JOURNAL OF MATERIALS SCIENCE 29 (1994) 4946–4952

Effect of frequency on the electrical characteristics of tin–antimony–oxide mixtures

A. OVENSTON, D. SPRÎNCEANĂ*, J. R. WALLS
Department of Chemical Engineering, University of Bradford, West Yorkshire BD7 1DP, UK
M. CĂLDĂRARU
Institutul de Chimie Fizica, Academia Româna, Spl. Independentei Nr. 202, Sector 6, Bucuresti 77208, Romania

The effect of frequency (100 Hz to 1 MHz) both on complex permittivity and on complex impedance data was used to study the conduction processes in Sn–Sb–O systems between 300 and 873 K. The conductance of tin oxide was increased by the addition of antimony oxide at all frequencies and a peak in conductivity was observed at 5 wt % Sb_2O_3. The effect of frequency on conductance was in agreement with the universal behaviour of solid dielectrics, whilst the atmosphere-dependent capacitance indicated surface dipole phenomena. The catalytic activity and selectivity patterns for the oxidation of propylene above 650 K may be correlated with the observed electrical behaviour, which is related to the mobility of lattice oxygen in the outer layers of the surface.

1. Introduction

The electrical conductivity of SnO_2 can be increased by several orders of magnitude by doping with Sb_2O_3 [1, 2]. This electronically conducting material is an effective catalyst for the oxidation and ammoxidation of hydrocarbons (e.g. [2–8]). An excellent review of this extremely controversial system was published by Berry [9]. Furthermore, the conductivity of the doped material is sufficiently high for it to absorb energy in a reactor heated by r.f. power [10]. Recently, the rates of diffusion of oxygen anions in various mixed oxides under catalytic conditions have been related to reaction rates for selective oxidation reactions [11]. The rates of oxygen diffusion were generally considered to be sufficient to carry out the reactions through rapid oxygen diffusion in the surface layers. But, on the other hand, by using $^{18}O_2$ tracer in propylene oxidation, Ono *et al.* [12] showed that the extent of participation of the lattice oxygen is only three or four layers deep for a system containing 10 at % antimony obtained by co-precipitation. This means that the interaction with the ambient atmosphere and consequent influence of adsorption on the electrical properties is strictly limited to the "skin" layers, at least up to 673 K as in their experiments. Thus, a better understanding of the conduction processes is needed. Conduction mechanisms and the influence of defect aggregates on activation and association energies in highly doped systems have been identified as items needing urgent attention if opportunities in highly conducting electroceramics are to be recognized [13]. In this report preliminary studies using a.c. techniques are discussed.

Pure polycrystalline SnO_2 is used as a sensor and the links between chemisorption and the electrical properties of the bulk and surface layers have been examined (e.g. [14–16]). The electrical properties of tin–antimony oxides have already appeared in the literature in some detail (e.g. [2, 17–20]). However, these investigations generally involved measurements of the conductance at d.c. or a single a.c. frequency only. Here, both conventional methods of measurement and impedance spectroscopy (a technique mainly used to separate bulk and grain boundary effects in solid-state electrolytes and ionically conducting sensors) have been used to study the a.c. properties between 300 and 873 K, over the frequency range 100 Hz to 1 MHz in argon and air atmospheres. Some experiments performed in Romania using powders of the materials are also described, together with their catalytic behaviour for the oxidation of propylene.

2. Experimental procedure

Powders of SnO_2 (BDH Chemicals, containing < 0.002% arsenic and < 0.05% lead) and Sb_2O_3 (May and Baker, purity > 99%) were mixed in proportions containing 0 to 15 wt % Sb_2O_3 with a small amount of water to form a thick paste. About 0.1 ml g^{-1} of ethylene glycol was added to assist lubrication in pelleting. After drying overnight at 350 K, pellets of 1 cm diameter, 5 mm thickness were made using 10 kg force for about 5 min. They were then heated in static air at a rate of 2 K min^{-1} up to 1273 K, calcined for 1 h and then cooled at 4 K min^{-1} in the same atmosphere. Under these conditions most

---

* On leave from Institutul de Chimie Fizica, Academia Româna, Bucuresti 77208, Romania.

of the Sb is likely to have formed a solid solution with the SnO_2. Powdered XRD measurements at Bradford showed no evidence of isolated patches of Sb_2O_4 or other oxides which have sometimes been observed when high proportions of Sb are present [3, 21]. The rutile structure is usually found for high-temperature calcined Sn–Sb–O systems with an Sb content up to 25% [9]. This was explained by solid solution formation, favoured by the comparable ionic radii of Sn^{4+} (0.067 nm) and Sb^{5+} (0.062 nm) ions [21].

