The behaviour of semiconducting rutile as the current collector in a sodium–sulphur cell

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The behaviour of tantalum-doped titanium dioxide (rutile) as the current collector in a sodium–sulphur cell has been investigated. The resistivity of the material has been measured and compared with the cell impedance. The sintering characteristics, micromorphology, mechanical strength and static corrosion resistance have also been studied.

1. Introduction

Sodium–sulphur cells, in common with a number of other electrochemical devices, especially those operating at elevated temperatures with molten salt electrolytes or electrodes, need a corrosion resistant electronically conducting element to serve as the current collector. In the case of the sodium–sulphur system, a variety of metals and alloys may be used as the sodium anode current collector but the cathodic melt of sulphur and sodium polysulphides at 575 to 625 K is extremely aggressive and virtually all metallic materials are corroded [1, 2]. A number of ceramic materials are stable in the cell environment but are not sufficiently conductive to use alone. They can, however, be used as a composite with a thin ceramic coating on a metal substrate to provide a short current path through the ceramic but this has proved to be difficult because of the high degree of coating integrity required. An alternative is to use a thin, impervious ceramic with a layer of metal to act as a current shunt on the surface away from the electrode. This approach has been described for tantalum-doped titanium dioxide (rutile) [3] but the material has not been tested in cells. The object of the present work was to study the behaviour of this material in sodium–sulphur cells.

The range of acceptable resistivity values can be determined by considering the overall resistance of a composite. For example, a ceramic tube 200 mm long with an outside diameter of 10 mm and a wall thickness of 1 mm, plated on the inner surface with 0.1 mm of nickel has an acceptable overall resistance of ~5 mΩ at 600 K if the resistivity of the ceramic is ~0.01 Ωm. Alternatively, an aluminium rod 200 mm long with a diameter of 10 mm and a 2 μm ceramic coating also has a resistance of ~5 mΩ at 600 K but in this case the resistivity of the ceramic considered is ~10 Ωm. Thus for use as a solid tube a resistivity of ~0.01 Ωm is required. Values as low as 0.002 Ωm at 600 K have been reported for tantalum-doped titanium dioxide [3].

The electronic conductivity of rutile is dependent on the concentration of charge carriers. These may be produced either by making the material sub-stoichiometric with respect to oxygen by reduction or by substituting titanium ions with pentavalent ions resulting in mobile electrons for charge compensation [4]. The latter approach is more likely to be successful for a current collector material in a sodium–sulphur cell as it will be intrinsically oxidation resistant. Niobium and tantalum are both suitable dopants but need to be homogeneously dispersed to be effective. This has been achieved by using tantalum pentafluoride as the source of the dopant [3]. The fluoride has a high vapour pressure and so on heating it is homogeneously distributed through the unfired (green) shape whilst simultaneously reacting with oxygen, firstly, to form TaO_2F which is substantially less volatile and, finally, Ta_2O_5. Sintering at 1675 K produced a dense material (~99% theoretical) with a uniform, fine grain size of the order of 10 μm. The resistivity adequately meets the requirements of a current collector material and

corrosion resistance in sodium polysulphide appears satisfactory.

In this work the behaviour of tantalum-doped titanium dioxide in sodium—sulphur cells has been studied. Polycrystalline ceramic tubes have been prepared and tested in cells with a central sulphur electrode. The resistivity of the material has been measured and compared with the cell impedance. The sintering characteristics, micromorphology, mechanical strength and static corrosion resistance have also been investigated.

