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# Electrodeposition of Si and Sn-based Amorphous Films for High Energy Novel Electrode Materials

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## ABSTRACT

In this work we report the electrodeposition parameters of Sn-graphene films in aqueous solutions and silicon films in propylene carbonate. The galvanostatic electrodeposition of tin-graphene films from a sulfate-based acidic solution on copper substrates has been studied evaluating the effect of stirring on the morphology and the electrochemical performance. SEM analysis films deposited galvanostatically at  $-10 \text{ mA}\cdot\text{cm}^{-2}$  for 20 minutes at  $25 \text{ }^\circ\text{C}$  and reveals that electrodeposition is suitable to generate continuous and homogeneous films with thickness values in the micrometer range. XRD analysis shows many intermetallic Cu-Sn crystalline phases are formed, as opposed to a pure amorphous tin layer. So far, electrochemical characterization has only been performed over a short number of charge-discharge cycles. The galvanostatic electrodeposition of silicon from propylene carbonate in galvanostatic mode has been carried out, but is currently extremely challenging to obtain continuous and homogeneous films. The XRD characterization has suggested the possible presence of amorphous phases in the films deposited at  $-1.0 \text{ mA}\cdot\text{cm}^{-2}$  for 30 minutes at  $25 \text{ }^\circ\text{C}$ .

## INTRODUCTION

In order to replace capacity-limited graphite anodes ( $372 \text{ mAh/g}$ ), this study aims to develop novel, high-density-amorphous anode materials for versatile applications to Li-ion batteries. In particular, we focus on the electrodeposition of Si- and Sn-based anodes to state if this technique is suitable to obtain amorphous materials to achieve long cycle life and durability. Electrodeposited electrodes do not need conductive agents or binders being therefore inherently more energy dense; electrodeposition is low-cost and easy to scale-up technique. Moreover, solid electrolyte materials such as ionomeric and/or ionically conducting ceramic films can be applied as artificial SEI-type films to suppress electrolyte decomposition at low voltages and prevent the growth of the SEI [1] increasing the electrode performance. This work shows the first results on the electrodeposition of tin and silicon in aqueous and organic media respectively.

Sn electrodes are susceptible to volume change ( $\approx 300 \text{ vol. } \%$ ), but this can be limited by using carbonaceous co-materials such as graphene to decrease the crystallite sizes [1] and increase in-plane electrical conductivity, surface area and excellent mechanical resistance [2]. In

this study, we investigated the effect on morphology, crystalline structure and electrochemical behavior of the electrodeposited films as graphene addition is made into a Sn-sulfate based aqueous solution.

Furthermore, the electrodeposition of silicon has been investigated in propylene carbonate as aqueous solutions are unsuitable due to high moisture-sensitivity of the silicon precursor and very negative deposition potential (-1.7 V/NHE) [3].

## **EXPERIMENTAL DETAILS**

The electrodeposition of Sn-graphene films is carried out in a Hull cell using a two electrodes setup: copper foil as WE and a Sn sheet as CE. The solution is commercial Bright Tin CULMO Technology (Schloetter) composed of tin sulphate ( $\text{SnSO}_4$ ) as the tin precursor, sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and CULMO Starter as an additive and few layer Graphene (XG Science) in a concentration of 5 g/L.

Electrodeposition of the films is carried out in galvanostatic mode for current densities of  $5 \text{ mA}\cdot\text{cm}^{-2}$  -  $20 \text{ mA}\cdot\text{cm}^{-2}$  for different deposition times between 10 and 30 minutes in static or stirred conditions at 300 rpm with the cell at a temperature of 25 °C.

Electrodeposition of silicon is performed in an Argon filled glove-box at 25 °C from propylene carbonate (PC-Sigma Aldrich) using 0.1 M tetrabutylammonium chloride (TBAC-Sigma Aldrich) as supporting electrolyte and silicon tetrachloride ( $\text{SiCl}_4$ -Sigma Aldrich).

