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Synthesis of sodium titanate composites by sol-gel method for use in gas potentiometric sensors

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Abstract

Mixtures of $Na_2Ti_3O_7/Na_2Ti_6O_{13}$ and $Na_2Ti_6O_{13}/TiO_2$ were synthesised by the sol-gel method using alkoxide precursors. XRD and SEM characterisations were performed. Semi-quantitative chemical analyses were carried out and the mixture ratio of $Na_2Ti_3O_7/Na_2Ti_6O_{13}$ was 3:1 wt. A qualitative estimation on the mixture $Na_2Ti_6O_{13}/TiO_2$ gives also a higher ratio. Such composites are well suited to be used directly as oxygen electrode materials in potentiometric gas sensor devices exchanging sodium and oxygen with the surrounding phases. Electrochemical impedance spectroscopy (EIS) was used to measure the total conductivity. A part of electronic conductivity depending on the partial oxygen pressure was observed in the mixture $Na_2Ti_6O_{13}/TiO_2$ due to the presence of rutile TiO_2.

Keywords: EIS; Electrode materials; $Na_2Ti_3O_7$; $Na_2Ti_6O_{13}$; TiO_2; SEM; Sol-gel processes; Synthesis; XRD; Gas; Conductivity

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1. Introduction

Alkali and alkaline earth titanates have been used in ion exchange processes, for ceramic capacitors, as dielectric resonators in microwave oscillators band pass,[1] as a reinforcing agent of plastic, as adiabatic materials[2] and as an oxygen electrode for potentiometric gas sensors.[3–5]

As discussed by Feist et al.[6] and Li et al.,[7] the alkali–metal titanates $A_2Ti_nO_{2n+1}$ ($n=3$ or 8, and A = Na, K, Li) crystallise into a monoclinic structure with almost the same *b* cell parameter. Such materials for $n=3$ or 4 consist of $(Ti_3O_7)^{2-}$ layers held together by alkali–metal ions (Na^+, K^+) as shown in Fig. 1. With a low alkali metal content (i.e. $n=6$ to 8), they present a tunnel structure (see Fig. 1) and exhibit a high insulating ability and a good chemical stability. Bouaziz et al.[8] and Gicquel et al.[9] have reported partial phase diagrams of the system Na_2O–TiO_2 using X-ray diffraction (XRD). These phase diagrams are commonly accepted by the scientific community.[10] Up to now, very few data are available in the literature about the electrical properties of alkali–metal titanates.

Different synthesis procedures are described in the literature[1–9] to prepare alkali and alkaline earth titanates. $Na_2Ti_3O_7$ and $Na_2Ti_6O_{13}$ are generally synthesised by solid-state reactions from the stoichiometric weights of Na_2CO_3 and TiO_2 or Na_2O and TiO_2, followed by an oxidation at 1250 °C.[4,8,9] The aim of this work is to obtain a new composite based on sodium titanate mixtures to be applied in oxygen or carbon dioxide sensor devices, as proposed first by Maier et al.[3] In this context, a mixture of two compositions of titanates was elaborated to allow a stable electrochemical system. The role of the electrode materials is to exchange sodium with a solid conductor (NASICON or β-alumina) and oxygen with the gas, for example according to the following equilibrium:

$$2Na_2Ti_3O_7 \Longleftrightarrow Na_2Ti_6O_{13} + 2Na^+_{(electrolyte)} + 2e^-_{(metal)} + \frac{1}{2}O_{2(gas)} \qquad (1)$$

If the ratio of titanates is not too high or not too low (i.e. about 1), such a system is buffered and can be stable a priori. A sol-gel route has been developed because this

