A NEW METHOD FOR THE PREPARATION OF FINE-GRAINED SnO₂ AND WO₃ POWDERS: INFLUENCE OF THE CRYSTALLITE SIZE ON THE ELECTROCHEMICAL INSERTION OF Li⁺ IN SnO₂ AND WO₃ ELECTRODES

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We propose an unconventional method to obtain fine-grained SnO₂ and WO₃ powders. It uses as precursors, polymer complexes between polyethylene oxide (POE) and SnCl₄ or WCl₆ respectively. By pyrolysis of these complexes in the 350-550°C temperature range, metal-oxide powders possessing small crystallite sizes are obtained. They are free from water and hydroxyl group contaminations, which is an added advantage where the application of these materials to Li-batteries is concerned. We have, indeed, demonstrated that these powders show good ability to insert reversibly lithium ions in the Li/Li⁺/SnO₂(WO₃) cells.

INTRODUCTION

SnO₂ is an n-type semiconductor with a tetragonal rutile structure¹ and a large indirect band energy gap (2.7 eV)². It has attracted considerable attention to the variety of applications related to its unique electrical, optical and catalytic properties. Among its applications, to mention only a few, are in transparent heaters for windshield defrosting, in anti-reflection coating for solar cells, as a transparent electrode for electrochromic devices, as a sensing material for combustible gas sensors, and as an electrocatalyst for organic oxidation³⁻⁸. In the last two applications mentioned above, fine powders of SnO₂ are used. These powders have generally been obtained through two different methods: one involves the oxidation of elemental tin with acids (HNO₃, H₂SO₄ etc.) and the other utilizes the well-known sol-gel route. The sol-gel method involves the dispersion of stannic hydrate in aqueous ammonia to give a sol. The sol is later ‘solidified’ through stages of stiffening and polymerization to give a gel (gelation). The gel so obtained is
thoroughly washed with distilled water, filtered, dried and finally heated to high
temperatures to obtain the required material\textsuperscript{9}. The sol-gel route has been found to
give finer crystallites compared to the former method. However, samples free from
water and hydroxyl groups are hardly achievable when low calcination tem-
peratures are used.

WO\textsubscript{3} is an \textit{n}-type semiconductor that displays three crystal polytypes: mono-
clinic, hexagonal and orthorhombic\textsuperscript{10}. WO\textsubscript{3} powders can be obtained using the
same preparation procedure used for SnO\textsubscript{2}. They have also been prepared using
other techniques. Cheng et al.\textsuperscript{11-12} obtained WO\textsubscript{3} powders from the thermal
decomposition of ammonium paratungstate while Zhong et al.\textsuperscript{13} used a similar
process with H\textsubscript{2}WO\textsubscript{4}. These authors were primarily concerned with making cath-
ode electrodes for secondary lithium batteries where high surface area is an
important parameter. The specific surface areas of the WO\textsubscript{3} powders obtained
from the thermal decomposition of H\textsubscript{2}WO\textsubscript{4} were between 12.2 and 4.3 m\textsuperscript{2}/g\textsuperscript{13}, and
so were of limited use for this purpose. Low specific surface areas are obtained not
only for the WO\textsubscript{3} powders but also for the SnO\textsubscript{2} powders obtained using the
preparation procedures quoted above. There is, therefore, a need to develop a
method to produce WO\textsubscript{3} and SnO\textsubscript{2} powders with higher surface areas for use as
cathode materials in lithium electrochemical cells. For this purpose the powders
will also have to be free of water and hydroxyl groups.

We propose here an unconventional and easy-to-carry-out method for the
preparation of fine particles of SnO\textsubscript{2} and WO\textsubscript{3} powders. It uses as precursors
complexes of the respective halides SnC\textsubscript{14} and WC\textsubscript{16} with polyethylene oxide
(PEO)\textsuperscript{14}. The method has been shown to give not only very fine particles, obtained
after eliminating the polymer by heating, but also particles free from water and
OH group impurities.

