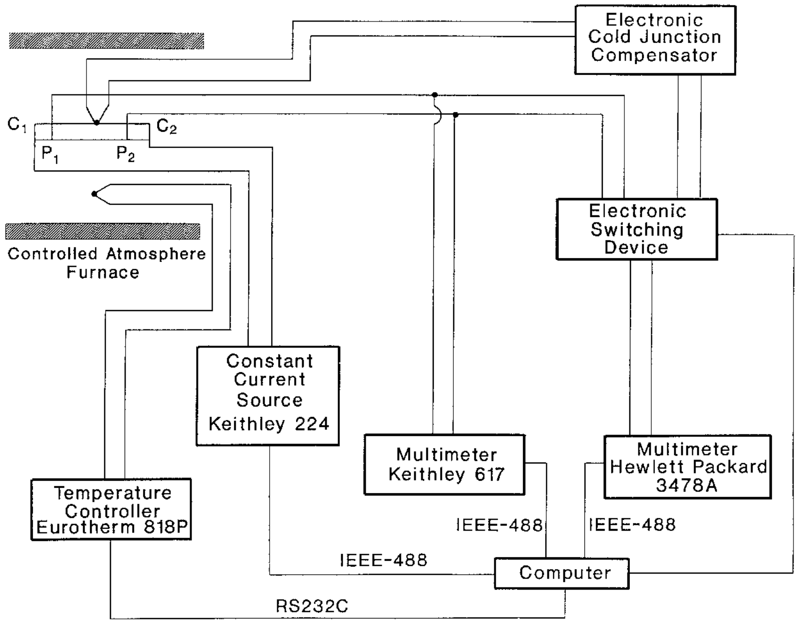

Fig. 1. A schematic diagram of the four-probe d.c. conductivity measurement apparatus.

(200 mV) or a Hewlett Packard model 3478A multimeter with an input impedance of $> 10^{10}\,\Omega$ and 0.1 μV resolution on the lowest range (30 mV). Both meters used for monitoring voltage are also fitted with an IEEE 488 interface. The temperature is controlled with a Eurotherm model 818P programmable temperature controller via a RS232C interface. The controller has only 16 temperature segments. In order to overcome the limited temperature segments available within the temperature controller, all the heating and cooling rates and dwell points are generated with the computer software. All the equipment is interfaced to an IBM compatible desk-top computer.

In addition to its use in measuring the voltage drop across the potential probes at high temperatures when the specimen resistance is low, the HP3478A multimeter, is also used to measure the temperature of the specimen. The meter is capable of accepting separate inputs from the front and rear terminals and the input is software selectable. This mode of operation is used for measuring the signal from the thermocouple which monitors the temperature of the specimen. The thermocouple input to the meter is through an electronic cold junction compensator (built in this laboratory) for the appropriate thermocouple. Although in most of our work, type R thermocouples are used for measuring and controlling the temperature, the equipment can be easily modified for other types of thermocouple. A table was generated within the computer software for converting thermocouple voltage readings to celcius temperature.

The raw data is displayed on the screen and stored on a disk. On completion of an experiment the data is processed and may be displayed on the screen in graphical form, printed and plotted. Data for each heating and cooling cycle and at selected dwell points as a function of time is stored in separate files to facilitate subsequent data processing.

2.1. *Measurement modes*

Measurements can be made in several modes. In the simplest form the heating and the cooling rates are preset, usually not exceeding 2° C min^{-1}, and the data are recorded for a constant current at regular time intervals while the temperature is changing. The zero reading (no current passage), the voltage signal for a given current and the thermocouple readings are recorded over a very short span of time (< 2 s). The value of the constant current may be altered during the measurement as the resistance of the specimen increases or decreases with changing temperature.

