PREPARATION OF TIN@CARBON FIBER COMPOSITES BY ELECTROLESS DEPOSITION

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Abstract

The synthesis of tin-coated carbon fibers (CFs) by electroless deposition method in aqueous solution was studied. Sodium hypophosphite was used as a reducing reagent. The composites were characterized by X-ray diffraction, energy-dispersive X-ray spectroscopy and scanning electron microscopy techniques. The experiment results showed that the car fiber surfaces can be fully deposited by tin layers and a continuous tin coating on carbon fiber was obtained by electroless deposition. These tin@carbon fiber composites can be used in some possible applications such as electrode materials, fiber-matrix composites, and so on.

Keywords: Electroless coating, deposition, tin, carbon fiber

1. INTRODUCTION

Carbon fibers (CFs) are well-known materials their superior properties such as high strength, high elastic modulus, high thermal and electric conductivity. Having these unique properties make CF a useful material not only for a reinforcement in light alloys but also for various electrical and electronic applications. In metal matrix composites (MMCs), wettability between reinforcement and metal matrix is a prominent issue and therefore, fabricating CFs reinforced MMCs with excellent interface bonding, and thus their further application is greatly limited. For this reason, many researchers studied electroless metal deposition on non-metallic surfaces and they suggested that the wettability between metallic matrix and CFs could be improved by using electroless deposition method. Several coating techniques including sputtering, electrodeposition, and electroless plating have been developed so far. Electroless plating method was recognized as a promising technique because of being low cost, simple handle, and environmental friendly. This type of coating, invented in 1946 by Brenner and Riddell, has been used in many fields owing to their unique properties. Composite powders prepared by this method show good dispersion, and the metal content in such composites can also be controlled effectively [1].

Tin (Sn) is widely studied as an alternative electrode material for commercial graphite anodes due to their high theoretical capacity (994 $mA{\cdot}h{\cdot}g^{-1}$). However, volume expansion during lithiation causes Sn pulverization and peeling from the surface and hence, rapid capacity fading. To overcome this problem, one possible approach is incorporating tin with a carbonaceous buffer matrix that presents good electrical conductivity and excellent volume stability. Carbonaceous materials can impede particle aggregation and effectively buffer the strain from the particle volume changes during cycles, which lead to the enhancement of the battery cycle properties. Carbonaceous materials, such as amorphous carbon, carbon nanotubes (CNTs), carbon fibers (CFs), graphite and graphene have been intensively studied and have exhibited enhanced electrochemical properties [2].

There are some studies in the literature that related to the electroless coating of carbon fiber with Cu [3-5], Ni [6-8], Ag [9], Sn [2] Fe [10] for different applications. In this study, we aimed to deposit a thin Sn layer on carbon fiber surfaces via the electroless plating method. We obtained promising results to produce well-suited nano-scale core-shell Sn-CF structure not only for light alloy applications but also negative electrodes for Li-ion batteries.

2. EXPERIMENTAL DETAILS

Carbon fibers (supplied by Alfa Aesar with the diameter of 7 μm and length of 1 mm) were used in this experimental study for producing Sn@CF composites. Before the Sn deposition process, the surfaces of pure copper powders were pretreated to obtain catalytic activity and then cleaned with acetone to remove any contaminants on the surfaces. Later, the surfaces of copper powders were micro-etched to provide sufficient bonding between CFs and Sn deposits. Following the micro-etching, CFs were filtered and washed with distilled water several times and the pretreatment of CFs was completed after drying of activated powders for 10 h in a vacuum oven at 60 °C. After the pretreatment process, the surfaces of CFs were coated with Sn by an electroless process. The surface of pure CFs was sensitized with SnCl2 solution. Later, the CFs were introduced to a $PdCl_2$ solution to obtain active metallic sites on CFs. All solutions were prepared with de-ionized water and reagent grade chemicals. Plating process was carried out at 70 °C temperature and optimum plating time was 10 min for the composites. The pH value of the plating bath was controlled continuously during plating between 12 and 13 by using NaOH as a buffering agent. After the plating process, tin coated copper powders were washed up with distilled water and then dried at 60 °C in a vacuum oven for 12 h. The basic composition of the bath, and the plating conditions are shown in **Table 1**.

