

Electrochemical behavior of ammonia at Ni/Ni(OH)₂ electrode

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ABSTRACT

The electrochemical oxidation of ammonia was investigated on a Ni/Ni(OH)₂ electrode prepared by potential cycling of a Ni electrode in 1 M NaClO₄. It was found that oxidation of ammonia is strongly pH dependent and proceeds mainly at pH values above 7. This indicates that NH₃ rather than NH₄⁺ is oxidized on nickel electrodes. Oxidation of ammonia occurs in the potential region of Ni(II)/Ni(III) redox activity resulting in formation of a clear peak. Ni/Ni(OH)₂ is not deactivated during ammonia oxidation even at high ammonia concentrations. A considerable fraction of the ammonia was oxidized to nitrate (11%), while the rest were gaseous nitrogen compounds. It is postulated that nitrogen was formed via a mechanism involving direct electron transfer from ammonia to the anode whereas the formation of nitrate involved oxygen transfer from water to an ammonia molecule.

KEYWORDS

Electrochemical ammonia removal; Nickel electrode; Nickel hydroxide; Nitrate formation; Urine treatment

1. INTRODUCTION

Ammonia containing wastewaters have detrimental effects on the environment, such as eutrophication and fish kills [1] and [2]. Consequently, ammonia removal is one of the main tasks for domestic wastewater treatment. Recently, electrochemical removal of ammonia has been shown to be a promising technique for the degradation of ammonia [3]. Several electrode materials have been tested so far, mainly Pt, Ru, Pd, Ir, Au, Pt–Me binary alloys and metal oxides (RuO₂, IrO₂, and PbO₂) in order to find the best electro-catalyst for ammonia electro-oxidation [4] and [5]. Electrolysis would be especially useful to degrade ammonia (and urea) in source-separated urine, which contributes about 90% of nitrogen to domestic wastewater [6] and [7].

In this work, the electrochemical oxidation of ammonia has been investigated on a nickel electrode in 1 M NaClO₄ at different pH values. Nickel is known to be an effective and cheap catalyst for the oxidation of small organic compounds [8]. However, there is limited previous research on the electro-oxidation of ammonia on Ni. The reported results showed that nickel has little to no activity to catalyze ammonia electro-oxidation in 1 M KOH [9] and [10]. Boggs et al. [6] showed that Ni electrodes can be used to degrade urea in urine. The authors propose that the process might be very useful to remove nitrogen and concomitantly produce hydrogen from urine. In reality, however, stored urine only contains little urea, because of biological urea hydrolysis in the collection system [11]. Thus, ammonia rather than urea might be the nitrogen compound that has to be degraded in urine.

2. EXPERIMENTAL

The electrochemical measurements were carried out in a single-

compartment three-electrode cell (50 mL) using a Eco Chemie potentiostat (Autolab PGSTAT 30). The counter electrode was a Pt wire and the reference electrode was Hg/Hg₂SO₄/K₂SO₄ (MSE). The working electrode was a Ni/Ni(OH)₂ electrode (0.785 cm²) prepared by potential cycling between –1.35 V and 0.7 V vs. MSE (200 scans) of a Ni electrode, at 100 mV s^{–1} in 1 M NaClO₄ + NaOH at pH 9 and 25 °C, in order to form a nickel hydroxide, as given in Eq. (1) [12]



The bulk electrolysis of ammonia was carried out in a one-compartment electrochemical cell (150 mL) using a Wane Kerr PDD 3502A galvanostat. The nickel electrode (16.47 cm²) was used as an anode and two zirconium electrodes were used as cathodes. The concentrations of total nitrogen, total ammonia, nitrate and nitrite were measured with a Hach Lange spectrophotometer DR 2800 using cuvette test Laton (LCK 338, 20–100 mg/l TNb), ammonium cuvette test (LCK 302, 47–130 mg/l NH₄–N), nitrate cuvette test (LCK 340, 5–35 mg/l NO₃–N, 22–155 mg/l NO₃), and nitrite cuvette test (LCK 342, 0.6–6 mg/l NO₂–N, 2–20 mg/l NO₂), respectively.

