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Electrical behaviour of compressed magnesia powder

D. S. SMITH, R. AVEDIKIAN, P. BOURG
Laboratoire de Matériaux Céramiques et Traitements de Surface, U.R.A. CNRS 320, Ecole Nationale Supérieure de Céramique Industrielle, 47 à 73 Avenue Albert Thomas, 87065 Limoges, France

A. LAVAL*, G. NUSSBAUM, J. M. BORIE
Pechiney Electrométallurgie, Laboratoire Central de Recherche, Usine de Chedde, 74190 Le Fayet, France

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Magnesia powder has an important application for electrical insulation. In order to study the leakage conduction mechanisms, test samples were made by compressing 10 cm long alloy tubes filled with industrial class magnesia between a central electrode rod and the outer casing. The electrical behaviour between the central electrode rod and the outer casing was characterized up to 1200 °C by measurement of the d.c. resistance and the frequency dependence of the a.c. impedance. Three regimes can be identified. Below 700 °C, an activation energy of 1 eV is attributed to second phase(s) containing silicon and calcium which acts as a bypass. Above this temperature ionic conduction in the magnesia grains becomes predominant with an activation energy close to 2 eV. Finally, at even higher temperature above 1000 °C, the activation energy increases further, indicating mixed ionic–electronic conduction. This last regime yields a voltage dependence to the resistance explained by blocking of the ionic component at the electrodes.

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1. Introduction

Magnesia (MgO) is an important electrical insulation material for high-temperature applications, such as heater elements and signal wires. For this function, the leakage conduction must be reduced to its lowest possible value. The object of the present work was to determine the predominant mechanism controlling the electrical behaviour of industrial class magnesia powder used as a filler between a central electrode rod and a containing alloy tube, a form corresponding closely to actual use.

The existing literature on MgO for single crystals and ceramics invokes different conduction mechanisms depending on the conditions of temperature and atmosphere [1–3]. At high temperature, MgO exhibits mixed ionic–electronic conduction. With high oxygen partial pressure, the electronic conduction is p-type with an activation energy of approximately 3 eV, whereas at low oxygen partial pressure, it is n-type with an activation energy close to 4 eV. Doping with trivalent ions such as iron or aluminium promotes ionic conduction through magnesium ion vacancies characterized by a smaller activation energy of 2 eV. At lower temperatures it is necessary to take into account parallel paths through impurity phases [4]. Because of the different activation energies, measurement of the resistance as a function of temperature should provide a useful test for evaluating the predominant conduction mechanism.

The insulating character of magnesia makes electrical measurement delicate. Typically, in the earlier work cited above, a three-electrode technique was used to avoid problems of parallel surface conduction. However, for the present work, the sample form of 10 cm long cylinders should reduce such effects, and thus, for simplicity, a two-electrode configuration has been used. Such a configuration is also relevant to the practical situation. In addition to direct current measurements, the interpretation of the electrical behaviour is based on study of the impedance as a function of frequency and temperature.

2. Experimental procedure

2.1. Sample preparation

The alloy tube samples of magnesia were prepared by Pechiney Electrométallurgie (Chedde). The raw material was melted in an electric arc furnace at 2800 °C. After solidification, the solid mass of magnesia was broken and milled for granulometric selection within different powder grades. Two grades were studied in particular detail. Grade B is a medium-quality commercial product and grade A is distinguished by a greater purity with respect to SiO_2, Fe_2O_3, and Al_2O_3

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* *Present address*: Usine Cebal (Groupe Pechiney), Vienne le Chateau, 51800 La Marne, France.

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content. A further powder type with a similar SiO_2 content to B (3 wt %) was made up of grade A with 1.5 wt % SiO_2 added. To make a sample for testing, the powder was packed by vertical filling into a 10 cm high temperature alloy tube containing a central electrode rod. The outer tube consists of a Fe–Cr–Ni composition (AFNOR Z6CNT) and the inner rod consists of a Ni–Cr (80%–20%) composition. After drawing the tube through a roller mangle in order to reduce its diameter, and a final heat treatment of 1000 or 1100 °C, the final body (calrod) had less than 10% porosity. The inner electrode diameter, the magnesia layer thickness, and the tube outer diameter were approximately 3, 2, and 8 mm, respectively. Electrical contacts were made by welding thin alloy rods to the calrod outer tube and the central electrode.

