



Investigation of multi-metal catalysts for stable hydrogen production via urea electrolysis

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ABSTRACT

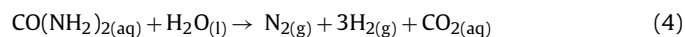
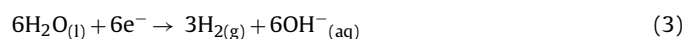
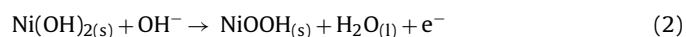
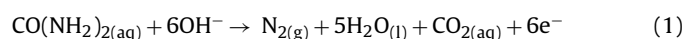
It has been shown that urea electrolysis is a viable method for wastewater remediation and simultaneous production of valuable hydrogen. Inexpensive nickel catalyst is optimal for the oxidation of urea in alkaline media but improvements are needed to minimize surface blockage and increase current density. Multi-metal catalysts were investigated by depositing platinum group metals on a nickel substrate. Rhodium and nickel proved synergistic to reduce surface blockage and increase catalyst stability. Rh–Ni electrodes reduced the overpotential for the electro-oxidation of urea and improved the current density by a factor of 200 compared to a Ni catalyst.

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1. Introduction

1.1. Urea electrolysis

Urea-rich waste waters can be remediated via urea electrolysis in alkaline media to produce valuable hydrogen fuel in support of the emerging hydrogen economy (Eqs. (1)–(4)). Urea is oxidized at a standard theoretical potential of -0.46 V vs. SHE (Eq. (1)) with competing oxidation of the nickel catalyst at 0.49 V vs. SHE (Eq. (2)). Hydrogen gas is produced at the cathode via water reduction at -0.83 V vs. SHE (Eq. (3)) to give 0.37 V standard theoretical cell voltage for urea electrolysis (Eq. (4)) [1–3]. In addition to direct production of fuel from waste, urea electrolysis prevents toxic ammonia emissions and nitrate contamination that currently results from leaving these waters untreated [4,5]. This technology has applications in industries such as wastewater treatment plants or farms and also as on demand fuel production for portable applications. However, the reaction rate for urea oxidation must be improved before successful application at the industrial scale.



1.2. Multi metal catalysts

It has been shown that nickel is the most active electrocatalyst for the electro-oxidation of urea in alkaline media when compared with Pt, Ir, Rh and Ru [1]. However, degradation of the nickel catalyst is a problem, as is observed in oxidation of many organic molecules for which NiOOH is the active nickel form (Eq. (2)) [6,7]. As a result, the high current density indicating initial fast reaction kinetics quickly decreases due to a deactivated catalytic surface. Various methods have been developed to regenerate the active nickel form by voltage cycling or polarity switching [7–9]. However, polarity switching to regenerate the catalyst would disrupt urea remediation and hydrogen production unless both anodic and cathodic electrodes are active for the oxidation and reduction reactions. Finding a catalyst combination that works well for both reactions would allow preparation of identical electrodes, such that polarity switching could be implemented to accomplish continuous urea remediation, hydrogen production, and catalyst regeneration. A suitable catalyst is needed to sustain higher current densities and remain stable for longer times.

Multi-metallic catalysts often provide enhanced activity compared with the individual metals because these metals may have different properties once combined. This can be manifested as a change in activity, stability, or resistance to poisoning and therefore could be beneficial to the kinetics or thermodynamics of an electrochemical reaction [10–12]. For example, platinum group metals such as platinum and iridium increase the kinetics of ammo-

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nia oxidation and thus have been proposed as catalysts [13,14]. In ammonia oxidation, hydroxide ions compete with ammonia for adsorption on active platinum sites [15]. This could also be the case for urea oxidation where the active nickel sites could be occupied by another adsorbed species present in the solution, such as hydroxide ions or unidentified intermediate species. Daramola et al. have performed theoretical investigations on the oxidation of urea in the presence of NiOOH catalyst [16]. The authors indicated that CO groups tend to be strongly adsorbed on the surface of the catalyst, which may be associated with the decrease in catalyst activity over time [16]. If the presence of CO adsorbed groups is limiting the catalytic activity of the electrode as reported by the authors [16], the addition of rhodium to a catalyst surface may selectively adsorb CO or OH⁻ thus preventing self-poisoning and leaving the active catalyst sites open for adsorption and oxidation of the compound of interest [17–20]. In an effort to decrease hydrocarbon, CO, and NO_x emissions in the automotive industry, Pt and Rh are used [19,21]. Hu et al. studied the use of an Rh–Pt catalyst for this purpose and found that these metals are synergistic in that Pt serves to regenerate active Rh sites [19]. Similarly, Hung et al. found that Rh–Pt catalysts are active for the oxidation of ammonia [22]. In general, the presence of noble metal catalysts has been shown to enhance the oxidation of ammonia [18,23]. This activity towards oxidizing CO and N–H bonds could be a contributing factor for urea electrolysis.

