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Impedance spectroscopy studies of orthorhombic $FeNbO_4$

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Electrical characterization of the $FeNbO_4$ compound, with orthorhombic structure, has been carried out. Compact bodies were prepared by sol–gel and ceramic routes. Pellets for electrical measurement were sintered in air, and samples for electrical tests were electroded with platinum, gold and silver paste. Equivalent circuit models were established that fit the impedance spectroscopy data with good agreement. Comparison of impedance responses showed that samples prepared by different routes have similar electrical behaviour. These measurements, in conjunction with *I–V* characteristic curves, indicate the existence of a small bulk resistance, which does not change at the higher experimental temperatures considered. Interfacial impedances due to the metallic contact regions contribute the greatest part of the overall impedance. The response of the sample with different electrode materials (platinum, gold, silver) was studied. *I–V* characteristic curves indicate a space charge-limited current phenomenon at the platinum contact, followed by a charge avalanche process at higher voltages.

1. Introduction

Some types of ABO_4 oxides containing transition metal elements are semiconductors, because of a valence mixed behaviour that results in the jumping of electrons to the conduction band. This kind of material is interesting owing to potential applications as gas sensors, catalysts and photodetectors.

Roth and Warring [1] studied the synthesis and structural characteristics of $FeNbO_4$, which exhibits the following polymorphism:

$$\text{monoclinic} \xrightarrow[1085\,^{\circ}\text{C}]{} \text{orthorhombic} \xrightarrow[1380\,^{\circ}\text{C}]{} \text{tetragonal (rutile)}$$

The monoclinic phase $FeNbO_4$ is isostructural with the wolframite; $FeNbO_4$ (orthorhombic) is isostructural with ioxolite mineral; and $FeNbO_4$ (tetragonal) is isostructural with rutile. No work has been found in the reviewed literature dealing with the electrical properties of $FeNbO_4$. Structural and magnetic properties have been studied by Harrison and Cheetham [2].

In previous papers on the synthesis and structural characterization of $Fe_xTi_{1-2x}Nb_xO_2$ rutile solid solutions [3,4], a phase with orthorhombic $FeNbO_4$ structure was detected. It was noted that the orthorhombic phase changed to rutile when the temperature was increased. Preliminary electrical characterization of the $FeNbO_4$ orthorhombic compound with platinum electrodes, by means of impedance spectroscopy (IS), allowed us to separate two conduction processes. The one taking place at the lower frequency values contributed the greatest part of the resistance to the overall impedance. It was tentatively assigned to an interfacial conduction–polarization process at the material–metal interface.

The present work was mainly devoted to establish which of the processes found in the impedance spectra was due to interfacial electrical phenomena at the metallic contacts. To this end, we studied in detail the IS data of a sample electroded with different electrode materials, and also the *I–V* characteristic curves. The results allow the high-frequency resistance found in the impedance spectra to be identified as the electrical resistance of orthorhombic $FeNbO_4$.

2. Experimental procedure

Samples of $FeNbO_4$ were prepared by ceramic and sol–gel methods. The starting materials used in the ceramic method were Nb_2O_5 (Merck) and Fe_2O_3 (Panreac). Two types of gel were processed: colloidal gel and polymeric gel. For colloidal gels, $NbCl_5$ (Merck) and $FeCl_3 \cdot 6H_2O$ (Panreac) of chemical quality reagent grade were used as raw materials. For polymeric gels, $NbCl_5$ (Merck) and Fe(III) acetylacetonate (Merck) were employed.

In the ceramic method, the appropriate amounts of starting materials were mixed and homogenized in acetone in a planetary ball mill for 20 min.

To obtain the colloidal gel samples, $NbCl_5$ was dispersed in water by vigorous stirring. Then $FeCl_3 \cdot 6H_2O$ was simultaneously added into suspension

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and stirred vigorously at 70 °C. After that, a solution of ammonium hydroxide was poured until gelation (pH = 5–6) took place. Finally, the obtained gel was dried with an infrared lamp.

In the polymeric gel method, a solution of $NbCl_5$ in ethanol was refluxed with continuous stirring at 70 °C for 15 h. Fe(III) acetylacetonate was added to the resulting solution, refluxed at 70 °C for 24 h and acidified with 3M HNO_3. These gels were dried by slow drying, covering the gel with a plastic film to slow down solvent loss by evaporation. The film was drilled with a needle to control the speed of evaporation.