In the more common mode the specimen is assembled in the furnace and initially taken to the starting temperature. The whole temperature range over which data are to be recorded is entered and normally divided into two zones for each heating or cooling cycle. The temperature intervals, heating and cooling rates, and the dwell time after which the measurements are to be taken on a computer instructed temperature change, may all be set differently for each temperature zone. Both temperature zones may be divided into any number of temperature intervals. Once these values are programmed they are used in all the subsequent heating and cooling cycles. The conductivity measurements are made just before the temperature is changed. On completion of measurements at a given set temperature, the temperature is ramped to the next dwell temperature at the preset rate. The software allows for recording of data for any number of heating and cooling cycles. It is also possible to record data as a function of time at the end of a heating or a cooling cycle. This mode of measurement is schematically shown in Fig. 2.

If the conductivity data are to be recorded as a function of time, at a constant temperature, then that temperature, the total time and the time intervals are

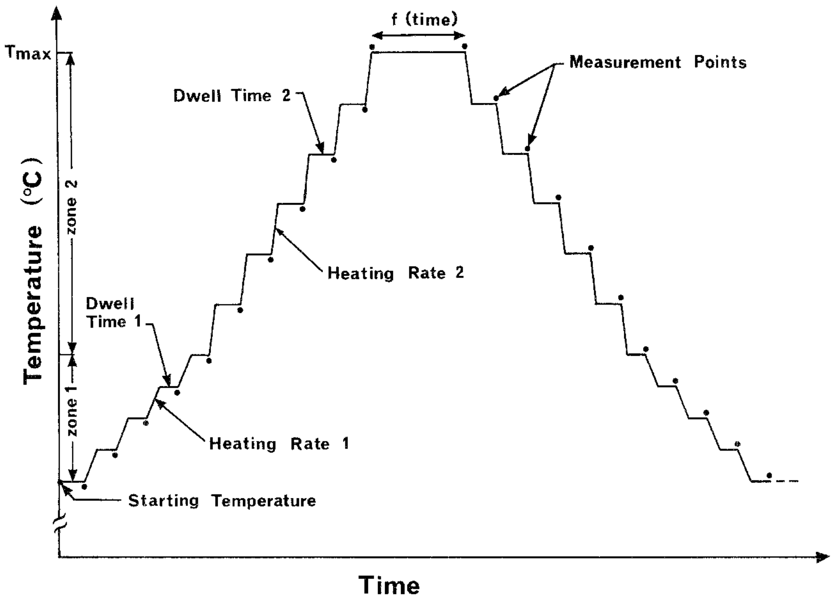

Fig. 2. A mode of data collection as a function of temperature and time.

all entered at the beginning before the run is started. The total time period may be divided into three segments each with a different time interval.

At each constant measurement temperature during heating or cooling cycles, measurements are made for three different current values and the resistance is averaged. The current settings at each temperature are determined by the maximum voltage cut-off point (< 50 mV) preset in the software for the entire temperature range. Thus, current values used for making measurements automatically increase or decrease as the temperature and the specimen resistance change. For specimens with high resistivity, especially at low temperatures, the software also allows for switching between an electrometer (high input impedance) at low temperature when the specimen resistance is high and an HP3478A multimeter for measurements at higher temperatures.

Several variations of the procedures described above are possible.

3. Experimental procedure for conductivity measurements

Most of our measurements have been carried out on oxygen-ion conducting solid electrolytes such as zirconia, ceria or bismuth oxide materials or on oxide and non-oxide electronic conductors. For this, sintered specimens, usually 20 mm long and in the form of circular rods or rectangular bars with cross-sectional area of 0.2–0.25 cm^2 were used. Potential probes were constructed by cutting a 0.3 mm wide groove around the specimen (approximately 4 mm from each end) with a diamond blade and wedging a platinum 13% rhodium wire in the groove. The depth of the groove was kept to a minimum (< 0.15 mm) just enough to hold the wire in place. Preliminary measurements were made on specimens with different groove depth to study its effect on the measured conductivity. In general, the error increased with increasing groove depths. The potential probes were typically 12 mm apart. Current probes were usually constructed by applying a thick layer of platinum paste to each end of the specimen bar or rod. The coated specimens were then spring loaded between either perforated platinum foils or platinum wire mesh and alumina discs. A schematic of the cell assembly is shown in Fig. 3. Two type R thermocouples in separate alumina sheaths were used for controlling and measuring the temperature. The thermocouple for measuring the temperature was either in direct contact with, or within 0.5 mm of,