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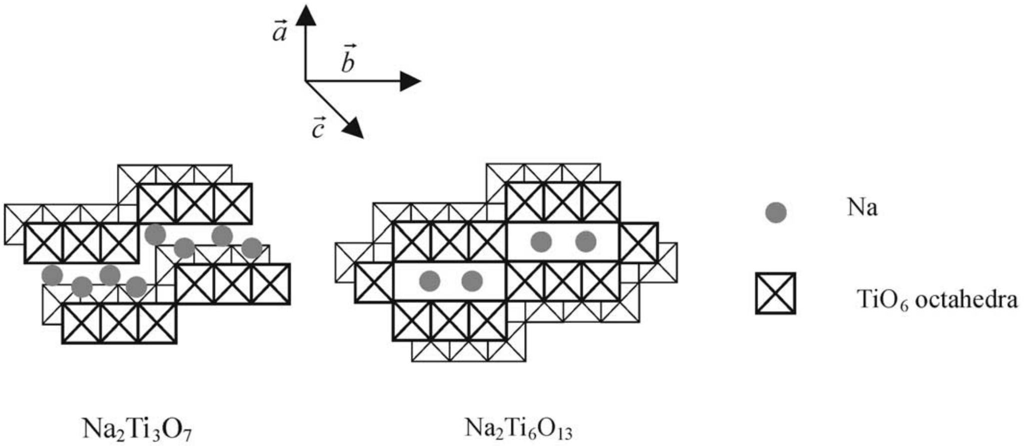

Fig. 1. Several layered titanate structures.[5]

process is well adapted for the synthesis of small grained powders homogeneous in composition. Consequently, exchange kinetics is expected to be improved. Moreover such a process allows the obtaining of compounds well mixed.

The present study is devoted to the elaboration of sodium titanate composites and to the characterisations of samples by XRD and SEM. Electrical properties of such composites were also investigated by electrochemical impedance spectroscopy (EIS) in different atmospheres (air, CO_2–air, argon). The characteristics of such materials in potentiometric sensor devices are described elsewhere[11,12] and the present paper is essentially dedicated to the elaboration and physical characterisations of the composites.

2. Experimental

2.1. Preparation of materials

To synthesise the compound based on $Na_2Ti_3O_7$ (referred to as Ti3), 21 g of $Ti(OET)_4$ (titanium(IV) *n*-butoxide 99%, $C_{16}H_{36}O_4Ti$, Jansen Chimica) were dissolved in 50 ml of butanol-1 (Chimie plus lab.). NaOH (1.6 g) (99%, Strem Chemical Inc.) dissolved in about 100 ml of distilled water was added simultaneously with an excess of distilled water (higher than 200 ml) to obtain a fast hydrolysis–condensation reaction. All the reagents were initially heated between 55 to 60 °C. After that, the powdered suspension was maintained at the same temperature for 40 min up to a complete reaction.

For the compound based on $Na_2Ti_6O_{13}$ (referred to as Ti6), 22.86 g of $Ti(OET)_4$ was dissolved in 50 ml of butanol-1. 0.88 g of NaOH dissolved in distilled water and an excess of distilled water was added according to the same process (temperature and time).

Whatever the compound, the gel was heated under continuous stirring to evaporate a maximum of water and residual alcohol, in order to get a very viscous solution, which was successively dried in ambient air at 100 °C. A residual white powder was finally obtained. In the following step, the dried powders were then ball-milled for 20 min, compacted in pellets (10 mm in diameter and 2–4 mm in thickness) by isostatic pressing at 250 MPa for 10 min. The pellets of Ti3 and Ti6 were subsequently sintered at 1000 °C for 16 h in air, similar conditions as for mixed oxide processing. The total sol-gel process diagram is given in Fig. 2 and the sintering program is represented in Fig. 3.

The final densifications of samples (Ti3 and Ti6) were approximately in the range 85–95% of the theoretical densities (about 4 g cm^{-3}).

2.2. Characterisations

X-ray diffraction analyses were carried out at room temperature using a Siemens D500 with a Cu $K_{\alpha 1}$ radiation ($\lambda = 1.5405$ Å), 2θ scanning rate of 0.04° min^{-1} from 10 to 80°. $Na_2Ti_3O_7$, $Na_2Ti_6O_{13}$ and TiO_2 phases were identified by comparison with the respective JCPDS cards.

The particle morphology of sodium titanates was observed by scanning electron microscopy (SEM Jeol JSM-35).