Samples were placed in a refractory crucible and calcined at temperatures between 300 and 1000 °C for 12 h soaking time. Calcined powders were ceramically conformed into disc pellets (0.8 cm diameter, 2–5 mm thick) and then sintered at 1450 °C in air for 2 h. The X-ray diffraction analysis indicated the presence of $FeNbO_4$ with orthorhombic structure as the unique phase from temperatures of 1000 °C. This orthorhombic structure was retained in the samples sintered at 1450 °C, and the rutile phase was not noticed in any of them. The attained densities were between 93% and 95%.

Samples for electrical tests were electroded onto both surfaces with platinum high-conductivity paste. These contacts were fired at 800 °C for 2 h. In order to check the dispersion effect of different contacts, gold electrode high-conductivity paste fired at 800 °C for 2 h and silver paste fired at 100 °C for 24 h were also applied.

For complex plane impedance analysis, a frequency analyser HP-4192A in the frequency range 10–10^7 Hz was employed. The *I*–*V* characteristic curves were obtained by using a Keithley 228A voltage source. Samples were put into a hot-sample holder regulated by a temperature controller and measurements were carried out between 20 and 800 °C.

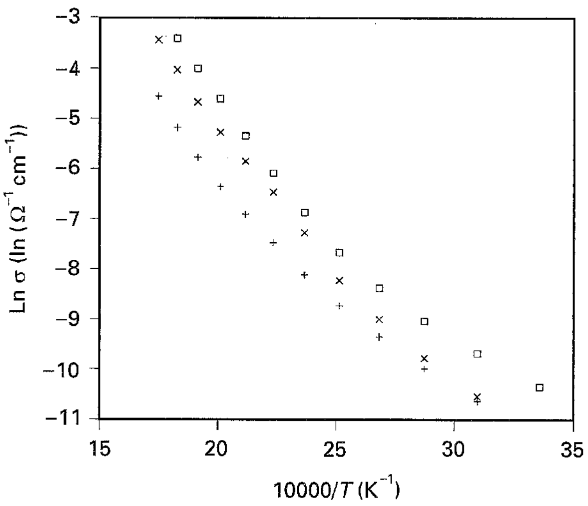

Figure 1 Total conductivity of samples electroded with platinum, versus the inverse of temperature. (+) Ceramic, (□) polymeric gel and (×) colloidal gel preparation routes.

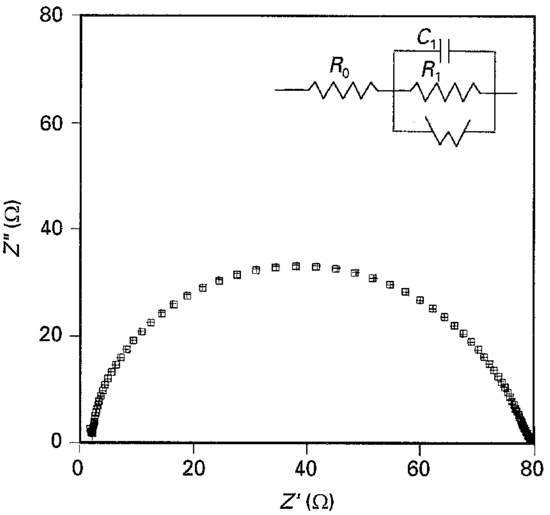

Figure 2 Impedance spectrum of the ceramic route sample electroded with platinum, at *T* = 250 °C. Shown are (□) measured data and (+) values simulated from fitted parameters.

3. Results

3.1. General electrical characteristics of samples prepared by different methods

A thorough analysis of the impedance spectra shows that the various samples, as prepared by different methods, present similar electric behaviour when electroded with platinum on both sides. The bulk material contributes a relatively small resistance with no measurable capacitive-associated effects. It was not possible, therefore, to separate electrically the porosity, grain boundary and the rest of the blocking-element contributions in the bulk material.

