



In situ study of electrochemical processes of metal nano-nuclei formation, growth, and stability on single carbon microfiber for surface multifunctionalization

Shuangqi Song^a, Karen Taniguchi^a, Li Sun^{a,b,*}, Zhonghou Cai^c

^a Department of Mechanical Engineering, University of Houston, Houston, TX 77204, USA

^b Texas Center for Superconductivity, University of Houston, Houston, TX 77204, USA

^c Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439, USA

ARTICLE INFO

Article history:

Received 14 July 2010

Received in revised form 13 August 2010

Accepted 24 August 2010

Available online 19 September 2010

Keywords:

Electrodeposition

Carbon fiber

In situ

XRD

Nucleation

ABSTRACT

With better understanding and control of metal layer formation on carbon surface, the electrical, magnetic, thermal, interfacial, and catalytic characteristics of carbon-based micro- and nanomaterials can be further improved for large-scale engineering applications. Experiments demonstrated that controlled metal electrodeposition on micro- and nanocarbon fibers can be realized in a cost-effective and reproducible fashion. Microbeam synchrotron X-ray diffraction and fluorescence techniques have been developed to provide *in situ* characterization capabilities to reveal the nuclei formation and growth processes on individual carbon microfibers with size, distribution, and microstructural information. The nuclei stability of the metal deposit is found to have strong dependence on its size as well as the deposition condition.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Since the discovery of carbon-based nanomaterials, represented by C₆₀, carbon nanofibers (CNFs), carbon nanotubes (CNTs), and graphene, increasing scientific and industrial efforts have been devoted to explore new physics and develop new applications of these materials. The unique physicochemical properties of carbon nanostructures can be further modified or improved by surface coating of other functionalized materials. Earlier studies on carbon microfibers surface functionalization included high-temperature wetting with liquid aluminum [1]; electroless deposition of copper [2,3], nickel [4,5], and silver [6]; and chemical vapor deposition (CVD) of titanium [7]. All these studies indicated the difficulty of achieving controllable metal growth on carbon surfaces, which was a result of the chemical stability of carbon atom sp² hybridized electron configuration and only weak van der Waals type interactions with metal atoms are favored [8,9]. However, recent studies showed that the electronic structures of single-walled carbon nanotube (SWNT) and multi-walled nanotube (MWNT) can be very different from a flat graphene layer due to chirality and surface curvature. *Ab initio* calculation [10] showed that Ni atoms can form a covalent type of bonding on certain sites of the SWNTs due to curvature-induced sp² and d-orbital rehybridization.

Recently, we demonstrated that metallic Ni can be effectively electrodeposited on assembled carbon nanofibers (CNFs) interconnected structure and significantly improved electric conductivity and better magnetic field alignment [11] could be achieved. Electrochemical surface coating provides multiple adjustable experimental parameters and is capable of simultaneously coating complex-shaped surfaces. Although industrial applications of electrochemical synthesis have a long history [12], only a very limited number of material characterization techniques can provide quantitative real-time analysis capability to reveal the complex electrochemical processes. Specifically designed atomic force microscopy (AFM) [13,14], scanning tunneling microscopy (STM) [15,16], and transmission electron microscopy (TEM) [17] techniques have been experimented to characterize the electrochemical nucleation and growth. But due to the existence of multiple species and phases, intertwined mass and charge transfer processes, and complicated surface reactions and diffusion, high-resolution *in situ* study has been proven to be challenging. In this study, we report on the study of utilizing *in situ* synchrotron X-ray microdiffraction and fluorescence techniques together with electrochemical characterization and *ex situ* microscopy to investigate the nucleation and growth of Ni on individual carbon microfibers.

2. Experiments

Considering the strong X-ray absorption by water molecule and ionic species, a custom-made three-electrode electrochemical cell was developed to minimize X-ray passage length for both diffraction and

* Corresponding author. Department of Mechanical Engineering, University of Houston, Houston, TX 77204, USA. Tel.: +1 713 743 4509; fax: +1 713 743 4503.