2.2. Electrical characterization

Electrical measurements were performed between room temperature and 1200 °C. The measured temperature profile in the furnace at 1000 °C revealed less than 10 °C variation along the 10 cm length of the calrod position. The standard test measured the two-terminal d.c. resistance, R, using a Keithley 617 Electrometer. In addition, the impedance, as a function of frequency, was measured with either a Lock-in amplifier or a Solartron 1260 impedance/gain phase analyzer. In order to avoid making assumptions about the conduction process, the activation energies, E_a, were calculated using the simplest expression

$$1/R = Ae^{-E_a/kT} \tag{1}$$

where A is a constant, k is Boltzmann's constant and T is the temperature. The current–voltage behaviour was studied above 900 °C using a 600 V Heinzinger voltage source and a Keithley 196 multimeter to measure the current.

3. Results and discussion

The discussion is divided into three temperature regimes.

3.1. Low temperature (25–400 °C)

Measurement of the calrods' d.c. resistance at room temperature yielded values of the order of 100 MΩ. This is surprising, because extrapolation of higher temperature data in the literature would suggest a value greater than 10^{12} Ω. Further unusual behaviour was observed as the temperature was increased. The resistance first decreased but then increased dramatically between 50 and 100 °C to a value greater than 200 GΩ (beyond the limit of the instrument in the constant current mode). Then finally at a temperature starting between 200 and 300 °C, the expected behaviour of an insulator was observed with a thermally activated decreasing resistance.

The simplest explanation is bypassing of the bulk resistance of the grains through surface conduction. Russian workers have studied the absorption of water which degrades the insulating properties [5]. The increase of resistance with temperature is then due to driving the moisture off with removal of the surface conduction path.

3.2. Medium temperature (400–800 °C)

In a first set of trials, d.c. resistance measurements for samples A and B showed thermal activation, Fig. 1. All samples exhibited a lower temperature range activation energy of 1 eV which steepened to 1.5 eV or more. Complementary impedance measurements indicated another feature. In the lower part of this temperature domain, the impedance spectrum is distorted at low frequency, suggesting two contributions, Fig. 2a. However, at higher temperatures, roughly correlating to larger activation energies, a well defined semicircle, indicating one dominating contribution was obtained, Fig. 2b. This can be modelled by a parallel RC circuit.

In either case, an estimate of the sample capacitance obtained from the frequency, f^*, at the semicircle maximum through

$$C = 1/(2\pi f^* R) \tag{2}$$

yields values of the order of 10^{-10} F. This implies that the measured response can be attributed to the ceramic and is not due to an electrode effect. An estimate for pure MgO based on a dielectric constant of 10 in the sample geometry, gives 0.35×10^{-10} F. Values for the capacitance in parallel to the resistance for an electrode–ceramic interface are typically several orders of magnitude higher. The absence of a blocking electrode response at low frequency (a steadily increasing imaginary component of the impedance with

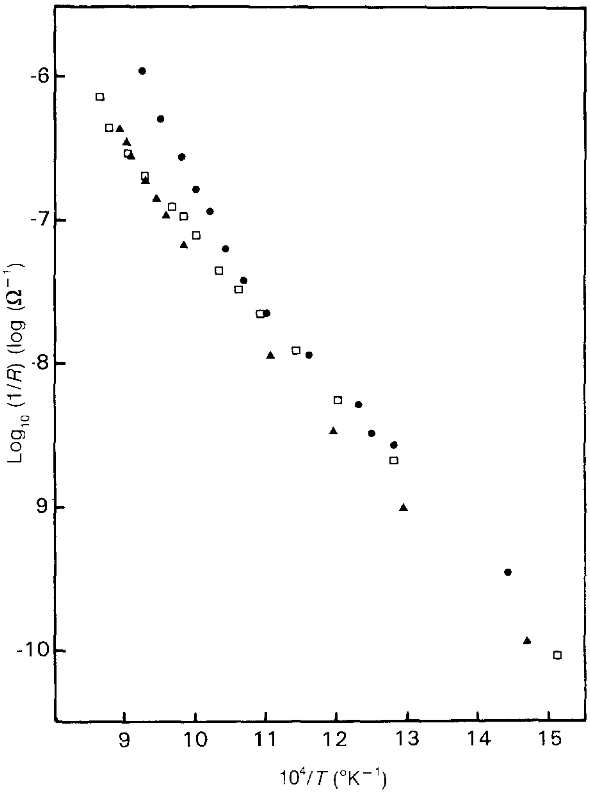

Figure 1 The d.c. conductance as a function of inverse temperature for different powder grades: (●) B, (□) A, (▲) A + 1.5.