Pt enamel contacts were fired on to the end faces of the pellets for 1 h at 1073 K. Using a Hewlett Packard 4194A analyser and a programmable Eurotherm gold reflecting furnace, the electrical characterization was conducted as described previously [22]. For conductivity ($\propto G$) and capacitance measurements the sample was represented by a capacitance C_p in parallel with a resistance ($= 1/G$). The real and imaginary components of the dielectric constant (ε' and ε'') are proportional to C_p and G/ω, respectively, where ω is the angular frequency. For complex impedance plots the samples were represented by a resistance Z' in series with a reactance Z''. The Boukamp "equivalent circuit" package from the University of Twente (using 200 frequency points between 100 Hz and 1 MHz) was used to study the dielectric dispersion data and the complex impedance data. Generally, for the most conducting samples with a high loss tangent, if G exceeds about 0.1 S the C_p and Z'' data were not sufficiently accurate to be used.

By monitoring the conductivity, no indication of moisture was found at lower temperatures and prior to measurements being made, the sample was allowed to stabilize for 15 min at each temperature concerned. The initial measurements were made in purified and pre-dried air flowing at 20 ml min^{-1} with the temperature increasing from ambient to 873 K. After slow cooling in static air, measurements were repeated in pre-dried argon at 20 ml min^{-1} and after cooling in argon, again repeated in air.

The fundamental Kramers–Kronig transformations relating the real and imaginary components of the dielectric constant (and consequently Z' and Z'') should be obeyed for all dielectric data. Hence for the highly conducting samples only data at intermediate frequencies may be used for complex dielectric and impedance analysis [23]. At the high frequencies, when the impedance of the leads is comparable to that of the pellets, the compensation for the leads is never totally accurate and errors will occur. For highly conducting samples, at low frequencies inductive loops may become apparent and can sometimes also be associated with the formation of intermediate species after chemisorption [23].

In order to compare the electrical conductivity data with other surface properties, some *in situ* single-frequency conductivity and catalytic activity measurements were performed on powdered samples (1.5 cm^3 grains, diameter 0.2–0.8 mm) of the calcined materials described above. Data were obtained using an integral flow reactor provided with two coaxial tantalum cylinders as electrodes as described elsewhere [24]. The electrical conductivity was measured using a semi-automatic precision Tesla BM484 bridge at 1592 Hz, during temperature-programmed heating at 2 K min^{-1} in atmospheres of argon, air, propylene–air and propylene–argon (1:10) mixtures, with a contact time between 0.5 and 2 s. After experiments using propylene mixtures, measurements using argon alone were repeated in order to check the possible influence of the mixtures on the surface conductivity of the samples. For catalytic experiments, the product distribution was monitored using on-line gas chromatography.

3. Results and discussion

3.1. Conductivity

It is difficult to compare the magnitude of the conductivity with other reports on polycrystalline samples since this will also depend on the method of preparation, the density of the sample and its porosity. An overall conductivity of the pellet can be estimated using $\sigma = G \times \text{depth/area}$ (here $\sigma \approx 35\, G\, S\, m^{-1}$). Samples in air at 1 atm at 300 and 700 K at 100 Hz showed the conductivity to be comparable in magnitude with those measured by Herrmann and co-workers [1, 2] and also to go through a substantial peak at around 5 wt % Sb_2O_3. At room temperature the addition of 5 wt % Sb_2O_3 leads to an increase in conductivity of order 10^5 whilst at 700 K the increase is reduced to below 10^3 (Fig. 1). The reasons for the peak are well

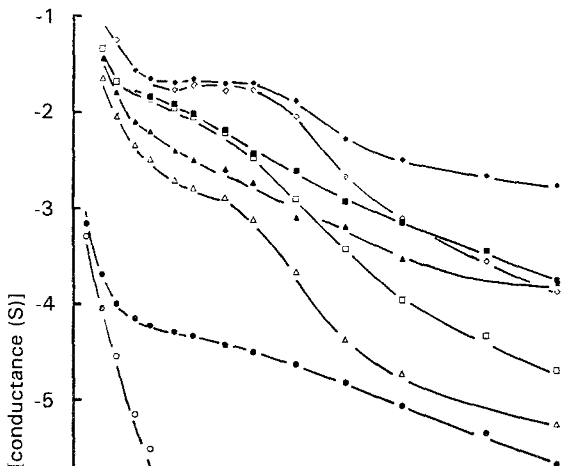

Figure 1 Conductance as a function of temperature for samples of SnO_2 containing 0 to 15 wt % Sb_2O_3 in air at 100 Hz and 1 MHz: (○) 0% 100 Hz, (●) 0% 1 MHz, (◇) 5% 100 Hz, (◆) 5% 1 MHz, (□) 10% 100 Hz, (■) 10% 1 MHz, (△) 15% 100 Hz, (▲) 15% 1 MHz.

described (e.g. [1, 2]). At $0 < \mathrm{Sb} < 10\,\%$, doping of Sb^{5+} cations dissolved in SnO_2 occurs and one electron per Sb atom is liberated giving rise to the large increase in conductivity. At larger additions of Sb, trivalent Sb ions are thought to be created with a subsequent decrease in free electrons and reduction in the conductivity.