E-mail address: lsun4@uh.edu (L. Sun).

fluorescence signals. A 0.05 M NiCl_2 aqueous solution ($\text{pH} \approx 3$ adjusted by HCl) was used. Individual carbon microfibers (from Sigmatex with a diameter of $6 \mu\text{m}$) were fixed on a frame to be used as working electrode. Synchrotron X-ray experiments were conducted using the 2-ID-D beamline at the Advanced Photon Source in Argonne National Laboratory. The energy of the photons was selected to be 10.4 keV. The micron beam size used in this experiment was $6.0 \times 6.0 \mu\text{m}^2$. The intensity of diffracted X-rays was recorded by a CCD detector. Scattered fluorescence signals were recorded by an energy-dispersive detector.

3. Results and discussion

Fig. 1 shows the first scan of the cyclic voltammogram measured on three substrates with the same potential sweep rate of 2 mV/s. The current density is based on deposition area calculated by the diameter and length of the fiber. The onset potential of significant Ni growth on the carbon microfiber and the glassy carbon surface is found to have much more negative value when compared to than that on the Au/Cr/Si substrate. For carbon microfibers, the ratio between the integrated oxidation reaction charge and the integrated reduction reaction charge has a much lower value than that for the other two substrates (on carbon fiber: 0.042, on flat carbon: 0.439, and on Au: 0.543). However, with the same reduction potential, the carbon microfiber has the largest current density during the reduction reaction. These observations indicate that Ni deposition on the carbon microfiber is more difficult than that on the Au surface with more significant hydrogen evolution. Sequential cyclic voltammogram measurements show that the Ni surface passivation intensifies and the Ni oxidation reaction on both the carbon and the Au surface diminishes with an increased number of cycles.

Fig. 2a is the schematic drawing of the electrochemical reaction cell used for synchrotron characterization. Figs. 2b–d show the simultaneously recorded time-dependent current transient, Ni X-ray fluorescent and X-ray diffraction signals for one of the electrochemical experiments. During this experiment, a potential of -1.1 V was first

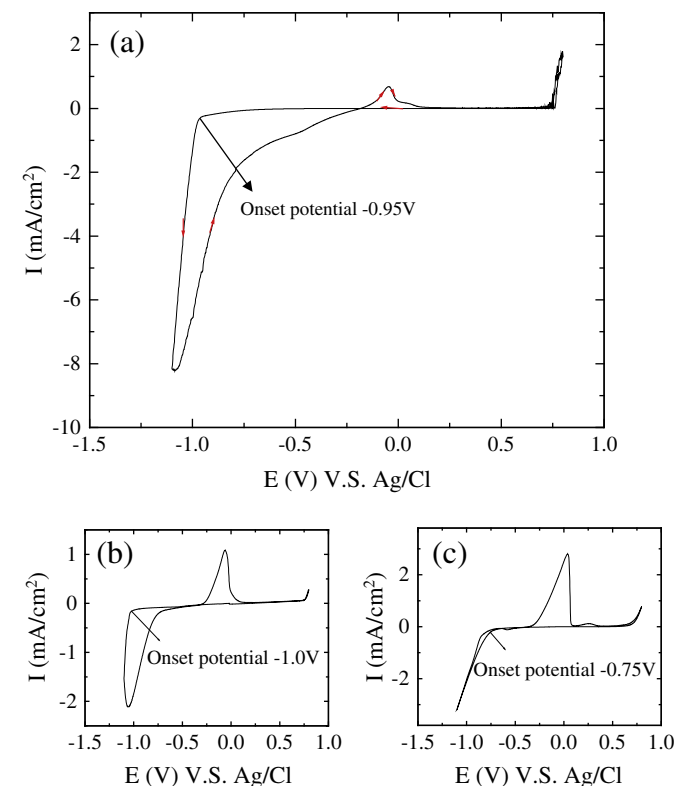


Fig. 1. Cyclic voltammograms for the 50 mM NiCl_2 solution on (a) a single carbon microfiber, (b) a flat glassy carbon substrate, and (c) a flat Au/Cr/Si substrate.

