Applied Surface Science 255 (2009) 4309–4315

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Study on the adhesion mechanism of electrodeposited nickel clusters on carbon substrates

M.F. De Riccardis [a,*], D. Carbone [a], V. Martina [a], M. Re [a], B. Bozzini [b], L. D'Urzo [b]

[a] ENEA Brindisi Research Centre, SS.7 Appia Km 712, 72100 Brindisi, Italy
[b] Dipartimento di Ingegneria dell'Innovazione, Università del Salento, via Monteroni, I-73100 Lecce, Italy

ARTICLE INFO

Article history:
Received 23 July 2008
Received in revised form 21 October 2008
Accepted 21 October 2008
Available online 21 November 2008

Keywords:
Ni clusters
Electrodeposition
SERS
TEM

ABSTRACT

Growth and adhesion mechanisms of Ni clusters electrodeposited on three different carbon-based substrates have been studied. Glassy carbon, carbon paper and PAN-based fibres have been used as working electrodes and Ni clusters have been electrodeposited from a $NiCl_2 \cdot 6H_2O$. Ni reduction on carbon substrates has been studied by cyclic voltammetry, chronocoulometry and in situ SERS, whereas the morphological and structural characterization of the interface between Ni clusters and carbon-based substrates has been performed by High Resolution TEM.

From our results we can conclude that the precipitation of Ni hydroxides and basic salts in the unbuffered catholyte promotes the adhesion of Ni clusters on the carbon-based substrates considered in this study. This feature of the investigated Ni clusters electrodeposition suggests that it may be a suitable fabrication route for applications in catalytic processes, such as metal-particle catalysed growth of carbon nanotubes.

1. Introduction

Electrodeposition is a versatile and inexpensive technique that allows the synthesis of metals in several morphologies and structures, including continuous metallic films and nanoparticles, also on 3D substrates. Electrodeposition of metallic clusters has a host of cutting edge prospective applications, such as the catalytic growth of carbon nanotubes (CNT) in CVD processes [1–3]. In order to obtain a reliable catalytic surface for CNT, and in general for the growth of carbon nanostructures (CNS), such as nanofibres or nanowalls, a key property is the adherence of the clusters to the substrate. Outstanding adherence is mandatory in catalytic reactions, in order to avoid clusters coalescence during heat-assisted processes. Nevertheless, in the growth of metal catalysed carbon nanostructures, strong interactions between support and metal catalyst, together with minimization of surface mobility of catalyst particles, are highly desirable process highlights. Well adhered metallic coatings can be produced by electrodeposition once the plating parameters, the substrate treatments and the electrolytic bath composition are optimized [4–6]. In previous papers the authors demonstrated that it is possible to obtain well adhered and uniformly distributed Ni clusters, on PAN-based fibres and carbon paper [1,2]. The good adhesion of electrodeposited Ni clusters was demonstrated by performing several experiments, consisting in immersion, magnetic stirring, centrifugation and ultrasonication into different liquids (such as deionized water, ethanol, acetone, *n*-butanol). Nevertheless, nano-scratch tests were performed on Ni coated supports by means of Atomic Force Microscope (AFM) equipped with a diamond tip; the metallic clusters were moulted and not removed by the diamond tip. The experimental details are reported in [2].

It is well known that Carbon and Nickel not form stable carbides [7]; so the reason of this evidenced strong bond between electrodeposited Ni and carbon support is still undefined. The aim of this paper is to provide a further piece of information to understand the grounds of adhesion between Ni clusters and carbon substrates; for this reason with insight we analysed the interface between Ni electrodeposit and carbon support.

Our attention has been directed to Ni and C because their jointed use is highly attractive. In fact remarkable catalytic activity of Ni and amphoteric properties of C make them able to be widely used in metal catalysed reactions as catalyst and support material respectively. Nevertheless, the nature of interfacial bond between metal/carbon or metal/polymer, has been extensively exploited in different technologies, e.g. microelectronics, composites, adhesive bonding and packaging. In particular, a lot of research effort has been devoted to the understanding of the interfacial interactions between carbon-based materials, especially HOPG, and metal deposits [8–11].

In the specific issue of metal-catalysed carbon nanostructure growth, the catalytic activity of metal particles can be more or less dramatically affected by both physical and chemical interactions

---

* Corresponding author.
E-mail address: federica.dericcardis@brindisi.enea.it (M.F. De Riccardis).

0169-4332/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2008.10.127

between substrate and catalyst [11]. For this reason, we are interested in characterising the nature of the bond between Ni clusters and substrate [1–3].

To this aim, we studied the Ni electrodeposition process by combining some classical electrochemical methods – such as cyclic voltammetry and chronocoulometry – with in situ SERS. This technique is typically carried out with precious-metal electrodes, exhibiting a remarkable degree of surface-enhancement. Nevertheless, it has been proved relatively recently (see e.g. [12] for an updated review) that the SERS effect – though at a significantly lower level with respect to precious metals – can be achieved also with Fe- and Pt-group metals. The use of SERS in electrodeposition studies in such transition metals has received very limited attention. Ni electrodeposition has been used in one case to achieve Ni electrode roughening prior to SERS work [13]. Electrodeposited Co, Ni, Pt and Pd nano-wire arrays have been shown to exhibit surface enhancement [14]. Co electrodeposition in the presence of coumarin has also been investigated [15].