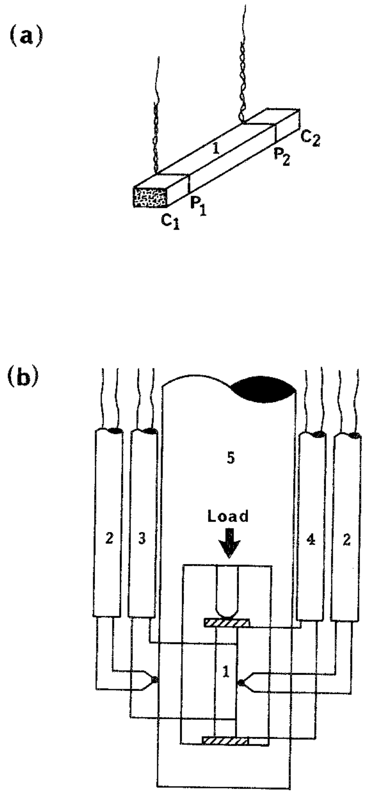

Fig. 3. A schematic of the ceramic specimen and specimen holder. C_1 and C_2: current probes. P_1 and P_2: potential probes. 1: specimen, 2: thermocouple sheaths, 3 and 4: twin bore alumina tubes for carrying potential and current lead wires, 5: alumina tube with a slit for loading specimen.

the specimen mid-way down its length. The furnace constant temperature zone was 5 cm long (within ±1° C).

The dimensions indicated for the specimens are commonly used in our work but the equipment is not limited to accepting specimens with these dimensions.

The majority of measurements were made over two heating and two cooling cycles for zirconia based materials over the temperature range 400–1000° C at 15° C intervals for the 400–600° C segment and 25° C intervals for the 600–1000° C segment. The heating or cooling rate was usually 50–100° C h^{-1} between various dwell points. After each temperature change 30–45 min were given before recording data for three different current settings at each temperature. The data at 1000° C were recorded as a function of time at the end of each heating cycle initially at 10 min and then at 30 and 60 min intervals. The current passed through the current probes varied between 100 nA at low temperatures to 2–5 mA at high temperatures depending on the specimen resistance. The current was kept low to ensure minimal polarization of the current probes and to avoid heating of the specimen as a result of current passage (I^2R heating). The input impedance of the voltage measuring circuit was several orders of magnitude higher than the specimen resistance.

All the measurements were made in a flowing atmosphere of dry air although it is possible to control gas atmosphere over the specimen.

4. Sources of error

The accuracy of the measurements was checked by constructing equivalent circuits of the specimens with high precision resistors and capacitors of known values. The simulated value of the specimen resistor was varied between 1 Ω and 1 MΩ (13 different values). In all cases the values measured by the four-probe d.c. conductivity equipment was within ±0.2% of the actual values. The average of three resistances measured by three different current values was typically within 0.1% for resistors. Similar scatter was observed for zirconia-based specimens above 500° C and it was slightly higher at lower temperatures. The error which results from positioning of the probes on specimens and measuring of the distance (usually 11–12 mm) between them was typically within ±0.6%. The temperature of the furnace was controlled to within 0.5° C. However, the measurement time is short (few seconds) and over this time period, the temperature fluctuation of not more than 0.1° C is expected to occur. Although the temperature of the hot zone in which the specimen (about 15–20 mm) is located was within ±1° C over 5 cm furnace length, slight temperature gradients across specimen length may generate thermal EMF's (thermoelectric effect). For example, for oxygen-ion conductors, a mere 1° C temperature difference between two voltage measuring probes, can give a signal about 0.5 mV. For all measurements, zero correction was applied, that is, the voltage reading in the absence of any current passage was subtracted from the voltage signal for a given current value. The only other main source of error is in the actual measurement of specimen temperature resulting from the thermocouple itself, compensation leads and electronic cold junction compensation box. The exact value is difficult to estimate but every possible precaution is taken (for example comparison of output of the thermocouples used with a precalibrated thermocouple, the use of high precision cold junction compensation etc.) to reduce this source of error.