Impedance spectroscopy measurements were carried out using an impedance analyser HP 4192A in a two electrode cell (platinum electrodes) and in a symmetrical mode with a signal of 0.1 V from 5 Hz to 13 MHz. Some measurements at very low frequencies (down to 10^{-2} Hz) were also carried out using a Solartron (Schlumberger 1186 with a SI 1250 interface).

A flux of pure and dried synthetic air, or CO_2 5% in synthetic air (19% of O_2) or argon (oxygen partial

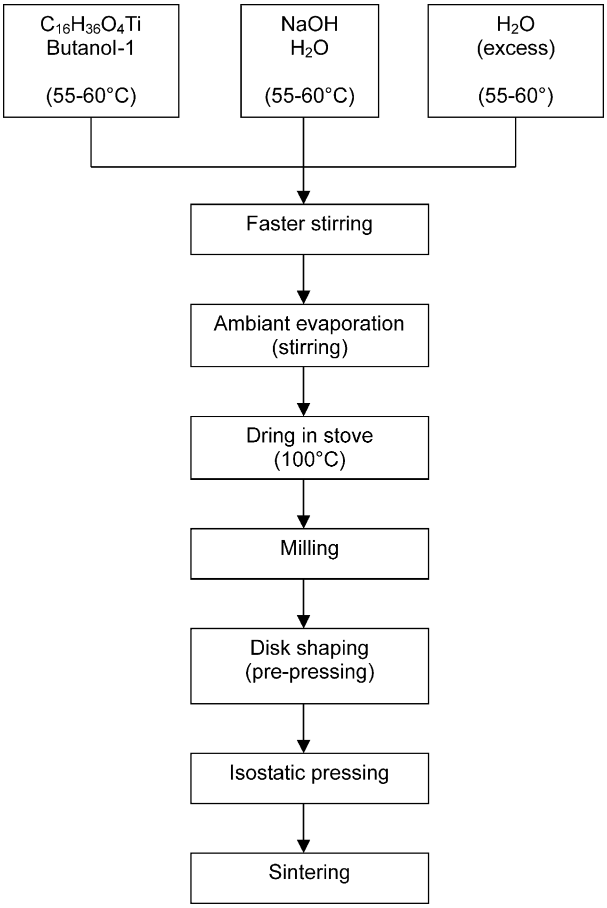

Fig. 2. Diagram of the sol-gel process.

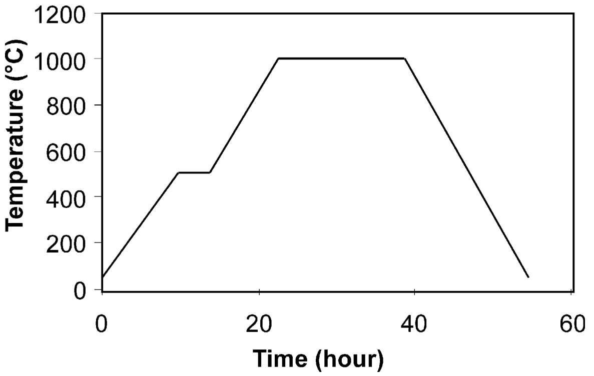

Fig. 3. Sintering program of pellets.

pressure about 10^{-5} atm) was used. An electrochemical pump-gauge device was also used to adjust the oxygen partial pressure at different values.

3. Results and discussion

3.1. XRD and lattice parameters

From the previously described sol-gel way, a mixture of two phases was identified in each sample as $Na_2Ti_3O_7/Na_2Ti_6O_{13}$ for Ti3, by comparison with 72-148 and 73-1398 JCPDS cards respectively, and $Na_2Ti_6O_{13}/TiO_2$ for Ti6, by comparison with 72-1398 and 78-1509 JCPDS cards respectively. The loss of sodium could appear during a step of the sol-gel process which is a very complex chemical reaction. For Ti3, which is a mixture of monoclinic phases, a semi-quantitative chemical analysis was performed using the ratios of intensities of 100 peak of each component. So the mixture ratio of $Na_2Ti_3O_7/Na_2Ti_6O_{13}$ was 3/1 wt. Such a ratio is not too much further than 1/1 which should be the ideal ratio for a buffered mixture in the oxygen electrode reaction used in potentiometric sensors [see Eq. (1)]. For Ti6, because $Na_2Ti_6O_{13}$ is monoclinic and TiO_2 is a tetragonal phase, similar analysis cannot be made rigorously. An example of XRD pattern is shown in Fig. 4 where the rutile phase of TiO_2 can be clearly observed in a noticeable ratio.

