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Characterization of the granular ceramic materials corundum and mullite by impedance spectroscopy

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The granular ceramic materials corundum and mullite are potential filter bed materials for electrically enhanced filtration at elevated temperatures. The dielectric response of the granular ceramics has been determined at temperatures between 420 and 920 K. It is shown that the response of these materials can be described by one equivalent circuit over the whole temperature and frequency (0.1 Hz–10 kHz) range. Thermally activated conduction in parallel with a dipole relaxation with a symmetrical logarithmic distribution of relaxation times (Cole–Cole relaxation) is the mechanism which determines the response at not too low frequencies.

1. Introduction

At the Delft University of Technology, research is performed on gas clean-up at high temperatures (up to 1120 K) by means of an electrically enhanced granular filter bed in order to obtain a high and controllable filter efficiency for particles smaller than 10 μm. The granular material to be used in the filter bed has to fulfil several demands concerning, among others, the mechanical and (di)electrical properties at high temperature. Concerning the dielectrical properties, a high dielectric constant is desired because a large gradient of electric field enhances the capture rate of the particles. A low conductivity of the filter bed material is also desirable, because the conductivity determines the energy consumption of the filter. Materials that fulfil these demands can be found in the classes of ceramics such as aluminium oxide, quartz and alumino-silicates.

It is well established that the dielectrical properties of granular materials strongly depend upon the volume fraction, shape and geometric distribution of the granules. Therefore, for the modelling of the filter characteristics (i.e. power efficiency and capture rate) it is of considerable interest to determine the dielectrical properties of the filter bed instead of those of the bulk material.

In this paper we will discuss the dielectrical properties of two ceramic granular materials: corundum (polycrystalline Al_2O_3) and commercially available sintered mullite (tradename K-ref). The chemical composition of the mullite, which was fired at a temperature of 2020 K, is given in Table I. The mullite granules with typical dimension between 1.5 and 3 mm, exhibited various colours, probably because mullite appears in different crystals [1, 2]. The typical dimension of the corundum granules was 2 mm. Apart from quartz-like granular materials [3], both corundum and mullite are possible candidates for application in the filter bed. The experiments were performed on the (highly nonspherical) granules as-received.

2. Experimental procedure

2.1. Apparatus

For the dielectric characterization of the granular materials, a cylindrical measuring cell made out of commercially available ceramic alumina was used [4]. The two coaxial cylinders of the cell define a capacitor with a 5 mm wide gap. The gap between the cylinders is closed at the bottom side by an alumina ring to allow filling with granules. The outside of the inner cylinder (with a diameter of 60 mm) and the inside of the outer one are coated with an approximately 20 μm thick Pt coating. Two guard electrodes, one at each side of the 60 mm high inner electrode, reduce the edge effects. The measurements reported in this paper were performed in an oven which can be heated up to approximately 1250 K by means of an electrical coil. The temperature of the measuring cell is controlled by a PID controller with a NiCr–Ni thermocouple inside the inner cylinder of the cell acting as a sensor. The temperature variation along the cell was about 3 K at a temperature of 1080 K. Because O_2 in the air may cause corrosion problems at the elevated temperatures where the cell is used, the measurements are performed in an atmosphere of dry N_2.

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TABLE I Chemical composition of mullite (wt %)

Al_2O_3	73.5	MgO	0.15
SiO_2	24.75	TiO_2	0.1
K_2O	0.75	CaO	0.05
Fe_2O_3	0.45	Fe	0.01
Na_2O	0.25		

The complex impedance of the measuring cell filled with the sample material is determined with a Solartron model 1250 frequency response analyser (FRA) and an integrating operational amplifier built at our institute (CPM–TNO). The computer-controlled experimental measuring system is shown schematically in Fig. 1. For the feed-back element Z_{fb}, different capacitors and resistors are installed automatically, depending on the impedance of the filled cell. The impedance of a low-loss dielectric is measured using a capacitor only. Dielectrics with high losses are measured using a resistor in parallel with a capacitor. The experimental set-up allows measurements on materials with a dielectric loss factor, tan δ, between 10^{-3} and 10^2, and a capacitance of the filled cell between 10 pF and 1 µF.

