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A low-temperature ammonia electrolyser for wastewater treatment and hydrogen production

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HIGHLIGHTS

- A Ni-Cu catalyst and Ni felt substrate was used for ammonia electrooxidation.
- A high current density was achieved (200 mA cm⁻² by CV).
- The system was scaled in a zerogap electrolyser.
- High Faradaic efficiencies for ammonia oxidation (88%) and hydrogen production (99%) were recorded .

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GRAPHICAL ABSTRACT



ABSTRACT

Ammonia is a pollutant present in wastewater and is also a valuable, carbon-free hydrogen carrier. Stripping, recovery, and anodic oxidation of ammonia to produce hydrogen via electrolysis is gaining momentum as a technology, yet the development of an inexpensive, stable catalytic material is imperative to reduce cost. Here, we report on a new nickel-copper (NiCu) catalyst electrodeposited onto a high surface area nickel felt (NF) as an anode for ammonia electrolysis. Cyclic voltammetry demonstrated that the catalyst/substrate combination reached the highest current density (200 mA cm⁻² at 20 °C) achieved for a non-noble metal catalyst. A NiCu/NF electrode was tested in an anion exchange membrane electrolyser for 50 h; it showed good stability and high Faradaic efficiency for ammonia oxidation (88%) and hydrogen production (99%). We demonstrate that this novel electrode catalyst/substrate material combination can oxidise ammonia in a scaled system, and hydrogen can be produced as a valuable by-product at industrial-level current densities and cell voltages lower than that for water electrolysis.

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Introduction

Currently, the energy consumed by wastewater treatment plants (WWTP) represents approximately 1–2% of global energy consumption [1,2]. To add, the energy consumption of plants is expected to rise further by 20%, by 2030, due to global population growth [3,4]. Several government reports mention that the wastewater treatment industry is the fourth most energy-intensive segment in the UK, consuming 7703 GWh y⁻¹ and accounting for as much as 4 million tonnes of greenhouse gases (GHG), approximately 1% of the annual UK's emissions [5,6], and adding to global warming [7].

Biological treatment of wastewater leads to the emission of potent GHGs, such as methane, carbon dioxide, and nitrous oxide. Nitrous oxide emissions are linked to the treatment of ammonia [8] and occur primarily in aerated zones owing to active stripping and ammonia oxidising bacteria. It is one of the dominant contributors to the destruction of the ozone layer and is considered to be up to 300 times more potent than carbon dioxide [9]. Moreover, a significant amount of additional electrical pumping energy is required to support ammonia treatment; 4.6 kg of oxygen is required to treat 1 kg of ammonium ions. Clearly, technological innovations are needed to reduce both, energy consumption in WWTPs and pollutants released into the environment. As such, resource recovery from wastewater, instead of destruction, has been gaining significant interest in the wastewater industry.

With the drive to increase WWTP sustainability, a new treatment process, thermal hydrolysis (THP), has been adopted by some water companies where waste sludge is heated using steam to break down and solubilise macromolecules [10]. The THP technology allows for a much larger production and capture of valuable biomethane [11]. However, the THP and subsequent anaerobic digestion (AD) process leads to increased ammonia concentration in dewatering liquor of $>1000 \text{ mg L}^{-1}$ and can even be in the region of 2500 mg L $^{-1}$ [12]. This raises the need for increased capacity to remove harmful ammonia either via traditional biological processes or using other techniques such as the Anammox process [13,14]. As dewatering liquor from AD contains increasing quantities of ammonia, a great opportunity for recovery of ammonia and reuse occurs in WWTP. With resource recovery, energy could be conserved and greenhouse gas emissions lowered [15].

In the last decade, technological solutions, such as ammonia air stripping, have been implemented to facilitate ammonia removal from wastewater [16–18]. New technology to generate purified ammonia solutions, after the stripping process, are also being tested at pilot plant scale [19]. This has provided the opportunity to use electrochemical processes for treating the recovered ammonia solution [20–23]. In an electrolyser, it is possible to couple the ammonia oxidation reaction (AOR) in alkaline media with the hydrogen evolution reaction (HER) [24]. When compared with water electrolysis (1.23 V), the overall ammonia electrolysis process (Eqs. (1)–(3)) could provide a theoretical reduction of 95% in power consumption [21,25,26].

