



Microwave-assisted solution synthesis of SnO nanocrystallites

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Abstract

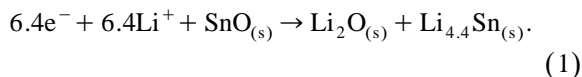
High-purity powders of SnO nanocrystallites with crystallite sizes less than 30 nm and surface areas up to 40 m²/g have been synthesized by a solution process, in which amorphous oxy-hydroxy precipitate of Sn⁺² is crystallized with microwave heating. Microwave heating was found to have selectively accelerated SnO crystallization but not the concurrent Sn⁺²-to-Sn⁺⁴ oxidation, which otherwise prevails in the conventional thermal heating process. Control studies give strong indication of a non-temperature effect of the microwave irradiation in the present process. © 2002 Elsevier Science B.V. All rights reserved.

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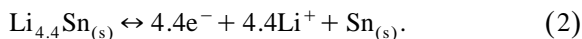
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1. Introduction

SnO has been recognized as a potential anode material for the lithium-ion secondary battery [1–6]. During the first charging step, Li ions react with SnO according to the following reaction:



The reversible anode half-cell reaction during subsequent discharging–charging cycles is expressed as:



The irreversible product Li₂O formed in reaction (1) helps to stabilize the anode structure by establishing a stable matrix [3]. The advantage, however, would

be counteracted by unnecessary excessive Li ion loss when SnO₂, rather than SnO, is used. As a result, one of the objects in synthesizing SnO powder for this application is to minimize oxidation of Sn⁺², which otherwise leads to the formation of SnO₂. Furthermore, the practical charge capacity is known to depend heavily on the crystallite microstructural properties [3–6]. A smaller crystallite size, and hence a greater surface area, for example, has been shown facilitate the solid-state redox reactions, giving a higher practical reversible capacity [6].

The low-temperature characteristic of the solution synthesis technique is particularly attractive for producing metal sub-oxides materials, which are mostly metastable at ambient oxygen pressure. We have previously developed a process in which SnO sub-micron crystallites with a size of ~0.2 μm were synthesized via hydrothermal crystallization of amorphous oxy-hydroxy precipitate obtained in an aqueous SnCl₂ solution (route 1 in Fig. 1) [7]. It was then

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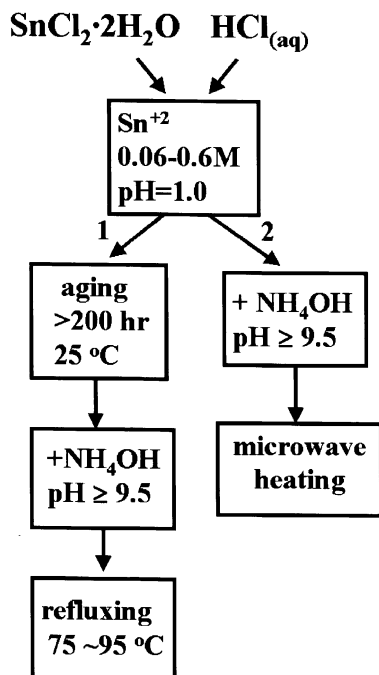


Fig. 1. Experimental procedures for two adopted crystallization processes that employ the conventional thermal heating (route 1) and microwave heating (route 2) methods, respectively.

found that during crystallization between 75 and 95 °C, oxidation of Sn^{+2} to Sn^{+4} took place simultaneously, leading to the formation of SnO_2 impurity. The oxidation rate was, nevertheless, effectively suppressed by adopting a prolonged (> 200 h) solution aging prior to the final crystallization step. The stability of Sn^{+2} against oxidation appeared to increase as the aquo-hydroxo complexes of Sn^{+2} condense to form longer chains of oxy-hydroxy colloidal polymers during aging [7]. The required long aging time, however, may not be practical.

Instead of reducing the oxidation rate, the other means to increase SnO selectivity is apparently to increase the SnO crystallization rate. Successful examples of applying microwave heating in accelerating solution crystallization of zeolites [8–12] have prompted us to employ the same heating technique in the present process. As demonstrated in this work, microwave heating has indeed resulted in a much greater SnO crystallization rate, but not the oxidation rate, than in the conventional heating process even at the same average temperature. As a result, SnO

crystallizes prior to oxidation, and the prolonged aging step is no longer necessary for reducing SnO_2 impurity. Furthermore, the fast crystallization rate allows for formation of nanocrystallites with large surface areas. Control studies give strong indications of a non-temperature effect by the microwave irradiation.

