



# *In situ* Raman spectroscopic analysis of the lithiation and sodiation of antimony microparticles



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## ABSTRACT

A one-pot sol-gel autocombustion synthesis for carbon coated antimony microparticles has been developed. The initial capacities of this material were 647 mAhg<sup>-1</sup>Sb vs. Li and 527 mAhg<sup>-1</sup>Sb vs. Na, with a rate capability (8C: 398 and 356 mAhg<sup>-1</sup>Sb vs. Li and Na respectively) and cyclability (cycle 120 capacity retention: 86% vs. Li, 91% vs. Na). The sol-gel synthesised Sb was found to be superior to commercial Sb of similar particle size (ca. 5–50 μm), which is attributed to carbon coating. *In situ* Raman analysis revealed differences between the sol-gel synthesised and commercial antimony materials, regarding their reversibility, during the 1st cycle, and additionally demonstrated that upon charge both materials do not return to a crystalline material, but instead to an amorphous phase represented by a broad feature centred at ca. 140 cm<sup>-1</sup>.

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## 1. Introduction

Lithium- and sodium-ion batteries are seeing increasing interest in their potential use for a wide range of areas, from transportation and portable electronic devices to both stationary and grid storage. However, with this comes an increasing demand to improve a range of properties to make them more suitable for those applications [1–6].

Intermetallic negative electrodes (anodes) have received some attention due to their potential use as high gravimetric capacity materials. However, their high gravimetric capacity is often accompanied by a large volume change during intercalation/deintercalation, which can lead to pulverisation of the particles. This in turn can result in loss of electrical contact within the anode and damage to the surface of the intermetallic particles, leading to continuous solid-electrolyte interphase (SEI) formation/breaking and irreversible capacity loss [7–10]. Nevertheless, due to their attractive properties there is still considerable appeal in developing and improving these types of materials, particularly for sodium-ion batteries [11,12].

The intermetallic anode material antimony (Sb) has a number of properties that make it of potential interest. Capable of alloying with both sodium and lithium with a theoretical gravimetric

capacity of 660 mAhg<sup>-1</sup>Sb (based on the capacity of M<sub>3</sub>Sb), even in its bulk form it is a reasonably attractive anode, with good reversibility at low to moderate current density [12–15]. Moreover, the use of antimony anodes offers a way to investigate and compare a wide range of lithium and sodium electrochemical systems. However, one key challenge is improving the electrochemical properties of antimony by increasing its rate capability and mitigating the stress and strain caused by volumetric changes during cycling.

One approach is to prepare new and unique micro- and nano-structures [12]. Consequently there has been interest in using antimony both as a pure anode and as a composite with other materials. Research has been carried out into the lithiation of bulk microcrystalline powders and vacuum evaporated thin-film materials [13,15], antimony/carbon nanotube composites [16] and high-energy milled or chemically synthesised antimony nanocomposites [17–21]. Stable and reversible sodiation has been demonstrated for bulk antimony and in thin films [13,15], with work also having been carried out into sodiation of antimony/carbon fibres [22] and mechanically milled antimony/carbon nanocomposites [23]. Recently, nano-sized antimony particles were synthesised and, after additional processing, were able to demonstrate excellent rate capability and cyclability during both sodiation and lithiation [14]. However, these also exhibited poorer coulombic efficiencies than bulk antimony in the initial cycle, which has attributed to the larger surface area of the nano-materials leading to increased decomposition of electrolyte during the formation of the SEI layer [11,14].

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Given that the surface stability of the antimony particles can dramatically affect the electrochemical behaviour of the resulting electrode, decorating the surface with carbon could well mitigate the effects of volume expansion and improve the cyclability of the material. One facile way to achieve this is to use a sol-gel synthetic route, as this method can often leave small traces of carbon residue on metal particles. Furthermore, since the chemistry of sol-gel syntheses has enabled the production of a wide range of materials with diverse nano- and micro-structures, some of which were used in lithium- and sodium-ion systems, a practical sol-gel route to produce antimony particles would be advantageous [24–31]. Given this, and thus the likely subsequent importance of electrochemistry occurring at surface, the use of *in situ* Raman spectroscopy presents an opportunity to investigate and understand these processes in relation to both the carbon decorated antimony surface and the near-surface of the antimony particle itself.

However, until now few sol-gel routes have been developed for pure antimony metal particles. In part this is due to the difficulty of forming a stable sol with an antimony salt precursor, as well as the problem of controlling the oxidation, and thus combustion, of the carbon gel without oxidising the antimony metal particles. Nevertheless, by using a citric acid sol-gel route it is possible to mitigate some of these problems – the citric acid not only forms the gel, but may also be capable of chelating metal ions to form a more stable sol as well as facilitating their reduction [31–33]. Moreover, citric acid sol-gel syntheses have previously been used to make nanoparticles of other metals [34] and metal oxides, implying that should a suitable route be developed it may then be possible to control and optimise the size of the resulting particles by controlling and optimising the synthetic conditions [35,36].