The lattice parameters of our samples were found close to the JCPDS cards (see Table 1) in which natural sodium titanates were elaborated by oxidation method at high temperature [8]. We can mention that the sol-gel method provides the same sodium titanates crystalline structures as those reported by other preparation methods.

3.2. SEM analyses

The scanning electron micrographs of sol-gel sodium titanate ceramics show particle sizes ranging from 0.3 to 6 μm (Fig. 5). Different morphologies can be observed: small spherical particles of 1 μm in diameter, cubic particles of about 6 μm in size and parallelepipedic shapes of 0.7–2 μm in width and 2–7 μm in length.

3.3. Electrical properties

For the Ti3 composite (Fig. 6), the impedance diagram consists of one loop in the frequency range higher than 40 Hz. This diagram is similar to that of a material for which bulk and grain boundary contributions cannot be separated when their characteristic frequencies are close. Such a diagram shape could also be due to the presence of two mixed phases $Na_2Ti_6O_{13}$ and $Na_2Ti_3O_7$. This part of the diagram is only partly modified as a function of the oxygen partial pressure. This is in accordance with a predominant ionic conductivity for example by Na^+.

In the frequency range lower than 40 Hz, an influence of the oxygen partial pressure was clearly observed. The determination of the capacitance, from the part of the semi circle in this range of frequency, leads to a value of about 1–3 mF cm^{-2} depending on the oxygen partial pressure. Moreover, at frequencies down to 10^{-2} Hz a Warburg straight line could be drawn (not represented in Fig. 6). This part of diagram is fully related to