5. Applications

The technique can, in principle, be used to investigate conductivity behaviour of a wide variety of materials such as semiconductors, ionic conductors and superconductors. The technique eliminates contribution of lead wires, contact resistance and, in the case of ionic or mixed ionic/electronic materials, electrode effects. Resistances from a few mΩ to 100 MΩ can be measured with high accuracy with the equipment described earlier. However, one drawback of the technique is that only the total specimen resistance is measured and any contribution from grain boundaries, which can have a dominant effect in many ionically conducting materials (e.g. zirconia, ceria, beta-alumina), can not be separated. Despite this limitation, as will be shown by examples in the following section, the technique is versatile for studying conductivity behaviour of single crystals and high purity materials, stability of the material in given environments, and for investigating phase transformations as a function of changing temperature or kinetics of precipitation and growth of secondary phases at a constant temperature. In the automated mode, because measurements are carried out continuously including after working hours, considerable time is saved and the data may be collected over narrow time or temperature intervals to obtain more accurate information about the conductivity behaviour.

In the simplest mode the conductivity measurements, as a function of temperature, can provide information about the absolute value of conductivity at a temperature, the activation energy for conduction and also about phase transformations if any are occurring during thermal cycling. Figures 4 and 5 show some examples for zirconia and bismuth oxide based electrolytes respectively. The hysteresis effects in the Arrhenius plots in partially stabilized zirconia occur due to transformation of the high temperature tetragonal phase to monoclinic zirconia on cooling and the reverse transformation on heating. Similarly, jumps in the conductivity curves in partially stabilized bismuth oxide occur as a result of phase transformation (Figure 5). The high temperature phase in doped Bi_2O_3 is the face centered cubic phase but the low temperature phase diagram is complex and the phase assemblage is determined by the type of dopant and