1.3. Objective

Within this context, the objective of this paper is to study various catalysts combined with nickel in order to increase the current density and electrode stability during the electrolysis of urea. To achieve the objective different electrodes (Pt–Ni, Pt–Ir–Ni, Rh–Ni, and Ru–Ni) were prepared by electrodeposition on nickel foils. The performance of the different electrodes was compared via cyclic voltammetry (CV), short time cell voltage step, polarity switching, and long time constant cell voltage.

2. Experimental

2.1. Electrode preparation

Nickel foil anodes were constructed by welding nickel wires (Alfa Aesar, 1.0 mm diameter, annealed, 99.5% metals basis) with a Sunstone Engineering resistance welder (CD200SP) to 2.5 cm × 2.0 cm nickel foils (Alfa Aesar, 0.127 mm thick, 99+% metals basis). The nickel foils were sanded with 220 grit Norton all-purpose sand paper under dry conditions and rinsed thoroughly with ultrapure water prior to electrodeposition. Pt, Pt–Ir, Rh, and Ru, were deposited on a 1.5 cm × 2.0 cm section of the electrodes as depicted in sections “b” and “c” of Fig. 1, leaving the top 1.0 cm × 2.0 cm portion (labeled as section “a” in Fig. 1) as bare nickel foils. The section labeled as “c” in Fig. 1, 0.5 cm × 2.0 cm strip, was cut from the end of each electrode after deposition and prior to testing for electrode characterization, leaving 2.0 cm × 2.0 cm as active area for electrochemical testing (sections “a” and “b” in Fig. 1). The top half of the active area (section “a”) was left as nickel foil to ensure both nickel and platinum group metal catalyst sites would be available for reaction.

Plating baths were prepared according to Table 1 using ultrapure water (Alfa Aesar, HPLC grade) with sodium hydroxide (Fisher, ACS grade) and sodium chloride (Alfa Aesar, 99.9%) as electrolytes. Metal salts used include ruthenium (III) chloride hydrate (Acros Organics, 35–40% Ru), rhodium (III) chloride hydrate (Alfa Aesar, 38.5–44.5% Rh), dihydrogen hexachloroplatinate (IV) hexahydrate (Alfa Aesar, 99.9% metals basis), and iridium (III) chloride hydrate (Alfa Aesar, 99.9% metals basis). Deposition of Rh is typically accom-

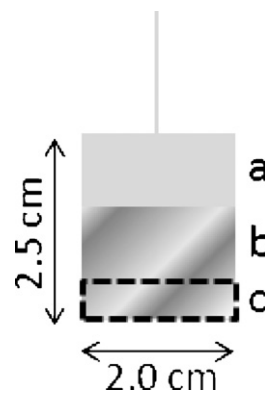


Fig. 1. Schematic of electrodes used during the analysis. Electrode dimensions for (a) bare nickel foil (b) Pt, Pt–Ir, Rh, or Ru deposited on nickel foil substrate and (c) sample section cut for SEM and EDX analysis. Sections (a) and (b) together make-up the total active electrode area used for electrochemical testing.

plished in acidic plating baths not compatible with the active nickel metal substrate desired here. Due to the tendency to form rhodium hydroxide precipitate, basic baths are not preferred [19]. Therefore, a sodium chloride bath was used to provide sufficient conductivity in a non-corrosive weak acid solution [24].

All electrodeposition experiments were performed using a Solartron 1287 potentiostat at a constant potential vs. an Hg/HgO reference electrode (electrodeposition potentials shown in Table 1). The experiments took place at room temperature; the plating solution was stirred with a magnetic stirring bar set at 60 rpm. A loading of 2.0 mg cm⁻² was achieved in each electrode, unless otherwise stated. An open beaker cell setup described previously [1] was used including a Luggin capillary and a platinum foil (Alfa Aesar, 0.127 mm thick, 99.9% metals basis) counter electrode.