The experiments discussed in this paper were performed in the frequency range from 0.1 Hz–10 kHz and at temperatures between 420 and 920 K. The a.c. voltage applied across the cell had an amplitude of 10 V. To allow accurate measurements, the impedance of the filled cell was measured using at least ten periods of the sinusoidal signal.

2.2. The measuring cell

Preceding the experiments with granular materials, the empty measuring cell was characterized dielectrically in the temperature range from room temperature to 1130 K. These experiments revealed that the dielectric behaviour of the cell can be described by a model consisting of an ideal capacitor in parallel with a resistor for the whole temperature and frequency range. The parallel resistance varied from 6×10^7 MΩ at room temperature to 60 MΩ at 1130 K. The capacitor of the parallel model circuit was calculated to be 22.1 pF, which corresponds to a (relative) dielectric constant of 1.02 using the appropriate geometry factor. From these measurements on the empty cell it is evident that the geometry of the cell is well defined and that disturbing edge effects (e.g. by the bottom ring) are successfully suppressed, even at high temperatures.

2.3. Volume fraction

One of the parameters involved in the characterization of granular materials is the volume fraction, ϕ, being the fraction of the volume of the cell filled with the granular material. The volume fraction is determined by measuring the total mass of the granules in the well-defined volume of the measuring cell (76.58×10^{-6} m^3) and the density of the material. The density is measured by means of a pycnometer with a volume of 25×10^{-6} m^3 filled with distilled water. Our experience is that porous materials have to be outgassed under vacuum to remove all air out of the material. For mullite a density of 2.89×10^3 kg m^{-3} was determined by this method. For corundum a density $\rho = (3.95 \pm 0.01) \times 10^3$ kg m^{-3} was determined. This value is almost equal to the density of 3.97×10^3 kg m^{-3} reported in the literature [5]. This correspondence proves that there was no significant volume of closed pores in the corundum used for our experiments. The volume fraction of corundum and mullite was 0.240 and 0.414, respectively, for the experiments discussed in this paper.

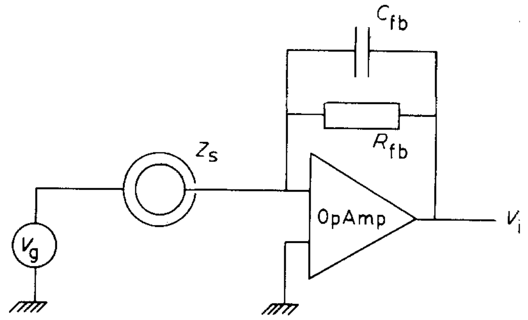

Figure 1 The measuring circuit for the impedance of a sample with an impedance, Z_s. The impedance, Z_{fb}, of the feed-back element of the integrating operational amplifier contains a variable capacitor C_{fb} in parallel with a variable resistor, R_{fb}. V_g, a.c. generator of the FRA; OpAmp, operational amplifier; V_i, input for the correlator of the FRA.

3. Theoretical background

3.1 Dielectric relaxation

The frequency dependent dielectric response of a material can be described by the complex dielectric constant

$$\varepsilon = \varepsilon' - j\varepsilon'' \qquad (1)$$

where $j = (-1)^{1/2}$, ε' represents the in-phase component of the dielectric displacement and ε'' the out-of-phase component. In the case of dipole relaxation with a single relaxation time, τ (Debye model), the real (ε') and imaginary (ε'') part of the dielectric constant $\varepsilon(\omega)$ are frequency dependent according to the dispersion relation (see e.g. [6])

$$\begin{aligned} \varepsilon(\omega) &= \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + j\omega\tau} \\ &= \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2\tau^2} - j\omega\tau\frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2\tau^2} \qquad (2) \end{aligned}$$

where ε_s and ε_∞ are the low- and high-frequency limits of the dielectric constant, and ω the angular frequency.