In Fig. 1 the log (conductance) versus reciprocal temperature characteristics show regions of well-defined activated behaviour. At $T < 400$ K there is a low activation energy as shown in Table I for values at 100 Hz in air. At $T > 700$ K there is a much higher activation energy. In general, the greater the conductivity of the sample the lower is the activation energy. The magnitudes for E_A are similar to those measured by Paria and Maiti [18] for samples containing up to 0.4 wt % Sb_2O_3 at 1592 Hz, and exhibit similar trends despite the much lower amounts of doping used. The high-temperature value for pure SnO_2, i.e. about 1.7 eV, is in excellent agreement. At 708 K a lower value of 1.13 eV has been observed for powdered samples under a constant pressure [2]. At temperatures near ambient, 0.81 eV lies within the range of activation energies (about 0.7 to 1.4 eV) tabulated for pure SnO_2 (e.g. [25]). At lower frequencies and intermediate temperatures the behaviour is somewhat erratic and superimposed peaks in conductance were sometimes observed. Space-charge effects at the Pt electrodes, which result in a blocking (i.e. non-ohmic) contact might also arise and retard the flow of electrons across the Pt–sample barrier [26]. Due to the difference in work functions between Pt and SnO_2 as well as possible surface property changes of Pt in oxygen, Pt may be a bad choice of electrode, although it has been generally used elsewhere in conductivity studies of Sn–Sb–O mixtures (e.g. [17, 18, 27]).

Fig. 1 shows the frequency to have most effect for the more insulating (0 and 15 wt %) samples. There is a minimum effect of frequency for the highly conducting samples at 5 wt % which indicates semi-metallic behaviour. As is usually observed for semiconducting and insulating materials, the effect of frequency decreases as temperature increases as shown in Fig. 2. In general, solid oxide materials exhibit non-Debye behaviour showing a low activation energy at low temperatures coupled with a large effect of frequency (with $\sigma \propto \omega^n$ where $n < 1$, often between 0.7 and 0.8). In this region, according to the interpretations of Hill and Jonscher [28], the dielectric behaviour is that of a "lattice" response from a regular array of permanent or induced dipoles. The higher the value of n the more perfect the lattice. High values of n are accompanied by activation energies which may approach zero if thermal activation plays a negligible role in determining the dielectric loss (or the a.c. conductivity $\sigma \propto \omega\varepsilon''$). In contrast, at high temperatures and low frequencies, strong low-frequency dispersion may be exhibited. The index n may approach zero and accompany high activation energies when thermally activated diffusion of hopping charge carriers completely dominates any frequency-dependent relaxation of dipoles in the material. In this region n has been related to screening effects due to "many-body" interactions between the charge carriers [28]. Values for n' (calculated near 300 K between 100 kHz and 1 MHz) and n'' (calculated at about 870 K between 100 Hz and 1 kHz) and are shown in Table II for samples measured in air. For the undoped material n' is a maximum as expected since it will be closest to a perfect regular array of dipoles. At 5 wt % Sb_2O_3 n' is significantly reduced to 0.2 since the material is now highly conducting even at low temperatures and electronic conduction (which is not sensitive to frequency) dominates the behaviour. At 15 wt % the material again becomes more insulating with $n' = 0.62$. In contrast, values of n'' approach zero as expected for the high-temperature behaviour.