The conventional and unconventional sol-gel methods will be compared here;
they will be referred to as method 1 (for the conventional one) and method 2.

We also investigated the ability to insert reversibly lithium ions into the
fine-grained SnO\textsubscript{2} and WO\textsubscript{3} powders in Li/Li\textsuperscript{+}/SnO\textsubscript{2} (WO\textsubscript{3}) electrochemical
cells. Related to that, we have reported elsewhere that electrodes based on
fine-grained transitions metal oxides (Li\textsubscript{x}Fe\textsubscript{2}O\textsubscript{3}, Li\textsubscript{2-x}NiO\textsubscript{2} etc.) in the form of
thin films exhibit highly efficient electrochemical (de)insertion of Li\textsuperscript{+} ions into
lithium conducting electrolytes\textsuperscript{15-17}. The electrode materials were symbolized as
NCIMs (nanocrystallite-insertion-materials). Indeed, by minimizing the crystallite
size, we favor the formation of dangling and weak bonds at the surface and,
thereby, the rate of reversible lithium insertion. Since the previously studied
NCIMs were based on transition metal oxides, we were more concerned in earlier
publications in the cationic “d” orbitals that were involved in the electrochemical
processes\textsuperscript{15-17}. In the case of SnO\textsubscript{2} based electrodes, it is the cationic “5s” orbitals
that would be of concern; as for WO\textsubscript{3}, the “5d” orbitals are involved. Therefore, it
is worthwhile to have an insight into the respective influences of “s” and “d”
orbitals on the electrochemical response using SnO\textsubscript{2} and WO\textsubscript{3} as examples. The
SnO\textsubscript{2} powders were prepared by both methods 1 and 2 for comparison; the WO\textsubscript{3}
powders were obtained by method 2.
EXPERIMENTAL

Sample preparation

a) Method 1

A colloidal stannic hydroxide was precipitated by the dropwise addition of ammoniacal solution (35%, Aldrich) to an aqueous solution chloride (99.99%, Aldrich) maintained at 2°C in an ice-water bath. Residual impurities of hydrogen chloride and ammonium chloride were removed by repeatedly washing with distilled water. The washing and filtering process were repeated until the pH of the solution decreased to 7.5 (from an initial value of 12.5). The as-obtained α-stannic acid gel was heated in dry oxygen for 2h at different temperatures (150, 350 and 550°C) in order to get powdery samples with different morphologies. The heating and cooling temperature rate (1°C/min) was controlled using a Eurotherm programmer. The samples are identified hereafter as 1-(150); 1-(350); 1-(550) “1” designates the method of preparation and the number within brackets represents the heat treatment temperature.

b) Method 2.

Four grams of polyethylene oxide (PEO: Aldrich, M. W. 500,000) was first added to 230 ml of acetonitrile. Immediately afterwards, SnCl₄·5H₂O or WCl₆ (Aldrich, 99.99%) were added to the solution in the proportions [-CH₂-CH₂-O] / M = 8, (M = Sn or W). The solution was stirred at room temperature for about 6 hrs, i.e., until a satisfactory homogeneity was achieved. Then, the ‘sol’ was cast in a teflon mould. Evaporation of the solvent at about 40°C under a stream of dry air gave an organo-metallic polymer film of typical thickness 100μm. Finally, fine-grained SnO₂ and WO₃ powders were obtained by eliminating the C, H elements of the polymer film with slow heating in dry oxygen. In order to get NCIMs (with different morphologies, the polymer films were heated up to 350°C, 450°C, or 550°C and soaked for 2hrs at those temperatures. The heating and cooling temperature rate value was 1°C/min.

The powdery SnO₂ and WO₃ samples are identified as 2-(350), 2-(450), 2-(550) and 2-(350)W, 2-(450)-W 2-(550)-W; as above, “2” designates the method of preparation and the number within brackets the temperature of heat treatment. The symbol “W” identifies the tungsten oxide samples.