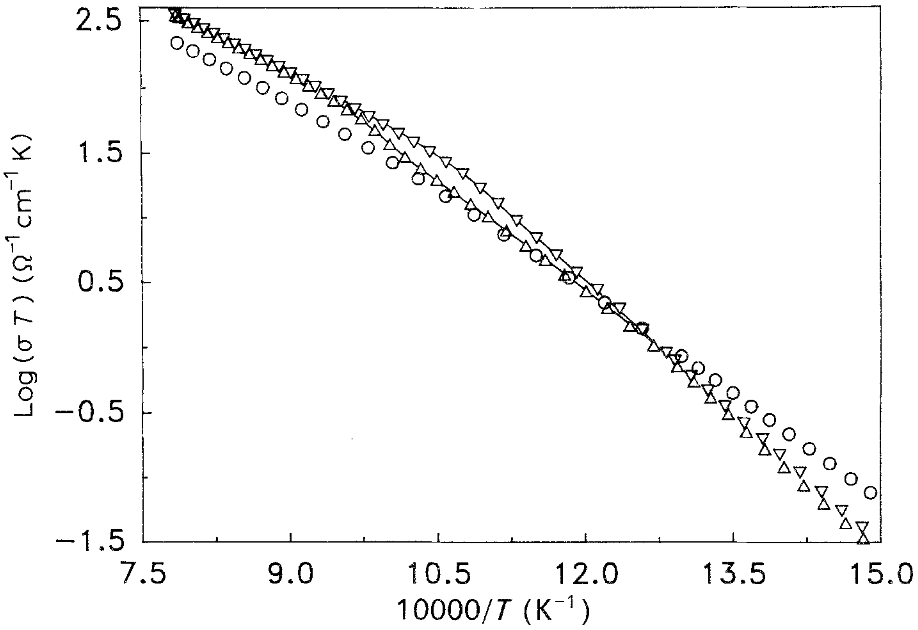

Fig. 4. Arrhenius plots for (○) 8 mol % Y_2O_3–ZrO_2; (△▽) 7 mol % Sc_2O_3–ZrO_2. △ – heating, ▽ – cooling cycle.

its concentration [1]. In zirconia-based materials, where no phase transformations occur during heating or cooling, a continuous change in the slope of the Arrhenius plots, which is a function of the dopant type and concentration, is observed towards lower activation energy with increasing temperature. In some fully stabilized bismuth oxide compositions instead a sharp change in slope is observed.

Figure 6 shows conductivity-temperature plots for the superconductor $YBa_2Cu_3O_{7-\delta}$. The data were collected at regular time intervals of 2.0–2.5 min in different oxygen partial pressures during the cooling cycle while the specimen was cooled at the rate of 0.5° C min^{-1} after it had been equilibrated in an oxygen partial pressure at 850° C for several hours. An inflection in the conductivity-time curve is observed at about the same conductivity value as shown by arrows. The inflection corresponds accurately to the tetragonal to orthorhombic phase transition temperature observed by in-situ X-ray and neutron diffraction studies [2]. At high temperatures the material has a tetragonal structure but on cooling, as oxygen uptake increases, a tetragonal to orthorhombic phase transition occurs which is a function of temperature and oxygen partial pressure.

In zirconia-based solid electrolytes ageing is commonly observed in the 800–1200° C temperature range [3–5]. The ageing is usually associated with the initial formation of metastable phases which slowly decompose into thermodynamically equilibrium phase assemblage. In single phase materials the ageing may occur as a result of formation of ordered compounds (growth of microdomains) at the annealing temperature. The four-probe d.c. technique, especially in the auto-

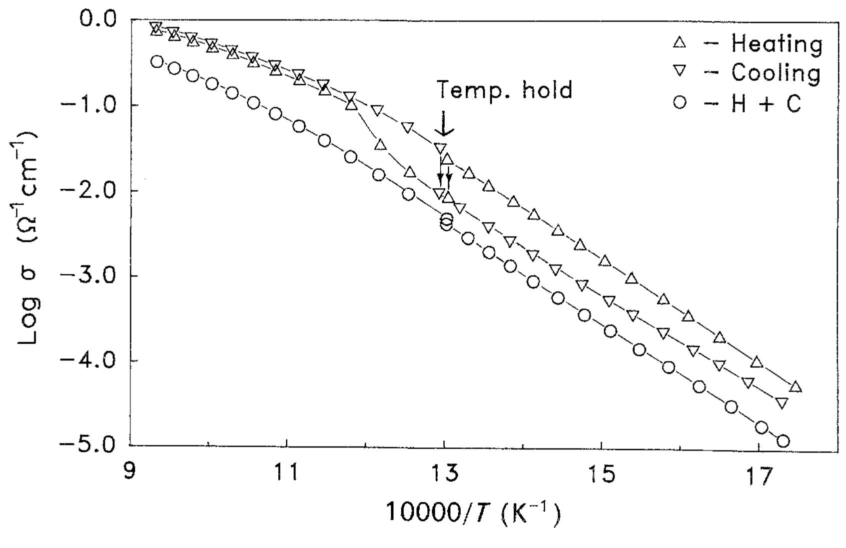

Fig. 5. Arrhenius plots for (△▽) 20 mol % Y_2O_3–Bi_2O_3 and (○) 30 mol % Y_2O_3–Bi_2O_3. △ – heating and ▽ – cooling cycle.