A:
$$2NH_3 + 6OH^- \rightarrow N_2 + 6H_2O + 6e^ E^\circ = -0.77$$
 V vs SHE (1)

C:
$$6H_2O + 6e^- \rightarrow 3H_2 + 6OH^ E^o = -0.83 V \text{ vs SHE}$$
 (2)

Overall:
$$2NH_3 \rightarrow N_2 + 3H_2$$
 $E^\circ = 0.06 V$ (3)

Moreover, the overall reaction does not consume water and 5.67 g of ammonia will generate 1 g of hydrogen. In essence, not only can ammonia electrolysis provide an inexpensive way to treat ammonia in wastewater and yield pure hydrogen fuel; it can also reduce greenhouse gas emissions by reducing the release of nitrous oxide from wastewater aeration tanks. Low temperature ammonia electrolysis has the potential to make hydrogen production more cost efficient, commercially feasible, and environmentally friendly than conventional hydrogen production processes such as hydrogen generation from natural gas and water [27].

Whilst the conversion of ammonia to benign nitrogen and the coupling of this reaction with the production of hydrogen is an attractive option, aspects, such as the stability and cost of the electrodes needed for the AOR, are barriers preventing industrialisation. Over the years, a variety of materials have been tested as catalysts for ammonia electrolysis in alkaline media, ranging from noble metals, such as gold and platinum, to cheaper alternatives, such as nickel and copper, [23,26,28-30]. Table S1 summarises the important results from the most promising electrode materials reported in the literature. Platinum is known to be the most active monometallic catalyst for ammonia oxidation, with an exceptionally low overpotential [28,31]. However, platinum group metals are rare and expensive and can be poisoned by nitrogen intermediates produced during ammonia oxidation due to high metal-N binding strength [31,32]. In contrast, while inexpensive transition metals such as nickel are inactive towards ammonia electrooxidation, nickel substrates, converted to Ni(OH)₂/NiOOH show good activity, making them promising candidates for long-term use in electrolysers [33,34]. Moreover, according to a theoretical study by Herron et al. [35], copper is second only to platinum in terms of potential for catalysing the electrochemical oxidation of ammonia. When incorporated as an oxide, copper has previously been shown to oxidise ammonia at +0.29 V (vs Hg/HgO) and could achieve high current densities for AOR [36]. However, copper and nickel based electrodes can undergo corrosion and become deactivated over time due to restricted stability in alkaline media [37,38].

Bimetallic nickel-based electrocatalysts have been shown to have good activity for AOR [39–42]. Recently, Xu et al. [42,43] reported that bimetallic nickel-copper (NiCu) catalysts, electrodeposited onto a carbon paper (CP) substrate, have high activity for ammonia oxidation. The NiCu catalyst showed significantly improved stability when compared to Ni and Cu alone. The prepared anode was tested in a beaker electrolysis cell achieving an ammonia removal efficiency of approximately 80%. The cell was operated at constant voltage (typical current density 3 mA cm⁻²) and was shown to operate efficiently at a low applied cell voltage. However, as an anode substrate for high current density operation, carbon is not an ideal material [44] and the authors speculate that the low efficiency at high applied voltage was due to carbon oxidation and oxygen evolution. Zhang et al. [21] also reported the synergistic effect of NiCu alloy nanoparticles, supported on carbon black, as an efficient anode material for ammonia electrochemical oxidation in a beaker electrolysis cell for hydrogen production. The electrolytic cell maintained a low cell voltage of 1.4 V (using a Pt foil cathode) whilst operating at 300 mA cm^{-2} . However, the energy efficiency was determined to drop significantly with increasing current density (50.2% at 300 mA cm^{-2}), due to oxygen evolution and carbon oxidation similar to that reported by Xu et al. Nevertheless, NiCu bimetallic catalysts have been proven to have high activity and stability for ammonia electrolysis at low current density.