The response of most dielectrics cannot be described by assuming a single relaxation time. Therefore, a distribution of relaxation times around the average value, τ, is introduced. The logarithmic distribution function $G(\ln\tau)$ is defined by

$$\varepsilon(\omega) - \varepsilon_\infty = (\varepsilon_s - \varepsilon_\infty)\int_{-\infty}^{\infty} \frac{G(\ln\tau')}{1 + j\omega\tau'}\,d\ln\tau' \quad (3)$$

One of the widely used distribution functions is (see e.g. [6])

$$G(\ln\tau') = \frac{1}{2\pi}\frac{\sin(\alpha\pi)}{\cosh\left[(1-\alpha)\ln\left(\frac{\tau'}{\tau}\right)\right] - \cos(\alpha\pi)} \qquad (4)$$

which leads to the well-known Cole–Cole dispersion relation

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (j\omega\tau)^{(1-\alpha)}} \qquad (5)$$

with α being a measure for the width of the distribution. In Fig. 2 the distribution function is shown for $\alpha = 0.1$ and 0.4. Typical values of α for the experiments discussed in this paper are 0.44 for mullite and 0.35 for corundum. Where the Debye model ($\alpha = 0$) gives a semicircle in the ε' versus ε'' plot with its centre on the real axis, the Cole–Cole model has its centre below the real axis. The position of the centre is determined by the distribution width, α.

It is very likely that, in general, both the average relaxation time, τ, and the distribution width, α, are a function of temperature. A good approximation for the relaxation mechanism might be that the process is thermally activated. In that case the average relaxation time, τ, is given by

$$\tau(T) = \tau_0\, e^{(E^{\tau}_{\text{act}}/kT)} \qquad (6)$$

where τ_0 is a characteristic time for the relaxation mechanism, E^{τ}_{act} the activation energy, k the Boltzmann constant and T the temperature.

3.2. Modelling

For the mathematical description of the dielectrical response of the filled measuring cell we used the method of equivalent circuits. This method is based on constructing an electrical analogon by means of capacitors, resistors and other components to describe the response of the material under consideration when an a.c. electrical field is applied. The experimental data were fitted to such a model, using the computerized algorithm of Boukamp [8].

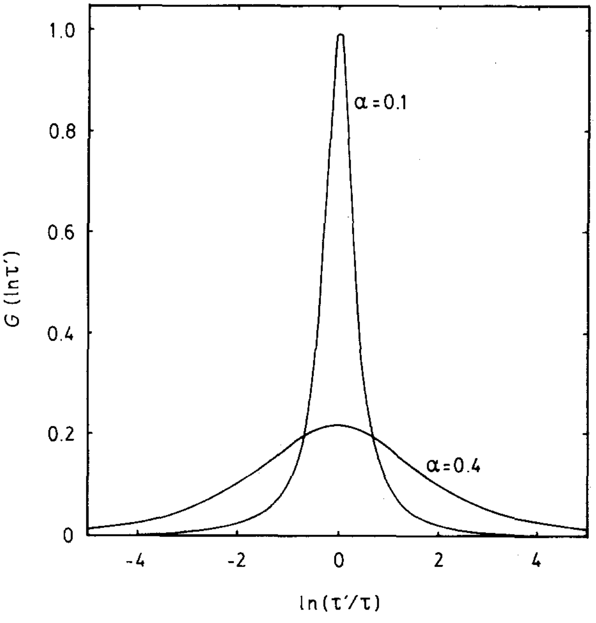

Figure 2 The logarithmic distribution function $G(\ln\tau')$ as a function of the normalized relaxation time $\ln(\tau'/\tau)$ for $\alpha = 0.1$ and $\alpha = 0.4$.

Several models for the dielectrical response of granular materials or powders on an applied a.c. signal have been proposed in the literature (see e.g. [6]). In the most simple models only ideal capacitors and resistors are used to describe the response of the system under consideration. One of those simple models for the characterization of granular materials is a series of elements each consisting of a resistor in parallel with a capacitor. It is assumed that each of these elements can be attributed to the response of a particular physical part (electrodes, grain boundaries, and granules) of the measuring cell filled with the powder. However, the interpretation in terms of the properties of the granules has to be considered with some reserve.

