

Characterization of electrochemically reduced dicadmium stannate

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The two stable species of dicadmium stannate, namely oxidized (yellow) and reduced (green), have been studied using X-ray diffraction (XRD), Auger, and electron spectroscopy for chemical analysis (ESCA) techniques. Semiquantitative ESCA showed a chemical formula of Cd_2SnO_4 for yellow and Cd_2SnO_2 for the green compound. It appeared that both tin and cadmium can undergo a change in valency state during the electrochemical reduction. This explains the high energy density of the compound when used as active material for the negative electrode in rechargeable batteries. The variation of electrical conductivity of dicadmium stannate prepared under different conditions can be explained in terms of the reduction of tin, cadmium or both in the original compound.

1. Introduction

Transparent conducting ternary oxides of cadmium and tin have been studied seriously for the last two decades. Dicadmium stannate has received more attention because of its interesting features for a number of solar energy conversion applications including heat mirrors, transparent electrodes and photo-anodes [1, 2]. The potential utility of this compound is based on its electrical conductivity as well as its chemical stability [3, 4]. Most of the previous work was mainly directed to the preparation and characterization of thin sputtered films [5, 6]. The data for the electrical conductivity of Cd_2SnO_4 reported by different authors vary over a wide range [7, 8] and attempts have been made to correlate the conductivity to the oxygen vacancies in the crystalline lattice of the compound [9].

It has already been reported that the compound Cd_2SnO_4 has two stable species [4]. The conventional methods of preparation normally yield the yellow species with high stability. By heat treatment of this compound under a controlled atmosphere, the green cadmium stannate with superior electrical conductivity can be produced. An alternative method for preparation of green cadmium stannate has been suggested by the present authors using electrochemical techniques [10]. The authors have also succeeded in using Cd_2SnO_4 as a novel cathode material for alkaline secondary batteries [11], by which a reasonable open circuit voltage, high energy density and extremely high corrosion resistivity could be obtained.

This paper describes the detailed results of characterization of dicadmium stannate in both oxidized and reduced forms. While this information is essential from the point of view of electrochemistry of the compound, it can provide additional insight into the unexplained electrical properties of Cd_2SnO_4 .

2. Experimental details

Test electrodes were prepared from an intimate mixture of $2\text{CdO} : 1\text{SnO}_2$ by isostatic pressing followed by firing at 900 to 1000°C for 5 h. The sintered bodies in the shape of rods of 7 mm diameter were then cut to proper sizes. The electrical resistivity was about $10^{-2} \Omega \text{ cm}$. Details of electrochemical experiments can be found elsewhere.

The Auger electron spectra were obtained using a Physical Electronics Auger/ESCA/SIMS system with the working pressure of 2×10^{10} torr. Part of the precise measurements of binding energies from X-ray photoelectron spectra of both oxidized and reduced cadmium stannate were carried out using a Kratos ES 300 ESCA spectrometer with $\text{AlK}\alpha$ X-rays as the excitation source. In order to calibrate the binding energy scale of the spectra, the carbon 1s level arising from oil contamination was taken as 285.0 eV. During the course of this study, there appeared some evidence of photoreduction under continuous X-ray illumination of the yellow samples. Attempts were made to minimize the effect by rapid data accumulation and using the lowest possible X-ray intensity.

X-ray diffraction patterns were recorded on a Siemens 500 spectrometer. In order to find the exact position of the X-ray diffraction (XRD) lines, silicon powder was mixed with cadmium stannate powder. Silicon has several XRD lines close to some of the major reflections of Cd_2SnO_4 and thus allows a comparison of XRD lines in different regions of the spectra.

3. Results and discussion

Our preliminary investigations showed no compositional and structural differences between the different types of dicadmium stannate using conventional

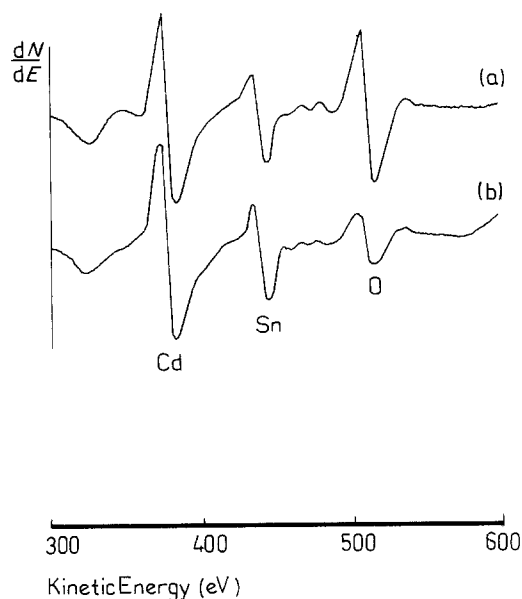


Figure 1 Auger electron spectra of dicadmium stannate: (a) in the oxidized state (yellow), (b) in the reduced state (green).