The deposition potential was determined by comparing preliminary cyclic voltammetry (CV) sweeps in the range of 0.1 to –0.95 V vs. Hg/HgO in the presence and absence of each metal salt. All CV sweeps performed throughout this work begin at open circuit potential for the first cycle and then proceed to the specified ranges. Multiple sweeps were performed in all experiments such that the voltammograms reported are the sustained periodic state achieved after 3–5 sweeps. The voltammograms of Fig. 2 reveal a reduction peak in the presence of each metal salt that is not present in the background electrolyte, indicating this peak is due to reduction and deposition of the metal salt. Fig. 2a displays peaks for reduction of Pt and Pt–Ir from 3 M NaOH baths at –0.65 and –0.74 V vs. Hg/HgO, respectively. Fig. 2b displays peaks for reduction of Rh and Ru from 1 M NaCl baths at –0.30 and –0.40 V vs. Hg/HgO, respectively. These potentials were chosen near the maximum reduction current for each metal in order to achieve the highest reduction current and deposition rate possible from diluted plating bath solutions. Deposition conditions were proven successful by examining the surface morphology and atomic composition of each electrode via scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) using a JEOL JSM-5300 SEM (1000× magnification, 15 kV) with a combined EDX from EDAX.

2.2. Electrochemical characterization

2.2.1. Cyclic voltammetry

Positive potential sweep CV was used to determine which metal combination was most active for urea oxidation. Sweeps were performed in 1 M KOH electrolyte (Acros Organics, 20607, analytical grade) in the presence and absence of urea (Acros Organics, Extra Pure, 98%) from 0 to 0.7 V vs. Hg/HgO reference electrode at 10 mV s⁻¹ in an open beaker cell [1] similar to that used for electrodeposition. An urea concentration of 0.33 M was used during the

Table 1
Electrodeposition conditions for multi-metal electrodes.

| Electrode | Metal salt added (mg) | Electrolyte | Bath volume (mL) | Deposition potential (V vs. Hg/HgO) |
|-----------|-----------------------|-------------|------------------|-------------------------------------|
| Pt | 134 | 3 M NaOH | 100 | -0.65 |
| Pt-Ir | 123 Pt, 188 Ir | 3 M NaOH | 100 | -0.74 |
| Rh | 127 | 1 M NaCl | 100 | -0.30 |
| Ru | 140 | 1 M NaCl | 100 | -0.40 |

CV experiments to simulate the concentration of urea present in urine. All electrochemical testing was performed at room temperature using a Solartron 1287 potentiostat unless stated otherwise. Similarly, negative potential sweep CVs were performed from 0 to -1.0 V vs. Hg/HgO at 10 mVs^{-1} to determine which combination was more favorable for the cathodic reaction since cathodic performance would be critical for application of polarity switching between two identical electrodes.

2.2.2. Voltage step and constant voltage experiments

Electrodes were compared in voltage step experiments where the total cell voltage was stepped from 1.35 to 1.60 V in 25 mV increments with a platinum foil cathode and stirred at 60 rpm. This range was determined by the CV experiments described above. The ratio of current density in the presence and absence of urea was used to quantify the amount of current due to urea electrolysis versus that due to water electrolysis, which contributes to a small portion of the current density. Constant voltage experiments were also

used to compare the current achieved with these catalyst combinations to previous results [1] achieved at 1.4 V in 5 M KOH electrolyte with each constituent metal alone in order to elucidate synergistic effects from the multi-metallic electrodes.

2.2.3. Polarity switching

Rh-Ni electrodes with loadings of 1.0 mg cm^{-2} and 0.5 mg cm^{-2} (4 cm^2) were employed as the anode and cathode in constant voltage operation at 1.55 V with polarity switching from 1.55 V to -1.55 V such that the role of the cathode and anode were reversed after each hour of testing. A 50 mL aliquot of 0.083 M urea (0.25 g dissolved in 1 M KOH) was subjected to a constant 1.55 V with polarity switching between these two Rh-Ni electrodes. A small concentration of urea was used for the polarity testing to prove the concept of urea remediation with hydrogen cogeneration. After electrolysis, urea concentration was determined using a heat treatment method described previously to quantify urea conversion [1].