More complex equivalent circuits contain, in addition to ideal resistors and capacitors, so-called constant-phase-elements (CPE). The admittance of such an element is defined by

$$Y_{\text{CPE}} = Q(j\omega)^{\alpha} \qquad (7)$$

where Q is the amplitude and α the phase. Consequently, this element is a capacitor for $\alpha = 1$ and a resistor for $\alpha = 0$.

The Cole–Cole relation mentioned in Section 3.1 can be described by the equivalent circuit shown in Fig. 3. The admittance of such a circuit is given by

$$Y = j\omega C_1 + \frac{j\omega C_2 Q}{Q + C_2(j\omega)^{(1-\alpha)}} \qquad (8)$$

with Q and α the amplitude and the phase factor of the CPE. The elements of this equivalent circuit are related to the parameters in the Cole–Cole relation (Equation 5) by

$$C_1 = \varepsilon_\infty C_0 \qquad (9a)$$

$$C_2 = (\varepsilon_s - \varepsilon_\infty)C_0 \qquad (9b)$$

and

$$Q = \frac{(\varepsilon_s - \varepsilon_\infty)C_0}{\tau^{(1-\alpha)}} \qquad (9c)$$

with C_0 the capacitance of the empty measuring cell.

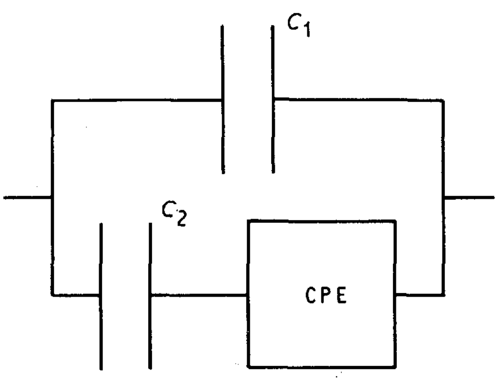

Figure 3 The equivalent circuit which gives a response on an applied a.c. signal that is identical to the Cole–Cole expression. C_1 and C_2 are ideal capacitors and CPE is a constant-phase-element.

If the relaxation mechanism is thermally activated as discussed in the preceding section (see Equation 6), then

$$\frac{1}{1-\alpha}\ln\left(\frac{Q}{C_2}\right) = -\ln\tau_0 - \frac{E^{\tau}_{\mathrm{act}}}{kT} \qquad (10)$$

and a straight line should be observed when $(1-\alpha)^{-1}\ln(Q/C_2)$ is plotted versus $1/T$. Both α and Q are a function of the temperature.

In addition to the relaxation described by the Cole–Cole relation, conduction might occur in the ceramic materials at high temperatures. The occurrence of this conduction can be described in the equivalent circuit model by a resistor in parallel to the elements which correspond to the dipolar relaxation mechanism. For highly insulating materials, the conductivity is mostly of a thermally activated nature. The charge carriers can be electrons, ions, or even both. The latter is the case in corundum [9]. For a thermally activated process, the resistor in the equivalent circuit is given by

$$R = A\,T\mathrm{e}^{(E^{\sigma}_{\mathrm{act}}/kT)} \qquad (11)$$

with A a constant, $E^{\sigma}_{\mathrm{act}}$ the activation energy, k the Boltzmann constant and T the temperature. Consequently, if only one type of charge carrier is present, a straight line should be obtained when $\ln(R/T)$ is plotted versus $1/T$. If two types of charge carriers with different activation energies are present, two different slopes will be observed in that plot. For ceramics, the activation energy and the pre-exponential factor are strongly affected by the presence of impurities, the diffusion path for the charge carriers and the partial oxygen pressure.

4. Results

The dielectric response of both granular materials could be described by the equivalent circuit shown in Fig. 4. The admittance of such a circuit is given by

$$Y = j\omega C_3 + \frac{j\omega C_2 Q_2}{Q_2 + C_2(j\omega)^{(1-\alpha_2)}} + \frac{j\omega C_1 Q_1}{Q_1 + C_1(j\omega)^{(1-\alpha_1)}} + \frac{1}{R} \qquad (12)$$

The upper two branches in the equivalent circuit (consisting of C_3, C_2 and CPE$_2$) represent the Cole–Cole relation. Parallel to this dipole orientation a conduction term, represented by the resistor, R, was observed. In addition to those well-defined processes, we observed an additional one which could be described by a capacitor, C_1, in series with a CPE (CPE$_1$).