The preparation procedure involved in methods 1 and 2 are schematically illustrated in Fig. 1. Let us note that the time required for the synthesis of the powders using the method 2 is much shorter (about 2/3 shorter) than that required for method 1: indeed, the filtering and milling processes intervene only in method 1.

Sample analysis:

Thermogravimetric analyses, using a Leco TGA-501 display, were performed in dry air between 22°C and 600°C with a Setaram thermobalance. X-ray diffraction measurements were obtained with a Phillips PW 1050 spectrometer and CuKα.
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diluted SnCl4 solution

\[ \text{NH}_4\text{OH} \]

colloidal precipitate

\[ \text{H}_2\text{O} \]

filtering

drying (60°C)

calcination

milling

SnO2 powder

SnCl4 hydrous (or WC16)

\[ \text{PEO} \]

\[ \text{CH}_3\text{CN} \]

stirring

drying (60°C)

calcination

SnO2 (or WO3) powder

**FIGURE 1** Schematic diagrams of the steps involved in obtaining fine-grained SnO₂ and WO₃ powders.

radiation. The average crystallite size, D, was calculated from the well-known Scherrer's formula

\[ D = \frac{0.9 \lambda}{\beta_{1/2} \cdot \cos \theta} \]  \hspace{1cm} (1)

\( \beta_{1/2} \) is the corrected width of the main diffraction peak at half height, \( \lambda \) is the X-ray wavelength, and \( \theta \) the diffraction angle. The specific surface area of the samples was measured by the single point Brunauer Emmett and Teller (BET) method with a Micromeretics Accu Sorb 2100 E. The samples were outgassed at 180°C for 5 hrs. The adsorbate gas was nitrogen. The IR spectra in the adsorbanse mode were recorded on a Perkin-Elmer 983G spectrometer between 4000 and 200 cm⁻¹ with an average resolution of 5 cm⁻¹. The experiments were performed on SnO₂ and WO₃ powders dispersed in Nujol and sandwiched between two cesium iodide disks. Conductivity experiments using the Van der Pauw four probe technique were carried on using samples that were pressed at 5 tons/ cm² in a steel die of diameter 13 mm. The analysis of the carbon content and the composition of the gases released during the sample pyrolysis were achieved using the TGA.
apparatus equipped either with an elemental analyser (LECO, CHN-1000) or with a gas chromatograph (Varian 3700).

**Electrochemical measurements:**

Electrochemical (de)insertion of lithium was realized in bottle-type cells having two electrodes. The cathode consisted of 35 mg of SnO₂ or WO₃ powder and 6 mg of carbon black (i.e. ~ 15w%). The cathode was prepared by intimately mixing the powders (previously outgassed at 180°C for 5 hrs) and pressing in the form of a disk in a 1.3 cm diameter stainless steel die. Lithium metal was used as both reference and apode. The electrolyte was a 1M LiCF₃SO₃-propylene carbonate solution impregnated into a glass filter paper. The propylene carbonate (Aldrich 99 + %) was further dried by fractional distillation under 4Å molecular sieves. The lithium triflate (Aldrich 97%) was kept under vacuum at 150°C during 72 hrs. The experiments were then carried out inside a glove box maintained under argon atmosphere and containing less than 1 ppm H₂O and O₂.

**RESULTS AND DISCUSSION**

**Sample composition**

a) Samples 1-(150), 1-(350), 1-(550)

The presence of adsorbed water hydroxyl groups in samples 1-(150) and 1-(350) is also revealed in the IR spectra (fig. 2). Adsorbed water is best characterized by its deformation mode δOH₂ occurring near 1620 cm⁻¹²⁸,¹⁹. This adsorption band is only observed in sample 1-(150). The broad features between 3500 and 3100 cm⁻¹ observed for samples 1-(150) and 1-(350) can involve stretching modes of water, hydroxyl groups. Traces of ammonium ions arising from the synthesis might also occur and contribute to the previous broad adsorption (ν₁ and ν₂ modes of NH₄⁺²¹). However, nothing is detected around 1420 cm⁻¹ (ν₄ mode of NH₄⁺).