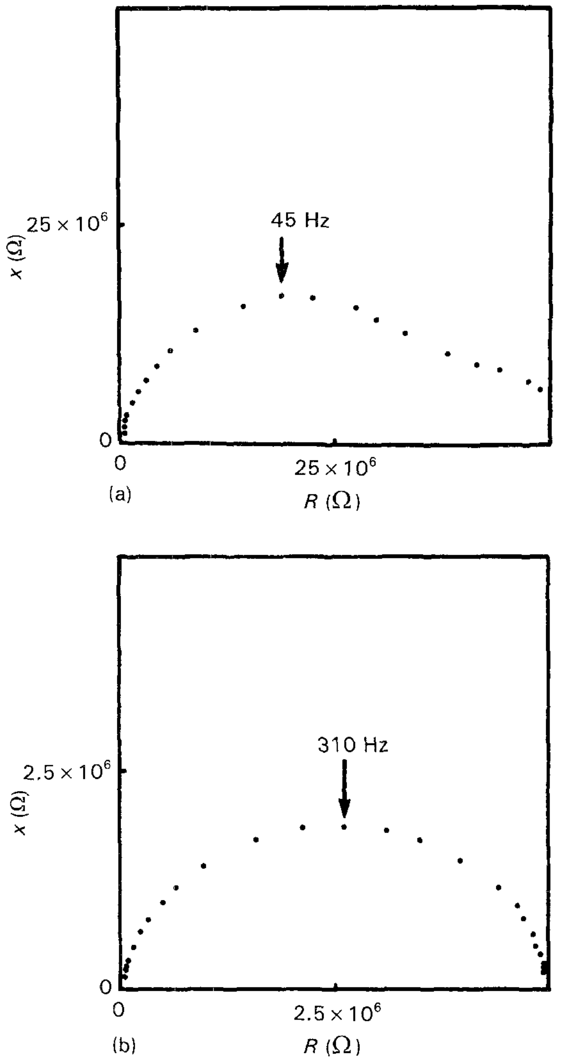

Figure 2 Impedance spectra for a sample B at (a) 600 °C and (b) 750 °C.

decrease of frequency [6]; Au/Na-β-alumina/Au is a well-known example), should also be noted.

The value of the activation energy at 1 eV suggests that the MgO grains themselves are not dominating the response. A simple model considers a parallel conduction path through second phase(s). The increase of activation energy is then due to the greater conductivity of MgO grains at high temperature, Fig. 1. Useful supporting evidence for this interpretation was given by X-ray mapping of the chemical distribution of elements using the EDS facility of the scanning electron microscope. This showed the presence of second phase containing silicon and calcium which could act as a bypass to the MgO grains in localized regions of the sample, Fig. 3.

3.3. High temperature (800–1200 °C)

From 700–1000 °C, measurements of the d.c. resistance yielded activation energy values in the range 1.5–2 eV, suggesting Mg^{2+} ion conduction in the grains, Fig. 4. Following Sempolinski and Kingery [1], the controlling charge-balance equation is

$$2[V''_{Mg}] = [I_{Mg}] + [Fe_{Mg}] \qquad (3)$$

where $[V''_{Mg}]$ is the concentration of magnesium ion

Figure 3 Micrograph of a sample B showing second phase containing calcium and silicon.