There are several ways to represent the dielectric response of a material graphically. Dielectric materials with low dielectric losses are often represented in an ε' versus ε'' plot. For conducting materials it is more illustrative to represent the response by an impedance plot (i.e. a plot of the real part Z' versus the imaginary part Z'' of the impedance). For the granular materials under consideration a modulus plot represents the experiments most clearly. The electric modulus $M = M' + jM''$ of a material is defined by $M = 1/\varepsilon = j\omega C_0 Z$, with C_0 the capacitance of the empty measuring cell and Z the impedance of the filled cell. Fig. 5 shows a modulus plot, corresponding to the equivalent circuit of Fig. 4.

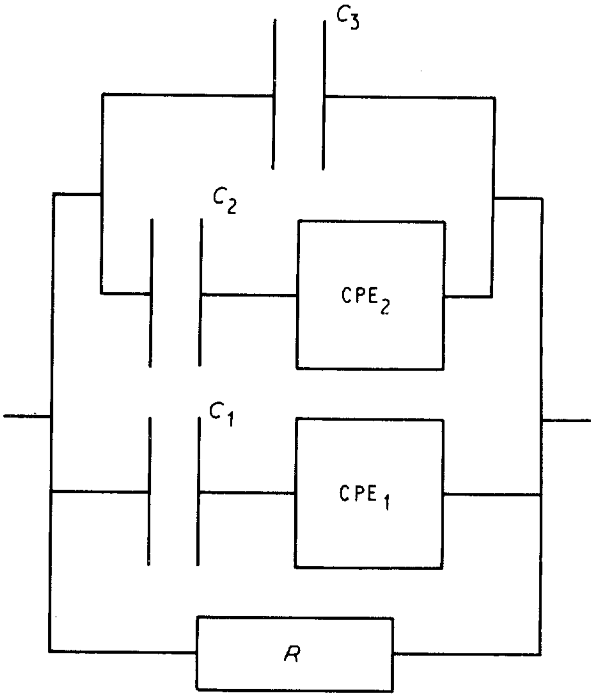

Figure 4 The equivalent circuit which was used to fit the experimentally observed dielectric response of the granular materials. C_1, C_2 and C_3 are ideal capacitors, CPE$_1$ and CPE$_2$ are constant-phase-elements and R is an ideal resistor.

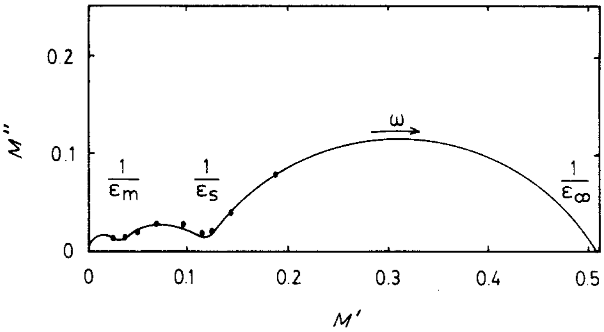

Figure 5 A typical modulus plot for the response of the granular materials discussed in this paper. For this particular plot, the numerical value of the parameters were obtained by fitting the experiments on corundum at 820 K. The dots represent some of the experimental data, the line the calculated response of the equivalent circuit over a much wider frequency range. The meanings of ε_m, ε_s and ε_∞ are explained in the text.