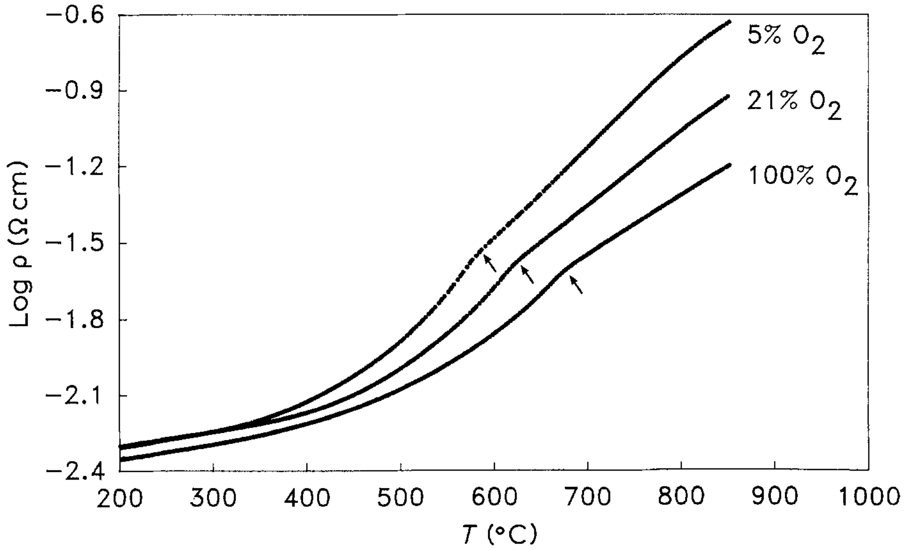

Fig. 6. Resistivity–temperature plots for the superconductor $YBa_2Cu_3O_{7-\delta}$ in three different oxygen partial pressures. The arrows indicate the inflection point at which tetragonal to orthorhombic phase transformation takes place on cooling.

mated mode, is extremely useful for studying such ageing behaviour and, when combined with phase and microstructure characterization techniques (X-ray diffraction, high resolution electron microscopy etc.), provides elucidating information about the ageing behaviour. Figure 7 shows conductivity–time plots for a number of zirconia-based electrolytes. In the case of the 7 mol % Sc_2O_3 + 1 mol % Y_2O_3–ZrO_2 composition, the conductivity deterioration occurs due to decomposition of the dopant-rich metastable t′-phase which is formed from the cubic phase on cooling from the sintering temperature [6]. In 3 mol % Y_2O_3–ZrO_2, this behaviour occurs as a result of this composition being in the two-phase field at the annealing temperature and consequent solute partitioning as required by the equilibrium phase diagram [7]. The 10 mol % Y_2O_3–ZrO_2 is in the single cubic phase field and no conductivity deterioration has been observed to occur with time at 1000° C.

As mentioned earlier the major drawback of the technique is that it provides information only about the total conductivity of the specimen. In polycrystalline electrolytes grain boundaries may make a significant contribution to the total resistivity as shown in Figure 8 for two materials of 3 mol % Y_2O_3–ZrO_2 composition with grossly different impurity levels. However, the relative contributions of the grain boundary and the volume resistivities change with temperature. The four-probe d.c. technique has been used effectively to demonstrate the diminishing effect of the grain boundary resistivity with increasing temperature as shown in Figure 9 for the materials of Figure 8. At 400° C, the total resistivity of the high impurity material was higher by a factor of about 6 but at 1000° C only by a factor of 1.3 compared with that of the relatively pure 3 mol % Y_2O_3–ZrO_2 composition.

