

Advances in Understanding Metal Electrolysis Process

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1. Introduction

Advancements in technologies related to the electrorefining and electrodeposition of metals—as important manufacturing process steps—continue to receive significant attention. Specifically, novel ideas that focus on the development of new approaches to the electrochemical synthesis of alloys and composites are important for advancing technologies that can promote increased supply sustainability in the future. This Special Issue, “Advances in understanding metal electrolysis process”, aims at the fundamental level of research with respect to novel approaches in areas of electrolysis and electrochemical mechanisms as well as their impact on the efficiency and quality of metal deposition. It consists of ten papers addressing various issues and their possible solutions around the electrolysis/-deposition of aluminum, copper, indium, rare earth metals, and their alloys, including Zn-Co coatings. One review paper provides an overview of the structure of metal powders produced by electrochemical methods.

2. Contributions

Rare earth elements (REEs) and their alloys are an increasingly important group of materials, considering their ongoing and potential future applications in everyday and advanced technologies. A combination of rapidly growing global demand for (REEs), the generation of large volumes of solid waste as the byproducts of primary production, and limitations in current technologies call for technological advancements in the increase of REEs available. In particular, the recycling, substitution, and efficient use of REEs is critical for developing a strategy towards a “green RE economy” and supplementing current supply channels. Examples of recent research focusing on several of these aspects are discussed in three papers: [1–3]. Articles [1,3] are focused on neodymium and praseodymium deposition, including the complete electroreduction mechanism of both metals, to enable better control over the process, greenhouse gas emission reduction during electrolysis, and better deposition efficiency. The key objective was to simultaneously deposit neodymium and praseodymium from a fluoride molten bath containing their oxides, as an alloy, by reducing the ecological footprint of the process. The environmentally improved process for neodymium and praseodymium co-deposition is performed in these studies under relatively small praseodymium deposition overpotentials on inert Mo and W cathodes resulting in very low levels of carbon oxide, fluorine, and fluorocarbon gas emissions due to the low anodic overpotentials. The application of the Nd and Pr co-deposition in a potentiostatic mode is a highly promising approach for recycling REEs from neodymium iron boron magnets if initially separated from the magnet in the oxide form [1,3]. The conditions for an anode effect during neodymium and didymium oxide electrowinning were discussed in paper [2]. The influence of decisive parameters on the anodic process (high current densities, low neodymium or didymium oxide content, high viscosity, electrolyte composition) was discussed and a mechanism proposed for the anode effect based on models used in aluminum electrolysis. Moreover, a mathematical model was



Citation: Friedrich, B.; Jovičević, J.N.; Feldhaus, D.; Cvetković, V.S. Advances in Understanding Metal Electrolysis Process. *Metals* **2023**, *13*, 307. <https://doi.org/10.3390/met13020307>

Received: 11 December 2022

Accepted: 9 January 2023

Published: 2 February 2023



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proposed to estimate the neodymium and didymium electrochemical cell voltage in an electrolytic cell with vertical electrodes [2]. The recycling route for materials containing precious metals, such as ruthenium (e.g., used catalysts from the chemical industry), is covered in paper [4]. A systematic study was conducted to address the oxidation behavior of ruthenium in copper electrowinning. Ruthenium is not directly electrochemically oxidized to ruthenium tetroxide at the anode. On the anode parallel to the oxygen evolution, the oxidants are formed; they oxidize ruthenium compounds to highly volatile ruthenium tetroxide through chemical reactions. The main variables influencing the rate of ruthenium oxidation were addressed, and suggestions for avoiding the emission of toxic ruthenium tetroxide were derived [4].

