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Optimization of the electrodeposition of Raney nickel on titanium substrate

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Abstract The electrodeposition of Raney nickel onto a titanium grid substrate was investigated. 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. A scale-up of the deposition process was performed to demonstrate the feasibility of the procedure using larger substrates. Reproducible electrodes were obtained which can find applications in fuel cells as well as electrolytic hydrogen generators.

Introduction

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

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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.

It has been widely accepted that the electrocatalytic performance of an electrode is a function of particle wt% in the deposit (r_a) [4]:

$$r_a = \frac{m_R - m_{Ni}}{m_R} \times 100 \qquad (1)$$

where m_R is the weight of the total deposit (Raney nickel and pure nickel combined) and m_{Ni} is the weight of pure nickel in the deposit. Percentage of Raney nickel in the deposit was calculated for each electrode in the study. This value is expected to be dependent upon the amount of current as well as the amount of charge passed in the electrodeposition [4]; these are the two independent variables to be tested in this study.

Experimental

Apparatus

All chemicals and supplies were high purity (above 99.9%) and were supplied by Fisher Scientific, Alpha Aesar or Sigma Aldrich. The electrodes were prepared by electrodeposition from a Watt's bath. The Watt's bath consists of H_3BO_3 30 g/l; $NiCl_2$ $6H_2O$ 45 g/l; and $NiSO_4$ $6H_2O$ 300 g/l [2]. The electrolytic cell used for the deposition of metals is shown in Fig. 1. The cell itself was a 400 ml Kimax beaker. The anode used in the trials consisted of a 2 cm × 2 cm sheet of nickel foil surrounded by approximately 100 g of nickel shot, all of which were enclosed within a cotton bag. A length of Ni wire held the anode. The anode supplied a large store of nickel for the electrodeposition, while the cotton bag served to filter noble metal impurities precipitated at the anode, retaining them in the bag and away from the nickel ion solution [4]. When depositing Raney nickel, 17.5 g/l of Raney nickel alloy powder was added to the Watt's bath before deposition.

In the interest of creating a large-surface-area electrode, a grid made of 18 mesh titanium wire was used as the substrate for Raney nickel electrodeposition. The cathodes used in the trials were titanium grids of similar size and geometry (2 cm × 1 cm). These grids were placed at an angle of 135° with respect to vertical in order to maximize the flux of Raney nickel powder on the surface and were fastened to a titanium wire. All wire leads to the cathodes were wrapped in Teflon tape prior to deposition, so that only the titanium grid (and not the titanium wire) was allowed to form a nickel deposit. Current for the study was supplied by an Arbin potentiostat BT–2000.

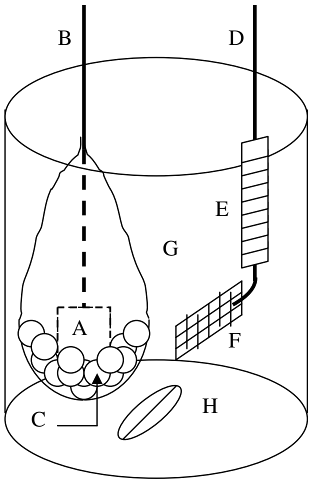

Fig. 1 Electrolytic cell used in deposition of Raney nickel particles: A = Ni foil; B = Ni wire; C = Ni beads; D = Ti wire; E = Teflon tape; F = Ti grid; G = Watts bath and Raney nickel powder; H = magnetic stir bar

Experimental design

The dependent variable of interest in this study was percentage of Raney nickel (r_a) in the deposited layer of each electrode; nickel deposition efficiencies were found in order to calculate r_a. The independent variables studied were current density and charge density; electrode shape and size, geometric positions in the experimental setup and stirring speed of the plating bath were held constant for all trials. Electrode shape and size were held constant for ease of comparison; geometric positions and stirring speed were set constant at settings which maximized the flux of Raney nickel powder on the grid.

Since there were two independent variables (current and charge density) considered in this study, a factorial design experimental method was utilized for the experimental design of the optimization. The power of this method lies in yielding information on the effects of not only parameters but also their interactions in a small number of experimental runs [11].

Dang et al. [4] report that the optimum current density for Raney nickel deposition on a stainless steel (rather than titanium) substrate is 60 mA/cm^2. However, preliminary results showed greater r_a values at higher current densities; in fact, below 60 mA/cm^2, little if any Raney nickel was found in the deposit. Therefore, the value reported by Dang et al. was used as the low value in the experimental range. The other values tested for the current density variable were 80, 100, and 120 mA/cm^2.

Optimum charge density for the Raney nickel deposition on stainless steel substrate was reported by Dang et al. to be near 250 C/cm^2. Again, preliminary results have pointed to this value being low for Raney nickel deposition onto titanium substrate; thus, this value was used as the low value for this experimental range. The medium and high variables for the charge density variable were 350 and 450 C/cm^2, respectively.