A new approach to improve the activity and stability of an electrodeposited NiCu electrode is to couple the catalyst with a high surface area, and stable, electrically conductive substrate such as nickel felt. Typically, nickel felt is used in alkaline water electrolysers, as a gas diffusion layer (GDL) and an electrode, and shows exceptional stability. Moreover, it can provide an excellent surface for electrodepositing the NiCu catalyst onto, and in so doing acts as a combined catalyst coated support and GDL for ammonia electrolysis. In this work, we establish a new method of depositing the NiCu catalyst onto nickel felt, at scale, for ammonia oxidation. The electrochemical activity of the NiCu catalyst/NF substrate at room and elevated temperatures was investigated and the long-term stability of the new electrode material assessed. Furthermore, scaled NiCu catalyst coated supports were tested in a low temperature flow cell anion exchange membrane ammonia electrolyser (AEMAE), at industrial-level current densities, for ammonia oxidation coupled with hydrogen production. Prior research in divided ammonia electrolysers utilised expensive and scarce platinum- or iridium-based anode materials [45,46]. It is our understanding that this is the first attempt at scaling such a process with non-noble electrode materials and evaluating long-term performance. The AEMAE should be capable of electrochemically decomposing ammonia recovered from wastewater streams at low cost, low cell voltage and high current efficiency for it to be considered a potential process for treating wastewater and resource recovery. If a process can be developed the benefits of ammonia oxidation as an alternative anode reaction to oxygen evolution are highly significant for the wastewater treatment industry; a pollutant can be removed and a valuable by-product, hydrogen, can be generated without the consumption of water.

Experimental

Materials

All chemical solutions were prepared with analytical grade reactants and ultrapure water (18.2 M Ω , Alto Type 1, Avidity Science, UK). Sodium dodecyl sulfate (SDS, 85%, Acros Organics, UK), nickel (II) sulfate hexahydrate (NiSO₄·6H₂O, 98%, Alfa Aesar, UK), and copper (II) sulfate pentahydrate (CuSO₄· 5H₂O, >99.0%, Acros Organics, UK) were used for catalytic layer precursor preparation. Nickel felt (300 µm, Dioxide materials, USA) or carbon paper (370 µm, AvCarb MGL370, Fuel Cell Store, USA) were used as electrode substrates for electrodeposition. Aqueous ammonia (35%), potassium hydroxide (pellets, 85%), hydrochloric acid (1 M), and acetone (99%) were purchased from Fisher Scientific, UK.

Electrode preparation

Nickel-copper/carbon paper (NiCu/CP) electrodes were prepared by following the procedure developed by Xu et al. [42] The nickel-copper/nickel felt (NiCu/NF) electrode was prepared by co-electrodepositing nickel and copper onto a nickel substrate, using constant voltage and current techniques with Metrohm Autolab potentiostat/galvanostat system а (PGSTAT204, Metrohm Autolab, UK). Before co-deposition, nickel felt was cleaned in the ultrasonic bath (40 kHz) by sonicating the substrate in acetone for 15 min, then ultrapure water for 3 min, followed by 1 M HCl for 10 min. Lastly, the substrate was sonicated in ultrapure water for 3 min to remove any residual HCl. The substrate was then dried in an oven at 80 °C for 2 h to ensure no moisture remained within the inner layers. The acid wash helped to remove contaminants from the surface of the fibres, Fig. S1.