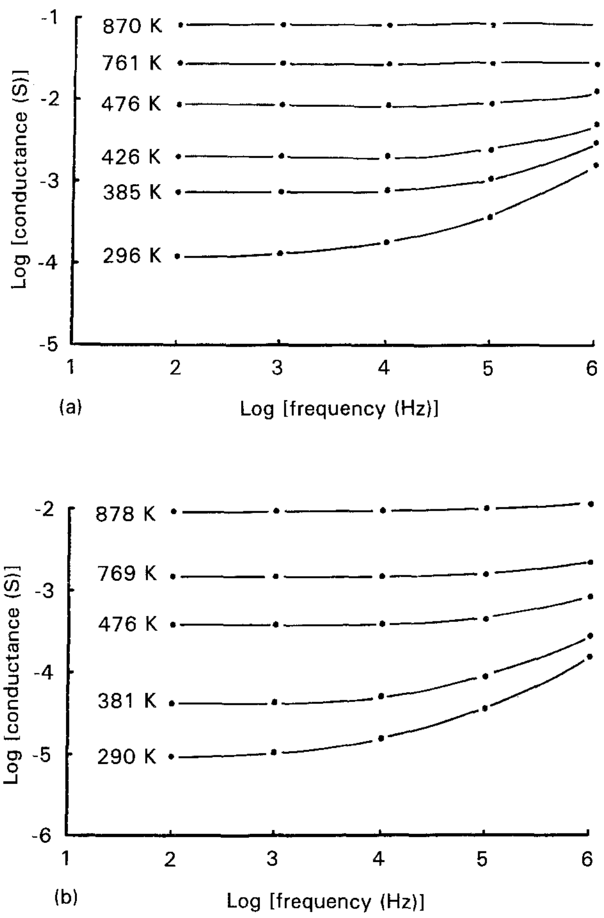

Figure 2 Effect of frequency on conductance for (a) 5% Sb_2O_3 in Ar and (b) 15% Sb_2O_3 in air.

TABLE I Low-frequency activation energies in air

Sb_2O_3 (wt %)	Activation energy (eV) Low temp. (300–400 K)	High temp. (800–900 K)
0	0.81	1.76
5	0.14	0.49
10	0.16	0.52
15	0.19	0.98

At low temperatures/high frequencies the conductivity power index n' increased as the air was replaced by Ar (due to the lattice becoming more perfect as surface impurities were removed) and decreased again on further exposure to air. The high temperature/low

TABLE II Effect of frequency on conductivity, index n in air

Sb_2O_3 (wt %)	Low temp., high freq. (n')	High temp., low freq. (n'')
0	0.73	0.037
5	0.2	0.01
10	0.31	0.006
15	0.62	0.006

frequency value of the power n'' remained close to zero in all cases, confirming that thermally activated charges dominated the behaviour in all cases.

3.2. Capacitance and dielectric dispersion

A marked change in the capacitance–temperature relationship was found between low and high frequencies. At 1 MHz the temperature had little effect, whilst at 100 Hz temperature had a negligible effect up to about 700 K, but as it was increased to 900 K the capacitance increased rapidly with a high activation energy of order 1.7 eV. Typical dielectric dispersion curves for 15% Sb_2O_3 at 665 and 878 K are shown in Figs 3 and 4. For the given geometry of the samples, a bulk capacitance of about 6 pF would be expected at room temperature for pure SnO_2 with a relative dielectric constant of about 24 [25]. The observed values at 100 Hz are many orders of magnitude higher and more typical of surface and grain boundary phenomena. In agreement with the conductivity data, the capacitances were generally highest for the most conducting material and lowest for the pure SnO_2.

Although the loss part of the dielectric dispersion ($\propto G/\omega$) measured at different temperatures could be normalized, i.e. superimposed by lateral shift of the frequency axes, the real part (capacitance) could not. Thus for these mixed oxide samples, the universal behaviour observed for many solid dielectrics [28] was not strictly obeyed, probably due to the presence of more than one loss process. This might arise from the surface, grain boundary and bulk contributions to the total capacitance having dissimilar activation energies.

The effects of changing the atmosphere from air to argon and back to air were relatively small, since after pelleting the specific surface area will be of order 1 $m^2\ g^{-1}$ and surface effects will consequently be low. For 5 and 10% Sb_2O_3 pelleted samples, the replacement of air by argon caused an increase in conductance at high temperatures only, but the reverse effect at low temperatures. The latter behaviour is somewhat surprising for a material usually claimed to be an n-type semiconductor, for which a change of atmosphere from air to argon would be expected to result in an increase in conductivity; further discussion is given in the Appendix. On a second exposure to air the conductance was significantly reduced for all the doped samples as expected. In the experiments on uncompressed powdered samples, the 5% sample showed erratic behaviour and the greatest effect of changes in atmosphere, whilst the 15% Sb_2O_3 sample exhibited typical n-type behaviour over the whole temperature range studied.