In addition to electrochemical analyses on Ni electrodeposition process, structural investigations at the interface between carbon supports (carbon paper, carbon-based fibres and glassy carbon) and the electrodeposited Ni clusters were performed by means of transmission electron microscopy (TEM).

2. Experimental

2.1. Ni electrodeposition

For Ni electrodeposition, a solution of 0.5 M $NiCl_2{\cdot}6H_2O$ with deionized water was prepared and pH was adjusted to 3.0 by HCl addition. Ni clusters were electrodeposited on different carbon substrates, such as PAN carbon-based fibres (obtained by pyrolysis of Polyacrylonitrile), carbon paper, commercially named Papyex, and glassy carbon.

Two different set-up of electrolytic cell were used, according to the nature of the substrates: (i) a cylindrical cell in the case of fibre bundles and (ii) a prismatic cell with carbon paper and glassy carbon. The cylindrical cell was equipped with a Pt spiral and a cylindrical assembly of PAN-based fibres as counter-electrode, in order to achieve a high degree of electrodeposit uniformity along both the fibre length and diameter. Uniform deposits on planar substrates were obtained with a plane-parallel electrode configuration in the prismatic cell, featuring a vertical cathodic specimen holder and Pt foil as anode.

Voltammetric and potentiostatic measurements were carried out by using a PAR potentiostat model 273A. The potentials were measured against a Ag/AgCl reference electrode and reported on this scale.

Different cleaning treatments were applied to the carbon substrates before Ni electrodeposition. PAN fibres, cut from a woven fabric, were treated at 650 °C for 1 h in air to remove the binder. Glassy carbon substrates were treated by boiling the coupons in a solution of HCl and HNO_3 (3:1) for 10 min and subsequently rinsing them in deionized water, to remove any organic residue. Carbon paper substrates were washed with acetone and ethylic alcohol, and rinsed in deionized water. The exposed area was 21 cm^2 for PAN-based fibres and 0.95 cm^2 for carbon paper and glassy carbon electrodes. Experimental details on the electrodeposition process are described elsewhere [2]. After Ni electrodeposition, morphological characterizations of Ni coated carbon substrates surface were performed by using XL40 LaB6 (Philips) SEM.

A monomodal narrow diameter distribution was found for the Ni clusters, around 50 nm, under different conditions for each substrate; in the case of glassy carbon at −0.85 V and 20 mC/cm^2 total charge, in the case of carbon paper at −0.8 V and 100 mC/cm^2 total charge, and in the case of PAN-based fibres at −0.75 V and 7.5 mC/cm^2 total charge.

2.2. SERS characterization

Raman spectra were recorded using a LabRam microprobe confocal system. A 50× long-working-distance objective was used and the excitation line at 632.8 nm was provided by a 12-mW He–Ne laser. The slit and pinhole were set at 200 and 400 μm, respectively, corresponding to a scattering volume of about 3 pL; Raman spectra were acquired with a 600 grid/mm spectrometer. The recorded Raman intensities are directly proportional to the discharge current of the CCD detector. In situ electrochemical measurements were performed in a glass cell with a vertical glassy carbon (GC) electrode (∅ 3 mm) embedded in a Teflon holder. A limited degree of SERS activity can be attained with GC [16] and Ni [17–19] that can be enhanced during the electrodeposition process, owing to the formation of active Ni clusters. The counter electrode was a Pt wire loop of total area ca. 2 cm^2, concentric and coplanar with the gold working electrode. An external Ag/AgCl reference electrode was used and all the potentials were reported on this scale. The applied potential was controlled by an AMEL 2049 potentiostat.

2.3. TEM characterization

Transmission Electron Microscopy (TEM) was carried out by TECNAI G^2 F30 operating at an acceleration voltage of 300 kV and with point resolution of 0.205 nm.

For TEM observations of electrodeposited Ni clusters, the samples were prepared with three methods, according to the characteristics and the nature of different substrates. With carbon paper, a powder sample surface was obtained by scraping it off the cathode surface and dispersing it in ethylic alcohol; the dispersion was cast on a carbon coated grid. In the case of glassy carbon substrate, two pieces of the same specimen were sandwiched and mechanically thinned down to about 20 μm of thickness, according to the standard preparation method of TEM cross-sections. The final thinning was performed by ion beam milling (PIPS Gatan) with Ar ions at 5 kV. For PAN Carbon fibres, a Pt thin layer was deposited by electron beam in order to protect the electrodeposited Ni, during the next Ion beam deposition of a thicker Pt layer necessary for TEM lamella preparation. Then a longitudinal cross-section was prepared with the in situ Lift Out technique with the FEI Strata 400 FIB/SEM system.

For all the samples, conventional Bright Field TEM images were obtained from many areas, in order to highlight global morphological features of the electrodeposited Ni clusters, such as size, distribution and shape, while High Resolution TEM images yielded insightful structural information regarding the microstructure of the clusters and the nature of the interface.

Nevertheless, High Angle Annular Dark Field (HAADF) STEM images were taken from cross-sections of Ni on glassy carbon and PAN fibres; this kind of analysis has highlighted chemical differences on large areas, thanks to compositional and thickness contrast mechanism. For chemical analysis, Energy Dispersive Spectrometry (EDS) was also carried out with the electron beam focused both on Ni clusters and on their interface with the substrate.

3. Results and discussion

3.1. Electrochemistry

The more appropriate term for the electrodeposition technique should be *electrocrystallization*, usually used for electrode pro-