chemical analysis technique, elemental analysis by electron probe microanalyser (EPMA), and X-ray diffractometry. In all cases the ratio of Cd/Sn remained the same. The colour and the conductivity changes, however, suggest that the different samples might have slight compositional differences even if there are no compositional variations due to the Cd/Sn ratio. That is, there is still the possibility of a compositional change due to the different oxygen content, a feature which is common in some non-stoichiometric oxides.

The oxygen content variation could, in principle, change the lattice parameter of the material under investigation. Because this change proved to be extremely small, the diffractometer was run with the slowest possible rate $\frac{1}{8}^{\circ} \text{min}^{-1}$ and a relatively high chart speed. This facilitates the peak positions to be read to an accuracy of four decimal figures.

Table I presents the d values, cell parameters and cell volumes of Cd_2SnO_4 samples prepared in different atmospheres. As is seen, the differences in cell constants and cell volumes are very small (about 0.9% in the b values and 0.07% in the a values). The difference in the volume is about 0.2% which reflects the changes in all three parameters. The immediate conclusion is that the variations in cell parameters and cell volumes are not really significant, taking into account the probable measurement errors.

Crystal structure similarity between oxidized and reduced species of cadmium stannate manifested by the above results offer a favourable condition for the material to be utilized in electrochemical secondary batteries. In certain conventional electrodes such as manganese dioxide, during a discharge cycle, the crys-

tal lattice undergoes an appreciable expansion which makes recharging difficult and reduces cycle life.

As electrode processes are basically surface phenomena, surface sensitive techniques such as Auger and X-ray photoelectron spectroscopy (XPS) seemed ideal techniques for further investigation of cadmium stannate electrodes prepared in different conditions. It must be stated however, that the green (reduced) samples proved to be sensitive to air oxidation. Because both Auger and electron spectroscopy for chemical analysis (ESCA) are UHV systems, the samples must be dried before insertion into the vacuum chamber. The drying and transfer processes present an inevitable problem in any analytical programme. Although great care was taken in the part of the study to exclude air as much as possible, even slight exposure to the atmosphere might have caused oxidation and/or adsorption of atmospheric oxygen and other contaminations. Nevertheless, during the course of this study it was proved that the problem can be solved to a great extent by careful handling of the samples. Fig. 1 shows Auger spectra of cadmium stannate in both oxidized and reduced states. It is evident that apart from the apparent change in O peak intensities, both spectra are essentially the same.

More detailed information about the chemical nature of the cadmium stannate species was sought by comparing their ESCA spectra. Fig. 2 shows full range spectra (1000 eV) for yellow (oxidized) and green (reduced) cadmium stannate.

A semi-quantitative analysis based on sensitivity factors established a chemical formula of Cd_2SnO_4 for the yellow and Cd_2SnO_2 for the green species. This confirms our previous suggestion of the existence of tin in the tetravalent state in the yellow and in the divalent state in the green compound, based on the indirect chemical and electrochemical method [11].

Figs 3 and 4 show XPS spectra of both cadmium stannate compounds in the regions of $\text{Sn}3d_{5/2}$ and $\text{Cd}3d_{5/2}$ respectively.

Evidently a chemical shift has occurred when the reduction has taken place in both tin and cadmium. This is in accordance with the chemical formula given above for oxidized and reduced compounds. The little shoulder on the $\text{Sn}3d$ spectrum (Fig. 3b) is due to air oxidation during the sample handling. Comparing the binding energies of $\text{Sn}3d$ and $\text{Cd}3d$ in the original mixture of CdO and SnO_2 it appears that in the case of the yellow compound the peak positions are very close to those of the original mixture. The chemical shift of 1.6 eV for $\text{Sn}3d$ and 0.8 eV for $\text{Cd}3d$ occurs only after the reduction process. In the original mixture it was noted that the spectrum of $\text{Cd}3d$ consisted of two peaks, one at 404.6 and the next at 406.0 eV. The peak at 406.0 eV was originally assigned by Hammond *et al.* [12] to be due to $\text{Cd}(\text{OH})_2$, CdCO_3