3. Results and discussion

3.1. Electrode characterization

Fig. 3a–d are SEM images of sanded nickel foil, Pt-Ni, Pt-Ir-Ni, and Rh-Ni electrodes, respectively. Samples of each electrode were taken for SEM and EDX prior to electrochemical testing and Pt-Ru was not examined due to poor performance during electrochemical testing as described in Section 3.2. The SEM image of Fig. 3a was included to show the surface conditions of the sanded nickel foil substrate prior to electrodeposition of Pt, Ir, or Rh. SEM imaging is informative from a morphological point of view in terms of the relative surface areas of the different deposited metals. The Pt-Ni electrode surface micrograph of Fig. 3b appears as a flat, cracked surface whereas the Pt-Ir and Rh deposits of Fig. 3c and d contain more surface features. The Rh-Ni surface in particular appears to provide the highest surface area due to the numerous spherical particles resulting from the deposition. Observing the form of deposition for each metal could impact future work in that Pt and/or Ir could be revisited upon improvement of deposition methods to increase surface area, perhaps by lower loading or employing an alternate substrate. EDX confirmed the success of electrodeposition of Pt, Pt-Ir, and Rh on Ni foil substrate with a high atomic composition of each desired metal quantified in Table 2. Nickel was not detected on the Pt-Ir-Ni electrode indicating the foil substrate was completely covered by the deposited metal.

3.2. Electrochemical catalyst comparison

Positive potential CV sweeps in the absence of urea, shown as dashed curves in Fig. 4, reveal peaks for the formation of NiOOH on the forward scan and $\text{Ni}(\text{OH})_2$ on the reverse scan, as expected (Eq. (2)) [1]. NiOOH formation begins at 0.45 V and 0.50 V vs. Hg/HgO for Rh-Ni and Pt-Ni or Pt-Ir-Ni, respectively, where the transition on Rh-Ni is more pronounced indicating more of the active NiOOH catalyst is formed. The solid CV curves of Fig. 4 in the presence of urea reveal that Rh-Ni is in fact the most active catalyst for urea oxidation in terms of current density perhaps due to the fact that more

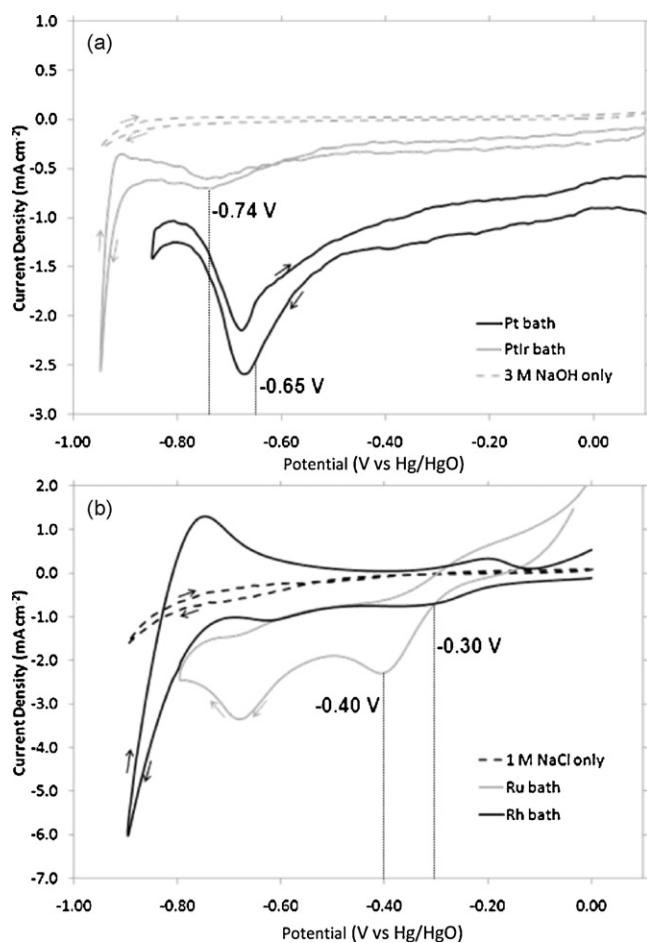


Fig. 2. Cyclic voltammetry determination of the deposition potential for the different metal salts used. (a) Pt and Pt-Ir metal salts in 3 M NaOH and (b) Rh and Ru metal salt in 1 M NaCl. Deposition potentials were chosen based on the maximum cathodic current densities observed for each of the plating salts.

