



# Anomalous Deposition of Co-Ni Alloys in Film and Nanowire Morphologies from Citrate Baths



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## ABSTRACT

Thin films and nanowires were deposited across the full range of Co-Ni solution compositions via templated electrodeposition in citrate baths. Spectroscopic analysis indicated a high degree of anomalous deposition across all alloy compositions, with no significant composition differences seen between films and nanowires. Electrochemical and microstructural analyses indicated notable differences between structures deposited in low- and high-Ni environments.

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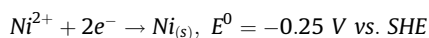
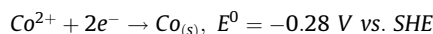
## 1. Introduction

Iron-group alloys and nanomaterials fabricated therefrom are a broadly applicable class of materials for a wide range of applications, thanks to their conductivity and magnetic properties. Nanowires consisting of cobalt and nickel in particular hold promise for applications in magnetic media [1,2], miniaturized magnetic drivers [2], and MEMS [3]. Nanowires consisting of compounds containing nickel and cobalt find applications in batteries [4,5] and thermoelectrics [6,7]. Understanding the doping behavior of the constituent elements is paramount to exerting full control over the synthesis of these nanomaterials.

Templated electrodeposition is a well-established technique [6,8–10] for the inexpensive synthesis of nanowire arrays and has the advantages of low cost, ease of scalability, and highly tunable size control from diameters of a few nanometers to microns or larger. Any template with well-defined pores may be used, but anodic aluminum oxide (AAO) or track-etched polycarbonate (PCTE) are common [10]. The technique may be used for the synthesis of nanowires [6,11], nanotubes [12–14], or intermediate structures [15,16], or even more complex geometries controlled by the choice of template and deposition protocol [10].

Anomalous deposition, wherein the less noble of two codepositing species deposits at a disproportionately higher concentration than the more noble species, presents an obstacle to the straightforward codeposition of Co-Ni alloys [17–24].

The half reactions for the cathodic deposition of Co and Ni are

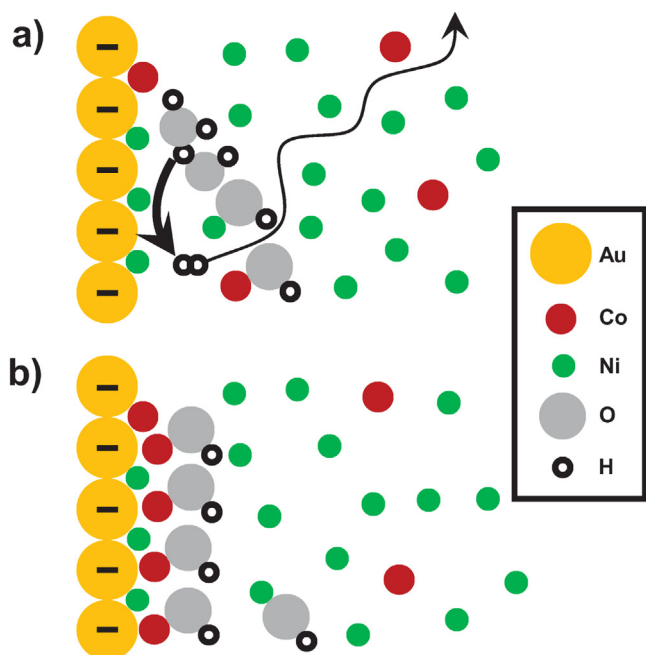


The deposition of Ni is thermodynamically favored over that of cobalt, though because their reduction potentials are so close, at a sufficiently high overpotential to drive the nucleation and growth [25] their thermodynamics would indicate that they would deposit in approximate proportion to their concentrations in solution. However, the highly preferential deposition of the less noble metal Co is observed in a wide range of deposition conditions, including those explored here.

The mechanism by which anomalous deposition (Fig. 1) occurs is still contested [26,27], but one mechanism is generally understood as follows [26,28,29]:

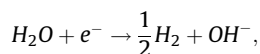
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**Fig. 1.** Cartoon of anomalous deposition. a) In normal electrodeposition, Ni (green) and Co (red) deposit on the Au (gold) electrode in approximate proportion to their concentrations in solution. Simultaneously water (oxygen, grey; hydrogen, small white circle) is electrolyzed, forming H<sub>2</sub>(g), which escapes, and OH<sup>-</sup> ions, which stay in solution and raise the local pH. b) Hydroxide ions bond with metal ions to form Co(OH)<sup>+</sup> and Ni(OH)<sup>+</sup>. The Co(OH)<sup>+</sup> adsorbs to the deposition sites more readily than the Ni(OH)<sup>+</sup>, effectively “crowding out” the Ni species and leading to the preferential deposition of Co over Ni. Excess water molecules and counterions such as citrates have been omitted for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