2. Experimental details

Rutile samples were prepared in the form of thin-walled, closed-ended tubes, 13 mm o.d. by 170 mm long and a wall thickness of 1.5 mm with a composition of 1.0 wt % Ta_2O_5, balance TiO_2. The material was made up from a sub-micron pigmentary anatase powder with a purity of 99.6 wt % TiO_2. The major impurities were: P_2O_5, 0.18 wt %; K_2O, 0.07 wt %; ZnO, 0.05 wt %; CaO, 0.03 wt %; Al_2O_3, 0.02 wt %. The tantalum dopant was added in the form of pure, reagent-grade tantalum pentafluoride. The starting materials were mixed by adding an aqueous solution of TaF_5 to an aqueous slurry of TiO_2. This was then evaporated to dryness, mixed with a solution of polyvinyl alcohol in hot water to produce ~ 3 wt % fugitive binder in the powder, re-dried and ground to break down agglomerates. A moderately coarse sieve fraction was isostatically pressed at 207 MN m^{-2} to form green tubes with a density of $\sim 55\%$ theoretical density of rutile. These were sintered at 1675 K for 3 h in air. A heating rate of ~ 50 K h^{-1} and a cooling rate of ~ 100 K h^{-1} were used. Tubes were finally annealed in a vacuum of 0.14 kN m^{-2} with a residual atmosphere of argon for 1 h at 1075 K. Analysis of sintered material by energy-dispersive analysis of X-rays (EDAX) showed that there were no significant losses of tantalum on firing and that it was uniformly distributed throughout the sample. Sintered densities were measured in water by a simple Archimedean technique. The microstructure was examined by optical microscopy after grinding with silicon carbide paper, polishing with 1 μm diamond paste and etching in hydrofluoric acid.

The tensile strength of the material was measured by diametral compression of rings 7 mm long cut from the tubes. Care was taken to minimize damage to the cut faces. A machine cross-head speed of 0.5 mm min^{-1} was used and

thin, soft aluminium shims were placed between the rings and the machine platens to prevent loading at asperities. The tensile strength was calculated from the specimen dimensions and the applied force at fracture using the approximations of thin-walled elasticity theory and taking into account any eccentricity in the rings.

The electronic resistivity along the tube axis was measured over a range of temperatures using a d.c. four-probe method to eliminate contact resistance. Four silver wires were wrapped around the tube and a small amount of colloidal silver was introduced between the wires and the tube. A current of ~ 50 mA was passed between the outer probes and the potential between the inner probes was measured. The resistivity in the radial direction was measured both using electroplated nickel contacts and a molten lead—tin alloy (60 wt % Pb—40 wt % Sn). For both contact materials a current of ~ 500 mA was passed and the potential
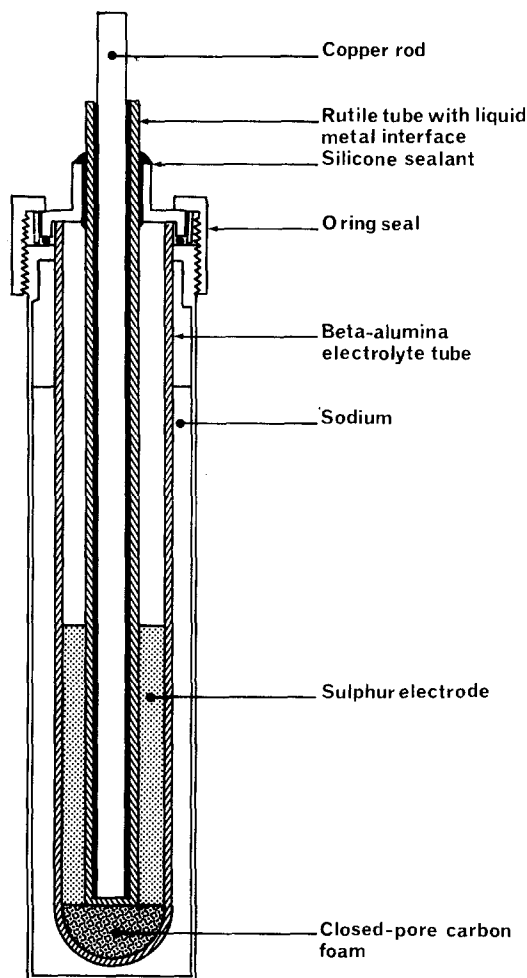

Figure 1 Schematic diagram of sodium—sulphur cell.

634

measured using silver wire probes. The resistivity was calculated directly from the measured resistance and dimensions of the samples.