At moderate temperatures (50–200 °C) the material–metal contact contributes by far the greatest part of the total resistance. Fig. 1 shows the total conductivity of the platinum–material interface versus inverse temperature, obtained from the impedance plots, for samples prepared by the colloidal gel, polymeric gel, and ceramic routes. Both total conductivity values and activation energies (with an approximate value of 0.42 eV) are very similar. Henceforth we focus next on the effect of the variation of the electrode material in a single sample, prepared by the ceramic method. Its size is 0.8 cm diameter and 3 mm thick, with the electrodes practically covering the whole sides.

3.2. Pt/Pt electrode configuration

Fig. 2 shows the impedance spectrum of the sample with a platinum electrode in both surfaces, at 250 °C, and the result of a fit by means of a non-linear least square method [5]. The agreement of experimental data with values simulated according to the equivalent circuit model (EC) drawn in the same figure, is excellent. To confirm the goodness of fit, Fig. 3 depicts the impedance bode diagram of the same data, and the simulated ones.

It is clearly appreciated in Fig. 2 that data deviate from a semicircle in the low-frequency region. Thus a proper fit requires a subcircuit with three elements in parallel (R_1C_1W), instead of the simpler, usual subcircuit (*RC*) with two elements in parallel. The Warburg impedance that accounts for the low-frequency

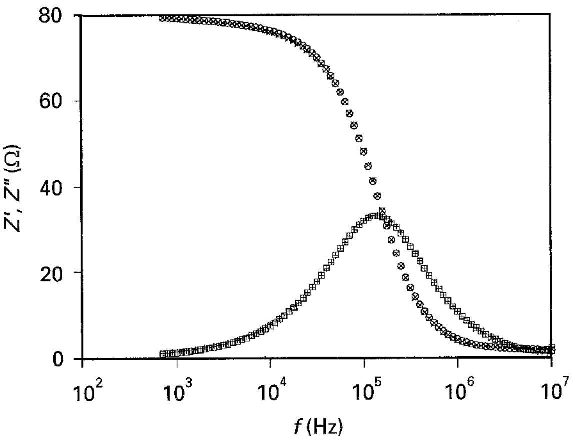

Figure 3 As Fig. 2, in an impedance bode diagram. (×) Z' simul., (+) Z'' simul., (○) Z' meas., (□) Z'' meas.

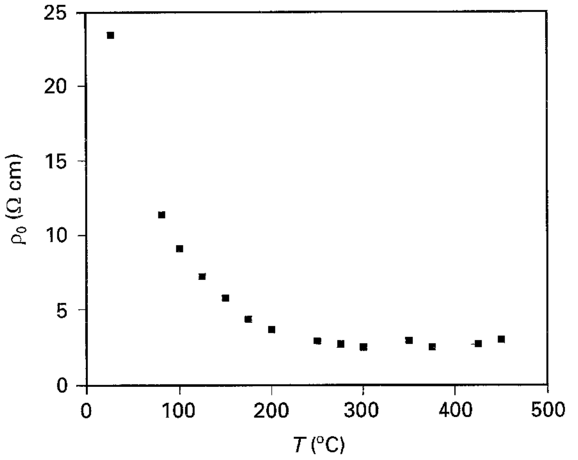

Figure 4 Bulk resistivity of the ceramic route sample versus temperature.

distortion indicates that diffusion effects are taking place at the metal–material interface.

In this Pt/Pt electrode configuration, the EC does not change as temperature is raised. If a d.c. bias of 0 to ± 10 V is applied, together with an a.c. stimulus of amplitude 0.1 V, the EC in Fig. 2 still accounts correctly for the impedance data. If the bias voltage is further increased, the impedance spectrum shows a pseudoinductance loop in the low-frequency region [6]. Moreover, a constant value of capacity $C_1 = 1.28 \times 10^{-8}$ F is found, despite the variation of bias and temperature. This precludes the possibility of a Schottky barrier formation at the material–metal contact.

The intercept with the real axis at high frequency yields the bulk resistance (R_0 value) of $FeNbO_4$. This resistance is unaffected by application of a bias voltage. Its behaviour under sample heating is shown in Fig. 4: it decreases slowly as temperature increases and then stabilizes at 250 °C. This effect is a typical response of an extrinsic semiconductor; it may be due either to the stabilization of charge-carrier concentration (if the intrinsic charge-carrier generation is not yet activated at the higher temperature considered), or to the stabilization of the charge-carrier mobility [7].