At temperatures from 420–520 K only one relaxation mechanism (one semicircle in the modulus plot) was observed for both corundum and mullite filter beds in the frequency range of our measurements (0.1 Hz–10 kHz). The intercepts with the real axis gave the dielectric constants $\varepsilon_\infty = 1.98$ and $\varepsilon_s = 8.32$ for the corundum filter bed and $\varepsilon_\infty = 2.36$ and $\varepsilon_s = 7.07$ for the mullite filter bed. These values for the dielectric constant gave the best fit over the temperature range where only one relaxation (represented in Fig. 4 by C_2, C_3 and CPE$_2$) was found. However, it should be mentioned that we observed an increase of the dielectric constant, ε_∞, and a decrease of ε_s by a few per cent when the temperature was increased up to 920 K. The value of ε_s for the corundum filter bed (with a volume fraction of 0.24) corresponds rather well to the dielectric constant of 8.23 reported in the literature [10] for porous Al_2O_3 ceramic with a volume fraction of 0.253.

If it is assumed that the relaxation mechanism is thermally activated as discussed previously, then a straight line should be observed when $(1-\alpha)^{-1}\ln(Q/C_2)$ is plotted versus $1/T$. This plot, which is shown in Fig. 6, reveals that this is the case for the materials under consideration. The correlation coefficient is -0.9996 and -0.9999 for corundum and mullite, respectively. An activation energy, E^{τ}_{act}, of 1.03 and 0.87 eV has been determined for the thermally activated relaxation of corundum and mullite, respectively. The characteristic time, τ_0, is calculated to be 17 ps for corundum and 67 ps for mullite. The phase factor, α, of the CPEs varied only about 10% with the temperature and was approximately 0.35 for corundum and 0.44 for mullite. Such a phase factor corresponds to a width in the distribution function of about two or three orders of magnitude (see Fig. 2).

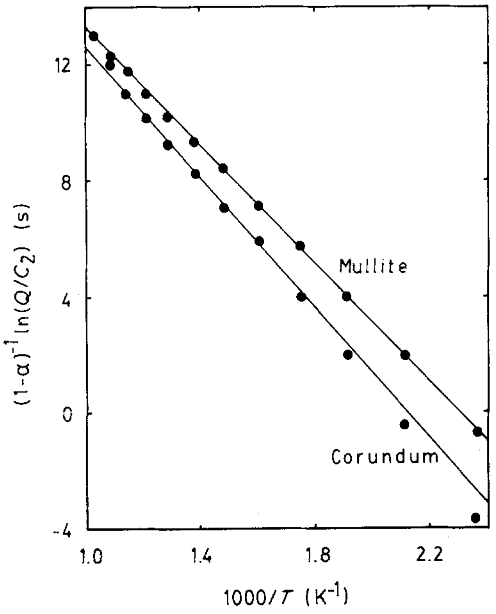

Figure 6 The activation energy, E^{τ}_{act}, and the characteristic time, τ_0 for the dipole orientation are obtained by fitting a straight line to $(1-\alpha)^{-1}\ln(Q/C_2)$ as a function of the inverse temperature $1000/T$. The dots represent the data as obtained by fitting the equivalent circuit shown in Fig. 4 to the measured data.

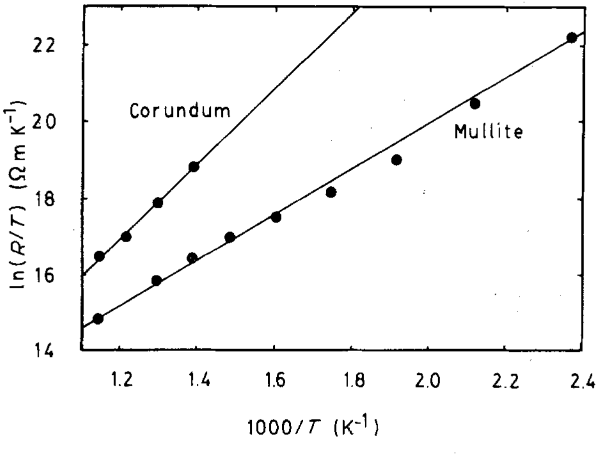

Figure 7 The resistivity of the granular materials in the form $\ln(R/T)$ as a function of the reciprocal temperature. R is the resistivity (Ωm) as obtained by fitting the experimental data to the equivalent circuit shown in Fig. 4.