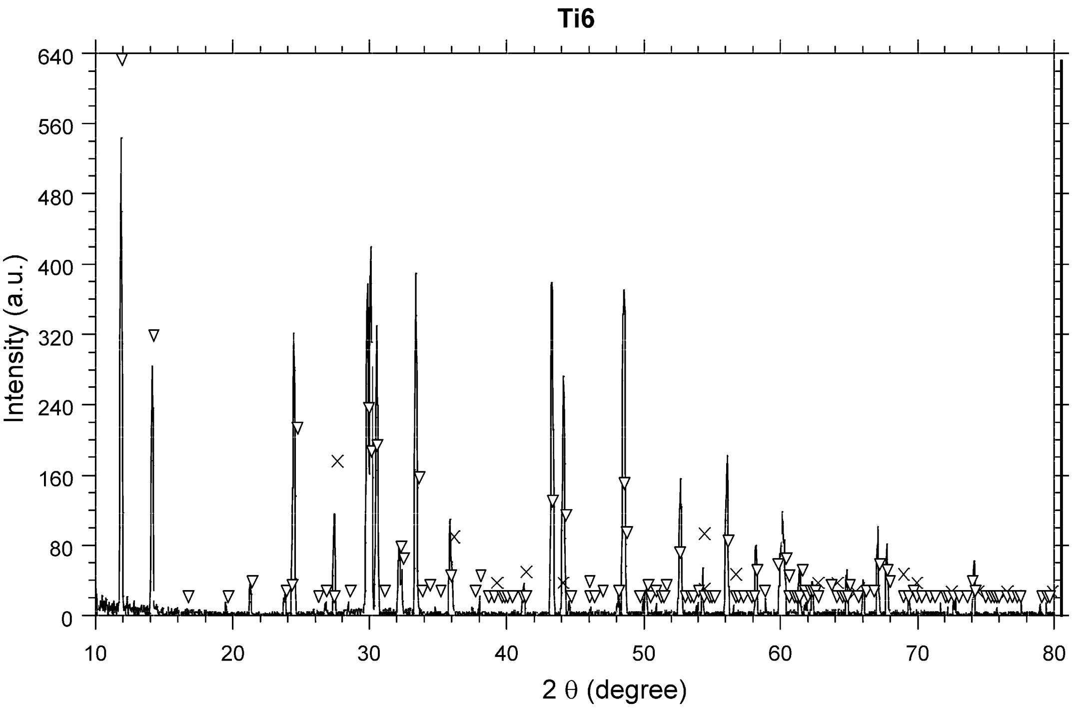

Fig. 4. X-ray diffraction pattern of Ti6 pellet ([▽] $Na_2Ti_6O_{13}$ and [×] TiO_2) elaborated by sol-gel method.

Table 1
Crystallographic lattice parameters

Compound	$Na_2Ti_3O_7$	$Na_2Ti_6O_{13}$	TiO_2
Crystalline structure (JCPDS)	Monoclinic (JCPDS 72-148)	Base-centered monoclinic (JCPDS 73-1398)	Tetragonal (JCPDS 78-1509)
Cell parameters	$a = 0.9128$ nm $b = 0.3806$ nm $c = 0.8566$ nm $\beta = 101.53°$	$a = 1.5120$ nm $b = 0.3746$ nm $c = 0.9162$ nm $\beta = 99.28°$	$a = b = 0.4594$ nm $c = 0.2958$ nm
Spatial group	$P2_1/m$ C^2_{2h}	$C2/m$ C^3_{2h}	$P4_1/mnm$ D^{19}_{4h}
Description	Alternating sheets of $(Ti_3O_7)^{2-}$ and 2 atoms of Na (viewed from *b*-axis, Fig. 1)	Somewhat similar to $Na_2Ti_3O_7$ in which the $(Ti_3O_7)^{2-}$ units have been closing up on the Na atomic layer, thereby the 2 Na atoms become boxed in by the titanate units (viewed from *b*-axis, Fig. 1)	TiO_6 octahedral connected by an edge-sharing pattern giving a ribbon-like formation along the *c*-axis
Phases in Ti3	$a = 0.8753$ nm $b = 0.3785$ nm $c = 0.8342$ nm $\beta = 99.65°$	$a = 1.4958$ nm $b = 0.3732$ nm $c = 0.8397$ nm $\beta = 101.2°$	Not observed
Phases in Ti6	Not observed	$a = 1.5117$ nm $b = 0.3746$ nm $c = 0.9215$ nm $\beta = 98.97°$	$a = b = 0.4598$ nm $c = 0.2956$ nm

phenomena which are taking place at the electrode–gas–electrolyte interface, and is not due to bulk and grain boundary contributions of the materials.

The total conductivity of Ti3 versus temperature is given in Fig. 7 and follows an Arrhenius behaviour. The average activation energy is 0.62 eV. On this diagram we can observe a slight influence of the oxygen partial pressure on the conductivity values, under argon atmosphere. Such a property could be due to a part of electronic conductivity or O^{2-} ionic conductivity depending on the oxygen pressure. This part does not excess 10% of the nominal value. Whatever its nature, such a mixed

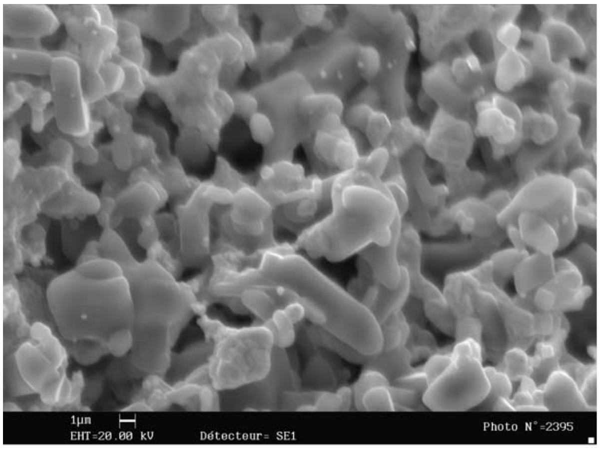

Fig. 5. Example of SEM micrograph of sodium titanate prepared by sol-gel method.