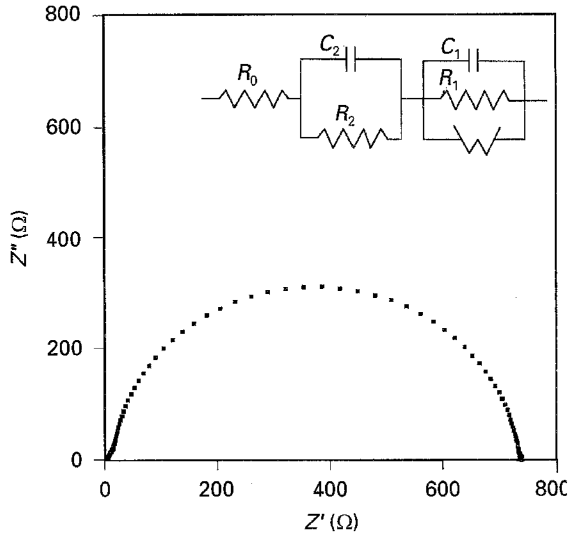

Figure 5 Impedance spectrum of the ceramic sample electroded with platinum on one side and silver on the other side, at $T = 150$ °C.

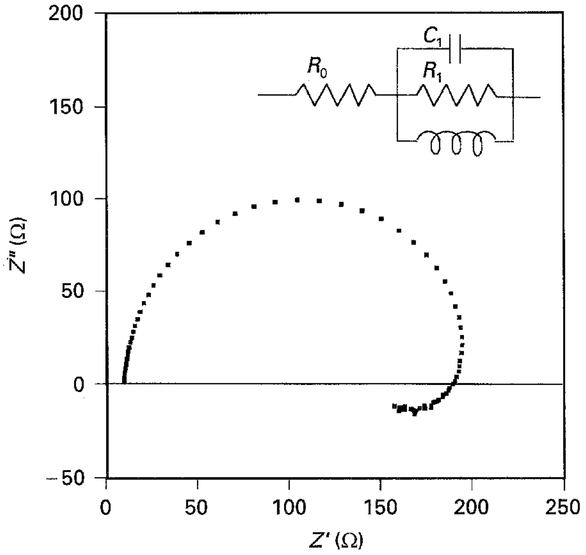

Figure 6 Impedance spectrum of the ceramic sample electroded with platinum on one side and silver on the other side, at $T = 150$ °C, with 35 V d.c. applied bias.

3.3. Different electrode materials at both sides

In the case of Pt/Ag electrode configuration (platinum on one side and silver on the other side of the sample), the impedance spectrum (Fig. 5) shows again a small R_0 resistance, an intermediate distorted semicircle and a large, low-frequency arc. Therefore, a subcircuit (R_2C_2) that accounts for the intermediate arc must be added, in series, to the EC ascribed to the Pt/Pt configuration in Fig. 2. The form of the impedance spectrum in Fig. 5 does not change in the temperature range between 25 and 150 °C. From 200–300 °C the intermediate subcircuit vanishes. When d.c. bias is applied from 5–35 V, the impedance spectrum (Fig. 6) exhibits a pseudoinductance loop, even clearer than in the Pt/Pt case.

In the case of Pt/Au electrode structure, the impedance spectrum at room temperature is similar to that

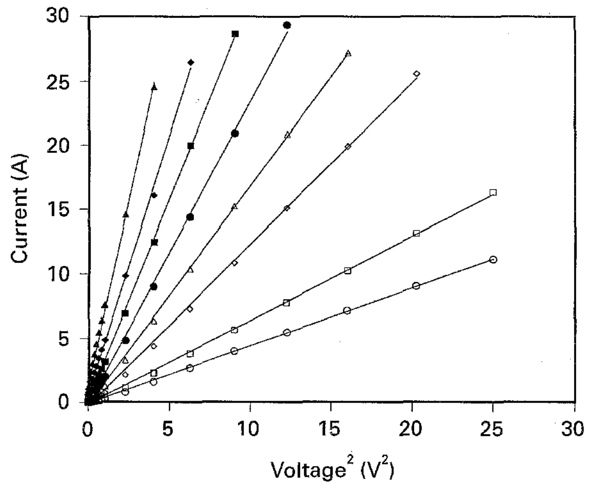

Figure 7 I–V^2 curves of the ceramic route sample electroded with platinum at different temperatures. Straight lines are linear fits of data. T (°C): (○) 25, (□) 97, (◇) 120, (△) 142, (●) 170, (■) 194, (◆) 219, (▲) 244.