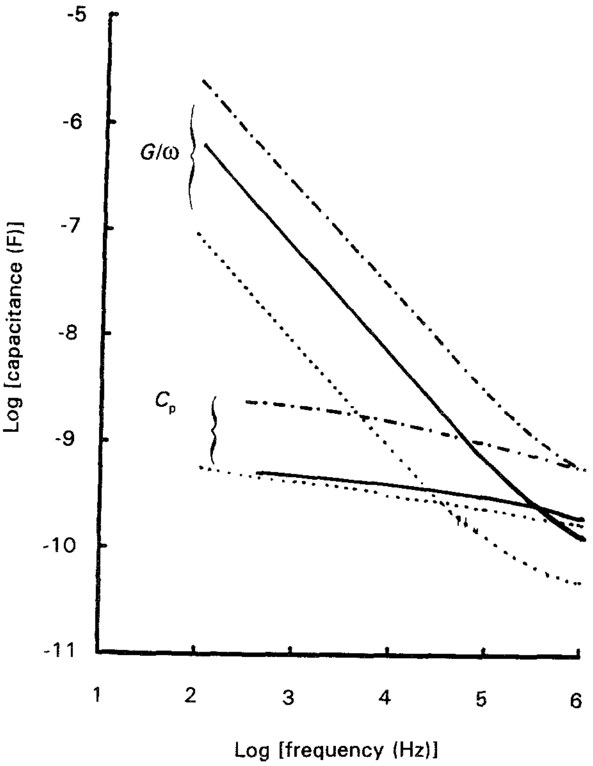

Figure 3 Dielectric dispersion for 15% Sb_2O_3 at 665 K (——) in air, (– · –) in Ar and (· · · ·) repeated in air.

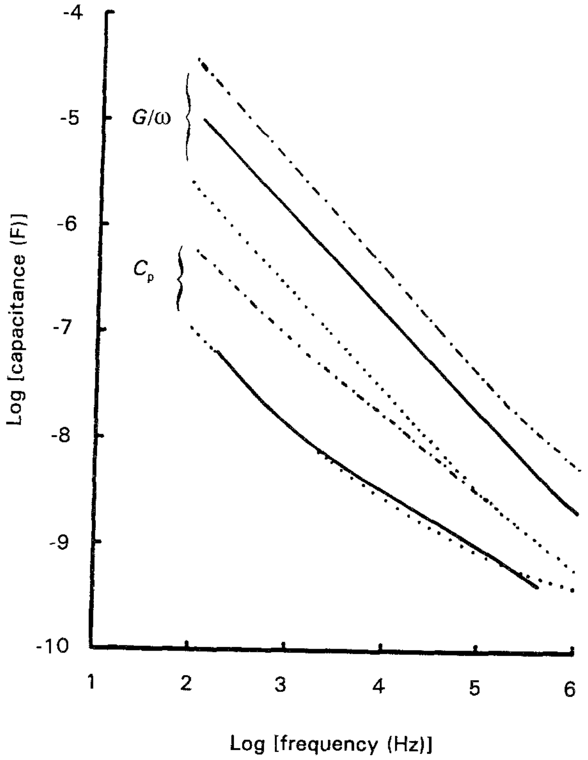

Figure 4 Dielectric dispersion for 15% Sb_2O_3 at 878 K (——) in air, (– · –) in Ar and (· · · ·) repeated in air.

These results are in agreement with those of Herrmann *et al.* [2, 29] who showed oxygen partial pressure to have a large effect up to 1.5% but almost no effect between 5 and 100% for powdered samples at 1592 Hz. Initially some excess surface oxygen will be removed by the Ar, oxygen anion vacancies will be formed and the electronic conductivity will increase. With further exposure to air this surface concentration of vacancies will decrease and conductivity again decrease. The capacitances in air are observed to be lower than those measured in Ar, probably due to the larger proportion of surface dipoles arising from induced surface defects in the lattice.

In Sn–Sb–O mixed catalysts calcination can lead to segregation of Sb and an epitaxial layer of Sb oxide may be formed [30]. The interaction between an oxide and a gas can lead to the formation of electric fields due to defect segregation which can influence the diffusive transport and gas–solid kinetics [15]. A large influence on the catalytic properties of an oxide can occur and may mask any influence on the bulk properties. A more detailed study of the effect of frequency on conductance of such systems may assist in the understanding of such phenomena.

3.3. Complex impedance

For ionic conductors the complex impedance diagrams, in which Z'' is plotted as a function of Z' as frequency increases, often exhibit a series of overlapping semicircles which may be attributed to different loss processes in the bulk, at grain boundaries and at the electrode interface [22]. Due to the high conductivity of the 5 and 10% samples it was not possible to obtain complex impedance diagrams over the whole frequency range at high temperatures. Typical curves for a 15% sample at 426 K and for a 5% sample at room temperature are shown in Fig. 5. In general, single shallow semicircles inclined at angles of about 16° to the real axis were shown at the lower temperatures, whilst little effect of frequency was observed for the highly conducting samples. For the 5% material, a significant intercept on the real axis occurred. This resistance, R_1, was almost independent of temperature and could be associated with electronic conduction, whilst the d.c. resistance R_2 (given by the value of Z' extrapolated to zero frequency, R_1) was thermally activated and associated with ionic conduction and relaxation losses in the material.