Materials scientists working with aluminum alloys may find interesting results for controlled vanadium and aluminum co-deposition from low-temperature chloroaluminate molten salts containing vanadium ions [5]. Intermetallic alloys were synthesized during aluminum underpotential deposition onto a vanadium metal that was previously deposited on the glassy carbon electrode. As a result of solid-state interdiffusion between the initially deposited vanadium and the subsequently deposited aluminum, Al_3V and AlV_3 alloys were formed. Not only did this provide a general introduction to the Al-V alloy generation, but addressed the influence of the vanadium ion concentration in the electrolyte on the deposition rate. This innovative research provides a solid foundation for the development of a controllable electrochemical synthesis of vanadium trialuminide (Al_3V) and Al5 alloy (AlV_3) intermetallics [5]. Contributing to the fundamental understanding of primary aluminum production, the electrochemical behavior of aluminum in the LiF-AlF_3 melt and the presence of the spent catalyst at 740–800 °C was presented in [6]. Experimental data obtained the optimal process parameters for aluminum reduction during the spent catalyst treatment and primary production, as well as key parameters; the effect of the catalyst content, temperature, and electrolyte composition was outlined. The mechanism of aluminum reduction in the LiF-AlF_3 melts appears as a diffusion-controlled two-step process. Both one-electron and two-electron steps occur simultaneously at close (or the same) potentials, which affect the cyclic voltammograms. The diffusion coefficients of electroactive species for the one-electron and two-electron processes were presented in [6].

Readers interested in composite materials may learn much from the investigation of electrochemically synthesized ceria-doped Zn-Co composite coatings. Some recent advances on the topic are well presented in study [7]. The morphology and corrosion resistance of the electrolytically synthesized novel ceria-doped Zn-Co composite coatings were examined and compared with pure Zn-Co coatings obtained under the same conditions. The effect of two ceria sources, powder and homemade sol, was investigated. Zn-Co, doped with ceria particles originating from ceria sol, exhibited superior corrosion resistance compared to Zn-Co- CeO_2 (powder) coatings. The application of ceria sol caused an increase in the ceria content within the resultant coating and favored the refinement from a cauliflower-like morphology (Zn-Co) to a uniform and compact coral-like structure (Zn-Co- CeO_2 sol) [7].

Another increasingly important field in electrolysis is metal coating electrodeposition, and one paper investigates advances in the electrochemical synthesis of Cu coatings. The influence of various electrolysis parameters, such as the type of cathode, composition of the electrolyte, and electrolysis time, on the morphology, structure, and hardness of Cu coatings is reviewed [8]. The critical relative indentation depth (RID), independent of electrolysis parameters, was established for all types of Cu coatings. This value separated the zone where the composite hardness could be equal to the coating hardness and the zone requiring an application of the Chicot-Lesage (C-L) composite hardness model to determine the absolute hardness of the Cu coatings [8].

A fundamental understanding of the electrochemical deposition process of indium and indium gold alloys formed from 0.1 mol/L InCl_3 in 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide ($[\text{P}_{\text{y1,A}}]\text{TFSI}$) was presented in [9]. Using the potentiostatic mode of electrolysis, compact and dense indium deposits composed of indium and an AuIn_2 alloy were obtained. Several processes preceding the formation of the Au-In alloy were involved, including the reduction of In(III) to In(I) and In(I) to In(0) [9].

The review article in this issue focuses exclusively on the morphology of electrolytically synthesized metal powder particles that are correlated to their crystal structure [10]. Metals belonging to a face-centered cubic (fcc) type of crystal lattice, such as Pb, Ag, Cu, and Ni, were analyzed. The shape of the powder particles depended on kinetic parameters, such as the exchange in current density and overpotential for hydrogen evolution reactions, strongly influencing the crystal structure of the particles. With the decrease in the exchange current density value, the crystal structure of the powder particles changed from the strong (111) preferred orientation obtained for the needle-like (Ag) and the 2D (Pb) dendrites to randomly orientated crystallites in particles with spherical morphology (the 3D dendrites, the cauliflower-like, and the spongy-like particles) [10].

3. Conclusions

This Special Issue, “Advances in Understanding Metal Electrolysis Processes”, covers research articles regarding advanced approaches to metal electrolysis processes.

The Guest Editors Professor dr Bernd Friedrich and Professor dr Jovan Jovičević expect this collection of papers to be a helpful reference for researchers working in this field.

Acknowledgments: The guest editors would like to thank all who have contributed directly and indirectly to the successful development of this Special Issue. The guest Editors thank all the authors for their contribution and all reviewers for their efforts to ensure high-quality publications. Credit should also be given to the Editors of Metals for their continuous help, and to the Metals Editorial Assistants. The Guest Editors would like to take this special opportunity to thank Vesna Cvetković, ICTM-University of Belgrade and Dominic Feldhaus, IME-Institute of RWTH Aachen University, for their valuable help in editing this issue.

Conflicts of Interest: The authors declare no conflict of interest.

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