Procedure

All experiments were performed on 2 cm × 1 cm titanium grids of the same geometry, realizing a total surface area (front and opposite side) of 4 cm^2. The experimental procedure for the study involved 3 steps: surface pretreatment, electrodeposition of nickel, and electrodeposition of Raney nickel alloy and nickel.

Surface pretreatment

Immediately before electroplating, the titanium grid used was placed in a 32 wt% NaOH solution for 5 min and then rinsed with distilled water. The titanium grid was then placed in a 1 M HCl solution for 5 min, and rinsed again with distilled water before electrodeposition began. These procedures removed most oils and impurities that may have been present on the surface of the titanium grid.

Electrodeposition of nickel

Pretreated titanium grids were placed into beakers containing 350 ml of stirred Watt's bath (containing no Raney nickel powder) and were electroplated at constant current and charge densities, with the former varying between 60 and 120 mA/cm^2 and the latter varying between 250 and 450 C/cm^2. To maintain an even coating thickness on the grid, the grid was turned over after every 250–350 C.

The purpose of this step was to obtain data, which along with data from step Electrodeposition of Raney nickel powder and nickel, would be used to calculate r_a for each trial. The electrodes produced during this step were not used again in the study.

Electrodeposition of Raney nickel powder and nickel

A new set of pretreated titanium grids were placed into a 350 ml stirred Watt's bath (containing 5.25 g Raney nickel powder) and were electroplated using the same experimental scheme as in step Electrodeposition of nickel. Dang et al. suggest that the factors influencing the efficiency of electrodeposition of the Raney nickel powder include solution agitation and grid inclination [4]; therefore, all trials utilized the same stir speed as well as the same grid inclination. As in step Electrodeposition of nickel, the grid was flipped after every 250–350 C to achieve a similar coating thickness on both sides.

Results and discussion

Effect of current density on nickel deposition efficiency

The amount of charge passed remained constant at 1400 C (350 C/cm^2) for trials in this particular test. Figure 2 shows the deposition efficiency for pure nickel (no Raney nickel); values shown in Fig. 2 have an experimental error of 0.2%. It is shown that nickel deposition efficiency is inversely related to current density, realizing efficiencies from 98.8% at 60 mA/cm^2 to 96.9% at 120 mA/cm^2. This phenomenon often occurs during electrodeposition due to parasitic reactions, such as the evolution of hydrogen from the aqueous medium of the electroplating solution; as current rises, the cell potential decreases, encouraging hydrogen evolution. The standard potential (E^0) for hydrogen evolution is –0.828 V, while E^0 for nickel deposition is –0.257 V. The current densities used in the described experimental scheme correspond to cell potentials roughly from –2.2 to –2.8 V. The evolution of hydrogen realized by these cell potentials helps to ensure a catalyst with high porosity.

The values for m_{Ni} used to calculate nickel deposition efficiency are also utilized in Eq. 1 to calculate r_a.

Effect of current density and charge density on percentage of Raney nickel deposited

Figure 3 shows how current and charge density affect r_a. It can be seen in Fig. 3 that r_a rises with increasing current density for all charge densities until reaching a maximum at 100 mA/cm^2; r_a decreases quickly once 100 mA/cm^2 is

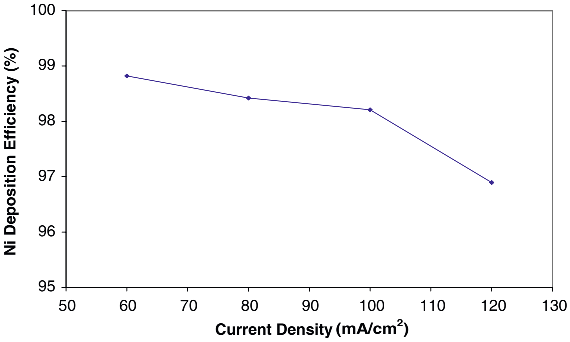

Fig. 2 Effect of current density on Ni deposition efficiency (error = 0.2%)

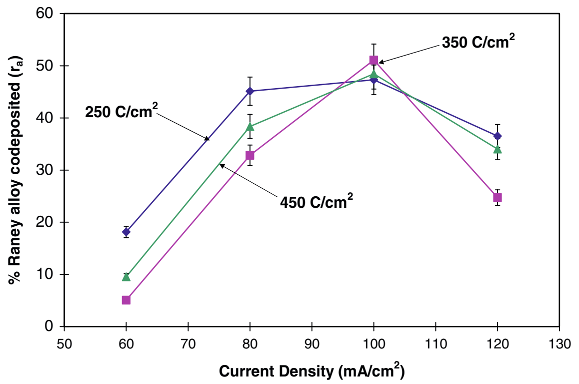

Fig. 3 Percentage Raney nickel deposited as a function of charge and current density

surpassed. These results are congruent with earlier studies by Dang et al. [4] on stainless steel substrate; while the quantitative data is dissimilar due to the differences in substrate, a similar phenomenon (r_a rising to a clear maximum, then a quick drop coinciding with increasing current density) is seen in both studies.