No evidence of clearly defined overlapping semicircles was found for all the data examined. Hence the conduction processes could not be separated into bulk, grain boundary and surface phenomena as is often possible for solid-state ionic or mixed conductors. It is interesting to note that closely overlapping semicircles were found for undoped samples of polycrystalline SnO_2 [27]. Elsewhere, simultaneous measurements of surface conductance (σ) and work function (ϕ) have been used to separate bulk and surface phenomena in undoped tin oxide [14]. At low temperatures, the change in ϕ was large and the change in σ was small, whilst at high temperatures the reverse was found. Since the effects of atmosphere were of similar magnitude at all frequencies for the doped samples examined here, it is likely that the observed behaviour largely stems from surface loss processes.

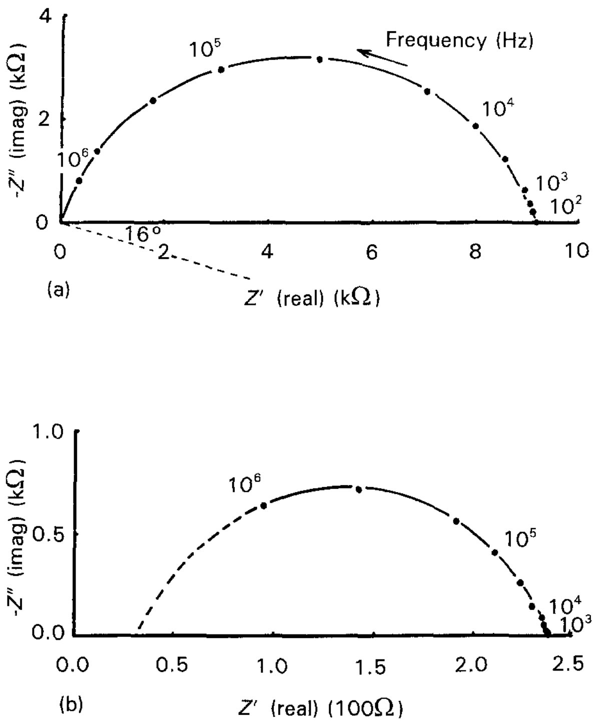

Figure 5 Complex impedance diagrams for (a) 15% Sb_2O_3 in air at 426 K and (b) 5% Sb_2O_3 in air at 300 K.

3.4. Catalytic activity

The catalytic activity and selectivity data for propylene oxidation in a propylene : air (1 : 10) mixture for a contact time of 2 s are shown in Table III. The

TABLE III Catalytic activity for propylene oxidation of Sn–Sb–O mixtures

Sb/(Sb + Sn) (%)	T(K)	C(%)[a]	S(%)[b]			
			CO	CO_2	CH_3CHO	CH_2CHCHO
0	653	53.8	–	96.2	Traces	Traces
5	648	5.6	1.6	30.7	5.8	61.9
10		2.7	2.2	15.5	9.2	73.1
15		4.4	3.5	14.7	9.2	72.6
5	673	9.6	1.0	34.8	2.9	61.3
10		8.7	3.3	18.5	4.8	73.6
15		7.0	3.9	25.3	5.4	65.4

[a] C = conversion of propylene.

[b] S = selectivity–moles of propylene transformed into product X per total amount of propylene transformed.

propylene transformation into oxidation products starts to be significant above about 623 K. This agrees well with the electrical conductivity data for both pelleted and powdered samples, which showed an increase in the activation energy (and hence a steep rise in conductivity) in this range of temperature. This correlation is presumed to arise from an increased mobility and a greater participation of lattice oxygen above 623 K. Antimony doping produces a sharp increase in the conductivity of SnO_2; this is accompanied by a marked decrease in the catalytic activity but an increase in selectivity to acrolein rather than production of carbon dioxide. For the doped samples, the greatest activity but least selectivity to acrolein is shown for the 5% Sb_2O_3 mixture which also exhibited the highest conductivity.

Up to 573 K, the electrical conductivity of powders of 5% Sb_2O_3 samples in propylene mixtures showed values intermediate between those for air and argon alone. At higher temperatures the conductivity in the propylene mixtures was slightly raised. For 10% Sb_2O_3 (up to 413 K) and 15% Sb_2O_3 (up to 573 K) the data were almost identical to those in air, indicating that there is no significant influence of propylene on the surface at these low temperatures. Hence these preliminary measurements indicate a good correlation between catalytic activity and electrical behaviour. A more detailed report concerning the catalytic behaviour will be the subject of a further article.