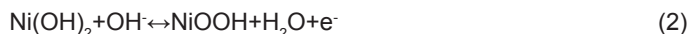
All solutions were prepared using ultrapure distilled water without further purification. The pH of the solution was adjusted with NaOH.

The speciation of ammonia (NH₃) was calculated from measured total ammonia concentrations using the simulation program PHREEQC [13]. The Pitzer approach had to be used to calculate the ion activities, because the ionic strength of the solution was very high (above 1 M). The PHREEQC database was enhanced with Pitzer parameters for ammonium and perchlorate [14], [15], [16], [17] and [18].

3. RESULTS AND DISCUSSIONS

3.1. Electrochemical oxidation of ammonia in 1 M NaClO₄ at pH 9

Figure 1 shows cyclic voltammograms recorded on the Ni/Ni(OH)₂ electrode in the presence of 10–150 mM NH₄ClO₄ in 1 M NaClO₄ at pH 9. The surface redox couple A₁/C₁, centred at ~0.35 V, can be attributed to Ni(II)/Ni(III) redox activity (Eq. (2)), according to [8]

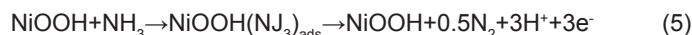


The ammonia starts to be oxidized in this potential region, resulting in an increase of the A₁ oxidation peak with the ammonia concentration. The appearance of the A₂ anodic peak at more positive potential suggests, however, that oxidation of ammonia takes place mainly after the oxidation of Ni(II) to Ni(III), i.e., in the potential region where only Ni(III) exists at the electrode surface. As a consequence, a clear separation of the Ni(II)/Ni(III) oxidation peak from that for ammonia oxidation is observed. Similar electrochemical behavior was reported during oxidation of organic compounds, such as methanol [19] or cyclohexanol [20], on nickel electrodes. In the literature, two mechanisms have been proposed for oxidation of organic compounds (R) on nickel electrode: (a) a direct electron transfer from the organic compounds to the oxide film (Eq. (3) [19]), and (b) an indirect oxidation of organics via Ni(III), resulting in formation of Ni(II) (Eq. (4) [8] and [20])



As shown in Figure 1, ammonia oxidation seems not to involve NiOOH reduction to Ni(OH)₂ because the C₁ reduction peak does

not decrease as the concentration of ammonia increases. Therefore, we might rather consider a direct electron transfer from ammonia to the anode (Eq. (5)) similar to the direct electron transfer postulated for organic compounds (Eq. (3))



The inset of Figure 1 shows the A₂ maximum current peak density as a function of ammonia concentration. The A₂ current peak density increases linearly with ammonia concentration suggesting that oxidation of ammonia on Ni/Ni(OH)₂ is controlled by diffusion. Considering a totally irreversible system, the diffusion coefficient of ammonia can be calculated with Eq. (6)[21]

$$i_p = (2.99 \cdot 10^5) \alpha^{1/2} A C D^{1/2} \nu^{1/2} \quad (6)$$

where i_p (A) is the current peak, A (cm²) is the electrode surface, C (mol cm⁻³) is the ammonia concentration, D (cm² s⁻¹) is the diffusion coefficient, ν (V s⁻¹) is the scan rate and α is the transfer coefficient calculated from Eq. (7)[21]:

$$|E_p - E_{p/2}| = \frac{1.857RT}{\alpha F} = \frac{47.7}{\alpha} \quad \text{mV at } 25^\circ\text{C} \quad (7)$$

where E_p (mV) is the peak potential and $E_{p/2}$ (mV) is the potential where the current is at half of the peak value, R (J mol⁻¹ K⁻¹) is the gas constant, T (K) is the temperature, F (C mol⁻¹) is the Faraday constant.