The morphology and crystallinity of the films is investigated using a FEG-SEM (Zeiss Sigma) and Panalytical Empyrean (Co target) X-ray diffractometer. Cross sections of the films are obtained using a FIB (Scios Dual Beam, FEI).

The electrochemical testing of the Sn-Graphene films is performed in 2032 coin cell (HOHSEN, Japan) hardware using lithium foil as counter electrode. The separator is PP/PE/PP microporous trilayer membrane (Celgard 2325) and the electrolyte is RD265 (PuriEL, SoulBrain, US). The cell was cycled galvanostatically using a Maccor battery test system (Series 4000, MACCOR, US) at C/20 for the formation cycle, then C/5 for the rest cycles.

## **DISCUSSION**

### **Electrodeposition of Tin-Graphene films**

Prior to electrodeposition of the films, and in order to understand the chemistry of the situation, cyclic voltammetry has been performed in tin sulphate based CULMO solutions without graphene (black line) and containing 5 g/L of graphene (grey line) in static conditions (Figure 1). Stirring of the solutions mitigates diffusion-limitations and increases the amount of electroactive species reaching the electrode surface. Figure 1a) (black line), shows the scan

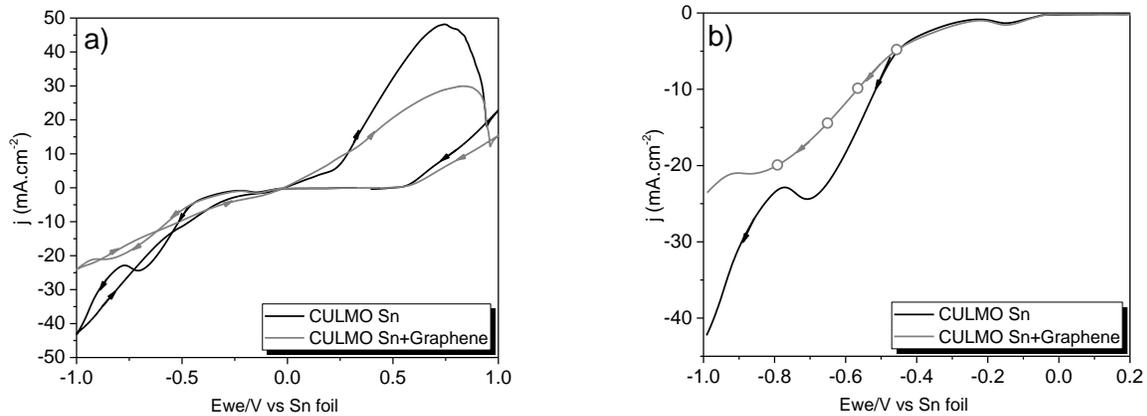
starting at the Open Circuit Potential (OCP) of the solution. The first reduction wave is observed close to  $-0.5\text{V}/\text{Sn}$  sheet (reaction (1)).



Subsequently, a second reduction wave is observed at  $-0.8\text{ V}/\text{Sn}$  sheet related to the reduction of protons and resulting in hydrogen evolution at the electrode according to the following reaction:

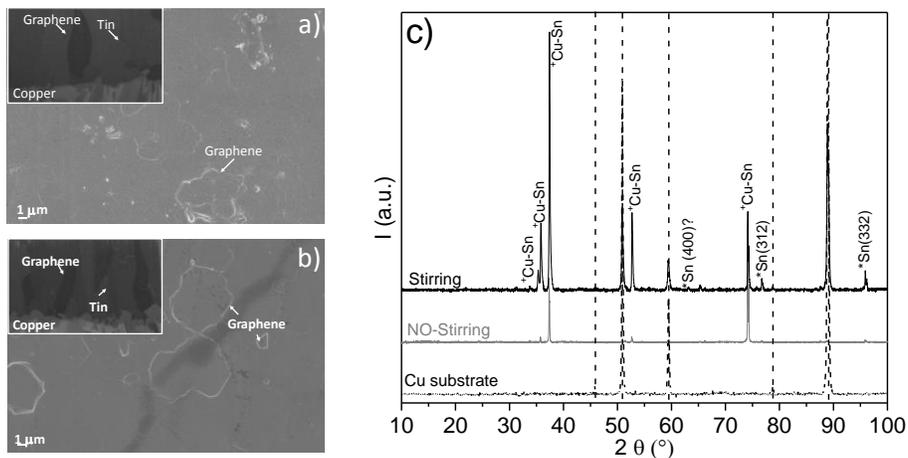


The anodic scan shows an oxidation peak corresponding to the re-oxidation of the deposited tin confirming the attribution of reactions (1) and (2). When graphene is added (grey line), the first reduction wave is shifted of  $0.1\text{ V}$  towards more negative potentials and the slope is lower compared to Sn-CULMO solution. Based on these results, Figure 1 b) shows the current densities that we have selected for electrodeposition (grey circles).



**Figure 1.** Cyclic voltammetry recorded at  $25\text{ }^{\circ}\text{C}$ ,  $\text{pH}=0$  on copper foil substrates in a) Sn-CULMO solution (black line) with no graphene, Sn CULMO solution with Graphene  $5\text{ g/L}$  (grey line) in static conditions. Sweep rate is  $20\text{ mV/s}$ . b) Direct scans of a).

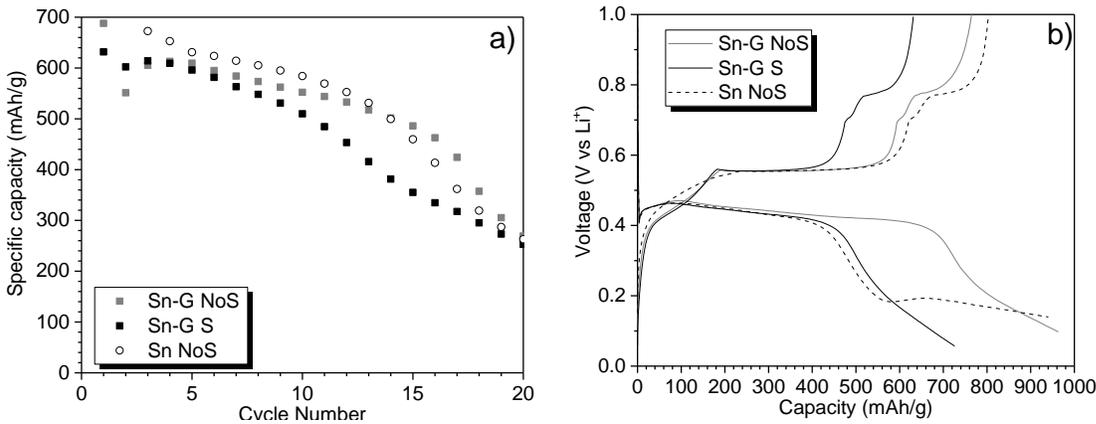
In this study, we will present exclusively the characterization of the films obtained at  $-10\text{ mA cm}^{-2}$  for 20 minutes. The morphology and X-Ray diffractograms are presented in Figure 2.



**Figure 2.** SEM micrographs of the films galvanostatically deposited on copper substrates at  $-10 \text{ mA}\cdot\text{cm}^{-2}$  for 20 minutes a) stirring the solution at 300 rpm, b) without stirring, c) X-ray grazing incidence ( $2\theta=6^\circ$ ) diffractograms of the films shown in a) and b).

As shown in Figure 2 a) and b) the films are continuous showing incorporation of graphene nanoparticles. In Figure 2 c), the reflections corresponding to the copper substrate are still visible (black line, PDF N.4-0836) in both films. The reflections characteristic of Sn films display very low intensity and the signals have a broad shape which could possibly indicate the presence of amorphous phases (PDF N. 40673). This is attributed to the high solubility of copper in tin at room temperature. Based on the works of Liao [4], Juskenas [5] and Tu [6] we have tried to assign the Cu-Sn alloy reflections. However, at this stage it is still very hard to attribute a preferential orientation to the deposited films, especially due to the complexity of Cu-Sn alloy diffractograms.