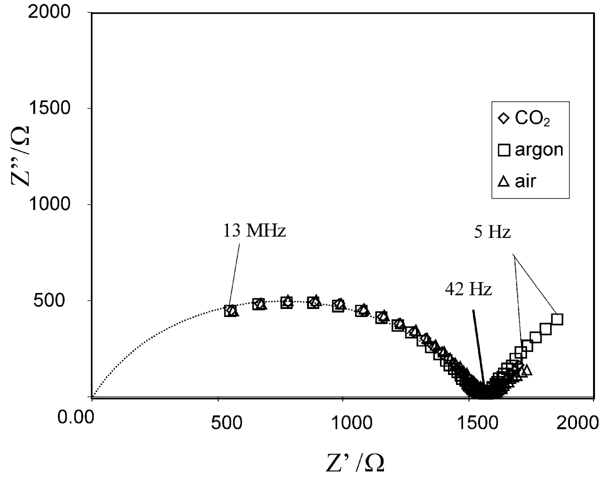

Fig. 6. Impedance plot for the Ti3 composite at 660 °C with Pt electrodes in argon, air and air-5% CO_2.

conductivity will be favourable to an electrode in which several species are exchanged (electrons, Na^+ and O_2 or O^{2-}).

Examples of impedance diagram obtained on the Ti6 composite are plotted in Fig. 8. In this case two loops can be distinguished (f°_1 about 10^5–10^6 Hz and f°_2 about 10^3 Hz). An influence of the oxygen partial pressure is shown. The separation into two semicircles was not sufficiently accurate to lead to a serious exploitation of the resistance values, nevertheless the order of magnitude of the capacitances can be determined. For the high frequency loop (f°_1 about 1 MHz), the capacitance is about 20–30 pF and is very low depending on the temperature. Such a value corresponds to the usual values of oxide materials (grain capacitance) for our geometric factors. For the loop observed in the lowest frequency range (f°_2 about 10^3 Hz), the value is about 5×10^{-8} F. Such a value cannot correspond to an electrode reaction capacitance (usually 0.1 to 1 mF cm^{-2}) and could be due to another phase than the first one. This phase can be another compound with a similar dielectric constant and with a thickness of about one or two orders of magnitude lower than the geometric thickness. It could also be due to a compound with the same order of magnitude in thickness but with a dielectric constant about 100 times higher. Because the dielectric constant of TiO_2 can be very high depending on the crystal orientation [14], both phenomena could lead to such a loop if TiO_2 appears as second phase in $Na_2Ti_6O_{13}$.

The values of the conductivity plotted in function of the temperature in Fig. 9 were calculated using the geometric factor of the sample. Of course it is an approximation because two phases are present in this composite. The conductivity corresponding to the first

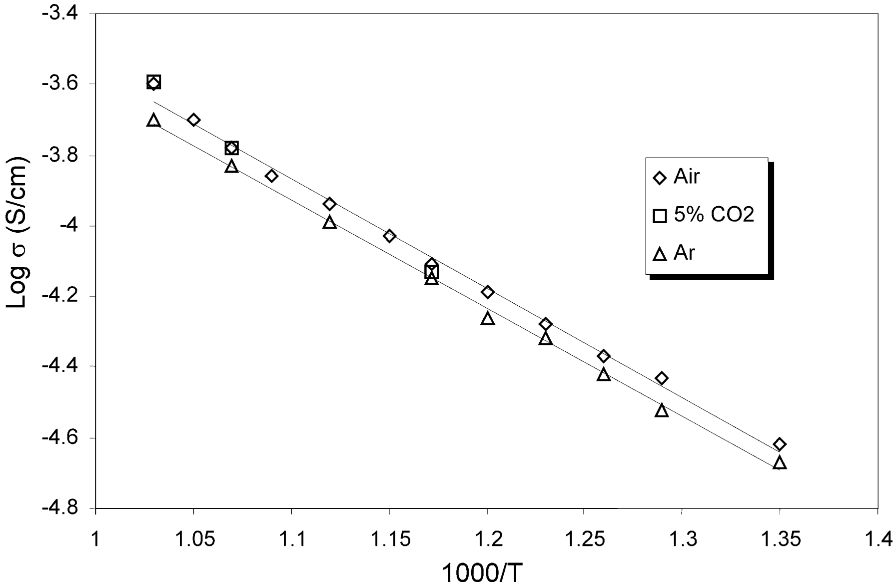

Fig. 7. Total conductivity of Ti3 composite versus temperature.