2. Experimental

The entire solution process (route 2 in Fig. 1) consists of the following procedures. A reaction solution containing 0.06 M $[\text{Sn}^{2+}]$ with $\text{pH} \sim 1.0$ was prepared by dissolving $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}_{(s)}$ in an aqueous HCl solution. Ammonia was immediately introduced into the solution to produce a white precipitate until the solution pH reached 9.5. The precipitate-containing solution in 200-ml capacity was heated in a household type microwave oven that has a wave frequency of 2.45 GHz and delivers a power level of 640 W. The product powder was collected either by completely drying the solution in microwave oven or by filtration.

Powder composition was characterized by X-ray diffraction (XRD; MAC M03XHF). Transmission electron microscopy (TEM) analysis was carried out on a Joel 2000 FX electron microscope, which operates at 200 kV and is equipped with Energy Dispersive Analysis of X-ray (EDX) analyzer. The samples were prepared by crushing and small particles were dispersed on a holey carbon film (Cu grid). Surface area was determined by nitrogen adsorption measurement (Micrometrics ASAP-2000).

3. Results and discussion

The macroscopic change of the solution during microwave heating was followed by interruptions at a 1-min heating interval. The observation time was limited to a few seconds. It was found that the solution reached its boiling temperature within 1–2 min and a small portion of the precipitate turned orange after totally 7 min of heating. The precipitate became completely brown after 10 min of heating, and the supernatant solution was clear. At this moment, the solution had only one-half of the initial

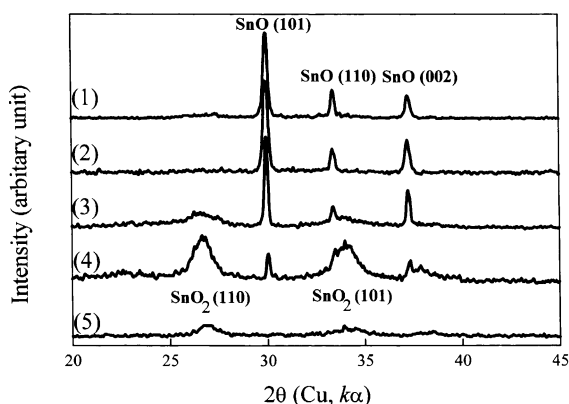


Fig. 2. XRD patterns for product powders via different solution crystallization processes. (1) and (2) are for powders subjected to microwave heating (route 2) for 10 and 15 min, respectively. (3) and (4) show typical powder compositions via thermal heating at 75–90 °C for 1 h (route 1) with and without aging of 240 h, respectively. (5) is for powder obtained in a control study where the solution is boiled (~ 95 °C) by thermal heating for 10 min.

volume left due to evaporation. With continuous heating, the precipitate turned darker, and finally became black as the solution was dried out after 15 min. (Precaution should be taken toward the complete dryness, because, as described later, the temperature of dry SnO powder rises rapidly under microwave irradiation.) When the brown precipitate obtained after 10 min of heating was filtered and dried at room temperature, it turned dark brown.

Ex-situ measurement showed that the solution has an initial boiling point of 90 °C. As the solvent evaporated, the boiling point gradually increased to 95 °C, and then became rather constant up to two-thirds of the evaporated solution.

Fig. 2 shows the XRD patterns of the 10- and 15-min microwaved powders. Both powders were found to contain predominantly tetragonal SnO [13]. For comparison, Fig. 2 also shows the XRD patterns of the powders that are typically obtained by thermal heating, i.e., via route 1 in Fig. 1. The effect of microwave heating is drastic. The SnO content can be quantitatively determined by using the Si internal standard in XRD measurements, as described in our previous study [7]. A nearly 95% purity (curve 2, Fig. 2) was achieved in the present process for as short as 15 min of microwave irradiation without the need of solution aging. This is in great contrast with

an SnO content of 75% via route 1 under the conditions of 720 h of aging plus thermal heating at 75–90 °C for 1 h [7].

Nitrogen adsorption measurements showed specific surface areas of 44 and 36 m²/g for the 10- and 15-min microwaved powders, respectively. They correspond to surface-weighted crystallite sizes of 25 and 30 nm, respectively, for non-agglomerated crystallites. The true crystallite sizes are expected to be smaller because these crystallites are in fact agglomerated. High-resolution TEM (Fig. 3) revealed severely defected structures, such as twins, deviations of planes, and voids, within the crystallites, which are presumably the consequences of fast crystallization rate.

In a control study, a reaction solution of 20 ml was subjected to thermal heating on a hot-stage set at 250 °C. The solution was heated to its boiling point in ~ 1.5 min and showed loss of one-half of the solution in 10 min, similar to the case of the microwave heating process for a 200-ml sample size. After 10 min of heating, the precipitate remained white and, as revealed by XRD (curve 5, Fig. 2), was mostly amorphous except for a minute amount of SnO₂.