Deposition electrolyte composition was 0.5 M NiSO₄·6H₂O + 0.05 M CuSO₄ \cdot 5H₂O + 0.5 M SDS (pH 3.5). The washed nickel felt was used as a working electrode, a mixed-metal oxide electrode as a counter electrode, and a Saturated Calomel Electrode (SCE) as a reference electrode. To determine the current density needed to deposit an equal amount of catalyst mass, potentiostatic coulometry experiments were carried out and the charge passed was calculated by integrating the area under the curves. As per the method specified by Xu et al., a potential of -1.34 V vs SCE was applied for the standard 20 s and the resulting current was recorded, Fig. S2(a). It was determined that the electrodeposition of the NiCu electrode should proceed by applying a current density of -45 mA cm⁻² to the electrode until a charge of 0.9C cm^{-2} was reached, Fig. S2(b). After the deposition was complete, the nickelcopper/nickel felt electrode (NiCu/NF) was rinsed thoroughly with ultrapure water and dried at 80 °C for 60 min. To determine catalytic loading, the electrode was weighed before and after deposition. Large scale electrodes (121 cm²) were prepared in a 5 L plating tank (TG 05, Walter Lemmen, Germany), where the Ni GDL was used as a cathode and a mixed-metal oxide was used as an anode. Conditions for the deposition remained the same as aforementioned.

Ni/NF and Cu/NF electrodes were prepared by following the NiCu/NF preparation procedure, but the deposition electrolytes used were either 0.5 M NiSO₄·6H₂O + 0.5 M SDS for Ni/NF or 0.05 M CuSO₄·5H₂O + 0.5 M SDS for Cu/NF electrodeposition.

Materials characterisation

The phases of the NiCu/NF electrode before and after electrolysis were characterised using a 3rd Generation Malvern Panalytical Empyrean X-ray diffraction (XRD). This was equipped with multicore (iCore/dCore) optics giving Cu K_{α 1/2} radiation and a Pixel 3D on the diffracted beam side. To analyse the valence states of the NiCu catalyst, X-Ray photoelectron spectroscopy (XPS) analysis was performed. The samples investigated in this study were attached to electrically conductive carbon tape, mounted onto a sample

bar, and loaded into a Kratos Axis Ultra DLD spectrometer which possesses a base pressure below 1 \times 10^{-10} bar. XPS measurements were performed in the main analysis chamber, with the sample being illuminated using a monochromated Al K α X-ray source ($h\nu$ = 1486.7 eV). The measurements were conducted at room temperature and a take-off angle of 90° with respect to the surface. The corelevel spectra were recorded using a pass energy of 20 eV (resolution approx. 0.4 eV), from an analysis area of 300 mm imes 700 mm. Morphology and elemental composition of the materials were characterised using scanning electron microscopy (1530 VP Field Emission Gun Scanning Electron Microscope (FEG-SEM), Carl Zeiss, Germany) and energy dispersive X-ray spectroscopy (X-MAX EDX, Oxford Instruments, UK). The material composition was further confirmed by high-resolution energy dispersive X-ray fluorescence (ED-XRF) spectroscopy (NEX DE, Rigaku, UK).

Electrochemical characterisation

Electrochemical analysis was performed in a standard threeelectrode cell using a Metrohm Autolab potentiostat/galvanostat system (PGSTAT204, Metrohm Autolab, UK). The working electrode used was the prepared 2 cm² NiCu/NF electrode, taped at the back and top by high-bond polyimide electrical film. The reference electrode used was Hg/HgO (1 M KOH, ALS, Japan) and a cylindrical platinum mesh was used as a counter electrode. The anode and cathode were washed with de-ionised water before each use. A glass jacketed cell was used for experiments. The temperature of the cell and solution was regulated using a temperature control unit (Haake C10/K10, Thermo Fisher, UK). Experiments were performed at room temperature (T = 20 $^{\circ}$ C) unless specified otherwise. Before analysis, the NiCu/NF electrode underwent electrochemical activation by cycling in 0.5 M KOH solution between 0.1 and 0.8 V vs. Hg/HgO for 200 cycles at 25 mV s⁻¹. Cyclic voltammetry (CV) measurements were performed between 0.1 and 0.8 V vs. Hg/HgO at a scan rate of 25 mV s^{-1} unless specified otherwise. The stability of the catalyst in various electrolytes was analysed by chronoamperometry, which was measured at a fixed potential (0.7 V vs Hg/HgO) for 3600 s. A platinum foil electrode and a thermally decomposed iridium oxide film on a titanium substrate (as prepared in literature [47]) were used to benchmark the chronoamperometry tests.