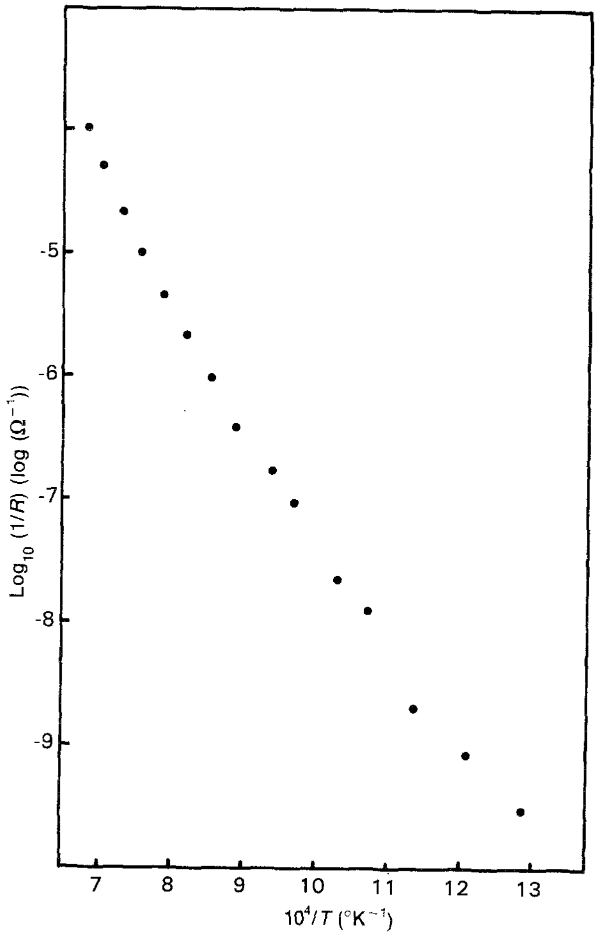

Figure 4 The d.c. conductance as a function of inverse temperature for a sample A + 1.5.

vacancies, $[\mathrm{I_{Mg}}]$ the concentration of fixed valence solutes such as aluminium, and $[\mathrm{Fe_{Mg}}]$ the concentration of $\mathrm{Fe^{3+}}$. Sample B contains 8500 p.p.m. trivalent ion impurities compared to 2900 p.p.m. for samples A and A + 1.5% $\mathrm{SiO_2}$ (A + 1.5). These are aluminium and iron in an approximate ratio of 3:1 for sample B and an approximate ratio of 6:1 for samples A and A + 1.5. Corresponding to Equation 1, above 750 °C the conductivity of sample B is significantly higher than A and A + 1.5, Fig. 1. Comparison of A and A + 1.5 suggests that the addition of silica has little influence on the high-temperature electrical behaviour.

The interpretation of ionic conduction has an important consequence for the experimental situation. The electrodes, though electronically conducting, should be blocking to $\mathrm{Mg^{2+}}$ ion discharge at the metal/electrode interface and vice versa. In the case of non-reversible electrodes the chemical potential is not fixed at the interfaces so that under d.c. polarization, the ionic component should be completely stopped [7]. However, in MgO, the resulting changes in $[\mathrm{V''_{Mg}}]$ may be alleviated by the electrode reactions

$$\tfrac{1}{2}\mathrm{O_2} + 2\mathrm{e^-} = \mathrm{V''_{Mg}} + \mathrm{O_O} \qquad (4)$$

$$\mathrm{V''_{Mg}} + \mathrm{O_O} = \tfrac{1}{2}\mathrm{O_2} + 2\mathrm{e^-} \qquad (5)$$

Osburn and Vest proposed this type of reaction in terms of singly ionized $\mathrm{V'_{Mg}}$ [3] but subsequently, Sempolinski *et al.* [2] deduced that because the energy of the $\mathrm{V''_{Mg}}$ acceptor is closest to the lowest energy donor state, it, and not $\mathrm{V'_{Mg}}$, is the stable state of magnesium vacancy. Reactions 2 and 3 are equivalent to a flow of neutral oxygen atoms through the solid. For sufficiently low currents, the electrodes can be considered as essentially reversible. This is supported by the observation of no significant low-frequency contribution in the impedance spectrum at 750 °C, Fig. 2, and a close correspondance between d.c. and impedance data, Table I.

There is a further increase in activation energy to 2.6 eV at even higher temperature, Fig. 4, as electronic conduction becomes significant. This regime of mixed ionic–electronic conduction has other interesting features. Direct current–voltage measurements were made up to ± 600 V. First of all it can be noted that after application of the voltage, considerable stabilization times, greater than 20 min, were necessary to achieve a steady current value, Fig. 5. Inversion of the polarity then gave initially a current of the same magnitude as the stabilized value with a subsequent increase (15 min) and another decrease. Fig. 6 shows the voltage–stabilized current data. The low-voltage response below ± 5 V was roughly ohmic but for higher voltages the current response is limited. However, this limitation is not complete (complete limiting is a standard situation in electrochemistry with an approach to a constant current value as the voltage increases) but instead reveals another ohmic-type behaviour with greater resistance. The behaviour suggests that the conditions for reversible electrode