applied (region I), followed by an open circuit period (region II), and finally a potential of 0.4 V was applied (region III). X-ray diffraction patterns were continuously recorded with an exposure time of 20 s. Fig. 2d shows the patterns recorded corresponding to the time of A to E indicated in Fig. 2b and c. The brightness of the image indicates the diffracted X-ray strength and the radial directions indicate the X-ray diffraction angle 2θ . The low 2θ angle halo is caused by liquid scattering. The narrow bright bands are caused by the diffraction from crystalline Ni. The partial diffraction rings are mostly continuous and reflect the polycrystalline nature of the Ni deposits. Unpredictable brighter spots can appear during electrodeposition, indicating the fast growth of random grains with certain orientations.

In region I, Ni diffraction bands emerge and intensify when Ni deposition progresses. By integrating the diffraction strength over the detector plane and subtracting the water-scattering signal, the X-ray diffraction strength resulting from the sample can be obtained as a function of 2θ . Fig. 2e shows such a diffraction spectrum, and uses the Ni (111) diffraction peak full-width at half-maximum (FWHM), the average grain size can be estimated using Scherrer's equation. An increase in average grain size is observed when the electrochemical deposition continues.

In the open circuit state of region II, although there were no electrochemical reactions, the deposited Ni still becomes unstable and chemical dissolution is evident. Both diffraction and Ni fluorescent signal strength decrease versus time. An interesting discovery is that the grain size estimation from the diffraction peak width shows a slow increase during this self-dissolution process although the total diffraction signal strength decreases. Scherrer's equation tends to underestimate grain size estimation because the peak broadening is mainly caused by small grains. The shift of remaining grain size towards larger values during dissolution indicates the quicker removal of small grains. Further studies also show that electrodeposited Ni grain stability improves with increasing amount of the total Ni deposits and also the average grain size when electrodeposition stops. Ni dissolution should be a result of the replacement reaction between Ni atoms and H^+ ions in the solution. Thermodynamically, the driving force for the Ni dissolution reaction increases with the Ni grain surface curvature. This is also the reason for the slower dissolution of thicker layers and larger grains.

In region III, a positive potential of 0.4 V was applied for electrochemical dissolution. A rapid intensity decrease of the Ni diffraction bands was observed indicating fast dissolution. Right after the positive potentials were applied, the fluorescent signal has a sudden increase and displays a peak before leveling off. This peak should come from the initial increase in nickel ion concentration around the carbon microfiber at the beginning of Ni dissolution. Fig. 2f also includes the data of grain size change during electrodeposition.

Ni deposition under seven discrete potentials ranging from -0.8 V to -1.5 V was studied and similar electrochemical behaviors were observed and self-dissolution at open circuit potential was present in all cases. When comparing the Ni grain sizes grown under different potentials with the same amount of charge transfer, it is observed that average grain sizes increase with increasing negative potential.

The stability of the deposited Ni strongly depends on grain size and the total amount of Ni deposits. As shown in Fig. 3, Ni deposited at -0.8 V will totally dissolve under open potential, the grain size after electrodeposition is about 16 nm. On the other hand, the Ni deposited at -1.5 V with a diameter of 38 nm is much more stable. Ni dissolution at open circuit is very limited and the grains remain stable even after applying a positive potential of 0.4 V. X-ray diffraction patterns confirm that the remaining material on the carbon fiber surface is mainly Ni.

To reveal the morphology of deposits, *ex situ* scanning electron microscopy (SEM) study was performed. A serial of samples corresponding to the different stages of electrochemical deposition at discrete potentials were prepared. Fig. 4 shows the representative SEM images of three deposition potentials of -1.5 V , -1.1 V , and -0.8 V . When comparing the deposits with the same amount of charge transfer, it is

Download English Version:

<https://daneshyari.com/en/article/180430>

Download Persian Version:

<https://daneshyari.com/article/180430>

[Daneshyari.com](https://daneshyari.com)