Electrolysis

Constant current bulk electrolysis was performed in a twoelectrode cell with the NiCu/NF as an anode, and a stainlesssteel plate as a cathode. Electrodes were carefully positioned, and the electrode gap was kept constant for experiments. A power supply (CPX200DP, Aim-TTi, UK) was used to apply a constant current of 100 mA cm⁻² and to monitor the cell voltage. The electrolyte in the reservoir was refreshed every 10 h to ensure the correct ammonia concentration was maintained throughout the experiment. Inductively coupled plasma - optical emission spectrometry (ICP-OES, Optima 7300, PerkinElmer, UK) was used to monitor the catalyst mass loss throughout the experiment.

For the flow cell electrolyser, an anion exchange membrane (15 µm thickness, PiperION-A15R, Versogen, USA) was sandwiched between а commercially available 2.5 cm \times 2.5 cm NiFeCo (350 μm , Dioxide Materials, USA) or Pt/ C (0.5 mg cm⁻², 365 μ m, Fuel Cell Store, USA) cathode and the prepared 3 cm \times 3 cm anode material. The membrane/electrode assembly was mounted into cell hardware (Dioxide Materials, USA) with a single-channel serpentine flow field (5 cm² active area). For appropriate cell compression and insulation, 300 μm PTFE gaskets were used for each electrode and a torque of 2 N m was applied to the cell. Electrolyte containing ammonia and KOH was fed at 10 mL min⁻¹ to the anode chamber, and KOH only to the cathode chamber from two separate Duran borosilicate glass bottles (500 mL, Cole Palmer, UK). The electrolyte was circulated back into the top of the containers, where gas/liquid separation occurred before the electrolyte was pumped back into the cell. Experiments were performed at room temperature unless stated otherwise. The electrolyser system was connected to a potentiostat/galvanostat for electrochemical analysis. Electrochemical Impedance Spectroscopy (EIS) was performed in a frequency range of 10 kHz to 0.01 Hz at an applied cell potential of 1.7 V. A constant current for electrolysis experiments was applied by a power supply and a digital multimeter (IDM91E, ISO-Tech, UK) was used to confirm cell voltages across the cell plates. At elevated operating temperature (40 °C, 60 °C), the electrolyte was heated by hot plates (C-MAG HS7, IKA, UK) and the temperature monitored by a digital thermometer.

Gas chromatography (GC) coupled with a thermal conductivity detector (Arnel Clarus 590, 9-inch Elite-Molesieve PLOT and 7/4-inch HayeSep columns, PerkinElmer, UK) was used to assess the purity of hydrogen produced at the cathode and to analyse gases generated at the anode. Helium/ nitrogen carrier gas (99.999%) was used for the analysis (BOC, UK). The gas chromatograph analysed the gases by a dose (not in real-time), with 11 min between samplings. To quantify and qualify the results, the instrument was calibrated by analysis of known H_2 , O_2 , and N_2 standard purchased commercially (PerkinElmer, UK). The GC results were collected when five consecutive samplings produced stable gas composition data (<0.5% variation). This acted as a check to ensure no air was left in the system. Gas flow rates were confirmed using an electronic gas flow meter (FlowMark, PerkinElmer, UK). A photometric cuvette system (DR2800, Hach-Lange, UK) was used to monitor the change in concentration of ammonia (LCK302), nitrite (LCK342) and nitrate (LCK339) over time. The data also allowed for the calculation of Faradaic efficiency, ammonia oxidation rate and selectivity (Eqs S4-S7).

