

273c Hydrogen Production from the Electrooxidation of Ammonia Catalyzed by Raney Nickel, Platinum and Rhodium

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Raney nickel alloys (such as NiAl and NiZn) have been used for years to produce active electrocatalysts for various reactions. The active catalysts are particularly suited for the liberation of hydrogen gas from water [1], but also find use as catalysts for fuel cells [2]. The main advantage of Raney catalysts is that they provide inexpensive high-surface-area substrates which may then be deposited or sputtered with a thin layer of noble metals; catalysts produced in this fashion combine large surface areas with low loadings of noble metals and can be utilized in numerous chemical processes.

Active Raney catalysts are made by leaching away the non-nickel metal (such as Al or Zn) from the alloy via immersion in a substance such as NaOH, leaving a high surface area “skeleton” of nickel metal behind. Though active Raney nickel has been used for years as an electrocatalyst, its preparation via electrodeposition has always been a challenge. Results published using earlier methods of Raney Ni electrodeposition [3] have been difficult to reproduce in the laboratory; a more reproducible method must be devised in order to make deposition a more prevalent technology in Raney nickel catalyst development.

Previous studies on Raney nickel deposition have utilized metals such as stainless steel [4] or copper [3, 5] as substrates. However, these substrates have disadvantages; stainless steel requires careful handling and extensive pretreatment to be suitable for electrodeposition, and copper can form surface oxides that reduce the electrical and mechanical integrity of the deposit. Titanium has found increased use in recent years as a substrate for electrodeposition [6,7] due to its strong mechanical properties as well as its readiness to accept an electrodeposit with little pretreatment. Furthermore, a titanium substrate can be used in both alkaline and acidic media at low temperatures with minimal corrosion problems. However, the electrodeposition of Raney nickel onto titanium substrate has not been studied.

This paper describes the procedure for creating a high-surface area electrode from the electrodeposition of Raney nickel powder onto a titanium grid. The procedure to obtain reproducible and scalable electrodes is presented. Although Raney nickel can be deposited onto a substrate in many ways, such as sintering [8], pressing [9], spraying [10], etc., the electrodeposition technique was chosen due to its simplicity, safety, and low cost. The electrodeposition of Raney nickel onto the titanium substrate involves electroplating nickel from a large nickel anode in a nickel plating bath containing suspended Raney nickel particles onto a titanium grid cathode. When current is passed through the solution, Raney nickel particles become embedded in the deposit formed by the reduction of nickel ions from the plating bath and anode. Thus, the electrodeposition method realizes two materials in the final deposit: pure nickel and Raney nickel particles.

The success of the electrodeposition process is known to depend upon two variables: current density and charge density. Optimization of current density and charge density was performed via a factorial design experimental method to maximize the percentage of Raney nickel powder deposited on the grid. Further statistical analysis was performed to show the reproducibility of producing Raney nickel electrodes through this method. Once these variables were optimized, a scale-up of the deposition process was performed to demonstrate the feasibility of the procedure using larger substrates. It is shown that reproducible electrodes were obtained which can find applications in fuel cells as well as electrolytic hydrogen generators.

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