As will be shown later (Figure 2), ammonia (NH₃) and not ammonium NH₄⁺ is the electrochemically active compound. At pH 9 and in 1 M NaClO₄, NH₃ accounts for 28.8% of total ammonia. Using this fraction, an ammonia diffusion coefficient of $2.8 \cdot 10^{-6}$ cm² s⁻¹ was obtained. This value is lower than the literature value ($1.5 \cdot 10^{-5}$ cm² s⁻¹[15]) indicating that oxidation of ammonia on nickel is not purely mass transfer limited. Despite this open

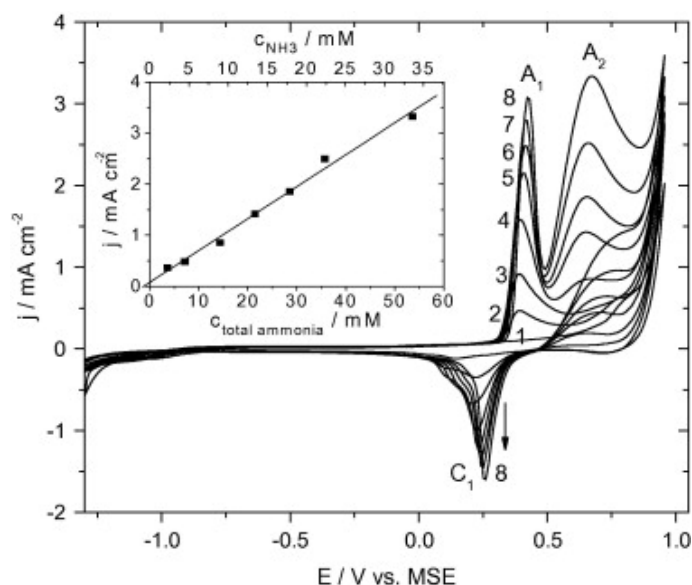


Figure 1: Cyclic voltammograms of (1) 0 mM, (2) 10 mM, (3) 20 mM, (4) 40 mM, (5) 60 mM, (6) 80 mM, (7) 100 mM, (8) 150 mM NH₄ClO₄ in 1 M NaClO₄ + NaOH at pH 9 and 25 °C recorded on Ni/Ni(OH)₂ at 50 mV s⁻¹.

The insets show the current peak density as a function of the total ammonia concentration (NH₄⁺ and NH₃) as well as the NH₃ fraction.

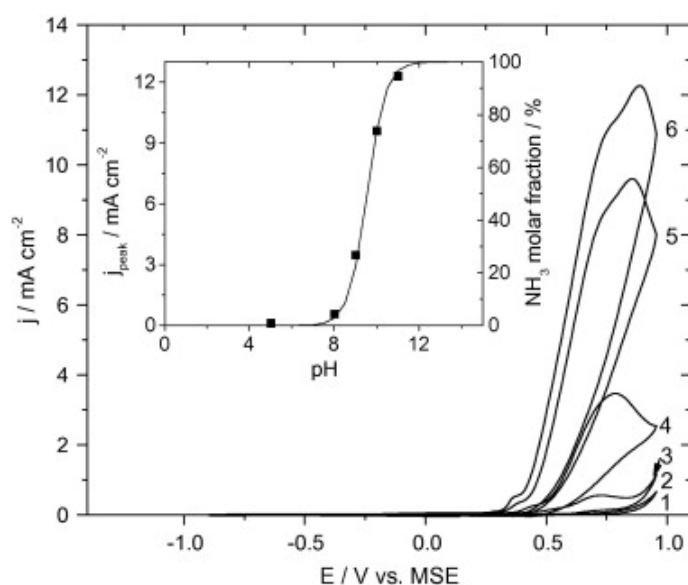


Figure 2: Cyclic voltammograms recorded on Ni/Ni(OH)₂ in the presence of ammonia at various pH values; scan rate 100 mV s⁻¹; the solution contained 150 mM NH₄ClO₄ + 1 M NaClO₄ + NaOH at pH (1) 5, (2) 6, (3) 7, (4) 8, (5) 9, (6) 10, (7) 11; temperature 25 °C. The inset shows: (■) the current peak density as a function of pH and (—) the mole fraction of the ammonia, as a function of pH.