Table 1 The bath composition and the plating conditions

Plating bath composition and the conditions	
$SnSO_4$	40 g/L
$NaH_2PO_2 \cdot H_2O$	20 g/L
NH_4Cl	100 mL
pH	12-13
Temperature	70 ºC
Powder concentration	2 g/L

The surface morphology of the CFs@Sn composites was characterized by SEM (JEOL 6060LV) equipped with EDS. Possible growth planes and the crystallographic relationship of CFs@Sn composites were performed by XRD method using a Rigaku D/MAX 2000 X-ray diffractometer.

Active sites are necessary for the electroless deposition of tin nucleation. The adsorption of hypophosphite on the surface of catalyst, the first non-Faradaic step is controlled by anodic processes. The schematic illustration of the electroless Sn process was demonstrated in **Figure 1** and described as follows.

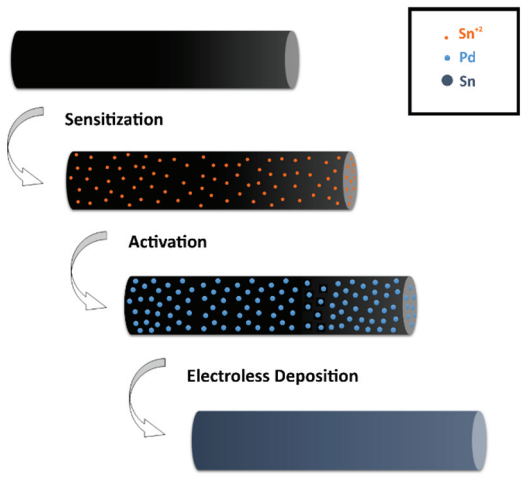

Figure 1 The schematic illustration of the electroless Sn process

The formation mechanism of the core-shell structure of Sn@CFs is schematically illustrated in **Figure 1**. Pre-treatment in the $SnCl_2$ solution enhances the adsorption of Pd ions on the surfaces of the CFs during activation. After sensitisation, Sn^{2+} ions are adsorbed on the surfaces of the CFs and act as seeds for the formation of Pd nuclei during the activation process [1].

3. RESULTS AND DISCUSSION

To investigate the tin deposition on the surface of the carbon fibers, SEM studies were performed. Typical SEM images of the tin deposited carbon fiber are presented in **Figure 2**. **Figure 2** presents an SEM image of the Sn-coated CF, and a relatively continuous uniform and dense tin layer is observed on the surface of the CF. **Figure 2b** demonstrates the microstructures of Sn coated CF with core-shell structure. As can be seen from the SEM observation in **Figure 1b**, homogeneous and uniform tin shell deposited on the CF surface. Due to the deposition time, it is expected that more particles would deposited onto the surface of a fiber, which grew larger, with “snowflake” shaped particles then aggregation of Sn particles [5]. In our samples, snowflake structures were obtained on the surface of the CFs.

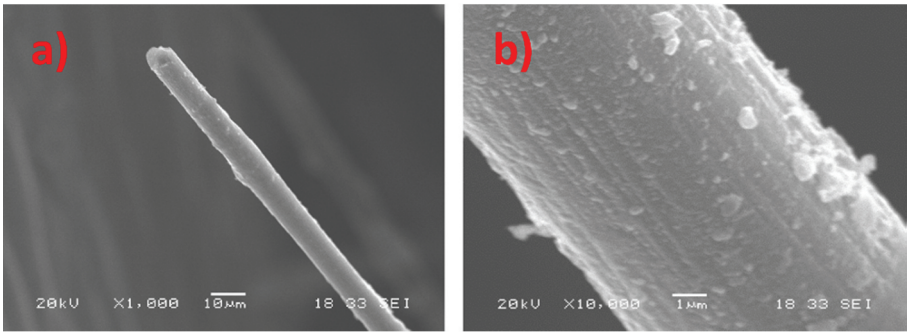

Figure 2 SEM images of surface morphology of Sn@CF structure at a) 1.000x and b) 10.000x

Subsequent EDS was applied to analyze the structure of the plated CFs with core-shell structure and presented in **Figure 3**. From **Figure 3**, it can be seen that Sn determined in the structure and peaks of Sn were clearly observed. Therefore, it can be concluded that the Sn covered the CF surface.