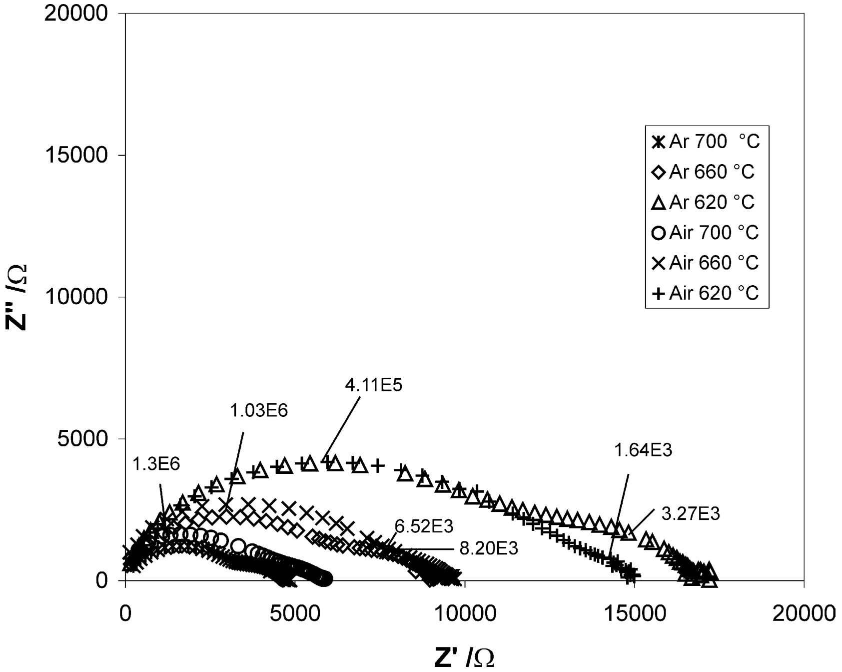

Fig. 8. Impedance plot for the Ti6 composite at different temperatures with Pt electrodes in argon and air.

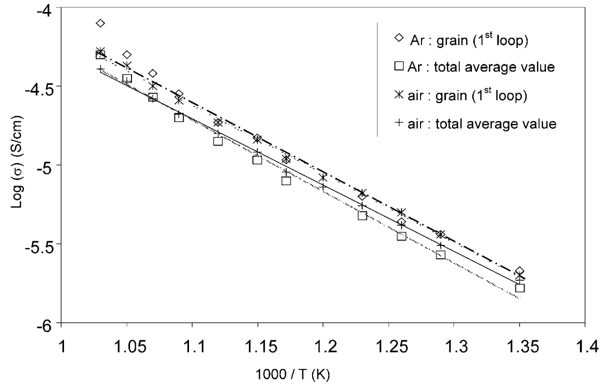

Fig. 9. Grain conductivity and total conductivity of Ti6 composite with Pt electrodes.

loop (f°_1) is not fully related to the oxygen partial pressure for temperatures lower than 900 K (dotted line in Fig. 9). The average activation energy is 0.82 eV for this conductivity. If we take into account the total resistance, the curves are slightly lowered and the crossing point between the values obtained in air and in argon is about 900 K. Such a phenomenon can be explained by the influence of oxygen partial pressure on the TiO_2 conductivity which is a well known phenomenon. It can be also remarked that the resistance value of the phase observed around f°_2 depends clearly on the oxygen pressure, for example it is approximately 0.6 times lower in air than in argon.