The conductivity in both granular materials seems to be of a thermally activated nature as Fig. 7 reveals. However, the data on corundum have to be interpreted with some precaution because no significant conductivity could be determined by the equivalent circuit model at temperatures below 650 K. Consequently, only a few data points are present in Fig. 7 for corundum. The activation energy is determined to be 0.85 eV for corundum and 0.52 eV for mullite. The activation energy for conduction in the corundum filter bed is lower than the typical values of about 2–3 eV for ionic conduction in corundum at temperatures above 1000 K [9]. On the other hand, the activation energy is higher than the value of 0.4 for pure corundum at temperatures between 830 and 1000 K [11]. The activation energy agrees rather well with the activation energy of 0.73 eV for the release of electrons from traps [12]. The conductivity of the filter bed at 830 K is about a factor of four lower than that of pure corundum at that temperature [11]. This observation is as expected because of the volume fraction, $\phi = 0.24$, of the filter bed.

At high temperatures, a second arc in the modulus plot, corresponding to the elements C_1 and CPE_1 in the equivalent circuit (see Fig. 4) was observed at the low frequency side of the plot. Such an arc could be interpreted as originating from a second relaxation mechanism of the Cole–Cole type, related to a dielectric constant ε_m as is indicated in Fig. 5. However, the calculated value for the capacitance, and consequently also for ε_m, increased strongly with the temperature. This observation in combination with the increase of both Q_1 and α_1 indicates that the second semicircle in the modulus plot does not originate from a simple relaxation mechanism. It is not clear to us what the origin of the observed second arc in the modulus plot is. It might be possible that (ionic) conductivity with a frequency-dependent character, leading to Maxwell–Wagner polarization at the grain boundaries or electrode interfaces, is the case. Such a frequency-dependent conductivity is often observed in rocks, for example. Because this conductivity is temperature dependent, the apparent dielectric constant is also temperature dependent.

For a comparison of the corundum and mullite filter beds, the characteristic parameters are summarized in Table II. In Figs 8 and 9 some fitting results are shown.

TABLE II The characteristic parameters of the filter beds

	Mullite	Corundum
ϕ	0.414	0.240
ρ_{bed} (10^3 kg m^{-3})	1.20	0.95
ε_∞	2.36	1.98
ε_s	7.07	8.32
E^{τ}_{act} (eV)	0.87	1.03
τ_0 (ps)	67	17
E^{σ}_{act} (eV)	0.52	0.85
A (Ωm K^{-1})	2860	190

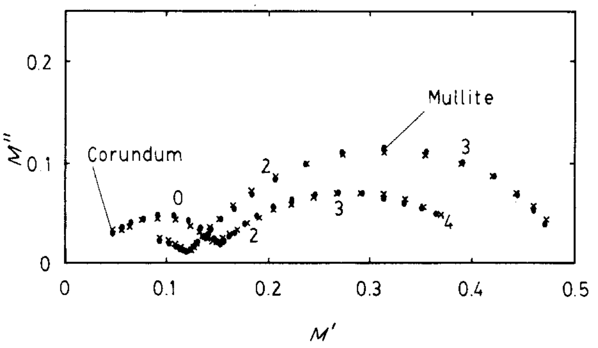

Figure 8 The modulus plot for the granular materials at a temperature of 620 K. Two semicircles corresponding to the two branches of a capacitor in series with a CPE are clearly observable. (●) Measured data (in the frequency range from 0.1 Hz–10 kHz), (×) best fit of the equivalent model to the measured data. The figures correspond to log (frequency).

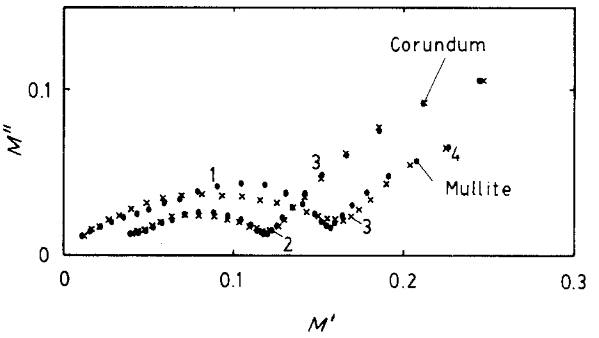

Figure 9 The modulus plot for the granular materials at a temperature of 770 K. (●) Measured data (in the frequency range form 0.1 Hz–10 kHz), (×) best fit of the equivalent model to the measured data. The figures correspond to log (frequency).