On the other hand, a weak and broad feature is observed at about 1200 cm⁻¹ in both 1-(150) and 1-(350) samples. It can be attributed to a hydroxyl bending mode. It can be attributed to a hydroxyl bending mode. Therefore, for sample 1-(350), which presents no water adsorption at 1620 cm⁻¹, it can be concluded that the protons are essentially involved in hydroxyl groups and the broad high frequency adsorption reflects mainly the stretching vibrations of these hydroxyl groups.

Finally, sample 1-(550) exhibits neither water nor hydroxyl group vibrations.

It is known that the presence of hydroxyl groups and adsorbed water in fine-grained SnO₂ powders favors protonic conductivity²²,²³. The latter can be evidenced from d.c. conductivity measurements, as shown below. First of all, the d.c. electric induced by an applied potential of 1 V across a disk of SnO₂ (1 mm thickness, 13 mm diameter) is shown in fig. 3 gold electrodes that are blocking to ionic motion insure the electrical contacts. The term “blocking to ionic motion” means the absence of any ionic transfer via the interfaces between the electrodes and the electrolyte.
FIGURE 2 IR absorption spectra of (a) 1-(150), (b) 1-(350) and (c) 1-(550) samples.

FIGURE 3 Electrical current across a pressed pellet ($d_{\text{exp.}}/d_{\text{theor.}} = 55\%$) of SnO$_2$ prepared employing method 1 and for an applied potential of 1 V.
With the blocking electrodes, the protonic conductivity causes the "polarization effect" illustrated in fig. 3 for samples 1-(150) and 1-(350): it can be noted that the current measured immediately after the potential has been applied is time dependent, accounting for an ionic (i.e., protonic) conductivity. The large concentration of the mobile enables, indeed, the progressive accumulation of a large number of charges within a thin thickness at the interfaces, causing the observed decrease of the current between 0 and 150 s (fig. 3). We are dealing, in fact, with the well known phenomena of the double electrical layer that which is produced at the blocked interface between an electronic conducting electrode and an ionic conductor. When $t > 150s$, the interfaces are built and the observed residual steady current (fig. 3) account for a residual electronic conductivity. The occurrence of protonic conductivity in samples heated only up to 350°C has also been observed by others. The constant current, observed uniquely for sample 1-(550) within the whole time range (fig. 3), accounts for the expected absence of ionic conductiv-

![Graph](image)

**FIGURE 4** TGA profiles of hydrated SnO$_2$ gel (a), SnCl$_4$·5H$_2$O-PEO and WCl$_6$-PEO (b), recorded in dry air with a heating rate of 1°C per minute.
Sample characteristics according to the preparation conditions.

| Preparation procedure | Method 1 | Method 2 | Method 2 |
|-----------------------|----------|----------|----------|
| Samples               | SnO₂     | SnO₂     | WO₃      |
| 'n' value in SnO₂·nH₂O/WO₃·nH₂O | 1.5 0.0 0.0 | 0.0 0.0 0.0 | 0.0 0.0 0.0 |
| Content carbon (wt%)  | 0.0 0.0 0.0 | ~ 15 ~ 5 0.0 | ~ 10 < 5 0.0 |
| Colour                | white pale yellow | black brown grey white | black brown pale green |

Moreover, the higher current observed for this sample results from an increased electronic conductivity due to an increase in concentration of oxygen vacancies. The latter introduce, indeed, ionized electronic donor centers that are responsible for an enhanced electronic conductivity.²⁶

Even though a small amount of ammonia not detectable by IR spectroscopy might occur, the compositions of samples 1-(550), 1-(350) and 1-(550) have been from the general formula SnO₂·nH₂O.²⁷ Then values have been deduced from TGA measurements (fig. 4a); they are reported in table I.