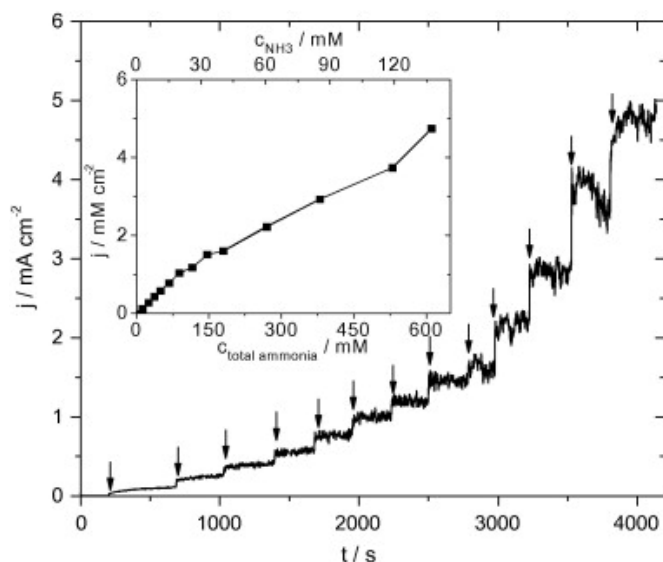


Figure 3: The current response of Ni/Ni(OH)₂ to step-by-step injections of ammonia (marked by arrows) to 1 M NaClO₄ + NaOH at pH 9 and 25 °C; polarization potential 0.65 V vs. MSE. The inset shows the current density as a function of the total ammonia concentration (NH₄⁺ and NH₃) injected to the solution as well as the NH₃ fraction.

question, the linear correlation of ammonia and current suggests that Ni/Ni(OH)₂ electrodes could be used as ammonia sensors. Further experiments would be needed to evaluate this promising application.

3.2. Effect of the pH on ammonia oxidation

Figure 2 shows cyclic voltammograms recorded on Ni/Ni(OH)₂ in the presence of 150 mM NH₄ClO₄ in 1 M NaClO₄ at pH 5–11. It can be seen that oxidation of ammonia is strongly pH dependent and proceeds mainly at pH > 7. As the pH increases, the oxidation peak of ammonia shifts toward higher potentials overlapping partially with oxygen evolution. In strong basic solution (1 M NaOH), the oxidation peak overlapped completely with oxygen evolution and was no longer visible (not shown here).

The inset of Fig. 2 shows the comparison of the A₂ anodic peak intensity with the theoretical curve of the NH₃ mole fraction. A good agreement between the experimental points and this theoretical curve indicates that only NH₃ is electrochemically active and can be oxidized on Ni/Ni(OH)₂. Similar results were obtained on IrO₂ electrode, as reported in [22].

3.3. Chronoamperometric study of ammonia oxidation

Figure 3 shows the current response of Ni/Ni(OH)₂ electrode, polarized at 0.65 V vs. MSE (approximately at A₂ peak maximum), to step-by-step addition of ammonia in a 1 M NaClO₄ supporting electrolyte at pH 9. The continuous increase of the current density with subsequent ammonia injections indicates that the nickel hydroxide electrode is not deactivated during ammonia oxidation even at high ammonia concentrations, on the contrary to other electrode materials such as IrO₂ or Pt [4] and [22]. The current density increases linearly with the ammonia concentration (inset of Fig. 3) although from 100 mM of ammonia, the oxidation of ammonia seems to slow down, probably due to the saturation of the active sites on the electrode surface. However, more studies need to be done in order to confirm this hypothesis.