In this work we report a one-pot sol-gel synthesis of pure antimony metal particles. Furthermore, we use electrochemical and *in situ* Raman spectroscopy to analyse the properties of the synthesised material, and to compare these to those of commercial antimony.

## 2. Experimental

### 2.1. Overview of sol-gel antimony synthesis

The citric acid sol-gel synthesis (Scheme 1) can be thought of as taking place over two general steps, i. Gelation and ii. Combustion.

During i. Gelation, the antimony precursor ( $\text{SbCl}_3$ ) and the gelation agent (citric acid) are dissolved in ethanol, allowing the citric acid to complex with antimony ions and preventing reaction with water during the addition of small quantities of aqueous oxidising agent ( $\text{NH}_4\text{NO}_3$ ). Given that citric acid has previously been shown to be able to act as a weak reducing agent [32], some degree of antimony reduction can take place during this stage. After heating overnight, the gel has expanded to form a white, porous, solidified foam which is then ready for combustion.

During ii. Combustion, the material is heated under an inert gas (argon). This initiates the thermal decomposition of the oxidising agent resulting in the release of, amongst others, oxygen gas, which then reacts with the hydrocarbon gel. It has previously been shown that thermal decomposition of nitrates in citric acid gels can result in the evolution of many gasses [34]. These include  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{NO}$ ,  $\text{CO}_2$ ,  $\text{NH}_3$  and  $\text{NO}_2$ .

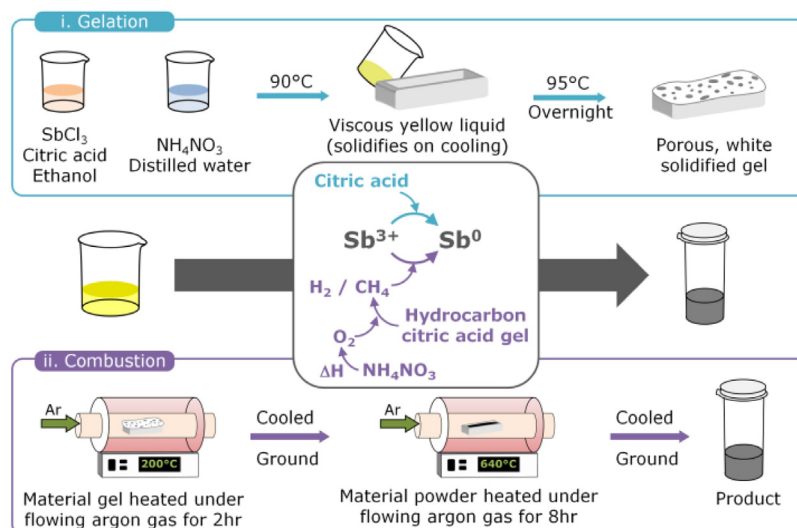
Given that  $\text{H}_2$  and  $\text{CH}_4$  are reducing agents it is expected that some degree of antimony reduction occurs during this step. After following a suitable heating regime (as described in 2.2.), the final product was obtained. Thus, by controlling the synthetic conditions (e.g. ratio of citric acid to antimony chloride, amount of  $\text{NH}_4\text{NO}_3$  oxidising agent, argon gas flow rate, etc.) it was possible to create the desired antimony product.

### 2.2. Synthesis of sol-gel antimony microparticles

Antimony trichloride (0.007 moles, 1 g) and citric acid (0.0083 moles, 1.6 g) were dissolved in ethanol (12 ml). Ammonium nitrate (0.025 moles, 2 g) was dissolved in water (2 ml). The two solutions were mixed and heated at  $90^\circ\text{C}$  for approximately 0.5 hr, forming a viscous yellow gel which was then poured into a ceramic boat and heated at  $95^\circ\text{C}$  for 12 hr. The resulting white porous material was then heated at  $180^\circ\text{C hr}^{-1}$  under a constant argon flow (approximately  $0.5 \text{ ml s}^{-1}$ ) to  $200^\circ\text{C}$  for 2 hr, before being cooled and ground. It was then heated again under argon at  $180^\circ\text{C hr}^{-1}$  to  $640^\circ\text{C}$  for 8 hr before being cooled and ground to obtain the final product.

### 2.3. Coin cell fabrication and testing

Sodium and lithium electrolytes were prepared from 1M sodium and lithium perchlorate (respectively) in dried, distilled



Scheme 1. Schematic diagram of sol-gel synthesis.

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