Letters

The electrical properties of monocadmium and dicadmium stannates

Conducting oxide materials are of interest for several energy conversion applications, including solid electrolytes for new types of storage and fuel cells, transparent electrode materials for some types of solar cells, and as photo-electrolysis electrodes for the direct conversion of solar energy to hydrogen. Two compounds of possible use as conduction oxides occur in the cadmium oxide–tin oxide system. The first reported preparation of any compound in this system [1] was that of monocadmium stannate, $CdSnO_3$, which was synthesized by solid state reaction between the two oxides. This synthesis was later repeated by Smith [2], who was also able to prepare polycrystalline dicadmium stannate, Cd_2SnO_4 by solid state reaction. Subsequent reported syntheses of both phases have involved thermal decomposition of cadmium hydroxystannates, precipitated from solutions of cadmium and tin salts by potassium carbonate solution [3], or by titration of sodium α-stannate with a cadmium salt [4]. The most recent reported preparation was a fluxed melt synthesis by Shannon *et al.* [5] of monocrystalline orthorhombic Cd_2SnO_4 and both orthorhombic and rhombohedral forms of $CdSnO_3$.

There is disagreement in the literature regarding the relative stability ranges of the monocadmium and dicadmium compounds. Smith [2] found that the dicadmium compound formed first, even in oxide mixtures of 1:1 stoichiometry, but completely converted to $CdSnO_3$ by heating to about 1100° C. On the other hand, an infra-red study of the thermal decomposition of cadmium hydroxystannate [6] was reported to indicate that the monocadmium compound thus formed converted at higher temperatures ($<1300°$ C) to Cd_2SnO_4.

The electrical conductances of $CdSnO_3$ and Cd_2SnO_4 monocrystals have been reported [5], as have the conductance, bandgap and optical properties of Cd_2SnO_4 thin films [7]. However, since no measurements of the photoelectrochemical properties of the cadmium stannates have yet been reported, this communication describes some experiments on sintered polycrystalline pellets, and, for comparision, an experiment on a Cd_2SnO_4 monocrystal.

The mono and dicadmium compounds were synthesized by thermal reaction of mixtures of the reagent grade oxides in the correct stoichiometric proportions. The syntheses were carried out at 1000 to 1050° C in alumina crucibles with closely-fitting lids. X-ray powder diffraction confirmed that both the polycrystalline monophase $CdSnO_3$ (orthorhombic) and the darker-coloured Cd_2SnO_4 could be prepared by careful control of the experimental conditions. No tin-rich phase could be prepared. Interdiffusion experiments between pellets of the reactant oxides suggest that the reaction mechanism is by diffusion of cadmium oxide (probably in the vapour phase) into tin oxide.

All electrical measurements were made on 1 cm diameter pellets of the pure phases, formed by pressing at 3×10^3 kg cm^{-2} and sintered at 1050° C for 2.0 h. in closed crucibles. The pellets thus prepared had densities of about 75 per cent of theoretical density. The room-temperature resistance of the pellets was measured by a four-point probe method using a Keithley model 225 current source with a model 163 digital voltmeter and model 530 type-all system. Photoelectrochemical measurements were made by cementing a contact wire to one face of the sintered pellet with silver dag sealed with epoxy resin, and immersing the complete electrode in a cell containing K_2SO_4–borax solution (buffered at pH 9.2) with a platinum counter-electrode. Reasonable ohmic contacts can usually be made by this silver dag method. The cell was irradiated with a xenon lamp having a luminous intensity of about 200 mW cm^{-2}. In other experiments, the variation of the photo-response with the wavelength of the incident radiation was measured using a mercury lamp and monochromator.

The room-temperature resistivity of $CdSnO_3$ and Cd_2SnO_4 pellets was found to be 3.0×10^{-3} and 1.3×10^{-2} Ω cm respectively. These values compare reasonably with the room-temperature conductance of thin amorphous films of Cd_2SnO_4, for which values of up to 1.33×10^3 Ω^{-1} cm^{-1} were reported [7], but are rather different from the reported resistivities of single crystal undoped orthorhombic $CdSnO_3$ and Cd_2SnO_4 [5], which

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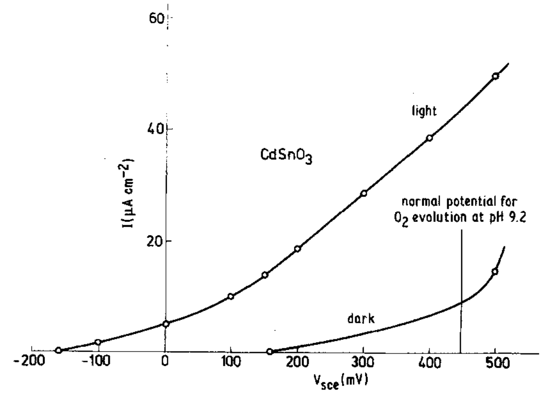

Figure 1 Photo-electrochemical behaviour of sintered $CdSnO_3$ pellet, pH = 9.2, Xe illumination (~ 200 mW cm^{-2}). Voltages measured with respect to saturated calomel electrode.

were described as insulating and semiconducting respectively. Since the conductivity of these materials is thought to be due to oxygen deficiency [5], the higher conductances of the present samples may be due to the introduction of anion defects during the solid state reaction between the oxide powders.