b) Samples 2-(350), 2-(450), 2-(550); 2-(350)-W, 2-(450)-W and 2-(550)-W

As reported above, the powdys SnO₂ and WO₃ samples result from the calcination of polymer-metal halide complexes at the required temperatures (350°C, 450°C, 550°C). The corresponding overall weight loss, as evidenced from TGA studies, is about 80%; it takes place in four stages as depicted in fig. 4b. The initial weight loss of ~ 12%, stage (i), is completed below ~ 100°C. It corresponds to the evaporation of the residual CH₃CN solvent. The stages (ii) and (iii) are completed between ~ 130 and 200°C and ~ 300°C respectively, they account for the emission of H₂O and HCl (~ 65% weight loss). The last step (iv) is completed at ~ 500°C, it corresponds to the departure of CO, CO₂ traces (~ 3% weight loss). Traces of carbon remaining in samples 2-(350), 2-(450), 2-(350)-W and 2-(450)-W give them a dark coloration (table 1), therefore IR spectroscopy measurements cannot be carried out. However TGA measurements reveal no measurable traces of water and hydroxyl groups in all samples. Consequently, the SnO₂ and WO₃ powders are likely to behave as the (quasi) water free and hydroxyl group free NCIMs whose electrochemical Li⁺ (de)insertion efficiency has already been demonstrated by some of us.¹⁵-¹⁷ To prove the occurrence of the similarity in the behavior of the SnO₂ and WO₃ powders to those of the NCIMs, we have to examine first the crystalline structure and texture prior to any electrochemical investigation.

Crystal structure and texture:

X-ray diffraction measurements were carried out on all samples listed in table 1 in order to know the evolution of the crystalline size as a function of calcination.
For the sake of clarity, the diffractograms, which are the most representative of this evolution, are shown in Fig. 5. The X-ray diffraction lines are very broad for 1-(350), 2-(450) and 2-(450)-W. However, their presence indicates that the samples are nanocrystalline in nature rather than glasses. The main size, $D$, of the microcrystallites, listed in Table 2, were estimated by considering the diffraction broadening of the peaks corresponding to the (110) plane for tin oxide and to the (001) plane for tungsten oxide.

We compare in Table 2 the specific surface areas of the SnO$_2$ powders 1-(550) and 2-(550) having rather similar crystallite size and being free from contamination by water and/or hydroxyl groups and carbon (originating from PEO). Most interestingly, a much higher value is obtained for the sample 2-(550). Consequently, prior to its complete departure, the organic part restrains the crystallite...
TABLE 2

Evolution of the crystallite size and specific surface area with calcination temperature using both methods 1 and 2.

| Samples | 1-150 | 1-350 | 1-550 | 2-350 | 2-450 | 2-550 | 2-350-W | 2-450-W | 2-550-W |
|---------|-------|-------|-------|-------|-------|-------|---------|---------|---------|
| Crystallite (a) size (±6Å) (110) (b) | < 20  | 30    | 75    | < 20  | 45    | 70    | < 30    | 60      | 308     |
| Surface (a) area (m²/g) | 25    | 55    | 150   | -     | -     | -     | -       | -       | -       |
| 122    | 148   | 39    | 16    | 104   | 75    | 16    | 38      | 25      |

(a) this study: let us quote that the surface areas reported here are related to the particle size and pore volume (the accepted definition being that many crystallites make a particle).
(b) from references 28-30