To verify such an assumption, a pellet of rutile TiO_2 was synthesised and its conductivity was measured. In the present paper all the experiments will not be developed in detail but only the main conclusions of the study [11] will be mentioned. For example similarly to Ti6, a crossing point on the Arrhenius plots, corresponding to the respective atmospheres previously mentioned, was also observed about 900 K ($1/T = 1.15$ 10^{-3} K^{-1}). When the measurements were carried out in a controlled atmosphere with a variable oxygen pressure fixed by an electrochemical pump-gauge system, in the range 10^{-4} to 1 atm, the evolution of the conductivity was similar to the literature data for micro-scale rutile thick films [15]. In a Log–Log representation, slopes of $-1/6$ and $+1/6$ were observed at low and high pressures respectively. Other values of the slopes were obtained depending on the size of the grains ($n = 1/4$ or $1/2$).[15,16] Because the conductivity of such a compound is strongly depending on the grain boundary effects,[16] the values obtained with a pure rutile phase cannot be rigorously compared to those obtained when this compound is mixed with another phase (e.g. in Ti6). We can only mention that the conductivity is lower about one order of magnitude than the one of Ti6. We can also remark that the total conductivity of Ti6 also depends on the oxygen partial pressure, but with a softening of the slopes in Log–Log scale (about 1/20 instead of 1/6), as shown in Fig. 10. The softening effect is certainly due to a short circuit of the $Na_2Ti_6O_{13}$ contribution, if it is a better conductor than TiO_2.

These results converge to the same assumption, i.e. the rutile TiO_2 phase plays a role on the total conductivity of Ti6 which is then a mixed conductor (conductive by sodium or/and oxide ions and by electrons or holes). Such properties could be interesting to improve

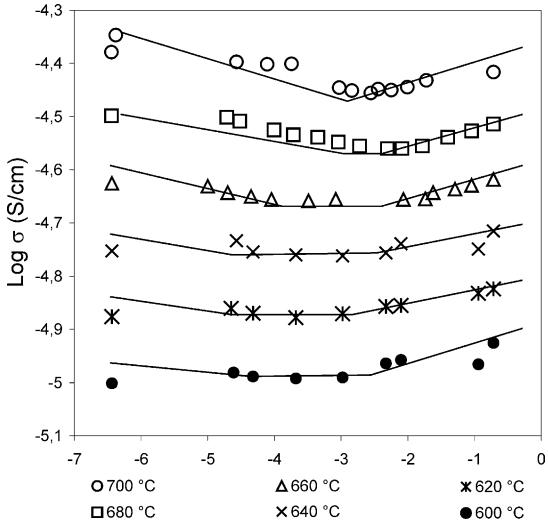

Fig. 10. Influence of the oxygen partial pressure on the total conductivity of Ti6.

the electrode reaction area, nevertheless the conductivity value of this compound is low compared to that of Ti3.

4. Conclusions

Two mixtures of sodium titanates, $Na_2Ti_3O_7$/$Na_2Ti_6O_{13}$ (Ti3) and $Na_2Ti_6O_{13}$/TiO_2 (Ti6), were synthesised by sol-gel route with a good densification. The particle size of Ti3 and Ti6 was of a few microns. The loss of sodium could be due to the sol-gel route. A work is in progress in our laboratory to obtain pure phases by sol-gel routes and to compare their electrical characteristics.

Such sol-gel method seems well adapted to an oxygen electrode in potentiometric sensor devices, because it provides an intimate mixture of two titanates and so the ionic exchanges can be improved for the electrode reactions. The Ti3 composite presents a good ionic conductivity, perhaps with a slight part of electronic or oxide ionic conductivity, which does not exceed 10%. The Ti6 composite has clearly a mixed conductivity (ionic and electronic) which influences strongly the impedance of the materials. Because Ti3 is a better conductor, it could be the best choice for an oxygen electrode compound. Our first results published elsewhere are promising in this field.[12,13] A good and small porosity size can be obtained by the sol-gel method and so the deposition by screen printing could be much easier to realise microsensors for future industrial developments.

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