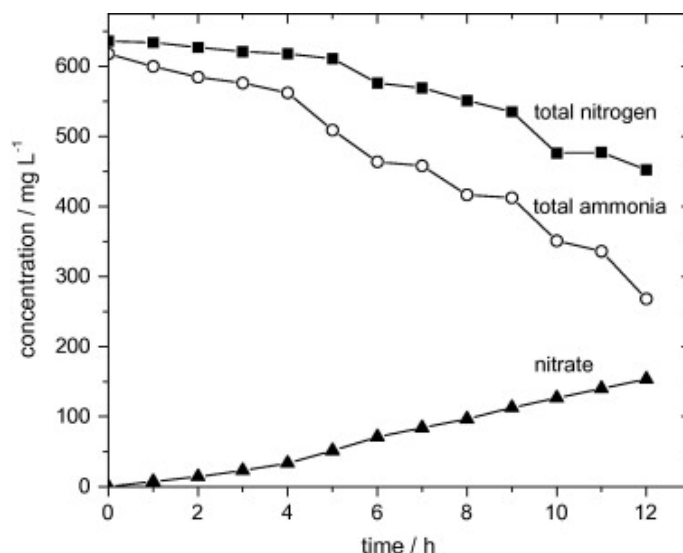
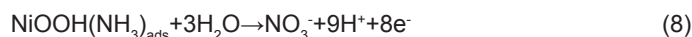


Figure 4: The concentration profile of total nitrogen, total ammonia (NH₄⁺ and NH₃), and nitrate during electrolysis of ammonia under galvanostatic conditions on Ni/Ni(OH)₂; solution: 50 mM NH₄ClO₄ + 1 M NaClO₄ + NaOH at pH 11 and 25 °C; current density 20 mA cm⁻².

3.4. Preparative electrolysis of ammonia

The bulk electrolysis of 50 mM ammonia on the Ni/Ni(OH)₂ electrode in 1 M NaClO₄ at pH 11 was performed during 12 h at 20 mA cm⁻². In a 12-h control experiment without applying current, 6% of ammonia was lost, most likely due to volatilization. Figure 4 shows the concentration changes of total nitrogen, total ammonia and nitrate during the electrolysis. Nitrite was measured as well, but its concentration was below the detection limit. Figure 4 shows that during electrolysis, the amount of total nitrogen and ammonia continuously decreases whereas the amount of nitrate increases. At the end of the experiment (after 12 h, taking into account the ammonia stripping), ~55% of the ammonia was degraded resulting in a degradation rate of ~0.14 mmol cm⁻² h⁻¹. 11% was recovered as nitrate, which leaves 34% for the production of volatile N-species (N₂ and maybe N₂O or NO). It is important to note that at the end of the electrolysis, the solution became grey suggesting corrosion of the electrode.

The direct electron transfer reaction proposed above (Eq. (5)) gives N₂ as a product of ammonia oxidation. However, as shown in Figure 4, a non-negligible amount of nitrate is formed as well. The nitrate might be formed during the oxygen transfer reaction (Eq. (8)) in which water is activated, resulting in a transfer of an oxygen atom to the ammonia molecule



Measurements under potentiostatic conditions would help to verify this hypothesis.

4. Conclusions

It has been shown that Ni/Ni(OH)₂ is a suitable electrode for the electrochemical oxidation of ammonia. The oxidation strongly depends on pH showing that NH₃ rather than NH₄⁺ is oxidized on nickel electrode. The main products of ammonia oxidation are

gaseous nitrogen compounds and nitrate.

Nickel is known to be a cheap electrode material what makes it attractive for wastewater treatment applications. The disadvantage, however, is the corrosion of the electrode and the concomitant release of Ni to the wastewater.

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