Results and discussion

Preparation and characterisation of NiCu/NF anode

The electrolyte used for NiCu electrodeposition was characterised by cyclic voltammetry to investigate the deposition process and determine appropriate potentials and current densities to achieve a good quality deposit. Cyclic voltammograms were recorded on a nickel felt electrode by scanning

from the open circuit potential (0 mV vs SCE) to negative potentials. The CV shown in Fig. 1 has a reduction peak which occurs at around -480 mV corresponding to Cu²⁺ ion reduction, followed by a decrease in the cathodic current, resulting from diffusion-limited Cu deposition. At approximately -900 mV, the current starts to increase rapidly due to the simultaneous deposition of Ni and Cu. In the reverse scan, the cathodic current starts to decrease up to -385 mV. Nickel and copper stripping peaks are observed at potentials of -200 mV and +500 mV respectively. Fig. S3 confirms these observations and shows CVs of nickel felt in an electrolyte containing only Cu²⁺(a) and Ni²⁺(b) with SDS. The CVs support the corresponding deposition potentials discussed in the experimental methods. However, the CV from the deposition electrolyte has a broader copper stripping peak and a more positive stripping peak potential. Similar results for NiCu alloy deposition have been reported in the literature, where the cathodic Cu^{2+} reduction peak occurs at approximately -300 mV vs. SCE and the cathodic Ni-Cu deposition occurs after -900 mV vs. SCE [48,49]. The broad larger peak observed at 500 mV is in good agreement with the previous reports [50] and suggests this is due to Cu dissolution from two separate layers; a pure copper layer and a bimetallic Ni-Cu layer deposited at more negative potentials.

Xu et al. [42] prepared NiCu electrodes on carbon paper (NiCu/CP) by applying a constant potential of -1.34V vs SCE. However, in this work, when electrodes with a larger geometric surface area (9 cm²) were prepared using potentiostatic control on nickel felt, Fig. 2(a), a severe edge effect was seen, as shown in Fig. 2(b). An uneven coating was obtained with most of the catalyst deposited at the edges of the felt as a poorly adherent powder. To improve the catalytic layer deposition and scalability, the NiCu layer was prepared by applying a constant current in a two-electrode cell, Fig. 2(c). Using this method of preparation a uniform coating was obtained with good adhesion to the underlying substrate. Using Fig. 1 as a guide it confirms that the applied current density of -45 mA cm⁻² was in the region where simultaneous NiCu electrodeposition occurred. Gravimetric



Fig. 1 – Cyclic voltammogram of nickel felt electrode in 0.5 M NiSO4·6H2O + 0.05 M CuSO4·5H2O + 0.5 M SDS, recorded at scan rate 25 mV s⁻¹, 20 °C.

measurements confirmed that 0.5 mg cm⁻² of catalyst loading was obtained using these conditions, matching the result obtained by the constant potential deposition method. To summarise, the electrodeposition of NiCu catalyst using a galvanostatic method achieved superior results (good coverage and adhesion) to a constant voltage preparation method. Furthermore, galvanostatic deposition requires only a two-electrode system and is more practical for larger-scale electrode preparation.

Whilst 2 cm² and 9 cm² electrodes are adequate for smallscale laboratory work, larger electrodes are likely to be required for practical applications. To evaluate the scalability of the suggested deposition technique, a 11 cm \times 11 cm nickel felt was used for the electrodeposition of NiCu catalyst using the described procedure. As presented in Fig. S4, the overall quality of the catalytic layer was of good standard, suitable for use in an electrolyser. This demonstrates that scaling up the process to coat larger substrates is viable.