The sodium–sulphur cells used in this work were of a central sulphur electrode design as shown schematically in Fig. 1. The sodium–beta-alumina tubes were 160 mm long and had an o.d. of 26 mm with a wall thickness of 1.5 mm. The beta-alumina was magnesium-doped with a composition, 8.0 wt % Na$_2$O, 2.0 wt % MgO, balance Al$_2$O$_3$. The manufacture and properties of this material are described in detail elsewhere [5]. The sulphur electrode had a matrix of graphite felt held under an axial compression of 2:1, impregnated with pure sulphur and surrounding the rutile tube. The base of the sulphur electrode compartment had a hemisphere of a closed pore carbon foam to prevent reaction in this area. The cells had an austenitic stainless steel case which also served as the sodium electrode current collector. The sodium electrode was filled to a level so that even when fully discharged, the sodium level was above the top of the sulphur electrode. The titanium dioxide was cored with a copper rod with a diameter of 9 mm and molten lead–tin alloy (60 wt % Pb–40 wt % Sn) was used to provide a conductive interface between the ceramic tube and copper rod. Nickel plating was also used on the inner surface of the ceramic tube of one cell. Cells were operated in a temperature gradient so that the electrodes could be sealed with silicone rubber "O" rings and a silicone sealant for the current collector as the temperature at the top of the cell was < 475 K. The 70 mm operating length of the sulphur electrode was held within a temperature range of ±10 K. Cells were charged and discharged over a range of current densities and the cell impedances and capacities were measured.

3. Results and discussion

The tantalum-doped titanium dioxide (rutile) tubes had an average sintered density of 4220 kg m^{-3} (99% theoretical density). They had a uniform black coloration and were impervious to helium.

Microscopic examination of the material before etching showed small rounded pores, often in clusters, with a size ranging from 1 to 5 μm. Etching revealed a uniform grain structure (grain sizes from 5 to 15 μm) with a complete absence of exaggerated grain growth or of any second phase (Fig. 2). The grain size remained uniform and in the same size range close to the surface of the samples. This is an important observation because grain growth in this material is inhibited by the tantalum dopant and confirms EDAX analyses of the tantalum distribution. Tantalum also has the effect of increasing the sintering temperature by decreasing the diffusivity as pure titanium dioxide of the same type used in this work may be sintered to high density at ~ 1475 K.

The distribution of measured tensile strength values σ_f for the rutile samples may be fitted to a Weibull distribution of the form,

$$P = \exp\left[-D(\sigma_f - \sigma_u/\sigma_0)^m\right]$$

where P is the survival probability, D the volume under stress, σ_u the zero probability stress, σ_0 a normalizing constant, and m the Weibull modulus. Consequently,

$$\ln \ln 1/P = m \ln (\sigma_f - \sigma_u) - m \ln \sigma_0 + \ln D$$

and thus a plot of ln ln 1/P against ln σ_f with σ_u set equal to zero yields a straight line with a slope equal to the Weibull modulus. Fig. 3 shows the survival probability of a group of samples tested in the form of rings that had an average tensile strength of 210 ± 26 MN m^{-2}. The data fit a Weibull

