



A possible scalable method for the synthesis of Sn-containing carbon nanostructures



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ABSTRACT

This paper presents a scalable and efficient method for the preparation of Sn-containing carbon nanostructures, based on the cathodic erosion of graphite electrodes in molten LiCl–SnCl₂ salt mixture. The product obtained was characterized by means of X-ray diffraction and electron microscopy. It was found that conducting the process in nominally pure argon containing a low concentration of oxygen leads to the formation of Sn-encapsulated carbon nanostructures as well as SnO₂-decorated carbon nanotubes (CNTs). On the other hand, CNTs decorated with SnO₂ nanocrystals could be synthesized in high yield in the presence of higher concentrations of oxygen. The oxidation of SnCl₂ to SnO₂ nanocrystals was found to be both thermodynamically and kinetically possible in atmospheres containing very small quantities of oxygen and to avoid the formation of tin oxides, it was necessary to perform the process under reducing conditions. The tin nanostructures encapsulated in carbon shells were found to be stable upon washing with water and drying. The results obtained provide essential knowledge to control the molten salt process.

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1. Introduction

Polycrystalline synthetic graphite (so-called graphite) can be corroded in molten alkali metal halides to form carbon nanostructures with a high degree of graphitization [1–4]. The corrosion/erosion of graphite in molten salts can be enhanced when a cathodic potential is applied to the graphite which makes the electrolytic conversion of graphite an attractive and economically viable emerging technology for the preparation of carbon nanomaterials. Using this method, the erosion product is in the form of CNTs and carbon nanoparticles which can be retrieved from the solidified salt by washing and filtering. An attractive feature of this technology is that CNTs and spherical nanoparticles can be produced by appropriately controlling the process parameters including the microstructural properties of graphite feed materials and electrolysis condition [5–11]. The molten salt approach was recently modified to develop a convenient and scalable process for reliable preparation of carbon nanostructures, in which the production rate could reach to 10 g h⁻¹ by cathodic polarization of a graphite rod of 15 mm in diameter, immersed in molten LiCl. The

method presented could be easily scaled up to provide significant quantities of carbon nanostructures [11].

Another attractive feature of the molten salt process is its capability of producing filled carbon nanomaterials, in which a metallic second phase is encapsulated by graphitic carbon. For example, Sn-filled carbon nanostructures have been produced by heating a mixture of LiCl and SnCl₂ to a temperature greater than 700 °C, followed by electrolysis of the molten salt using graphite electrodes. The cathodic reactions that occurred during the electrolysis can be described as follows: (a) Sn²⁺ ions are first reduced to Sn on the surface of the graphite cathode, (b) Li⁺ is reduced at the graphite cathode to form carbon intercalation compound or carbon-Li intermediate phases, (c) sheets of graphite are extruded which encapsulate the tin to form tin-encapsulated carbon nanostructures. When cooled down, the solidified salt can be washed off by distilled water and the carbonaceous product retrieved [12–15]. The material produced by this method was examined as anode material for lithium-ion batteries, and showed a promising electrochemical performance [16].

It should be noted that tin-filled carbon nanostructures with enhanced anode performances in lithium ion batteries have also been fabricated via various other methods including chemical vapor deposition [17–20], capillary-loading [21] sol-gel [22], ion exchange [23], aerosol spray pyrolysis [24,25] and electrospinning [26].