The SEM images of the prepared NiCu/NF electrode, Fig. 3(a), showed the co-deposited NiCu nanoparticles were evenly distributed, and larger clusters of nanoparticles were observed throughout the surface. The cluster size ranged from 200 to 400 nm. Xu et al. [42] reported the co-deposited NiCu cluster size to be lower (100 nm) but an agglomeration of particles was observed. A higher magnification SEM image, Fig. 3(b), showed the deposited NiCu presented with an isolated, amorphous, cauliflower-like structure. According to EDX measurement data, Fig. 3(c), the overall mass ratio of Ni:Cu on the electrode surface was approximately 9:2 (atom ratio 5:1). Xu et al. reported an atom Ni:Cu ratio of 5:6 on carbon paper. The higher ratio observed is because the EDX technique is not considered surface sensitive. The X-rays are typically generated to a depth of about 2 μ m [51] so an additional signal is picked up from the nickel felt substrate. To determine accurately the composition of the catalytic layer, it was carefully removed and analysed by XRF; the mass ratio of Ni:Cu coating was determined to be 6:4, Fig. 3(d). The catalytic layer had a high copper content even though the nickel/copper salt ratio in the deposition electrolyte was 10:1. This is not surprising and is consistent with standard reduction potentials for these metals. The EDX map (Fig. S5) shows that the deposition of Ni and Cu are non-homogeneous, the particles have copper and nickelrich regions as well as intermediate areas. This could also account for the broad anodic stripping peak of the NiCu deposit. The surface of the catalyst is also rich in copper and the metal displacement reaction between Ni and copper(II) ions could also play a part in enriching the deposit with surface copper [52].

Cross sections of the NiCu/Ni-foam and NiCu/Ni-felt show that the catalyst-coated substrate maintained a porous structure, Fig. S6, after electrodeposition. The cross sections of the catalytic coatings show that the NiCu catalytic layer exhibited a thickness of 400 nm–700 nm. The thickness of the coating was significantly lower than the pore size (5 μ m–50 μ m) of the substrates, indicating that the NiCu layer would not prevent the Ni substrate from functioning as a GDL.

XRD analysis of the NiCu catalyst was performed on carbon paper, to prevent nickel felt interference, to determine the crystalline structure of the as-prepared electrode, Fig. S7. However, while a slight increase in Ni(111) and Cu (111) peak



Fig. 2 – Images of (a) nickel felt (b) NiCu/NF prepared by applying a constant potential of -1.34 V vs SCE (c) NiCu/NF prepared by applying a constant current of -45 mA cm⁻².



Fig. 3 – (a) and (b) SEM images of the NiCu/NF. (c) EDX spectrum and composition data of NiCu/NF electrode. (d) XRF spectrum and composition data of NiCu catalytic coating.

region of $40-45^{\circ}$ was observed, the scattering planes were too weak to produce sharp peaks, suggesting the catalyst formed in this work was more an amorphous, thin-layered structure of NiCu clusters.

Nickel felt as substrate

Carbon paper has been widely used as a gas diffusion layer in electrolysers due to its high porosity and low cost. However, commercial carbon paper is susceptible to corrosion under oxidising conditions through dissolution or the formation of undesirable by-products [44,53]. Typical products of carbon electrooxidation are CO and CO₂, both of which have been linked to the chemical adsorption on the surface of nickel metal, potentially leading to a decrease in electrochemically active sites [54,55]. On the other hand, nickel-based substrates are low cost, have good stability in alkaline media [56,57], and have been used for water and ammonia electrolysis extensively [33,34,58–62]. The intrinsic activity of nickel-based substrates towards ammonia oxidation could lead to the enhanced catalytic activity of the NiCu system and improve long-term electrode stability.

To confirm the benefits of nickel as a substrate, electrochemical characterisation of the NiCu catalyst on Ni felt and carbon paper substrates were compared. The catalytic layer of both electrodes was deposited and preconditioned as detailed in the methodology. For both electrodes, during preconditioning, consecutive scans showed increasing current density of peaks A_1/C_1 with progressive scan number, Fig. S8, attributed to the oxidation of Ni(OH)₂ to NiOOH, Eq. (4) and (5). This is likely due to the formation of a thickening NiOOH layer [33,62,63].

$$Ni^0 + 2OH^- \leftrightarrow Ni(OH)_2 + 2e^-$$
 (4)

$$Ni(OH)_2 + OH^- \leftrightarrow NiOOH + H_2O + e^-$$
 (5)