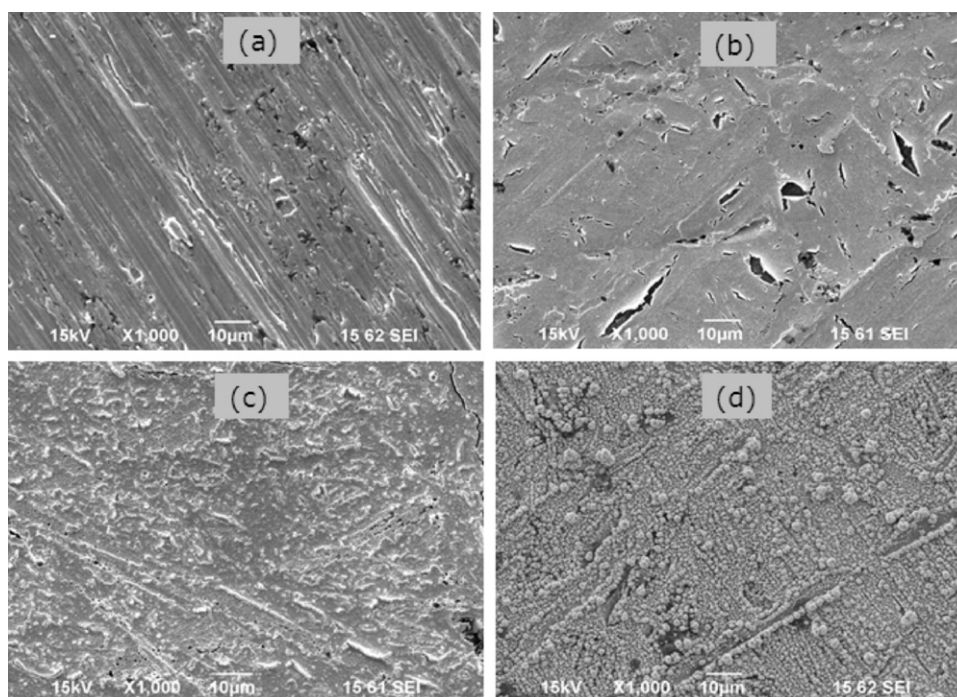


Fig. 3. Scanning electron microscope images of the electrodes used. SEM characterization of (a) bare sanded Ni foil (b) Pt-Ni (c) Pt-Ir-Ni and (d) Pt-Rh electrodes. The Pt-Ni electrode surface micrograph appears as a flat, cracked surface whereas the Pt-Ir and Rh deposits contain more surface features.

NiOOH is present on the electrode surface. The lower onset potential for NiOOH formation resulted in a lower potential required for the onset of urea oxidation on the Rh-Ni surface, which is seen as a shift towards less positive potentials in Fig. 4 as compared with other multi-metal catalysts. The presence of Rh or Pt-Ir diminishes the surface blockage peak near 0.63 V vs. Hg/HgO inherent to the Ni catalyst itself, indicating that a more stable electrochemical reaction can be sustained. Ruthenium activity was evidenced by nearly identical CV curves regardless of the presence of urea in solution and was thus eliminated from further investigations. Preparation and characterization of Rh-Ti and Ti electrodes has been described previously where Rh-Ti refers to Rh plated on Ti with no Ni present [1]. Comparing previous results [1] obtained with Rh-Ti electrodes reveals that Rh is not active for the electrooxidation of urea alone as shown in Fig. 5. This suggests a synergistic catalysis between Ni and Rh because Rh-Ni provides higher, more stable current than either Rh or Ni is capable of alone. Negative potential sweep CVs of these electrodes shown in Fig. 6 reveal that Rh-Ni is also the most favorable catalyst for water reduction whereas Ni alone will not be a feasible catalyst to accomplish polarity switching due to low current densities. Voltage step analyses versus a Pt foil cathode shown in Fig. 7 further confirm that Rh-Ni is the most active electrocatalyst over a wide range of cell voltages. Also, both Rh and Pt-Ir are capable of sustaining a constant current at higher cell potentials, whereas Ni and Pt alone are not, in agreement with the anodic CV sweeps displayed in Fig. 4. The current due to urea electrolysis is maximized at a cell voltage of 1.55 V, calculated as 93% due to urea electrolysis when compared with the same experiment in background electrolyte only.

Table 2
Electrodes characterization via EDX.

| Electrode | Atomic composition (%) | |
|-----------|------------------------|---------|
| Pt-Ni | 72.5 Pt | 27.5 Ni |
| Pt-Ir-Ni | 53.7 Ir | 46.3 Pt |
| Rh-Ni | 83.3 Rh | 16.7 Ni |

3.3. Polarity switching

Rh-Ni electrodes were implemented as both the cathode and anode and held at constant cell voltage of 1.55 V for 24 h with polarity switching each hour using an Arbin BT2000 potentiostat. Absolute current decreases as time progresses through each cycle as shown in Fig. 8 because lower reactant concentrations are present as urea is removed from the solution. Arrows indicate the direction of cycle progression. The bold curves in Fig. 8 demonstrate that Rh-Ni electrodes maintained their original performance upon replenishing the urea solution to its original concentration after 24 h of testing. This indicates that the decreasing current for each cycle could be due to the consumption of urea and that the electrode activity does not decrease with use. Therefore, polarity