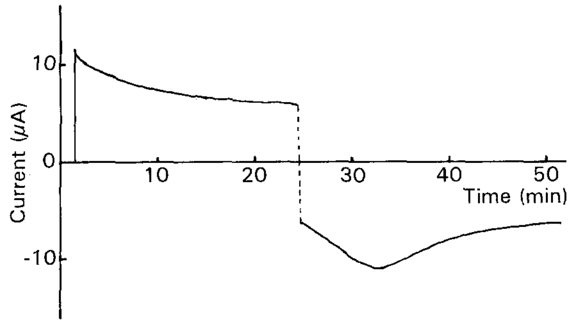

Figure 5 Current as a function of time for application of + 20 V and then − 20 V at 1020 °C. Sample A + 1.5.

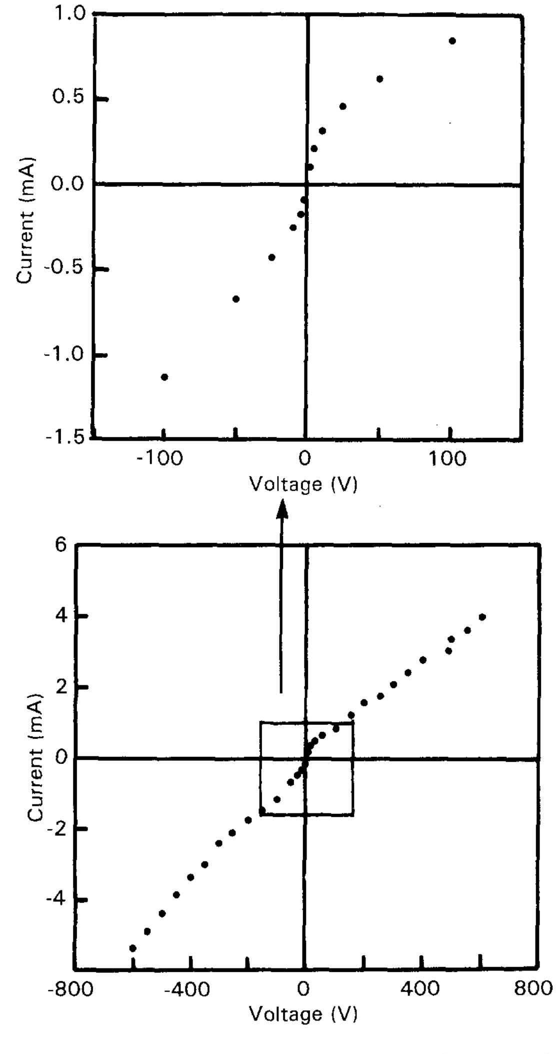

Figure 6 Current–voltage behaviour at 1100 °C for a sample A + 1.5.

TABLE I Comparison between d.c. resistance, $R_{\mathrm{d.c.}}$, after 30 s stabilization, and the low-frequency intercept of the impedance spectrum with the real axis, R_{LF}, for a calrod containing grade A powder + 1.5 wt % $\mathrm{SiO_2}$ (A + 1.5)

Temperature (°C)	R_{LF} (250 mV$_{\mathrm{rms}}$) (MΩ)	$R_{\mathrm{d.c.}}$ (MΩ)	Measurement current (nA)
811	9.0	9.05	10
900	1.85	1.91	100
940	0.99	0.98	100

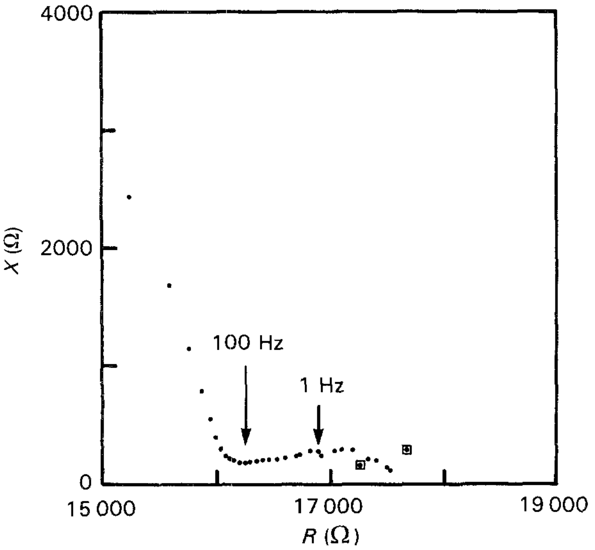

Figure 7 Low-frequency portion of the impedance spectrum at 1170 °C. The powder grade of the sample is in between A and B.

behaviour are no longer respected and a partial blocking occurs due to the higher currents involved.