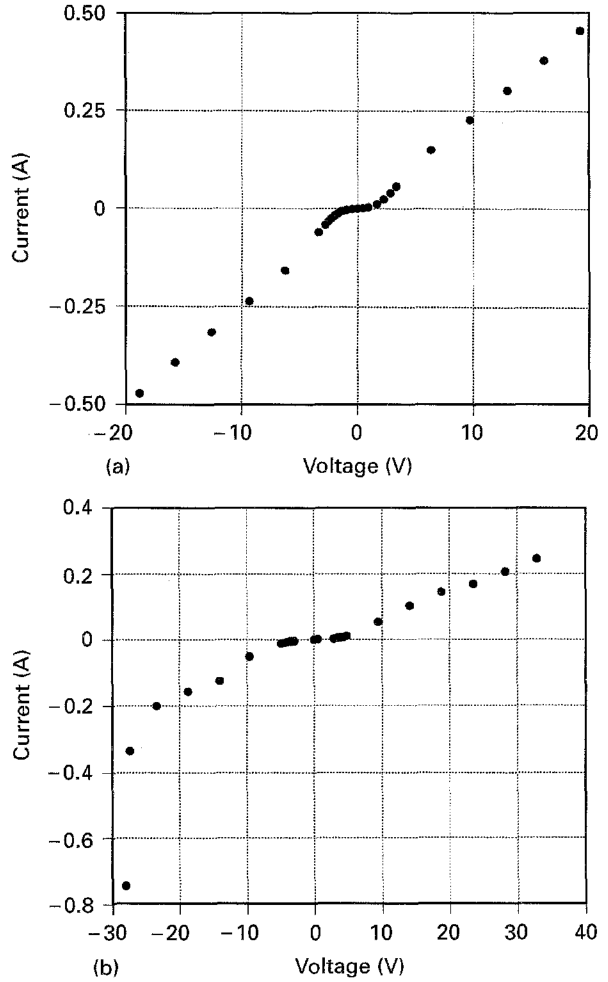

Figure 8 I–V characteristics at room temperature. (a) Pt/Au electrode configuration. (b) Pt/Ag electrode configuration. In both cases, platinum was on the lower potential electrode.

of Fig. 5 (Pt/Ag structure case), a pattern that is not altered when d.c. bias is applied. As temperature is raised from 100 °C to 200 °C the intermediate subcircuit also disappears. From 250–300 °C the impedance is exactly a pure resistance.

3.4. *I–V* characteristic curves

In samples with Pt/Pt electrode structure, Fig. 7, the form of the I–V^2 curves suggests a space charge-limited current phenomenon at the electrode contact [8]. If the applied voltage is again increased, a typical charge-carrier avalanche process takes place in the sample. At the lowest voltages, an ohmic region is found, whose associated resistance coincides closely with the interfacial resistance value found from impedance spectra.

No rectification effects were found in the Pt/Au electrode structure, Fig. 8a. The curve presents an almost ohmic characteristic over the entire range of applied d.c. voltage, at room temperature. When Pt/Ag electrode structure is applied, however, a significant rectifying process is observed (Fig. 8b). The IS results indicate that this behaviour is basically controlled by the material–metal contact, but this phenomenon is not completely understood as yet, and further experiments are needed.

4. Conclusion

$FeNbO_4$ is a highly conductive extrinsic semiconductor whose total conduction mechanism is ascribed to a mixed valence semiconduction.

IS measurements allow bulk and interfacial properties (but not the effect of blocking phase elements in the material such as pores, boundaries, etc.) to be separated. Both contributions have semiconducting properties. The bulk resistance, R_0, only changes with temperature, but not under d.c. bias. In all cases, an interfacial dispersion due to the electrode–material interface is observed, eventually separated into two dispersion semicircles. One (the intermediate arc), which also changes with temperature and d.c. bias, can be ascribed to the gold or silver contact interface. The second one, trend habit did not vary in any of the experiments carried out, must be ascribed to the platinum–material interface. In the Pt/Ag and Pt/Pt electrode structures, a pseudoinductance appears at high d.c. bias voltage.

Finally, space charge-limiting current behaviour accounts for high field effects.

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