The electrochemical testing of the Sn-Graphene films (Figure 2) in comparison with the Sn films is presented in Figure 3.



**Figure 3.** Comparison of a) Specific capacity vs Cycle Number for the first 20 cycles and b) Voltage vs Capacity of 1<sup>st</sup> cycle of the films deposited from Sn CULMO solution with 5 g/L graphene, at 25 °C,  $j= -10 \text{ mA}\cdot\text{cm}^{-2}$  for 10 minutes without stirring (grey dots/line) and stirring at 300 rpm (black dots/line).

Both films display a strong capacity fade after 20 cycles (Figure 3 a) with the films obtained in static condition showing a slightly higher capacity retention. In Figure 3 b), the 1<sup>st</sup> cycle discharge voltage profile shows that lithiation to a capacity of 700 mAh/g of the Sn-graphene films in both conditions occurs.

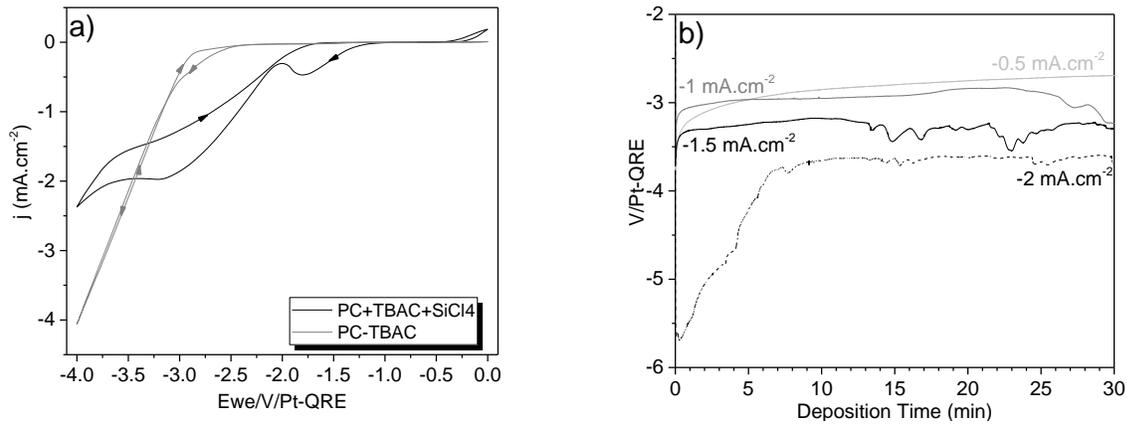
### Electrodeposition of silicon films

In order to establish the optimal current density to perform electrodeposition, and based on the findings of Nicholson et al. [2], voltamperometric studies have been performed in PC with TBAC as supporting electrolyte (Figure 4 a) grey line) and with the addition of  $\text{SiCl}_4$  (Figure 4 a) black line). The potential vs. time profiles during the electrodeposition of the films at different

current densities for deposition times of 30 minutes are shown in Figure 4 b). In Figure 4 a) (grey line), the reduction wave observed in the PC-TBAC solution starting at -3.0 V/Pt-QRE is associated with the cathodic decomposition of the solvent. When silicon tetrachloride is added (black line), a reduction wave starting at -1.0 V/Pt-QRE possibly associated to the reduction of residual protons in the solvent is observed. A second reduction wave associated to reaction (4) in agreement with the literature [3] starts close to -2.0 V/Pt-QRE:



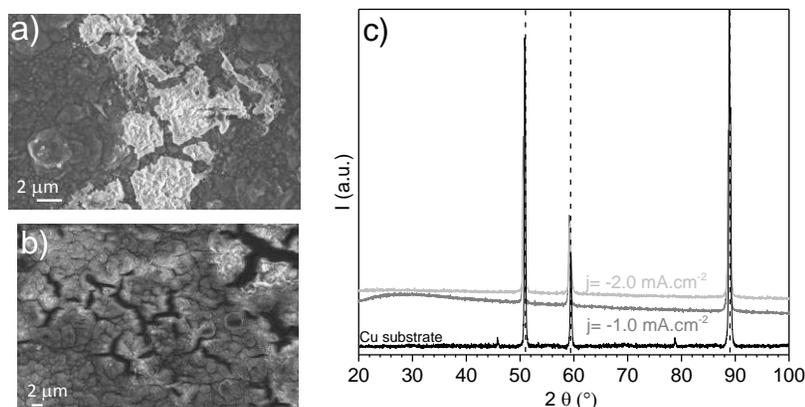
A diffusion plateau is observed between -3.0 V/Pt-QRE and -3.5 V/Pt-QRE followed by a current density increase due to the cathodic decomposition of the solvent.