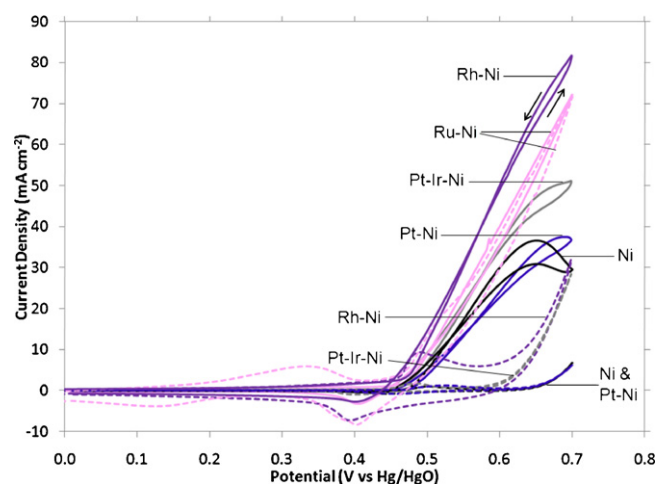


Fig. 4. Cyclic voltammetry comparison of the different electrodes used for the oxidation of urea. Cyclic voltammetry of each catalyst combination was performed from 0 to 0.7 V vs. Hg/HgO at 10 mV s^{-1} in 0.33 M urea, and 1 M KOH electrolyte. Dashed lines represent electrolyte only. The Rh-Ni electrode shows the highest activity towards the oxidation of urea.

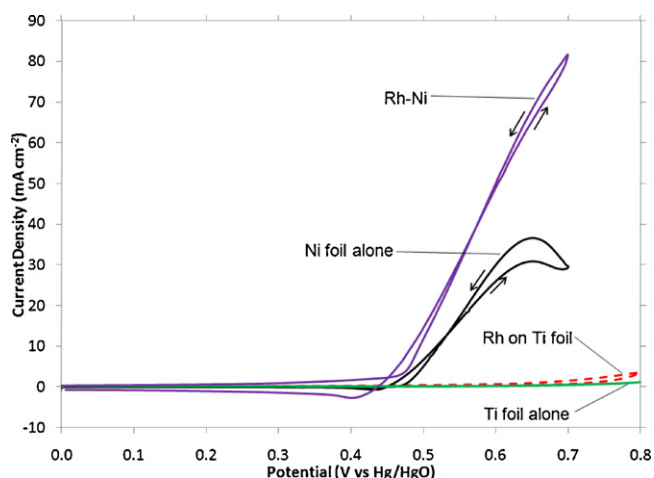


Fig. 5. Comparison of Rh-Ni with Ni, Rh-Ti, and Ti [1] electrodes for the oxidation of urea. Data for Rh-Ti and Ti were reported by others [1]. Cyclic voltammetry experiments were performed from 0 to 0.7 V vs. Hg/HgO at 10 mV s^{-1} in 0.33 M urea and 1 M KOH electrolyte. Rh on Ti is not active for the oxidation of urea as reported by Boggs et al. [1] while Rh-Ni shows a strong activity towards the oxidation of urea.

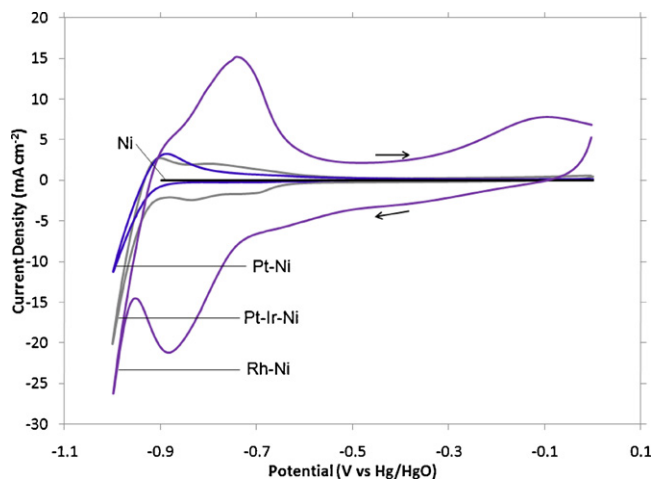


Fig. 6. Comparison of the different electrodes for the reduction of water. CV sweeps from 0 to -1.0 V vs. Hg/HgO, at 10 mV s^{-1} in 0.33 M urea and 1 M KOH.