4. Conclusions

Tin oxide is well known for its sensing properties. When doped with antimony oxide it has good catalytic properties, which are thought to be associated with its enhanced electronic conduction and related concentration of oxygen anion vacancies, particularly in the surface layers. A better understanding of charge transport and reaction mechanisms at and along interfaces and boundaries has been defined as a critical research need in electroceramics and catalysts [13, 30]. Here, the a.c. electrical properties of pellets containing 0 to 15 wt % Sb_2O_3 have been measured in air and argon atmospheres. The conductivity was optimum for intermediate amounts, with both frequency and temperature having relatively small effects. For the more insulating materials the effect of frequency became important at temperatures approaching ambient, and thermally activated conductivity was exhibited at high temperatures and lower frequencies. The observed frequency and temperature dependencies are typical of lossy solid dielectrics in accordance with the universal theory of dielectric response. At high temperatures, thermally activated charge carriers dominate the loss processes whilst dipole relaxation losses dominate at high frequencies and lower temperatures. Both processes are likely to be predominantly surface phenomena up to 1 MHz, and the high conductivity of the 5 wt % solid makes it a good candidate for consideration as a catalyst to be heated by r.f. power.

The catalytic oxidation of propylene was found to correlate well with the observed electrical behaviour, the greatest conversion being shown for pure SnO_2 but the greatest selectivity to acrolein for the doped material. In future investigations, care should be taken to avoid any loss of Sb by volatilization, e.g. by calcining pellets enclosed in a powder of the same composition [18]. Possible segregation of the antimony phase should also be studied [31]; work function changes in addition to a.c. properties could be helpful in studying the effect of chemisorption of oxygen [15]. Apart from electrical properties, other important criteria such as thermal and chemical stability, mechanical strength, formability and porosity should also be considered.

Appendix: The effects of the Sb^{5+}/Sb^{3+} ratio in Sn–Sb–O mixtures

According to thermodynamic data [32] the stability of SnO_2 in the presence of oxygen is considerably higher than that of SnO up to 1573 K, whilst for antimony oxides the situation is complex. Sb_2O_5 is the stable form up to 1243 K, but Sb_2O_3 is more stable at higher temperatures and the limit is shifted to lower temperatures for Sb^{5+} and Sb^{3+} ions contained in Sb_2O_4 and Sb_6O_{13} (oxides with mixed antimony valencies). The Sb^{5+}/Sb^{3+} ratio will depend both on the temperature and on the concentration of ambient oxygen. In addition, the relatively high ionic radius of Sb^{3+} (0.09 nm) practically excludes the participation of these ions in a solid solution. However, in the surface layers exposed to the atmosphere, due to incomplete co-ordination, fluctuations in the Sb^{5+}/Sb^{3+} ratio are possible and the conductivity may vary in an unusual manner due to the process

$$Sb^{5+} + 2e \rightleftharpoons Sb^{3+}$$

The solid-solution formation produces free electrons according to the scheme [32]

$$Sn^{4+}_{1-2x}Sb^{5+}_{x}Sn^{3+}_{x}O^{2-}_{2} \rightleftharpoons Sn^{4+}_{1-x}Sb^{5+}_{x}O^{2-}_{2} + xe^{-}$$

For powders prepared by co-precipitation and calcination, Mössbauer data have proved the existence of both ions [20, 33]. However, for the pellets used here (for which a typical ceramic method was used for the preparation with a relatively short time of high-temperature calcination), grains of SnO_2 may only contact and react with Sb_2O_3 at the interface and the extent of a true solid solution may increase upon further heating. It is thus possible that the structure may not be completely stable and deposition of islands or segregation of antimony oxides may occur at the surface. Such processes may explain the apparent p-type behaviour observed at lower temperatures and the reduced conductivity of the 10 and 15% Sb_2O_3 mixtures in comparison with those containing 5% Sb_2O_3. This is in excellent agreement with the catalytic activity data, since Sb_2O_4 is known to have low activity but high selectivity for acrolein conversion. It is probably that the electrical conduction is strictly related to the concentration of Sb^{5+} ions and the apparent p-type behaviour sometimes observed reflects a fluctuating ratio of Sb^{5+}/Sb^{3+} in air or argon.

Acknowledgement

The authors are grateful to the SERC for the provision of equipment.