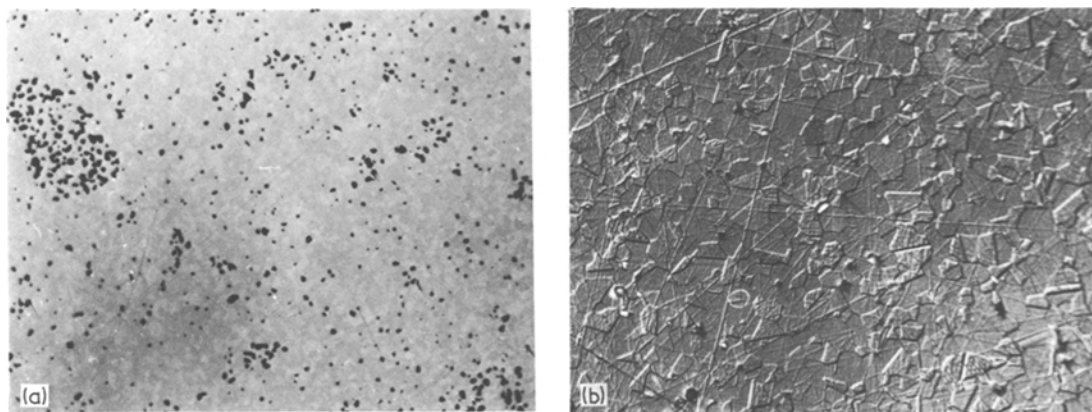*Figure 2* Microstructure of tantalum-doped rutile showing, (a) porosity distribution, × 190, (b) grain structure, × 480.
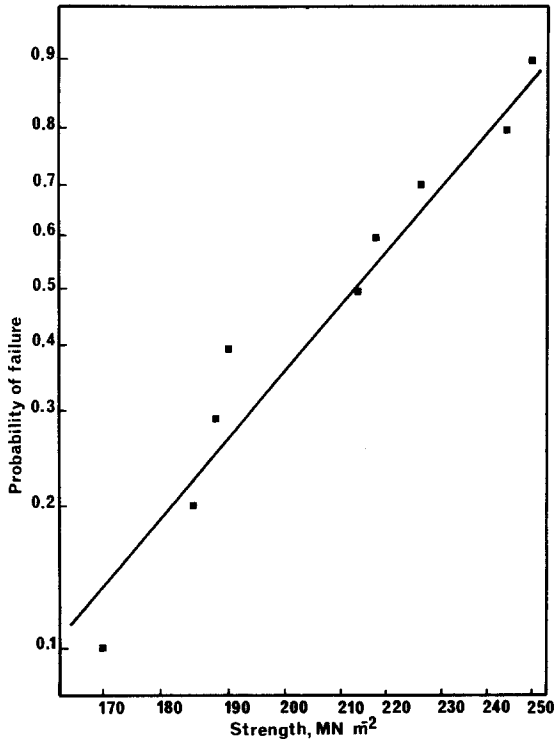
Figure 3 Cumulative probability of tensile failure of tantalum-doped rutile (plotted as $\ln \ln 1/P$ versus $\ln \sigma_f$).
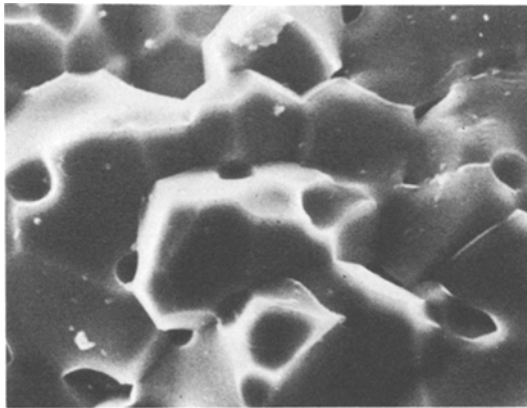

Figure 4 Scanning electron micrographs of the fracture surface of tantalum-doped rutile showing intergranular fracture and residual porosity, $\times$ 3200.

distribution quite reasonably and give a value of m of 7.3 that compares favourably with other engineering ceramics. On a macroscopic scale the fracture surface was flat and on a fine scale the fracture path appeared to be predominantly inter-granular (Fig. 4). The residual porosity was clearly visible on the fracture surface with pores concentrated at grain boundaries and occasional larger pores several grain diameters across.
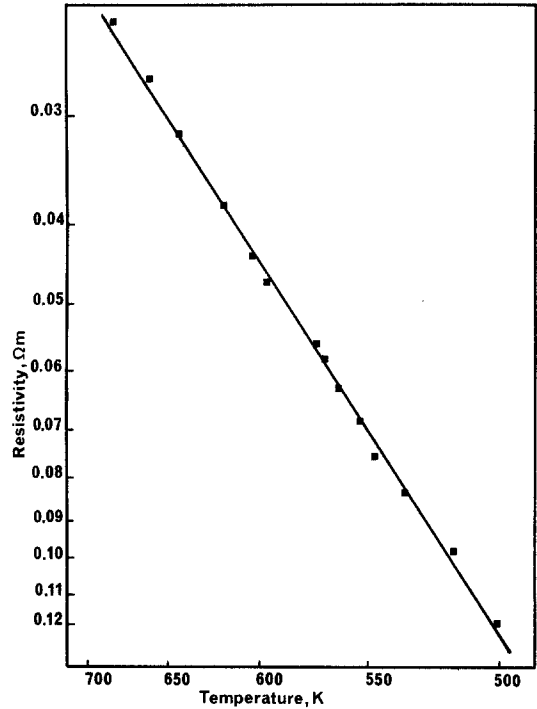
636