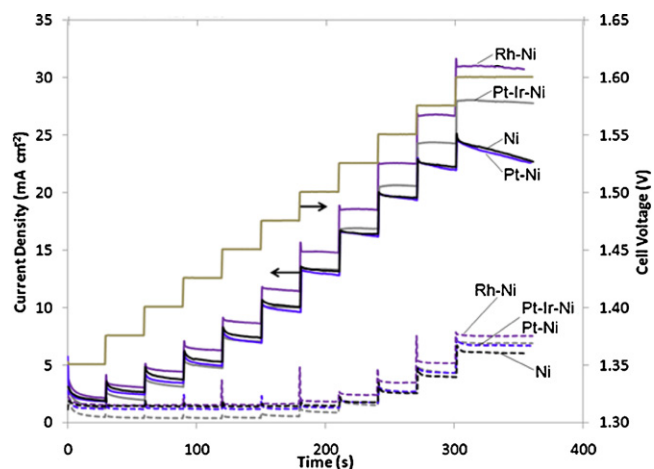


Fig. 7. Step voltage change in the cell. Cell voltage was stepped from 1.35 to 1.60 V with each electrode of interest held as the anode with a platinum foil cathode in 1 M KOH and 0.33 M urea. The solution was stirred at 60 rpm. Dashed lines represent KOH electrolyte only with no urea.

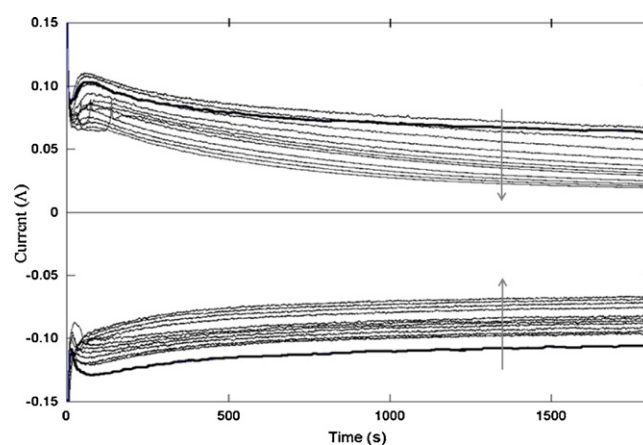


Fig. 8. Polarity switching between Rh-Ni electrodes. The cell voltage was kept at 1.55 V in 1 M KOH and 0.083 M urea, stirred at 60 rpm. The polarity was switched every 1 h such that the anode (Rh-Ni) and the cathode (Rh-Ni) alternated. The curves show decreasing current for each hour cycle in the 24-h test. The bold curves show that the current density is maintained after replenishing the urea in solution to its original concentration.

switching of Rh-Ni electrodes may not be necessary to provide a stable current. The concentration of urea was determined using a heat treatment method [1] after 24 electrolysis hours and revealed that 80% of the urea was consumed, from a 0.083 M initial solution concentration to a final concentration of 0.018 M.

Long-term constant voltage tests were performed at 1.55 V cell voltage without polarity switching to determine the length of intervals that could be sustained before reactivation or polarity switching is needed. Rh-Ni electrodes with loadings of 1.0 mg cm^{-2} and 0.5 mg cm^{-2} (4 cm^2) served as the cathode and anode for the long-term test, respectively. Fig. 9 shows that the current was stable for more than 17 h, with a reduction from 200 to 150 mA absolute current due to urea consumption from solution. It can be concluded that the Rh-Ni catalyst can provide a stable current without polarity switching for up to 17 h provided the reactant concentration is held constant. Further research is needed to determine the stability limit of Rh-Ni electrodes and whether polarity switching is needed in the long term.

Constant cell voltage testing was repeated in 5 M KOH electrolyte to compare with current densities achieved in previous urea electrolysis studies using Ni foil as the catalyst for the electrolysis of urea in alkaline media [1]. Constant voltage performance of the coupled Rh-Ni catalysts cell (loading of 0.5 mg cm^{-2} for the anode and 1.0 mg cm^{-2} for the cathode) shown in Fig. 10 resulted in an increase of current density by 200 times in comparison with the Ni foil alone, providing a steady current density of 50 mA cm^{-2} at a cell voltage of 1.4 V and 60 rpm stirring. The current density (30 mA cm^{-2}) of the electrochemical cell using the coupled Rh-Ni electro-catalysts as anode and cathode in 1 M KOH at 1.4 V is higher than the current density (5 mA cm^{-2}) of the Rh-Ni (anode, loading of 2.0 mg cm^{-2}) and Pt foil (cathode) cell shown in Fig. 7. These results suggest that the choice of cathode also has an effect in the electrolysis of urea. These results are in agreement with Fig. 6, which indicates that the overpotential for the reduction of water in alkaline media is lower in Rh-Ni electrodes than in Pt electrodes.