References

1. B. BENAICHOUBA and J.-M. HERRMANN, React. Kinet. Catal. Lett. **22** (1–2) (1983) 209.
2. J.-M. HERRMANN, J. L. PORTEFAIX, M. FORISSIER, F. FIGUERAS and P. PICHAT, *J. Chem. Soc. Faraday Trans. I* **75** (1979) 1346.
3. W. D. R. PYKE, R. REID and R. J. D. TILLEY, *ibid.* **76** (1980) 1174.
4. I. BROWN and W. R. PATTERSON, *ibid.* **79** (1983) 1431.
5. L. T. WENG, N. SPITAELS, B. YASSE, J. LADRIÈR, P. RUIZ and B. DELMON, *J. Catal.* **132** (1991) 319.
6. L. T. WENG, B. YASSE, J. LADRIÈRE, P. RUIZ and B. DELMON, *ibid.* **132** (1991) 343.
7. L. T. WENG, P. PATRONA, E. SHAM, P. RUIZ and B. DELMON, *ibid.* **132** (1991) 360.
8. L. T. WENG and B. DELMON, *Applied Catal. A* **81** (1992) 141.
9. F. J. BERRY, *Adv. Catal.* **30** (1981) 97.
10. A. OVENSTON and J. R. WALLS, *Trans. Inst. Chem. Eng.* **68** (1990) 530.
11. O. Yu. OVSITER and V. D. SOKOLOVSKII, *Catal. Lett.* **17** (1993) 239.
12. T. ONO, T. YAMANAKA, Y. KUBOKAWA and M. KOMIYAMA, *J. Catal.* **109** (1988) 423.
13. W. J. WEBER, H. L. TULLER, T. O. MASON and A. N. CORMACK, *Mater. Sci. Eng.* **B18** (1993) 52.
14. K. D. SCHIERBAUM, H. D. WIEMHÖFER and W. GÖPEL, *Solid State Ionics* **28–30** (1988) 1631.
15. W. GÖPEL, K. D. SCHIERBAUM, H. D. WIEMHÖFER and J. MAIER, *ibid.* **32–33** (1989) 440.
16. K. D. SCHIERBAUM, U. WEIMAR, W. GÖPEL and R. KOWALKOWSKI, *Sensors & Actuators B* **3** (1991) 205.
17. J.-M. HERRMANN, M. R. NUNES and F. M. A. DA COSTA, *J. Chem. Soc. Faraday Trans. I* **78** (1982) 1983.
18. M. K. PARIA and H. S. MAITI, *J. Mater. Sci.* **17** (1982) 3275.
19. G. W. GODIN, C. C. McCAIN and E. A. PORTER, in Proceedings of 4th International Congress on Catalysis, Moscow, 1968, edited by B. A. Kazanski, Vol. 1 (Akademiai Kiado, Budapest, 1971) p. 271.
20. J. L. PORTEFAIX, P. BUSSIÈRE, M. FORISSIER, F. FIGUERAS, J. M. FRIEDT, J. P. SANCHEZ and F. THEOBALD, *J. Chem. Soc Faraday Trans. I* **76** (1980) 1652.
21. M. CROZAT and J. E. GERMAIN, *Bull. Soc. Chim. Fr.* **49** (1973) 1125.
22. A. OVENSTON and J. R. WALLS, *J. Catal.* **140** (1993) 464.
23. B. A. BOUKAMP, University of Twente, personal communication (1993).
24. M. CALDĂRĂRU, D. SPRINCEANĂ and N. I. IONESCU, *Ber. Bunsenges. Phys. Chem.* **97** (1993) 369.
25. G. V. SAMSONOV, in "The Oxide Handbook" (Plenum, New York, 1982).
26. A. J. MOULSON and J. M. HERBERT, "Electroceramics" (Chapman and Hall, London 1990) p. 169.
27. J.-H. LEE, S.-J. PARK and K. HIROTA, *J. Amer. Ceram. Soc.* **73** (1990) 2771.
28. R. M. HILL and A. K. JONSCHER, *Contemp. Phys.* **24** (1983) 75.
29. J.-M. HERRMANN and J. L. PORTEFAIX, *React. Kinet. Catal. Lett.* **12** (1979) 51.
30. P. J. GELLINGS and H. J. M. BOUWMEESTER, *Catal. Today* **12** (1) (1992) 37.
31. Y. M. CROSS and D. R. PYKE, *J. Catal.* **58** (1979) 61.
32. C. A. VINCENT, *J. Electrochem.* **119** (1972) 515.
33. I. P. SUZDALEV, A. A. FIRSOVA, U. ALEXANDROV, L. YA. MARGOLIS and D. A. BALTRUNAS, *Dokl. Akad. Nauk. SSSR* **204** (1972) 408.

Received 9 March
and accepted 22 April 1994