Figure 5 Variation of axial resistivity of tantalum-doped rutile with temperature (plotted as $\ln \sigma_e$ versus T^{-1}).

The corrosion resistance of the material in a cell environment was measured by immersion of a small coupon in the sulphur electrode of a cell with a solid graphite rod current collector. The cell was discharged until the open circuit voltage corresponded with a melt composition of Na_2S_3 and held in this condition at 575 K for 300 h. The cell was then cooled and the sample recovered by dissolution of the sulphur electrode melt in water. There was no apparent attack or weight change (< 0.01 wt %). Similarly, rutile tubes removed from cells after cycling showed no signs of attack. The material was also stable on oxidation in air at 675 K. There was no change in resistivity as measured by the four-probe technique over a period of ~ 400 h.

To a close approximation, the electronic conductivity of rutile, σ_e, follows an Arrhenius relation of the form,

$$\sigma_e = k \exp -(E_a/RT)$$

where k is a constant, T is the absolute temperature, E_a the activation energy and R the gas constant. The results of axial resistivity measurements obtained using the four-terminal technique are shown in Fig. 5 as a graph of $\ln \sigma_e$ against reciprocal temperature, and the activation energy

TABLE I Variation of cell impedance with temperature

Cell temperature (K)	Ah discharged	Cell impedance (mΩ)	Electrolyte resistivity (Ωm)	Electrolyte impedance (mΩ)	Sulphur electrode resistivity (Ωm)	Sulphur electrode impedance (mΩ)	Rutile impedance (mΩ)	Rutile resistivity (Ωm)
601	0	353	0.104	31	0.013	18	304	0.488
601	1.7	281	0.104	31	0.013	18	232	0.372
586	2.5	323	0.113	33	0.014	19	271	0.435
568	3.2	381	0.126	37	0.015	20	324	0.520
551	3.9	496	0.141	41	0.016	22	433	0.695
535	4.3	574	0.159	46	0.018	24	504	0.809
522	5.7	714	0.176	51	0.019	25	638	1.024
600	6.7	242	0.114	33	0.013	18	191	0.307
631	7.6	177	0.087	25	0.011	15	137	0.220
562	14.0	400	0.131	38	0.016	21	341	0.547
615	14.3	238	0.100	29	0.012	16	193	0.310

was determined from the slope. The resistivity at 600 K was 0.044 Ωm with an activation energy of 6.6 kJ mol^{-1}. The resistivity is greater than that reported by Johnson and Miller [3] but is adequate to demonstrate the feasibility of using the material as the current collector in a sodium–sulphur cell. The high resistivity may have a number of causes: the tantalum doping level or distribution may be inadequate; impurities such as aluminium may act as sinks for mobile electrons; or grain-boundary layers of oxidized material may be formed during sintering or cooling. There was microstructural and analytical evidence that the dopant was uniformly distributed, and the doping level is more than adequate to compensate for the adverse effects of impurities unless these segregate to grain boundaries. The formation of grain-boundary layers of high resistivity by diffusion of oxygen along grain boundaries to form thin layers of oxidized material is associated with the higher activation energies that were observed. This is supported by effects noted in exploratory work in which the rate of heating and cooling were found to have a marked effect on resistivity. Higher resistivity values were observed before the vacuum heat-treatment at 1075 K but more extensive reduction at 1475 K for 4 h in a vacuum of 0.14 mN m^{-2} with a residual atmosphere of hydrogen and nitrogen produced a material with a resistivity of 0.0020 Ωm at 600 K with an activation energy of 4.1 kJ mol^{-1}. Under these conditions, the material was substoichiometric with respect to oxygen and its resistance was unstable in air at 675 K making it unsuitable for use as a current collector.