Further information was obtained by impedance measurements using an alternating signal of 500 mV_{rms} between 1 mHz and 10 mHz as a function of d.c. bias voltage. Firstly, under zero bias, a low-frequency contribution was observed, Fig. 7. The time constant is compatible with an impedance at the electrode/ceramic interface. However, a charge transfer resistance in parallel with the double layer capacitance is not sufficient in itself as a model, because a well-defined semicircle would have been obtained. A plausible explanation for the observed shape is that a Warburg impedance is also involved. The regime of mixed ionic–electronic conduction should permit the required concentration changes of species involved in the electrode reaction and would be consistent with a limitation by diffusion [8, 9], presumably of magnesium vacancies. Unfortunately, the size of the effect and the distorted nature of the spectrum does not allow clearer identification. However, it can be noted that such distortion will occur for two contributions with closely overlapping time constants.

Application of a d.c. level yielded another observation. Instead of simply increasing the impedance of the low-frequency contribution due to current limiting, the high-frequency "semicircle" increased, Fig. 8. Although the low-frequency measurements were limited to 1 Hz because of the filter which separates the alternating signal from the d.c. response, no electrode contribution was detected. In addition, the resistance given by the semicircle diameter gave a close agreement to the resistance dV/dI obtained from the current–voltage measurements.

This can be explained by a decrease of $[V''_{Mg}]$ in the layers next to the negative electrode which then blocks the ionic current. The application of higher voltages essentially selects the electronic component for the passage of current with a subsequent increase in bulk ceramic resistance. In addition, charge transfer at the metal/ceramic interfaces becomes restricted to hole creation and annihilation, presenting no significant impedance. To test this hypothesis, I–V measurements were made as a function of temperature. The resistance values, dV/dI, calculated from the low- and high-voltage regimes, yielded activation energies of 1.8 and 2.7 eV, corresponding to the ionic and electronic components, Fig. 9.

It is instructive to compare the above situation with the Pt, O_2/zirconia interface above 700 °C under low