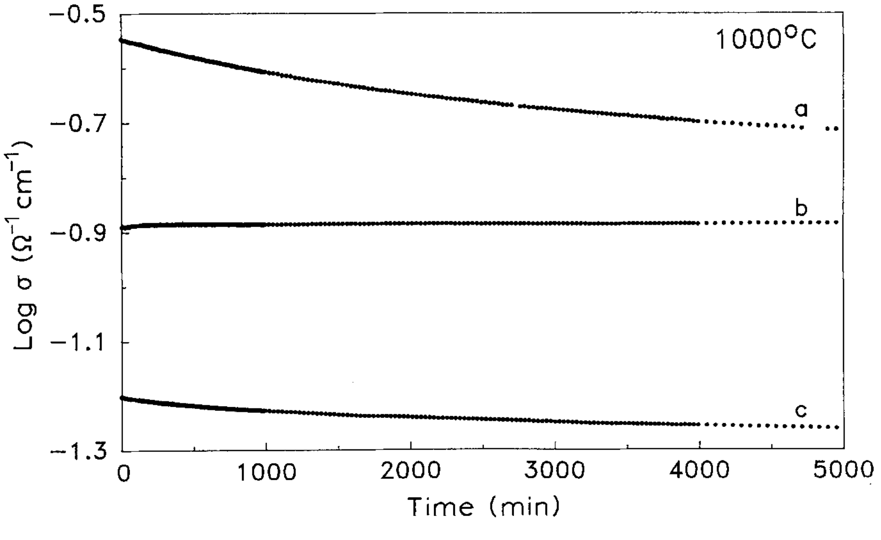

Fig. 7. Conductivity versus time plots at 1000° C for (a) 7 mol % Sc_2O_3 + 1 mol % Y_2O_3–ZrO_2; (b) 10 mol % Y_2O_3–ZrO_2; and (c) 3 mol % Y_2O_3–ZrO_2.