The results of the photo-electrochemical experiments on sintered $CdSnO_3$ and Cd_2SnO_4 pellets are shown in Figs. 1 and 2 respectively, from which it is seen that $CdSnO_3$ shows a much larger photovoltage and photocurrent than that of Cd_2SnO_4. The dark current from $CdSnO_3$ was also significantly greater than in Cd_2SnO_4, in which no background current was observed even at normal oxygen evolution potentials. This increased dark current in $CdSnO_3$ could be due to greater porosity of the sample pellet, which might also explain the lower reproducibility of measurements on that phase. Both $CdSnO_3$ and Cd_2SnO_4 pellets were stable in water and alkaline solutions for periods of several weeks, and showed no apparent tendency to dissolve or disproportionate, even at potentials up to those of oxygen evolution.

Tests were also conducted on a Cd_2SnO_4 pellet which had been sintered in an open vessel, losing some Cd from the outer surface, thereby forming an outer layer of $CdSnO_3$. This mixed-phase sample gave a smaller photovoltage than pure $CdSnO_3$, but showed a much larger photocurrent (Fig. 3). In all other respects, the sample had similar electrical properties to the pure $CdSnO_3$ and Cd_2SnO_4 phases. Although there was some slight variation in the as-tested densities of the various pellets due to differences in sinterability of the two stannates (the dicadmium compound sintered more readily than the monocadmium), the differences in photocurrent densities of the various samples are less likely to be due to this factor than to differences in the oxygen nonstoichiometry of the various phases, which has been shown by Shannon *et al.* [5] to exert a considerable influence on their electrical properties.

In all samples oxygen evolution was observed under intense illumination, even at potentials below the usual threshold for such a reaction. Since this effect was observed only on the anodic side, this result is consistent with n-type semiconduction behaviour. This is in agreement with the previous observation [7] that thin films of amorphous Cd_2SnO_4 exhibit n-type semiconductivity, with oxygen vacancies providing the donor states. The absence of physical disintegration of the samples suggests that the oxygen is derived from the electrolyte rather than the anode material, although some loss of oxygen from the pores may be possible without causing observable disintegration of the pellets.

The experiments with monochromatic radiation showed a photoresponse down to approximately 5300 Å, but the cut-off was not sharp, possibly due to the polycrystalline nature of the samples, and the low intensity level of the available monochromatic radiation. Nevertheless, this

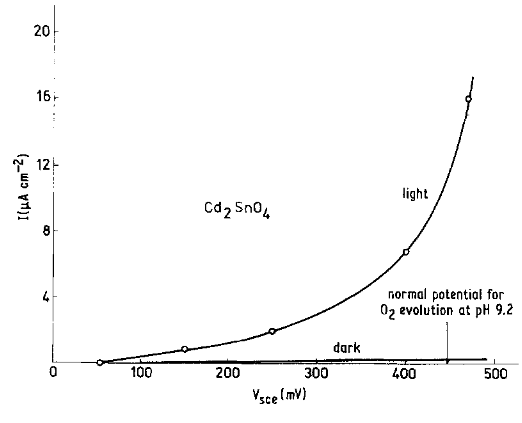

Figure 2 Photo-electrochemical behaviour of sintered Cd_2SnO_4 pellet, pH = 9.2, Xe illumination (~ 200 mW cm^{-2}).

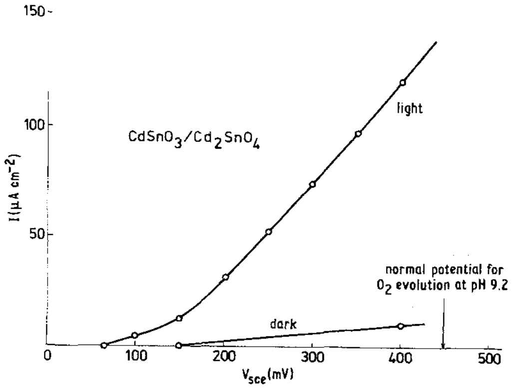

Figure 3 Photo-electrochemical behaviour of mixed $CdSnO_3$–Cd_2SnO_4 pellet, pH = 9.2, Xe illumination (~ 200 mW cm^{-2}).

cut-off wavelength corresponds to about 2.3 eV, in reasonable agreement with the optical bandgap of 2.06 eV reported for Cd_2SnO_4 thin films [7]. The present results indicate no significant difference in the bandgap of $CdSnO_3$ and Cd_2SnO_4, within the limitations of the experiment. Comparison of these data for the cadmium stannates with previously published photo-electrochemical data for SnO_2 [8] shows that SnO_2 behaves quite differently. As would be expected from the larger bandgap in SnO_2 (3.5 eV), the onset of photoconductivity occurs at about 350 mm, with V_{oc} of about −400 mV referred to a saturated calomel electrode at pH = 9. Photoconversion in SnO_2 below 350 nm is considerably more efficient than in the stannate samples. The lack of similarity between the photo-electrochemical behaviour of SnO_2 and the cadmium stannates confirms that the results for the stannates reflect their intrinsic behaviour, and are not simply due to traces of unreacted SnO_2 remaining in the sample.