1) Hydrolysis at the cathode surface produces free OH<sup>-</sup>, raising the local pH:



$$E^0 = -0.414 \text{ V vs. SHE}$$

2) The free OH<sup>-</sup> ions complex with the Co<sup>2+</sup> and Ni<sup>2+</sup> ions, forming Co(OH)<sup>+</sup> and Ni(OH)<sup>+</sup> respectively

3) The Co(OH)<sup>+</sup> adsorbs to the electrode surface more readily than the Ni(OH)<sup>+</sup>, simultaneously reducing to Co<sub>(s)</sub> as well as blocking deposition sites, thereby reducing the deposition rate of Ni species.

$$E^0 = -0.414 \text{ V vs. SHE}$$

The extent to which anomalous deposition occurs is dependent on solution composition, pH, overpotential and current density and has been observed in pores [20] as well as on planar electrodes [21,23,30].

Previous studies do not address the full range of Co-Ni compositions, instead exploring the role of deposition potential [30], pH [22], or counterion [27]. Furthermore most studies do not explore what role a porous template plays in the presence or severity of anomalous deposition. In our study we focus specifically on deposition within citrate baths. The proclivity of the citrate ion to form complexes [31], is useful in modifying the deposition potential of species when co-depositing elements with a large difference in reduction potential [6], but also complicates the phenomenon of anomalous deposition and warrants detailed investigation. We seek to expand this investigation to all

compositions in the fully miscible Co-Ni alloy system, in order to better understand the extent to which anomalous deposition is present at all compositions, and the extent to which it may be mitigated by the proper choice of solution composition. The large difference in deposition conditions and mechanisms within a pore versus on a flat electrode, as well as the popularity of electrodeposition as an effective and scalable mechanism for nanowire formation [10], motivate the study of whether the deposition of nanowires differs significantly from the deposition of films in composition or mechanism.

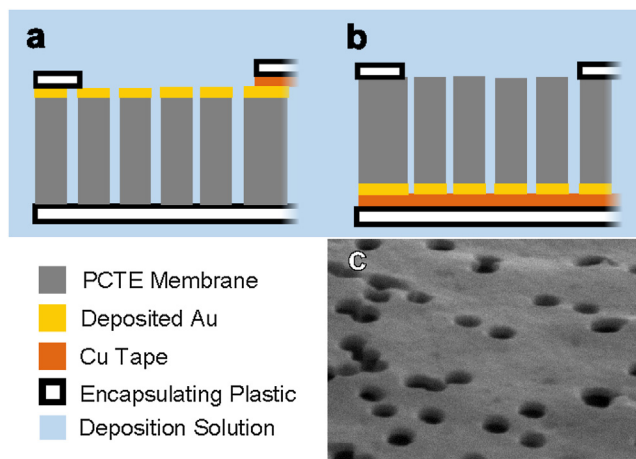
## 2. Methods

Sample electrodes were constructed from track-etched polycarbonate (Sterlitech, Inc.) with an average pore size of 200 nm and thickness of 7 μm. Membranes were metallized with Au via sputter deposition to achieve an electrode with a thickness of approximately 50 nm. A copper tape current collector with Ni-free conductive adhesive (Ted Pella, Inc.) was attached to the Au side of the membrane, and the membrane was encapsulated in plastic tape (Brother international Corporation) except for a 1/4 in. diameter hole exposing the membrane surface. For film deposition the electrode was constructed with the Au electrode exposed to the solution; for nanowire deposition the non-coated side was exposed to solution, forcing deposition to occur within the pores (Fig. 2).

Film electrodes were electrochemically annealed with 10 cycles of cyclic voltammetry (CV) in 50 mM H<sub>2</sub>SO<sub>4</sub> solution from 0 to 1.5 V prior to deposition. Nanowire electrodes were treated with *n*-butanol for 10 minutes and sonicated in deposition solution for 10 minutes prior to deposition.

The deposition solutions were composed of: 0.17(x) M Nickel Sulfate Heptahydrate, 0.17 (1-x) M Cobalt Sulfate Heptahydrate, 0.2 M Citric Acid and 0.125 M Potassium Citrate Monobasic with x=0, 1, 2, 3, 5, 9, 20, 30, 40, 50, 60, 70, 80, 90, 95, and 100. All chemicals were purchased from Sigma Aldrich and dissolved in DI water. Prior to deposition, solutions were sparged with nitrogen for at least 20 minutes to remove dissolved oxygen.

Deposition was performed in approximately 50 mL of solution stirred at 250 rpm, using a Pine Instruments Potentiostat, an Au counter electrode wire, and an Ag/AgCl reference electrode (0.194 V vs. SHE). All potentials are reported hereafter are vs. Ag/AgCl. The deposition procedures proceeded as follows:



**Fig. 2.** Schematic of deposition substrate construction for the growth of a) thin films and b) nanowires. c) shows a plan view SEM micrograph of the Au-coated surface of a PCTE membrane with 200 nm diameter nanopores.

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