In the cell design used in this work, a composite rutile current collector would have a resistance of 27 mΩ at 600 K if treated as a radial resistor with rutile having a resistivity of 0.044 Ωm. Similarly the resistance of the sulphur electrode would be 18 mΩ (resistivity, 0.013 Ωm) and the electrolyte, 33 mΩ (resistivity, 0.104 Ωm), giving a total cell impedance of 78 mΩ. Results obtained in cells with this material gave values considerably higher than this value. A cell with a liquid metal interface only (no nickel-plated layer) had an impedance of 180 mΩ at 595 K at an open circuit voltage of 2.0 V. This was stable over several charge/discharge cycles and did not vary significantly over the cycle except at the end of re-charge due to polarization. A similar result was obtained with a cell that had a nickel-plated inner layer in addition to the liquid metal interface. This cell had a capacity of 17 Ah on the first discharge (98% theoretical capacity based on discharging the cell to Na_2S_3). The capacity declined in subsequent cycles due to sulphur loss as a result of the poor sealing characteristics of the silicone material used to seal the current collector. The cell impedance was measured as a function of temperature and the data are summarized in Table I and in Fig. 6. Table I also shows the separate contributions from the electrolyte, the sulphur electrode and the balance due to the rutile current collector. The impedance of the sodium electrode and of the nickel plate/liquid metal interface/copper rod are negligibly small compared to the rest of the cell and the different elements were treated as radial resistors. The change of electrolyte impedance with temperature was calculated for ionic resistivity values determined earlier [5]. The impedance of the sulphur/sodium polysulphide melt varies not only with temperature but also with composition depending on the state of charge [6]. The resistivity of the graphite felt matrix increases with temperature.
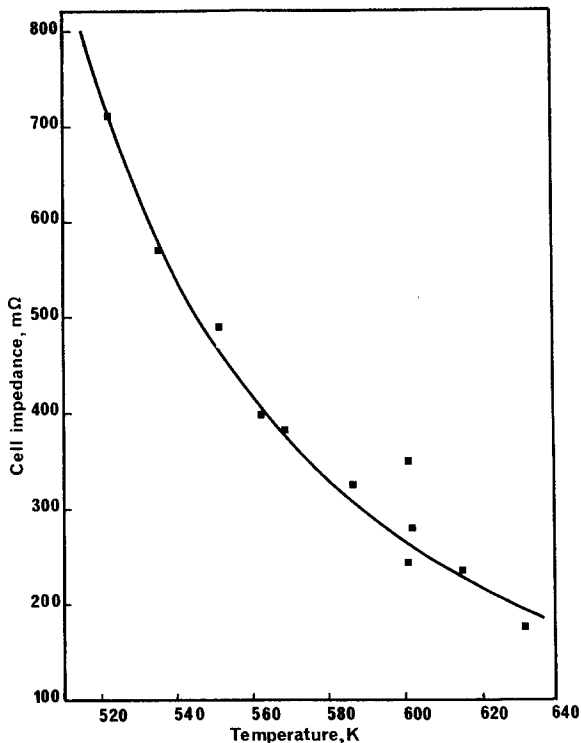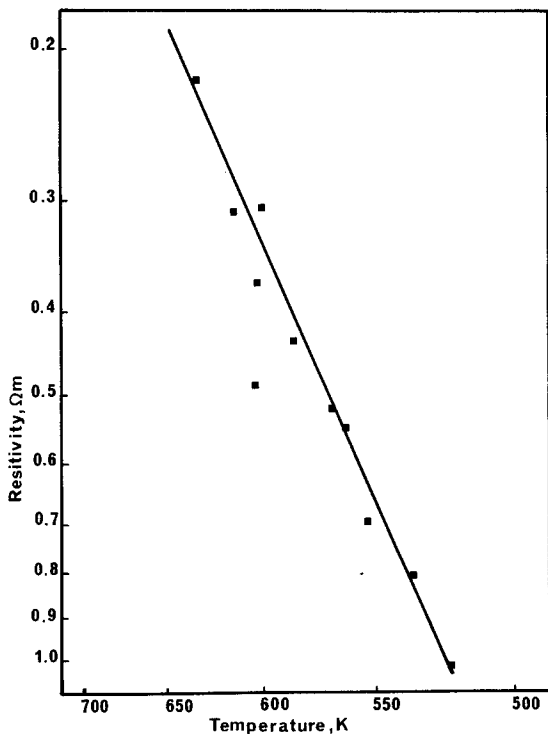
Figure 7 Variation of radial resistivity of tantalum-doped rutile measured in a sodium–sulphur cell (plotted as ln σ_e versus T^{-1}). The contributions to the cell impedance due to the beta-alumina electrolyte and the sulphur electrode have been subtracted from the total cell impedance at each temperature.