4. Conclusions

This research has demonstrated that the combination of rhodium and nickel offers a synergistic effect towards the electro-oxidation of urea where nickel provides current density and rhodium reduces overpotential and enhances stability. Rh-Ni catalysts stabilized and increased the current density by 200 times

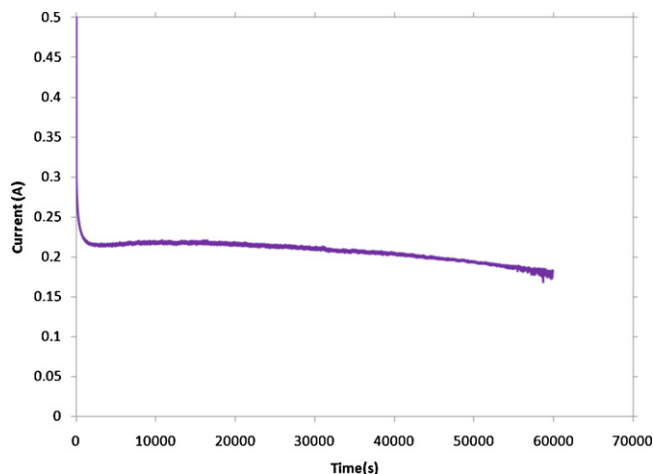


Fig. 9. Electrochemical response of the cell at constant voltage. The cell voltage was kept at 1.55 V between two 4 cm² Rh-Ni electrodes with no polarity switching in 5 M KOH and initial urea concentration of 0.33 M. Anode and cathode were 0.5 mg cm⁻² and 1.0 mg cm⁻², respectively.

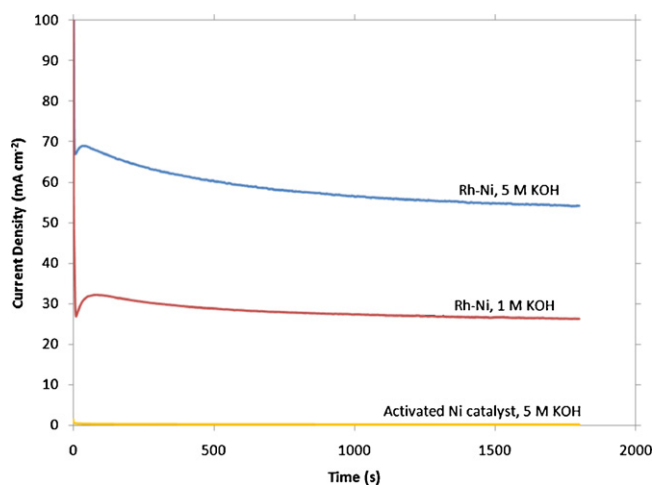


Fig. 10. Comparison of the electrochemical performance of the Rh-Ni electrodes (loading of 0.5 mg cm⁻² and 1.0 mg cm⁻², anode and cathode, respectively) for the electrolysis of urea developed in this paper with previous publications [1]. The cell voltage was kept at 1.4 V. Different electrolyte concentrations were used (1 M KOH and 5 M KOH). The initial concentration of urea in the cell was 0.33 M. The Rh-Ni electrodes show much higher current density than the activated nickel catalyst reported by Boggs et al. [1].

compared to previous Ni catalysts [1]. Addition of Rh to Ni catalysts also greatly enhances electrode life as evidenced by the maintenance of original current density after multiple long-term tests. The faradaic efficiency for the production of hydrogen, hydrogen production rate, and energy consumed during the electrolysis of urea for the production of hydrogen had been demonstrated in the literature [1]. However, the hydrogen production rate was affected by the stability of the anode during the electrolysis of urea and the poor current densities. Therefore, as a result of the improvements performed in this paper with respect to the increase in the current density and the stability and durability of the anode during

the oxidation of urea, it can be concluded that Rh-Ni electrodes can provide stable hydrogen generation while simultaneously remediating urea waste. Nitrate remediation from a dilute urea solution was demonstrated with 80% removal.

The need for polarity switching should be further investigated by conducting longer-term potentiostatic experiments with the urea concentration held constant. Furthermore, the optimization of Rh-Ni catalyst should be pursued with regards to optimal loading and ratio of Rh to Ni along with determination of a minimal loading needed for stability. Various substrates capable of providing higher surface area and hence lower loading requirements should be investigated.

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