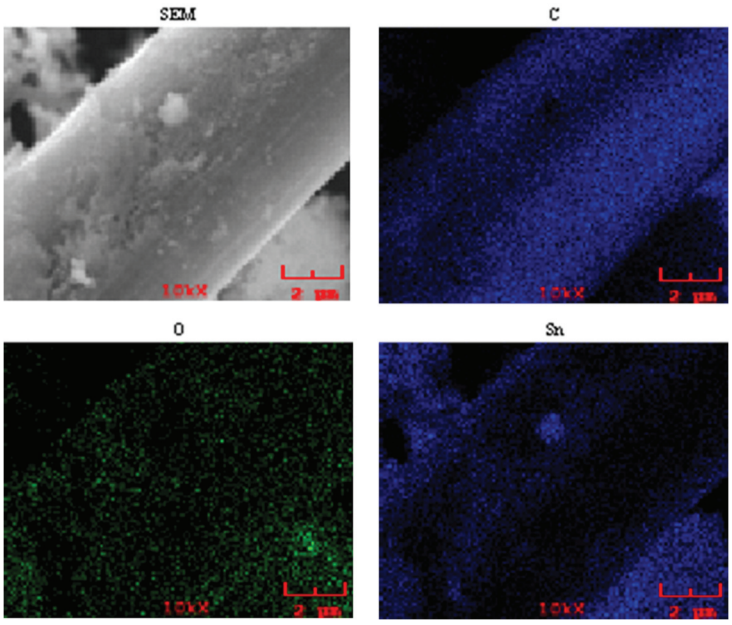

Figure 3 EDS-dot mapping image of Sn@CF composite

Distribution of Sn, C and O atoms was revealed by X-ray color mapping carried out with a SEM, as shown in **Figure 4**, indicating that the deposited elements are homogeneously dispersed on the CF. **Figure 4** represents SEM image, EDS dot-mapping of Sn@CF composite. SEM images of produced composite displays clearly visible tin atoms on the carbon fiber surface. In our samples, a coating thickness was measured between 600-800 nm. Therefore, electroless deposition of CFs were consisted of thin Sn layers resulting in a dense carbon dots and a tenuous Sn dots in EDS-dot mapping.

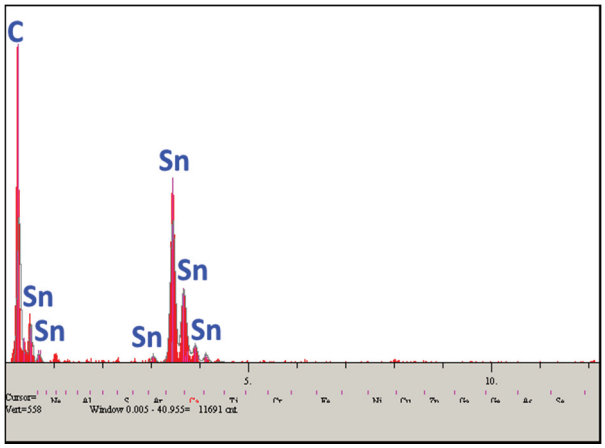

Figure 4 EDS spectra of Sn@CF composite

The obtained XRD patterns for the Sn@CF structure is shown in **Figure 5**. As can be seen from the XRD pattern in **Figure 5**, the deposited Sn gives the sharp diffraction patterns because of the crystalline form of tin deposition on CFs. It is clearly seen from XRD patterns of Sn@CF composite that carbon reflection peak was observed at 26.3. The XRD result clearly indicated that the Sn layers were successfully deposited on the surface of CFs by electroless plating process.

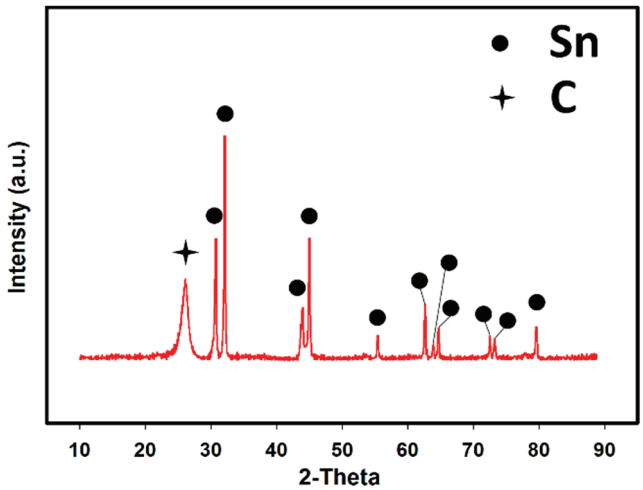

Figure 5 XRD patterns for the Sn@CF composite

4. CONCLUSION

In conclusion, Sn-coated CFs have been successfully synthesized via an electroless deposition method, which could effectively prevent tin particles from aggregation and oxidization. The current approach can be extended to the fabrication of copper coatings on other substrates and hence it is expected to have various applications in catalysis, sensors, and other fields.

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