TABLE I The d values, cell parameters and cell volumes of dicadmium stannate before and after electrochemical reduction

Sample	110	120	001	140	211	041	221	320	a (nm)	b (nm)	c (nm)	Cell volume (10^{-3} nm^3)
Cd_2SnO_4	4.857	3.698	3.195	2.263	2.055	1.958	1.934	1.739	0.5572	0.9905	0.3197	176.4
Cd_2SnO_2	4.857	3.697	3.194	2.268	2.054	1.959	1.934	1.741	0.5579	0.9925	0.3194	176.6

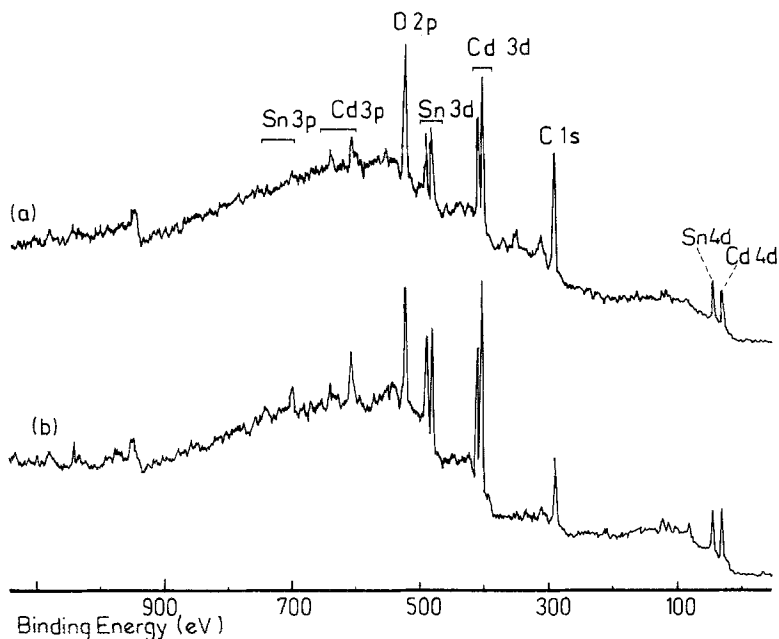


Figure 2 X-ray photoelectron spectra of dicadmium stannate: (a) in the reduced state (green), (b) in the oxidized state (yellow).

or CdO_2 . More detailed work by the present authors revealed, however, that this peak might be due to Cd_2O , a suboxide of CdO resulting from a disproportionate reaction [4]. This peak is absent in the spectrum belonging to the yellow compound, but the direction of the shift and the peak position suggests that the $\text{Cd}3d_{5/2}$ peak in the green compound is indeed due to Cd_2O . This is also consistent with the very nature of the electrochemical reduction process in which the reduced compound will always be found in the lower valency state. The reduced compound, if

heated in the atmosphere, will readily oxidize to the yellow species. Figs 3c and 4c are the spectra of the oxidized green compound obtained by heating in the atmosphere for 40 min at 250°C . All relevant binding energies are given in Table II.

The above results show a significant property of this material to be used as an active material in rechargeable batteries. That is if both tin and cadmium undergo a reduction process during the charging cycle, the system can produce much higher electrical energy in

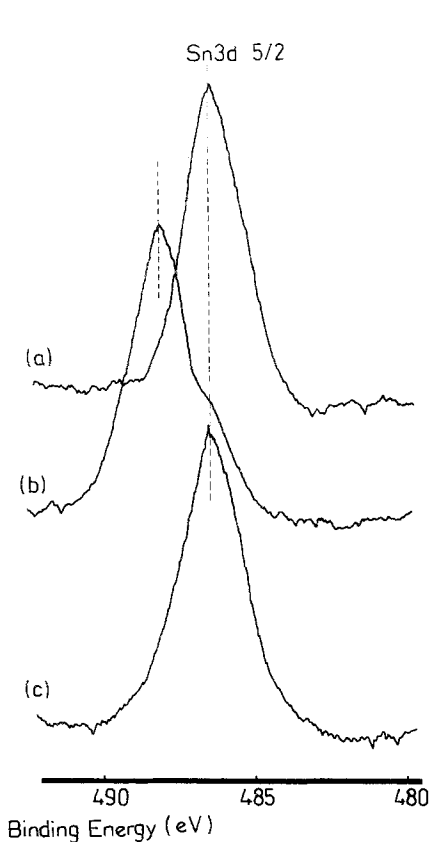


Figure 3 X-ray photoelectron spectra of dicadmium stannate in the $\text{Sn}3d_{5/2}$ region: (a) in the oxidized form (yellow), (b) the same sample after being electrochemically reduced, (c) the same sample heated in air for 40 min at 250°C .