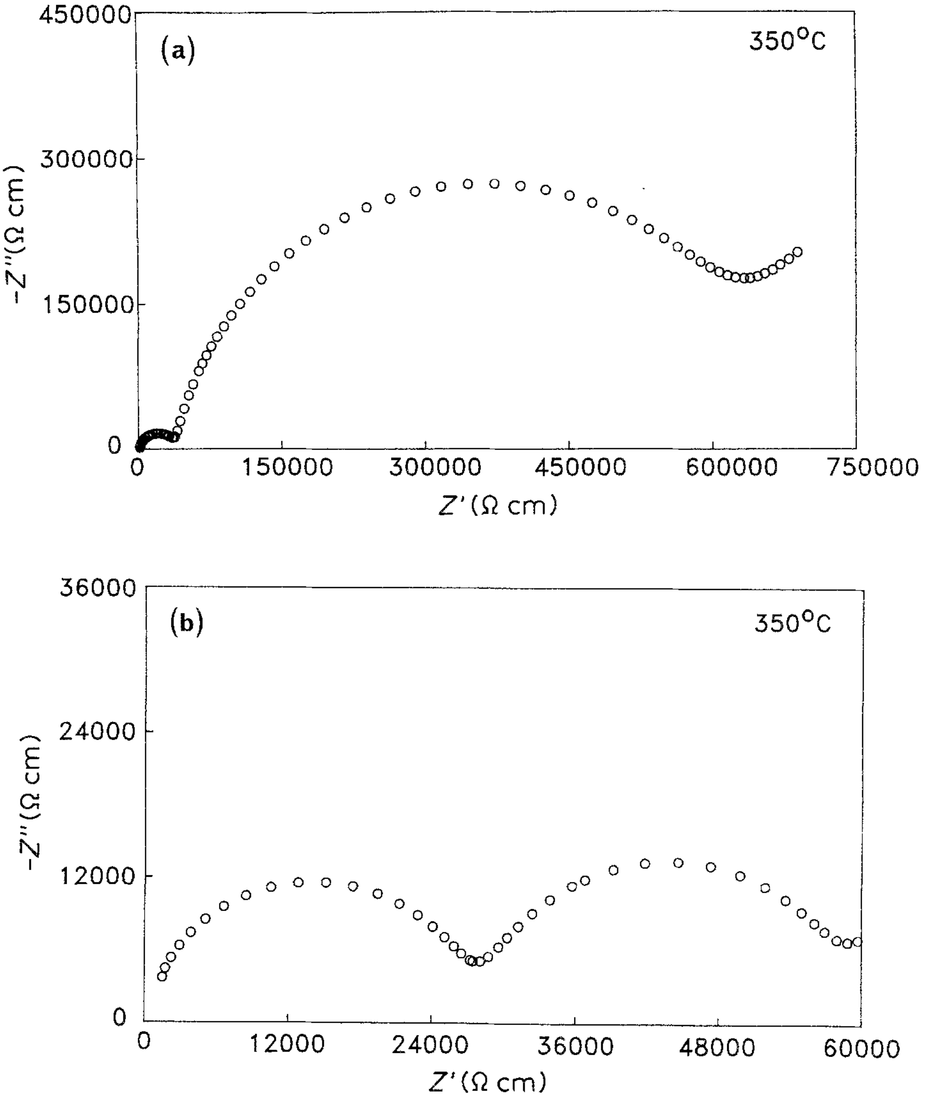

Fig. 8. Impedance curves for two 3 mol % Y_2O_3–ZrO_2 ceramics containing different levels of glassy phase (a) – high, (b) – low at the grain boundaries. Note high grain boundary (arc on the right side) resistivity for the ceramic with large amount of the glassy phase (a). The data presented here were collected with an HP4192 LF impedance analyser interfaced to a desk-top computer over the frequency range of 5 Hz–10 MHz.

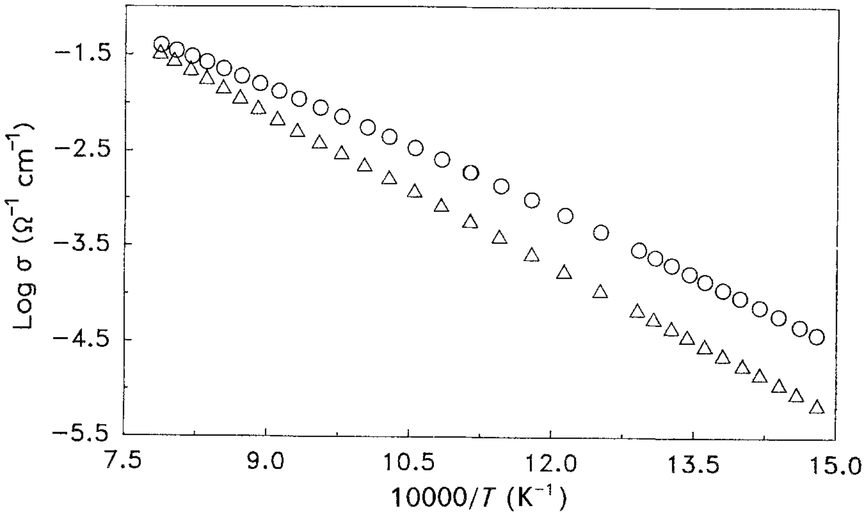

Fig. 9. Arrhenius plots (four-probe d.c. data) for the two ceramics as in Fig. 8 showing diminishing effect of the grain boundary resistivity with increasing temperature. (○) ceramic with relatively small and (△) ceramic with large amount of the glassy phase at grain boundaries.

7. Conclusions

The four-probe d.c. technique is simple, fast and can be used over a wide temperature range. For studying time dependent conductivity behaviour at a constant temperature this technique is inherently more accurate compared with a number of other techniques used for measuring ionic or electronic conductivity. In the fully automated mode, it is much more flexible, reduces time and effort required for data collection and removes all uncertainties associated with manual recording of data. The technique can be used to study a large number of materials and with the equipment described in this paper resistances varying from a few mΩ to 100 MΩ can be measured with high accuracy.

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