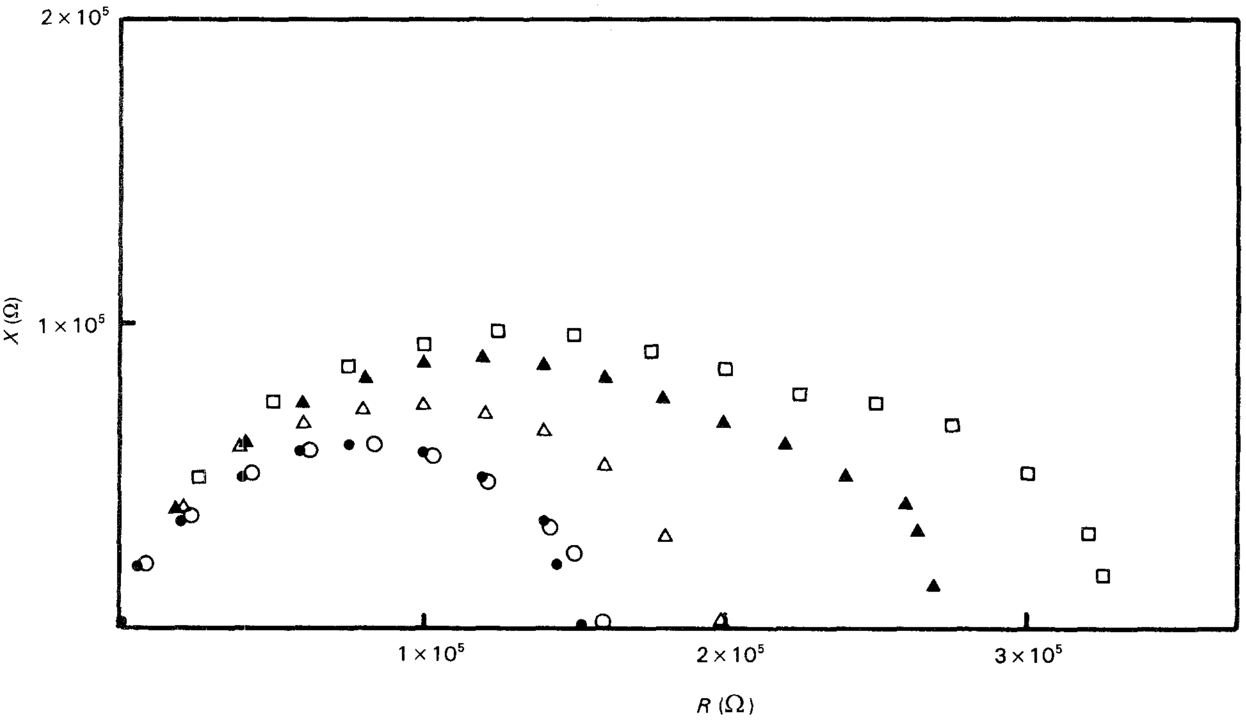

Figure 8 Impedance spectra at 1020 °C as a function of applied d.c. voltage for sample A + 1.5. The reactance maxima are at 9.1, 10.9, 7.6, 6.4, and 5.3 kHz for (●) 0, (○) 5, (△) 10, (▲) 25, (□) 40 V, respectively.

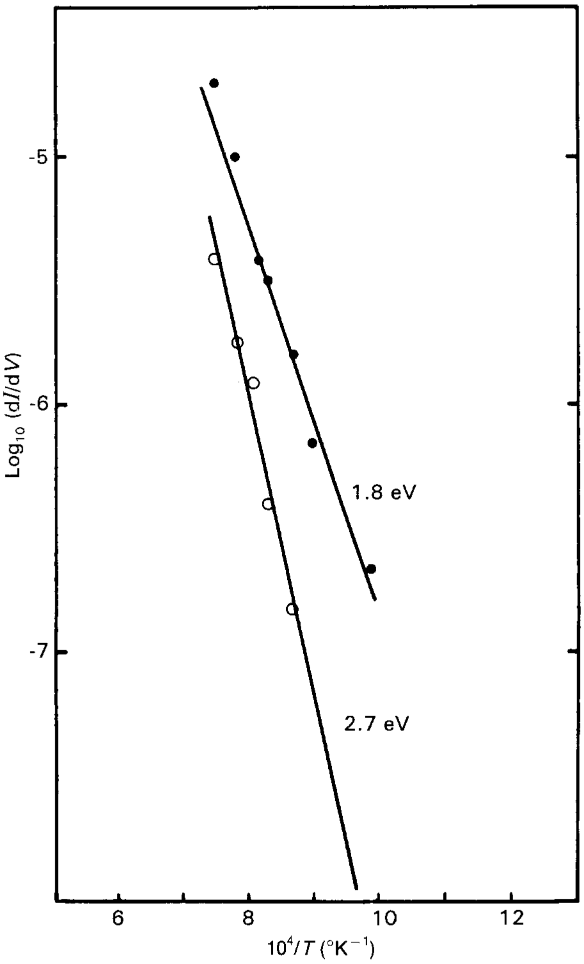

Figure 9 Plot of dI/dV at low and high applied voltage as a function of inverse temperature for sample A + 1.5.

oxygen partial pressure. For the Pt, O_2/zirconia interface, the low-frequency impedance exhibits two contributions; a "semicircle" attributed to charge transfer, and a Warburg impedance attributed to a limitation of the electrode reaction by diffusion [10]. Cathodic polarization increases the total impedance of the system but, in this case, it is due to the low-frequency electrode processes. The bulk ceramic impedance measured at high frequency remains unchanged. But zirconia, in contrast to magnesia, has only one mobile charge species, the oxygen ion.

4. Conclusion

These results demonstrate that the detailed picture of the electrical behaviour which has been developed for MgO can be related to leakage conduction in a practical situation. Three regimes can be identified: impurity phase conduction, ionic conduction, and mixed ionic–electronic conduction, which successively predominate as the temperature is increased. The ionic conductivity depends on the trivalent ion content and this is a factor which determines the quality of the magnesia powder. The mixed ionic–electronic regime presents the interesting feature of partially blocking electrodes. There is a significant increase in resistance at higher applied voltages as the ionic component to conduction is restricted. This is of direct relevance to industrial tests of leakage conduction which involve high temperatures and voltages.

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