The data presented indicate that while current density greatly influences r_a in the deposit, charge density appears to play a lesser role; this is confirmed in section Statistical analysis. The current density which realizes the highest percentage of Raney nickel in the deposit ($r_a = 51.1 \pm 3.1\%$) is 100 mA/cm^2. The value of r_a for this optimized case compares favorably with those found in an earlier study by Choquette et al. [3], which returned r_a values of 35–40%. This phenomenon is most likely attributable to titanium being a more feasible substrate than copper for Raney nickel deposition. The authors believe this is due to the titanium substrate spontaneously forming a uniform, conductive oxide layer on its surface [12]; conversely, spotty coverage of poorly-conductive oxides can develop on copper substrates [13], leading to deposits with lower r_a values.

Statistical analysis

As mentioned earlier, one of the largest difficulties in producing active Raney nickel catalysts is overcoming poor reproducibility over trials. A common way to measure reproducibility is percentage error of mean ($\%_{\text{error}}$):

$$\%_{\text{error}} = \frac{\sigma}{\bar{m}} \times 100 \tag{2}$$

where σ is the standard deviation of the masses of electrodes produced in this study and $\bar{m}$ is the arithmetic mean of these masses. The value of $\%_{\text{error}}$ for the 18 electrodes produced using the optimized plating parameters is only 6, which reflects satisfactory consistency of the deposits formed by the procedure.

The software program Minitab was used to evaluate the effects of current and charge density on r_a. An initial analysis was performed using a low and high value of 60 and 120 mA/cm^2, respectively, for current density and a low and high value of 250 and 450 C/cm^2, respectively, for charge density. The 94% confidence normal probability plot for this data is given in Fig. 4; in this type of plot, the farther a variable's point is from the central line, the greater the effect of the variable on the response of the system. It can be seen that the dominant effecter for r_a in the range tested is current density; charge density as well as charge and current density interactions are of less importance. Given these conclusions, it was clear that greater attention should be placed on the effects of current density; thus, the additional trials at 80 and 100 mA/cm^2 were performed. Since charge density and its interaction with current density were not as significant, only one other level (350 C/cm^2) was considered for the charge density factor.

In Fig. 3 it is shown that similar r_a values are found when using varying values of charge density for a given current density. Though an optimum was found at 100 mA/cm^2 and 350 C/cm^2, the uncertainties of the r_a values allow any of the charge densities tested at 100 mA/cm^2 to be an optimum. This, along with the conclusions of the statistical analysis, lead the authors to believe that during deposition the charge density (which is directly related to the final weight of the deposit) may be raised or lowered according to the needs of the application, and the deposit should reflect an $r_a > 50\%$ as long as a current density of 100 mA/cm^2 is utilized.

Scale-up of Raney nickel deposition procedure

While a 2 cm × 1 cm electrode is suitable for laboratory work, larger preparations would likely be necessary for industrial applications. In order to test the scalability of the proposed deposition procedure, a larger (2 cm × 2 cm)

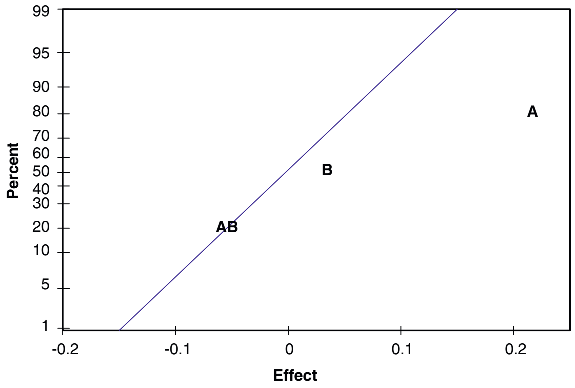

Fig. 4 About 94% confidence normal probability plot for percentage Raney nickel deposited: A = current density; B = charge density; AB = current and charge density interactions

titanium grid was electrodeposited with Raney nickel using deposition parameters of 100 mA/cm^2 and 350 C/cm^2. Since the 2 cm × 2 cm grid's dimensions realize an 8 cm^2 geometric area when considering both sides of the grid, the current applied for this test was 800 mA for a span of 2800 C of charge. These plating values realized a deposit containing 50.7% Raney nickel. This compares well with the values found using the smaller 2 cm × 1 cm grid, and proves that scale-up of the procedure to accommodate larger substrates is feasible.

Conclusions

Titanium metal shows promise as a substrate for Raney nickel deposition from a Watt's bath containing Raney nickel. The deposition of Raney nickel along with Ni ion was optimized by adjusting current and charge densities in the deposition procedure to maximize the percentage of Raney nickel in the deposited layer. It was found that upwards of 50% Raney nickel composition in the deposited layer can be achieved with acceptable reproducibility by applying a current density of 100 mA/cm^2 using the described experimental procedure; the amount of charge passed as well as charge and current density interactions were found to have little influence on the Raney nickel content of the deposit. Scale-up of the deposition procedure to accommodate a larger substrate was proven to be feasible.

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