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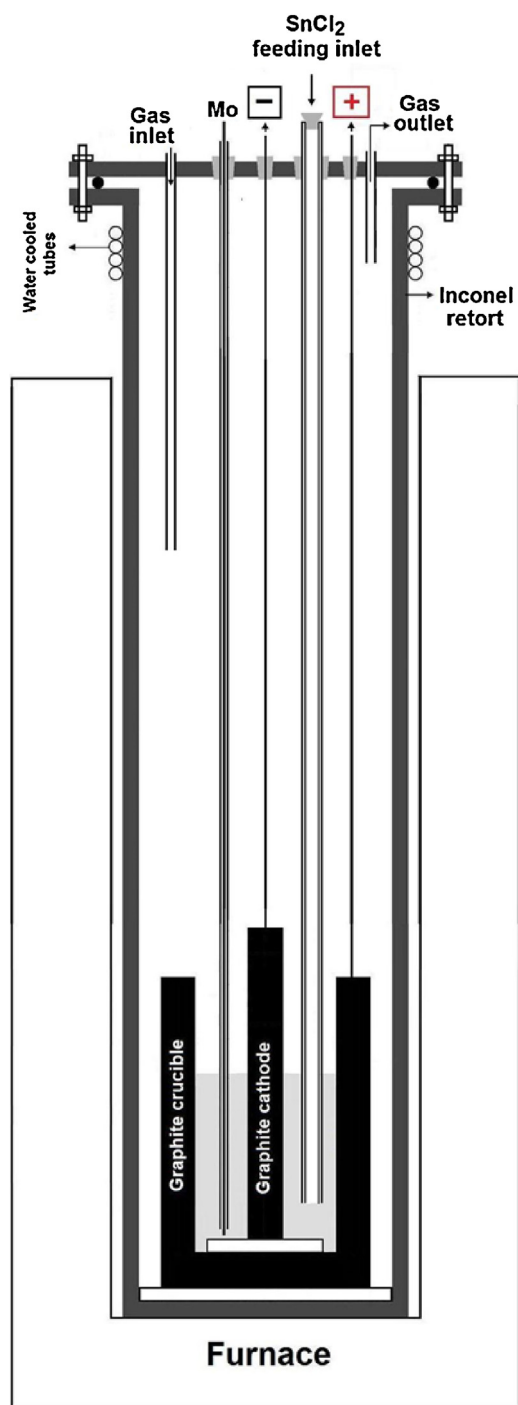


Fig. 1. Schematic representation of the experimental set-up used for the large-scale preparation of Sn-containing carbon nanomaterials in molten LiCl. It includes a graphite rod immersed in molten LiCl, which is used as the cathode during the electrolysis process, and a graphite crucible which is used as the anode. SnCl₂ pellets could be introduced into the molten LiCl through the alumina tube shown at different intervals during the electrolysis.

The molten salt technology, however, offers a much faster and perhaps more economic route for the preparation of Sn-filled carbon nanomaterials, in comparison with the other available methods [27]. Despite the interesting features of the molten salt process, some main issues need attention before the process can be successfully scaled-up.

First, it has been found that the above-described process may lead to the formation of Sn-filled carbon nanostructures if, and



Fig. 2. Photographs of a graphite rod (a) before and (b) after being used as the cathode during the electrolysis of LiCl-30 wt% SnCl₂. The molten salt electrolysis was conducted at 770 °C for 2 h at the constant current of 33 A, corresponding to an initial cathode current density of about 1 A cm⁻². Details of the set-up used can be found in [11].

only if, the SnCl₂ content of the initial salt mixture is less than about 2 wt%. At higher concentrations of SnCl₂, the formation of carbon product is completely suppressed which was attributed to the excessive deposition of Sn on the electrodes restricting the access of Li⁺ ions from the melt to the graphite, which suppresses the erosion of graphite cathodes and the formation of nanostructured carbon product. Furthermore, it was found that only 1 g carbon product, containing 16 wt% Sn, could be produced during 25 min electrolysis using graphite electrodes of 6.5 mm diameter in a salt mixture containing 200 g LiCl and 2 g SnCl₂ [15]. It is obvious that the process needs to be modified if it is to be considered as a method for the production of tin-filled carbon nanostructures. Two issues are addressed in this paper: the continuous addition of tin chloride to the melt and the avoidance of the creation of tin oxide during the process as these oxide phases have a detrimental effect on the performance of lithium ion batteries.

It should be noted that carbonaceous product fabricated by the electrolysis of molten LiCl–SnCl₂ in argon atmosphere contained a considerable amount of tin oxides as well as a minor amount of Li₂SnO₃ in addition to carbon and tin [15]. In the literature, the formation of SnO₂ has been solely attributed to the hypothesis that Sn inside the cavity of carbon nanostructures partly reacts with oxygen during washing, drying or storage to form SnO₂ [15]. This hypothesis, however, needs to be explored as it does not take into account the reactions which may take place during heating the mixture of LiCl and SnCl₂ from room temperature to high temperatures in laboratory grade argon. Furthermore, carbon layers usually provide an effective barrier against oxidation of the encapsulated metals. In fact, no oxidation of Sn was observed even after six months of exposure to air of Sn-filled CNTs [28].

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