In order to see whether the photoelectrochemical properties of the cadmium stannates might be impaired by the polycrystalline nature of the samples, single crystals of Cd_2SnO_4* in the form of long needle-like whiskers of about 1 mm × 1 mm cross-section were also tested. Although these crystals clearly showed n-type behaviour, the photocurrents were extremely small, even at high potentials and light intensities. These single crystals were too small to permit conductance measurements to be made, but if they possessed similar insulating properties to the Cd_2SnO_4 monocrystals grown by Shannon *et al.* [5], their poor photoresponse is understandable. Thus it appears that the photo-electrochemical properties reported here for polycrystalline samples may depend on their oxygen vacancy concentration, which in turn is a function of the method of their preparation.

The following conclusions can be drawn:

(1) Polycrystalline compacts of both $CdSnO_3$ and Cd_2SnO_4, prepared by solid state reaction between the pure oxides in closed crucibles at between 1000 and 1050° C, show high room-temperature electrical conductance (7.7 to 3.3 × $10^2\ \Omega^{-1}\ cm^{-1}$), the conductance of the mono-cadmium compound being higher than that of the dicadmium.

(2) A small but significant photoelectrochemical effect is shown by polycrystalline pellets of both compounds, the photocurrent (and background current) of $CdSnO_3$ being greater than that of Cd_2SnO_4. Both stannates are stable in water and alkaline electrolytes for periods of up to several weeks.

(3) Both stannates show n-type semiconductivity, with a bandgap of about 2.3 eV, estimated from the wavelength dependence of the photocurrent.

(4) The photo-electrochemical properties of polycrystalline Cd_2SnO_4 are better than those of a single crystal sample tested under similar conditions, possibly due to a lower concentration of oxygen vacancies in the latter.

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The morphology of the aluminium–palladium (Al-rich) eutectic

The aluminium–palladium phase diagram (Al-corner) presents a eutectic at 25 wt% Pd [1] or at 23% Pd [2] at 88 K. A compendium of the most important characteristics of this system, made by the authors on the basis of known data [1, 2] is given in Table I.

As reported in the literature [3], if the structure of this alloy is properly oriented, a high strength is gainable at elevated temperatures (673 K). Moreover, under hot-rolled conditions, it exhibits a fine-grained superplasticity manifested by a substantial elongation (~400%) [4]. However, the structure of this interesting system is not well established and some additional information is needed in order to clarify the doubtful points. For that reason a study was made of the microstructural characteristics under conditions of *in situ*-grown morphology.

The unidirectional solidification technique leads to a much simpler arrangement of the phases in comparison to that achieved under random casting conditions. The results of the research are reported here.

The master alloy was prepared by induction furnace melting (Al_2O_3 crucible) under a positive pressure of argon with the constituent elements mixed in a ratio nominally equal to the eutectic composition: 23 wt% Pd [2]. The base materials were of commercial purity: Al 99.998% and Pd 99.98%. After fusion, the ingot was cleaned and swaged at room temperature into a rod of 8.5 mm final diameter. Seven sections of length 20 cm were obtained and used as a charge for unidirectional solidification trials. Each section of the rod was placed in a cylindrical graphite crucible, remelted and unidirectionally solidified at a constant growth rate. The equipment has been described elsewhere [5]. The solidification rates were respectively: 3.3, 5.6, 6.5, 13.8, 14.7, 41.9 and 73.6 cm sec^{-1} × 10^{-4}, and the thermal gradient was about 100° C cm^{-1}.

The most important morphological features revealed by the metallographic observations (electro-etching in a solution of perchloric acid and acetic acid) are summarized in Table II, together with the corresponding growth rates and also weight compositions determined by chemical analysis. The alloys 1 and 2 were found to be slightly hypo-eutectic. However, such deviations from eutectic compositions are assumed not to have affected the basic microstructure. Chadwick

TABLE I Characteristics of the Al–Pd (Al-rich) eutectic [1, 2]

Solute element	Pd
Composition	23 wt % Pd [2], 25 wt % Pd [1]
Phases	
Matrix	Al (Pd solubility non detectable)
Second phase	Al_3Pd
Eutectic melting point	888 K
Composition	56.9 wt % Pd
Transformation temperature	1058 K
Transformation type	Peritectic Liq. (50 % Pd) + $Al_3Pd_2 \rightarrow Al_3Pd$
Crystal structure	Orthorhombic
Theoretical density	4580 kg m^{-3} *
Vol. % at eutectic temperature	28.8*

*Calculated by the authors

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