

Potentiostatic Co-deposition of Nickel and Graphite Using a Composite Counter Electrode

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Abstract

Nickel and graphite was potentiostatically co-deposited using a composite nickel-graphite composite counter electrode (CCE) with tunable-friability. This was done to achieve steady introduction of graphite into the electrolyte without intermittent mechanical infusion and stirring, thus facilitating a potentiostatic deposition route and promoting homogeneity of deposition. Graphite electrodes were produced at densities of 0.920, 1.026 and 1.188 g/cm³ and their suitability for constitution in a HCE assessed. The surface area of the nickel component of the HCE was varied from 100% to about 60 and 30% surface area and combined with the graphite electrode to form HCE constitutions designated as triplet, doublet and singlet respectively. Deposition was done for about 8 hours in 1 M NiSO₄ using the different HCE constitutions, an Ag/AgCI reference electrode unraveling was observed to be the formation of oxygen and CO_2 due to oxidation reactions at the HCE. Graphite electrode of density 0.920 g/cm³ was selected for the HCE due to its extensive surface porosity, a characteristic determined as favourable to the mechanism of electrode unraveling. Co-deposition of graphite with nickel was observed to increase as nickel surface area was reduced from the triplet to singlet. SEM micrographs show partially and fully embedded graphite particles in the nickel matrix while the presence of nickel and graphite was affirmed.

Keywords: Electrodeposition; Nickel; Graphite; Optical microscopy

Introduction

Electrodeposition has remained an attractive route for the synthesis of materials and complex structures due to its relative simplicity and low-cost setup. Co-deposition, referring to the simultaneous electrodeposition of multiple metallic and non-metallic phases, has been receiving considerable attention lately.

It has been used for the synthesis of metallic alloys [1,2], metalceramic composites [3,4] and 3D micro architecture [5].

In many of these applications the galvanostatic or constant current approach is often employed due to precise control of deposition rate achievable [6]. However the variously named additives - wetting agents, leveling agents, brighteners - needed to control deposit morphology and deposition current introduces bath complexities.

Different atomic interstitial elements or their intermetallic compounds derived from these additives contaminates the electrodeposited films [7]. In potentiostatic deposition voltage is constant. This confers on the process the advantages of close control of the deposition voltage, bath simplicity and avoiding the use of contaminating additives.

However, in the potentiostatic mode, deposition current is not constant; it tends to decrease as the concentration of the ionic species decrease in the solution [8]. This makes deposition rate control difficult.

Often, co-deposition involves the use of multi-species ionic baths or solid-particulates in an ionic suspension [9,10]. The latter approach is used mostly for the synthesis of metallic-nonmetallic composite films. However, co-deposition using particulates suspended in solution is fraught with problems. These stem from the tendency of the particulates to settle in the solution, resulting in inhomogeneity of the deposits.

Systems for introducing fresh particulates and keeping them in suspension through bath agitation or the use of surfactants have been proposed [11-14]. However, agitation of solution under potentiostat control may lead to instability and loss of control of the working electrode potential.

This work reports a method of co-deposition of nickel and graphite that avoids the need for continual introduction of particulates and suspension agitation by using a composite nickel-graphite electrode with built-in friability.

The effects of composite electrode constitution and the optimal conditions of graphite electrode unraveling and were investigated.

Materials and Methods

Graphite electrode

The graphite electrode assembly comprises a Teflon cup filled with compressed graphite powder from a lot of <63 μ m powder. The electrode assembly is shown in Figure 1.

Three electrodes compressed to densities of 0.920 g/cm^3 , 1.026 g/cm^3 and 1.188 g/cm^3 were produced. The stainless steel backing disc provides electrical contact with the powder.



Nickel electrode

The nickel electrode was formed from three pieces of 15 mm by Ø 9 mm sections of nickel (GoodFellow, Pennsylvania). They were electrically connected together and then mounted with epoxy inside a Teflon cup in such a way that only their circular cross-sections were exposed. Figure 2 shows the nickel electrodes with the exposed circular cross-sections.



Figure 2: Nickel electrodes showing the respective circular cross-sections.

Deposition bath

The deposition bath was 1 M NiSO $_4$ prepared using de-ionised water. The bath's pH was adjusted to a starting value of 2.5 using drops of concentrated hydrochloric acid.

Deposition head

The deposition head assembly is shown in Figure 3. It comprises an aluminium disk with an attached electrical lead.

The stainless steel ring placed on aluminium creates a cylindrical cavity inside which the deposition takes place. This assembly forms the working electrode in the three-electrode deposition setup.

Sections of the aluminium and the stainless steel ring that were excluded from deposition were coated with air-curing silicone rubber. The aluminium surface was cleaned prior to electrodeposition according to ASTM B322 [15] and ASTM B253-87 [16].