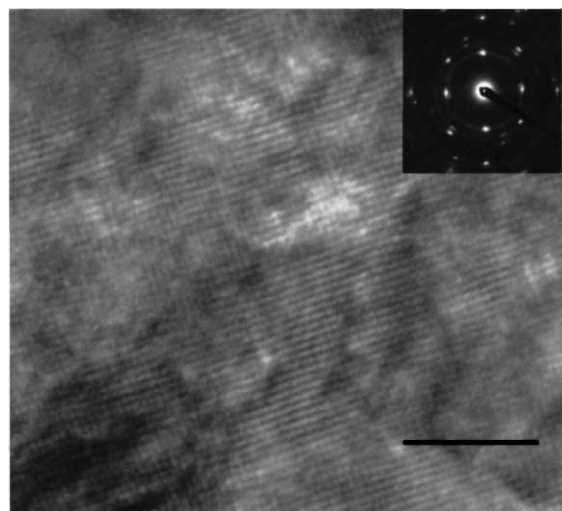


Fig. 3. TEM micrograph showing severely defected structures, such as twins and voids, within SnO nanocrystallites synthesized by microwave-assisted solution synthesis (the scale bar marks a length of 5 nm). The inset shows the corresponding diffraction pattern.

Study using microwave heating on dry powders indicates that SnO absorbs microwave much stronger than SnO₂. By inserting a thermocouple into the powders immediately after 30 s of microwave irradiation, 10 g of SnO powder in Al₂O₃ crucible showed a temperature of ~ 170 °C, while SnO₂ showed only 50 °C. In another control study, it was found that introducing already formed SnO crystallites into the reactant solution did not significantly affect the crystallization process, other than shortening the time for reaching the boiling temperature from 2 to 1 min. The macroscopic evolution process described earlier for the solution during the course of microwave heating remained about the same, irrespective of being with or without pre-introduction of SnO crystallites.

Slangen et al. [11], in their study on synthesis of zeolite NaA, have suggested that the microwave-accelerated zeolite crystallization is most likely caused by inhomogeneous heating and superheating, which overall cause higher temperature than in thermal heating. However, these two causes fail to account for what were observed in the present process. As described earlier, in the control study of thermal heating with a smaller (20 ml) sample size, the heating temperature (250 °C) was selected to give approximately the same power input into unit volume of the solution as in microwave heating. Furthermore, the solutions were constantly heated at their boiling temperatures with self-sustained vigorous agitation. The temperature distributions in both cases are expected to be rather uniform, and there is no concern of possible difference in their temperatures. Yet, the microwave heating process produced SnO crystallite, while the thermally heated precipitate remained amorphous.

Local hot spots could occur at the surfaces of SnO crystallites because of its strong absorption of microwave. However, the experiments with pre-introduction of SnO crystallites into the starting solution did not show significant effect on the crystallization, nor have we observed sign of autocatalytic effect, which was suggested by Chatakondur et al. [9] in their synthesis of VO(PO₄)·2H₂O. In fact, both the oxidation and crystallization are thermally activated reactions, and therefore, a “pure” thermal effect would have accelerated both reactions. The present results, however, have shown rate enhancement only

in crystallization but not in oxidation. That is, the microwave-heated powders, which showed 95% SnO phase purity, have a less *absolute* amount of SnO₂ than in any of the thermally heated powders.

In view of the results described above, we tend to believe that the microwave-accelerated SnO crystallization in the present study is a non-temperature effect, and that the enhancement is more likely due to the coupling of microwave energy with certain reactive sites associated with the reactants and/or intermediate structures. Being the nature of this kind, the coupling would be reaction-selective. Identification of this/these absorption site(s) is, however, difficult.

Crystallization of oxide from an amorphous oxy-hydroxy precursor consists of consecutive steps of dehydroxylation and oxolation reactions, nucleation, and nuclei growth. We noted that in a simpler system involving drying of silica gel, Rodrigues and Wilkes [14] observed accelerated gelation rate. The rate enhancement was attributed to the coupling between the microwave and the hydroxyls, which are the principle reactive sites and are strongly dipolar. The possibility of similar enhancement mechanism in the present crystallization process cannot be ruled out [15]. Indeed, enhanced dehydroxylation and oxolation would produce a higher degree of supersaturation for nucleation, which in turn results in an increase in nuclei, and hence, a smaller average crystallite size. This is also consistent with our findings.

In summary, adopting microwave heating in the solution crystallization of SnO was found not only to selectively accelerate crystallization rate against oxidation of Sn⁺² but also to facilitate the formation of nano-scaled crystallites. Both effects have been attributed to the coupling of microwave energy with the reactions involved in the crystallization process.

Acknowledgements

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