FIGURE 6 Reversible 10th discharge curves of (a) Li/Li⁺/LiₓSnO₂ and (b) Li/Li⁺/LiₓWO₃ cells between voltage limits of 1.5-3.1V (a), and of 1.8-3.1V (b), vs Li. The current density was 50µA/cm² for an electrode weight of 35 mg.
and particle growth. The crystallite and particle growths are, indeed promoted only when the organic part is almost eliminated. As expected, the specific area increases as the crystallite size is reduced, from 2-(550) to 2-(450) on the one hand, and from 2-(550)-W to 2-(450)-W, on the other hand (table 2). Finally, the low surface area values reported in table 2 for samples 2-(350) and 2-(350)-W are due to the incomplete elimination of the polymer-residuals at 350°C; the carbon content (measured using atomic adsorption spectroscopy) is indeed as high as 15% (table 1). It may be possible that the SnO₂ and WO₃ crystallites are bound together through O-C bonds; consequently very small surface areas are observed for 2-(350) and 2-(350)-W.

Electrochemistry: influence of grain and particle sizes on the reversible electrochemical insertions of lithium in SnO₂ and WO₃ NCIM electrodes:

As pointed out above in the experimental part, the obtained samples were intercalated with lithium in the following electrochemical cells: Li/LiCF₃SO₃ in propylene carbonate/SnO₂ and Li/LiCF₃SO₃ in propylene carbonate /WO₃. The measurements were carried out at room temperature. The lithium insertion process was conducted, using the well known cyclic manner, by (dis)charging the cells with a constant current of 50 \( \mu \)A/cm².

Fig. 6 illustrates the reversible 10th discharge curves of the cells for the samples free from contamination by water, hydroxyl groups, and residues of PEO (table 1). In agreement with our model¹⁵–¹⁷, the highest rate of lithium insertion occurs for the NCIMs 2-(450) and 2-(450)-W, which possess the highest specific surface area. Our results concerning WO₃ are also in agreement with Zhang³¹ who showed that powdery LiₓWO₃ electrodes having surface areas of 4.3m²/g and 12.2m²/g reversibly insert \( x = 0.28 \) and \( x = 0.48 \) lithium, respectively, between 1.8 and 3.2 V vs Li. In our work, the rate of lithium reversibly inserted is higher (\( x = 1.2 \) for 2-(450)-W) because of the higher specific surface area. Within the same voltage range (fig. 6), the amount of Li inserted is larger in the case of WO₃ compared to SnO₂: it is indeed related to the electron affinity of the W⁶⁺/W⁵⁺ couple, which is larger (in absolute value) than that of the Sn⁴⁺/Sn²⁺ couple. Fig. 7 illustrates the good cycling reversibility observed for 2-(450) and 2-(450)-W electrodes.

**FIGURE 7** Series of charge-discharge curves for Li/Li⁺/LiₓSnO₂(--) and Li/Li⁺/LiₓWO₃(-----) cells using 2-(450) and 2-(450)-W electrodes (1-50\( \mu \)A; electrode weight = 35 mg).
CONCLUSIONS

In this paper we have distinguished two methods for preparing fine-grained tin oxide powders. The method 2, to our knowledge, seems to be original and leads to SnO₂ powders free from water and/or hydroxyl groups and with small crystallite and particle sizes. Method 2 also has been used to prepare powdery WO₃ samples having the finest crystallites. Related to the fine-grained texture of the samples, we have shown that they are able to sustain long-term electrochemical cyclability. In fact, they behave like other NCIMs that we have recently investigated¹⁷. Indeed, by minimizing the size of the crystallites, the formation of defect bonds is favored, particularly at the crystallite surface, acting as reversible grafting sites for Li⁺. Moreover, the cation-anion bonding would be weakened not only in the grain boundary region, but also within a grain close to its surface. Therefore, the electrochemical insertion of Li⁺ would also occur through an easy bonding rearrangement.

Let us point out that for WO₃ these “non-conventional” insertion mechanisms should occur in addition to the well known intercalation mechanisms of Li within the crystallites and allowed by their tunnel type structure. However, in order to check the validity of the discussions and conclusions made here, further investigations of in situ IR and Raman spectroscopy and of the evolution of the electrode-equilibrium potentials as a function of the Li insertion rate are necessary.

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