Deposition procedure

The exposed surface area of the nickel electrode was varied by coating the electrode surface in the manner shown in Figure 4. This creates configurations referred to as "singlet", "doublet" and "triplet". These were combined with a single graphite electrode to form a "composite" nickel-graphite counter electrode (CCE).

The composite nickel-graphite counter electrode, the Ag/AgCl reference electrode and the aluminium backing plate in the deposition head constitute the 3-electrode setup for deposition. The deposition was done, whilst maintaining a bath pH of between 2.5 and 3.0 and an imposed potential of -1400 mV (vs. Ag/AgCl).





SEM and optical microscopy characterisation

The co-deposited nickel-graphite was characterized using FEI-Quanta 600 scanning electron microscope and Oxford EDX detector.

Optical microscopy characterisations of the compressed graphite electrodes and the co-deposited nickel-graphite were done on an inverted metallurgical microscope, using the extended depth of focus (EDF) software, Helicon Focus⁵.2.

Theory

The unraveling of the graphite particles of the graphite electrode component of the composite counter electrode occurs due to the formation oxygen and carbon dioxide gas bubbles at the electrode.

The process is illustrated in Figure 5.



Figure 5: a) Setup for the potentiostatic co-deposition b) illustration of co-deposition involving low-zeta potential graphite particles.

These bubbles grow and eventually "pop", causing the compacted graphite particles to spew into the bath. However, for the compacted graphite to unravel, the density of compaction must not be too high to cause coalescing or fusing together of the graphite particles. The reactivity of the graphite surface is enhanced by its surface porosity which provides increased reaction sites.

The spewed-out graphite particles migrate to the working electrode due to electrophoresis, and co-deposit with the growing nickel. The friable graphite electrode thus ensures the following:

- There is a guarantee of the presence of sub-micron size particles unravelling into the bath. The electrode gradually reduces in size as a result of this.
- There is no need for bath agitation because sub-micron sized particles that have high zeta potential is co-deposited by electrophoresis into the deposition mould.

Results

Characterisation of graphite electrodes at different compression densities

Optical micrographs at 104 magnification (using EDF) for graphite electrode samples A, B and C are shown in Figures 6-8 respectively. For sample A, formed to a density of 0.920 g/cm³, the micrographs show pores (marked Y in the micrographs) and distinct particles (marked X in the micrographs) on the surface. There is little coalescing or fusing together of the graphite particles.



Figure 6: Sample A (graphite formed to 0.920 g/cm3) at 10^4 (using EDF).

The pores were smaller in sample B compressed to a density of 1.026 g/cm³, as can be seen in the micrograph.



Figure 7: Sample B (graphite formed to 1.026 g/cm3) at 10^4 (using EDF).

In the micrograph in Figure 8, the relatively high density of 1.188 g/cm³ has caused an almost total coalescing of the particles with pores virtually eliminated.



Figure 8: Sample C (graphite formed to 1.188 g/cm3) at 10^4 (using EDF).

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Characterisation of nickel-graphite from composite electrode configurations

Figure 9 show the micrograph at 10^4 (using EDF) of nickel deposited solely with a 100% nickel counter electrode.



Figure 9: Nickel deposited with 100% Nickel counter electrode at 10^4 (using EDF).

Figures 10-12, also at 10⁴ (using EDF) shows micrographs of nickelgraphite film deposited with nickel triplet, doublet and singlet composite counter electrodes respectively. The deposits produced with 100% nickel counter electrode show a microstructure free of any codeposited particles. Figure 10 show few scattered specks of codeposited graphite.



Figure 10: Nickel-graphite co-deposited with nickel triplet + graphite at 10^4 (using EDF).

The co-deposited graphite tends to increase in Figure 11 for deposition with nickel doublet.



Figure 11: Nickel-graphite co-deposited with nickel doublet + graphite at 10^4 (using EDF).

This increased further for deposition done with the triplet in Figure 12.



Figure 12: Nickel-graphite co-deposited with nickel singlet + graphite at 10^4 (using EDF).

SEM and EDX characterisation of co-deposited nickelgraphite film

The SEM micrograph of the co-deposited film is shown in Figures 13 and 14, while the EDX spectrum is presented in Figure 15.



Figure 13: SEM of nickel-graphite film at 10000× showing pore and co-deposited graphite.



Figure 14: SEM micrograph of the nickel-graphite film at $2500 \times$ showing co-deposited graphite.



Figures 15: A) Focus area for EDX analysis and B) EDX spectrum of the co-deposited nickel-graphite.

The micrograph shows pores, partly embedded and fully embedded graphite particles in the nickel matrix. Also, the EDX spectrum indicates the presence of carbon.