5. Conclusions

The experiments reported here, show that for temperatures between 420 and 920 K the dielectric response of granular corundum and mullite at sufficiently high frequencies can be described by a thermally activated relaxation mechanism with a symmetric logarithmic distribution function for the relaxation times, in combination with thermally activated (electronic) conduction.

The activation energy for the dipole relaxation mechanism is observed to be almost equal for the mullite (0.87 eV) and corundum (1.03 eV) filter beds. The characteristic time constant, τ_0, however, was observed to be almost a factor four larger for mullite (67 and 17 ps, respectively). This implies a larger relaxation time for mullite at all temperatures. The low-frequency dielectric constant, ε_s, of the corundum filter bed is higher than that of the mullite filter bed. Because in addition, the volume fraction of the corundum filter bed is smaller than that of the mullite, the dielectric constant of the corundum granules will be higher than that of the mullite granules. This implies that the gradient of the electric field in the corundum filter bed and, consequently, also the capture rate for the particles will be higher.

The conductivity of the corundum filter bed material with an activation energy of 0.85 eV, was observed to be lower than that of the mullite with an activation energy of 0.52 eV. The pre-exponential factor for the conductivity in the corundum filter bed was about a factor of 15 lower than in the mullite filter bed. However, for temperatures up to 920 K the conductivity of the corundum filter bed is lower than that of the mullite filter bed and therefore the energy consumption will be less.

From the experiments reported in this paper we conclude that corundum is preferable to mullite for electrically-enhanced filtration at elevated temperatures.

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References

1. E. TKALČEC, D. NAVALA and M. ĆOSIĆ, *J. Mater. Sci.* **25** (1990) 1816.
2. I. M. LOW and R. McPHERSON, *ibid.* **24** (1989) 926.
3. C. A. P. ZEVENHOVEN, P. J. DROPPERT and R. H. M. van de LEUR, in "Proceedings of the 2nd World Congress on Particle Technology", Kyoto, Japan, September 1990 (Society of Powder Technology, Japan) Part I, pp. 289–296.
4. P. H. de HAAN, P. J. NEDERVEEN, P. J. DROPPERT, K. E. D. WAPENAAR and B. SCARLETT, in "Proceedings of the 3rd International Conference on Electrostatic Precipitation", Albano, Italy, October 1987, edited by M. Rea (University of Padua) p. 1065.
5. R. C. WEAST (ed.), "CRC Handbook of chemistry and physics", 65th Edn (CRC Press, Boca Raton, 1984) p. B-29.
6. C. J. F. BÖTTCHER and P. BORDEWIJK "Theory of electric polarization", Vol. II (Elsevier, Amsterdam, 1978) p. 45.
7. J. R. MACDONALD and W. B. JOHNSON, in "Impedance Spectroscopy, Emphasizing Solid Materials and Systems", edited by J. R. Macdonald (Wiley, New York, 1987) p. 1 of text ref: Fundamentals Impedance Spectroscopy.
8. B. A. BOUKAMP, "Equivalent circuit, the computer assisted electrochemical ac-immittance data analysis system", (Department of Chemical Technology, University of Twente, 7500 AE Enschede, The Netherlands, 1988).
9. E. DÖRRE and H. HÜBNER, "Alumina Processing, Properties and Applications" (Springer, Berlin, 1984), and references cited therein.
10. F. BROUERS, A. RAMSAMUCH and V. V. DIXIT, *J. Mater. Sci.* **22** (1987) 2759.
11. O. T. ÖZKAN and A. J. MOULSON, *Brit. J. Appl. Phys.* **3** (1970) 983.
12. G. P. SUMMERS, in "Structure and Properties of MgO and Al_2O_3 Ceramics", edited by W. D. Kingery (The American Ceramic Society, Columbus, 1983) p. 43.

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