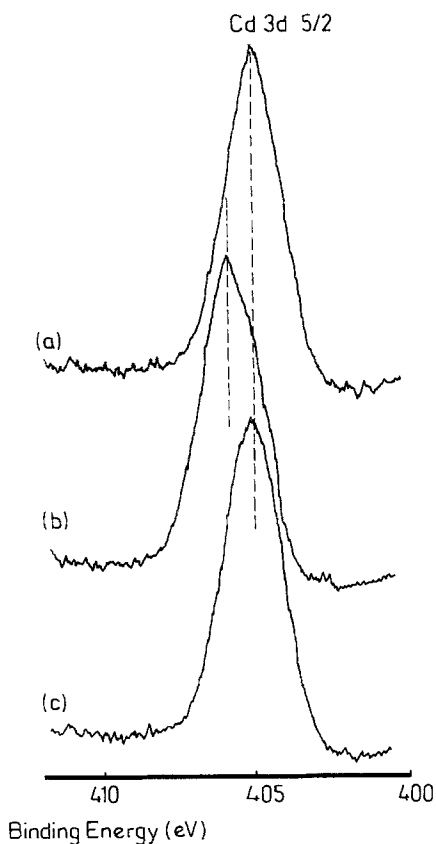


Figure 4 X-ray photoelectron spectra of dicadmium stannate in the $\text{Cd}3d_{5/2}$ region: (a) in the oxidized form (yellow), (b) the same sample after being electrochemically reduced, (c) the same sample heated in air for 40 min at 250°C .

TABLE II Binding energy values for the original mixture, oxidized (yellow) Cd₂SnO₄ and reduced (green) cadmium stannate

	Binding energy (eV)	
	Cd3d _{5/2}	Sn3d _{5/2}
CdO	404.8, 405.8	–
SnO ₂	–	486.4
Cd ₂ SnO ₄ (yellow)	404.8, –	486.3
Cd ₂ SnO ₂ (green)	–, 405.5	487.8

the discharging cycle compared to the energy produced in the system with the sole reaction of $\text{Sn}^{4+} + 2e \rightarrow \text{Sn}^{2+}$. Judging by the high energy density of Cd₂SnO₄, in our previous paper we suggested that perhaps the CdO component of Cd₂SnO₄ compound might also undergo an electrochemical reduction [11]. Present results support this view in that an additional transition of $\text{CdO} \rightleftharpoons \text{Cd}_2\text{O}$ also takes place during the charging and discharging cycles.

Electrical resistivity measurements were made on a variety of sintered dicadmium stannate samples prepared under different conditions of firing. This showed that the resistivity varies between 10⁻¹ and 10⁻³ Ω cm depending on the oxygen partial pressure during the firing process. The same measurement on electrochemically reduced samples showed an even higher conductivity of 10⁻⁴ Ω cm.

Based on the results obtained in this work we suggest that in Cd₂SnO₄ both tin and cadmium can undergo a reduction process imposed by an external force either by exposure to a reducing atmosphere or by electrochemical reduction. In either case, the reduction (electronation) of the compound leaves it with much higher electron density, which is responsible for higher conductivity. The more vigorous the conditions for reduction, the higher would be the electrical conductivity.

4. Conclusions

X-ray diffraction studies of dicadmium stannate in oxidized and reduced states showed no significant differences. This is an interesting feature of dicadmium stannate in connection with rechargeable batteries.

Auger electron spectra of the two cadmium stannate species also showed no major differences apart from oxygen content. ESCA examination of the samples revealed a chemical formula of Cd₂SnO₄ for yellow (oxidized) and Cd₂SnO₂ for green (reduced) species. Obviously both cadmium and tin undergo a reduction process. Binding energy measurements supported the results.

On the electrical conductivity of cadmium stannate, it is concluded that the high electrical conductivity in the green compound of cadmium stannate observed previously, is due to a reduction (electronation) process, because of the greater availability of electrons.

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