**Figure 4.** a) Cyclic voltammety obtained in PC-TBAC (grey line) and PC-TBAC-SiCl<sub>4</sub> (black line) at 25 ° C, sweep rate of 10 mV/s, b) Potential versus time profiles for the galvanostatic deposition of silicon films.

The potential vs time profiles of the galvanostatic deposition of the films shown in Figure 4 b) highlight that for the films deposited at -0.5 mA.cm<sup>-2</sup>, -1.0 mA.cm<sup>-2</sup> and -1.5 mA.cm<sup>-2</sup>, the potential initially increases, before reaching a plateau. For the film deposited at -2.0 mA.cm<sup>-2</sup>, the potential at the beginning is very negative (close to -5.5 V/Pt-QRE) suggesting that parasitic reactions from solvent decomposition may take place. The fluctuations of potential observed during the electrodeposition could be due to the insulating character of the films [7].

Due to the poor adhesion and/or strong charging effects observed on the samples deposited at -0.5 mA.cm<sup>-2</sup> and -1.5 mA.cm<sup>-2</sup>, exclusively the SEM and XRD analysis of the films deposited at -1.0 mA.cm<sup>-2</sup> and -2.0 mA.cm<sup>-2</sup> are presented in Figure 5.



**Figure 5.** SEM micrographs of the films deposited on copper substrates for 30 minutes at a)  $-2 \text{ mA}\cdot\text{cm}^{-2}$ , b)  $-1.0 \text{ mA}\cdot\text{cm}^{-2}$ . c) X-ray grazing incidence ( $2\theta=6^\circ$ ) diffractograms of the films shown in a) and b).

The film deposited at  $-2 \text{ mA}\cdot\text{cm}^{-2}$  (Figure 5 a) displays a continuous morphology with several aggregates possibly due to the interference of the cathodic decomposition of the solvent as observed in Figure 4 b) (dashed black line). The film deposited at  $-1.0 \text{ mA}\cdot\text{cm}^{-2}$  (Figure 5 b) displays a more continuous morphology with some cracks. In addition, strong charging effects are observed on this sample, suggesting insulating properties of the deposited film. X-ray diffractograms (Figure 5 c) show mainly copper substrate reflections (PDF N. 4-0836). However, for the sample deposited at  $-1.0 \text{ mA}\cdot\text{cm}^{-2}$ , a broad signal at  $2\theta=29.3^\circ$  is observed suggesting the presence of amorphous silicon phases [8]. Due to the poor homogeneity and mechanical properties of these films, the electrochemical testing was not carried out.

## CONCLUSION

Electrodeposition of Sn-graphene films from a commercial Sn-plating solution was successfully carried out leading to homogeneous and continuous films composed mainly of Cu-Sn intermetallics. The early stage electrochemical characterization has shown that the presence of graphene in the tin films did not result in significant improvement of the electrochemical performance. To firmly conclude the potential influence of the graphene on the resulting Sn and composite film properties requires additional exploration into the effect of the type of graphene used and how this influences or is a control parameter of the resultant Sn film crystallinity.

The electrodeposition of silicon films from organic propylene carbonate electrolytes has shown initial challenges in obtaining homogeneous and stable amorphous silicon films. Clearly to generate stable anodes for Li-ion batteries the stability issue warrants further investigation regarding post-deposition treatments to mitigate decomposition reactions. One recommended approach focuses on the electrodeposition of silicon from different ionic liquids due to the reported increase in the stability of the deposited films.

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