The figure used in Table I is compensated for the effects of temperature for an arbitrary single-phase melt composition of Na_2S_4. The errors introduced by neglecting the effects of melt composition are relatively small. The radial electronic resistivity of the rutile current collector in a cell is shown in the form of an Arrhenius plot in Fig. 7. The resistivity at 600 K was 0.35 Ωm and the activation energy, 8.4 kJ mol^{-1}. In order to determine whether the high resistivity obtained in a cell was due to a difference in the axial and radial resistivities, measurements were made of the radial resistivity of separate rutile samples using nickel-plated contacts backed up with liquid metal as in the cell. The resistivity at 600 K was 0.70 Ωm which is substantially higher than that measured in the cell, but the activation energy was similar at 8.1 kJ mol^{-1}. Equivalent results were obtained with liquid metal contacts alone. The resistivity values measured in a cell are the result of either a high contact resistance or a thin layer close to the tube surface with a higher resistivity. The results suggest a combination of both these effects. Contact resistance is relatively independent of temperature and so whilst the apparent impedance of the rutile tube would increase there would be little change in activation energy. There would, however, be a significant increase in activation energy for a surface layer of rutile that was more extensively

oxidized as observed but the lower resistivity obtained in the cell as compared to radial measurements suggests that contact resistance between the sulphur electrode and the tube is rather less than between the metallic contacts and the tube. Oxidation has taken place during manufacture, rather than by sulphur attack in cell operation and therefore attention should be given to improving the manufacturing route in order to make this material an effective current collector for a sodium—sulphur cell.

4. Conclusions

Polycrystalline tantalum-doped titanium dioxide (rutile) tubes have been prepared using tantalum pentafluoride to disperse the dopant. Sintered material had a high density and a uniform, fine-grained microstructure which led to a high tensile strength. Static corrosion tests showed the material was stable in an oxidizing environment. Measurements of the axial resistivity of the samples indicated that much lower values for the impedance of sodium—sulphur cells using composite rutile current collectors could be expected than were obtained in practice. The discrepancy results from a combination of contact resistance and a high resistivity surface layer and may be correlated with radial resistivity measurements measured in separate experiments. A considerable amount of development is clearly necessary to make this material useful as a current collector in the form of a solid tube but it could be used as a surface coating on an aluminium or copper rod if a suitable coating method could be devised.

References

1. G. J. MAY and I. W. JONES, *Metall. and Mat. Technol.* 8 (1976) 427.
2. R. BAUER, W. HAAR, H. KLEINSCHMAGER, G. WEDDIGEN and W. FISCHER, *J. Power Sources* 1 (1976) 109.
3. O. W. JOHNSON and G. R. MILLER, *Ceramic Bull.* 56 (1977) 706.
4. F. A. GRANT, *Rev. Mod. Phys.* 31 (1959) 646.
5. G. J. MAY, *J. Mater. Sci.* 13 (1978) 261.
6. B. CLEAVER, A. J. DAVIES and M. D. HAMES, *Electrochim Acta* 18 (1973) 719.