Discussion

Influence of graphite electrode density

The influence of the compaction density on the surface porosity of the compressed graphite could be seen on the optical micrographs in Figures 6-8. As compaction density increase, the surface pores reduce and the particles coalesce. This has two main effects on the codeposition process. Rough, pore-filled surfaces have a higher surface area for reactions to take place; hence such a surface could be described as more reactive. Also, less unraveling of the compacted particles would occur if compression density was too high; the goal of co-deposition of graphite would thus not be realized at higher compaction densities. Graphite sample A was selected for the composite electrode due to its low density and exhibiting more of favourable surface features.

Co-deposition mechanism

In potentiostatic deposition it is the potential of the working electrode that is controlled by the potentiostat. The controlling current flows through the counter electrode and fluctuates whilst controlling electrolyte concentration, and thus indirectly the working electrode potential. If the fluctuation of current through the counter electrode was minimal, the potential (negative) at the counter electrode may be considered approximately equal in magnitude but of opposite polarity to the potential (positive) at the working electrode. This positive potential at the graphite counter electrode is sufficient to cause its electro-oxidation to CO_2 .

The -1400 mV (vs. Ag/AgCl) is imposed at the working electrode is equivalent to -200 mV (vs. SHE). In the nickel-water Pourbaix diagram [17], at a pH of about 3.0, the reduction of Ni^{2+} to nickel takes place at about -260 mV (vs. SHE) while a potential higher than 1000 mV (vs. SHE) is required to decompose water into oxygen at the counter electrode. Hence, the potential of -1200 mV (vs. SHE) was imposed so that its approximate positive mirror at the counter electrode could achieve the oxidation of the graphite.

The deposition of dual phase in which one is a non-metal is fraught with challenges stemming from the inability of the non-metal to ionize and thus be deposited electrochemically. Effort was made by Lee et al. [18] to synthesis dual phase manganese - nickel oxide films. This was achieved via the anodic electrodeposition of MgO whilst encouraging the in-situ co-deposition of NiO by precipitation from the NiOH component of the electrolyte.

Mahapatra et al. [19] co-deposited aniline using the in-situ electropolymerisation of aniline at graphite electrodes. Co-deposition of dual phase in which one is non-metallic particulates is often achieved with the use of mechanical infusion and agitation of particulates in the electrolyte as in Bates et al. [20].

In these instances, homogeneity of deposit cannot possibly be guaranteed because particulate concentration is unsteady and decreases with deposition time; this becomes of particular concern for long deposition times. Additionally, the mechanical infusion of particulates and bath agitation to keep them in suspension introduces perturbations in the electrolyte which upsets a potentiostatic process, causing potentiostat stability problems.

Hence, these processes are often done galvanostatically. For electrochemical deposition, the potentiostatic process often desirable due to its bath simplification and close control and monitoring of deposition kinetics. The gradual and long-term unraveling of the compacted graphite component of the CCE ensures a steady presence of graphite particle in the electrolyte and eliminates the need for bath agitation and the problems of electrolyte perturbations.

Nickel-graphite structure

The SEM micrograph in Figure 13 shows a network of pores created by the co-evolution of hydrogen gas. Hydrogen co-evolution causes pH increases near the region of working electrode as a result of water's decomposition and accompanying local production of hydroxide ions [21]. This makes the bath alkaline, increasing the risk of nickel hydroxide production.

Hence, a continual lowering of bath pH with droplets of concentrated HCl to within the 2.5-3.0 window was necessary. The micrograph also shows partly co-deposited graphite particles (arrow A) measured to be about 5 μ m. Hyam et al. [22] reported similarly-size particles as being more favoured for electrophoretic deposition due to their high zeta potential which enables them to remain in suspension for longer. The micrograph in Figure 14 show an embedded graphite particle co-deposited within the nickel matrix.

The EDX spectrum show peaks indicating the presence of carbon and nickel phases. These indicate nickel and graphite co-deposition. The aluminium and oxygen peaks are believed to arise due to the method use for the removal of the aluminium backing layer which involves its dissolution inside sodium hydroxide while the sulphur peak is traceable to nickel sulphate bath.

Conclusion

This work demonstrated the co-deposition of nickel and graphite using a composite or composite nickel-graphite counter electrode with built-in friability. The electrode's friability is tunable by a variation of the compaction density of the graphite electrode and its constitution with the nickel. The mechanism of the graphite electrode's friability was the formation of carbondioxde and oxygen at its surface which unravels compacted graphite particles into the bath.

This approach maintains a quiescent bath that is favourable for the potentiostatic deposition approach and would help guarantee deposit uniformity and homogeneity. The co-deposited nickel graphite thick film is characterized by microporosity and an embedded graphite

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phase in a planar 2D surface. With the porosity, the film is permeable to gases and liquids. This attribute could be exploited in the fabrication of gas diffusion electrode for fuel cells and electrochemical sensors. These applications would benefit from the planar surface which will prevent flooding of reaction sites while catalysts could be more effectively deposited electrochemically within the porous nickel matrix (current collector).

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