The micro-nano structures after electrode activation were determined to contribute to a high electrochemical surface area (ECSA). The ECSA calculated by the double-layer capacitance method for the activated NiCu/NF electrode was observed as 85 cm² cm⁻² (170 cm² mg⁻¹), Fig. S9(a), significantly higher when compared to 24 cm² cm⁻² observed for a non-activated NiCu/NF, Fig. S9(b). The electrode exhibited a higher electrochemically active surface after the cyclic voltammetry conditioning, due to the restructuring of nickel felt substrate as mentioned above, by forming Ni(OH)₂ and NiOOH, as well as the formation of Cu₂O/Cu(OH)₂ [64–67], Eq. (6) and (7), and Ni(OH)₂/NiOOH on the catalyst.

$$2Cu^{0} + 2OH^{-} \leftrightarrow Cu_{2}O + H_{2}O + 2e^{-}$$
(6)

$$Cu_2O + 2OH^- + H_2O \leftrightarrow 2Cu(OH)_2 + 2e^-$$
(7)

The difference in ECSA when compared with an uncoated nickel felt (4 cm² cm⁻²) substrate is substantial, Fig. S9(c), indicating the deposited NiCu catalytic coating dramatically increased the electrode's active sites. Additionally, the experiment determined that NiCu catalyst coated onto nickel felt had approximately 8 times higher ECSA when compared to NiCu coated onto carbon paper (11 cm² cm⁻², 31.5 cm² mg⁻¹, Fig. S9(d)). This is a substantial increase and warrants its investigation as a high surface area catalyst for the AOR reaction.

Ammonia oxidation on NiCu/NF

To study NiCu/NF electrode activity for the AOR, electrochemical analysis was performed in a three-electrode cell. Cyclic voltammograms recorded in 1 M KOH solution with and without the presence of ammonia, Fig. 4(a), showed a pair of Ni(II)/Ni(III) redox peaks A_1/C_1 centred around $E_{anodic} = 0.45$ V vs Hg/HgO [62,68]. In the presence of ammonia, a large increase in the anodic current was observed in a potential region between 0.5 and 0.8 V. A high current density of 250 mA cm⁻² was achieved with 0.3 M NH₃ added to the electrolyte although the background current density at 0.8 V was 50 mA cm^{-2} . Nevertheless, 200 mA cm⁻² is the highest recorded current density reported in the literature for a non-noble metal-based electrode, see Table S1. ECSA normalised CVs, Fig. S10, show 3 mA cm⁻²_{ECSA} was achieved at 0.8 V vs Hg/HgO. The current density for ammonia oxidation increased linearly with ammonia concentration at 0.8 V, suggesting an enhanced

performance of the electrode for ammonia oxidation which is controlled by diffusion. Additionally, as seen in Fig. 4(b), NiCu/ NF reached a significantly higher current at 0.8 V as opposed to the NiCu/CP combination reaching only 90 mA cm⁻² under identical conditions.

The CVs show the Ni(II)/Ni(III) anodic peak is seen before ammonia oxidation takes place, indicating the NiOOH species is the main species acting as an electrocatalyst for ammonia oxidation. However, recent studies have shown that in alkaline media, copper in NiCu composites is typically used to enhance the electrocatalytic activity of nickel without participating in redox activities by filling Ni d-band vacancies with Cu electrons [69,70]. This leads to inhibition of volume expansion of Ni²⁺ in alkaline media. Besides, nickel-copper alloys are often employed in harsh conditions due to their well-known stability and performance in corrosive environments [71–73]. The presence of copper on the surface and in the structure of the deposit suggests copper is an important component of the catalyst and could be contributing to activity and stability through these mechanisms.

To further study the enhanced activity of the NiCu/NF electrode, cyclic voltammetric analysis of preconditioned NF, Ni/NF and Cu/NF was performed in 1 M KOH +0.3 M NH₃, the results are presented in Fig. 4(c) and background current are presented in Fig. S11. The cyclic voltammogram of the nickel felt exhibited comparable Ni redox curves observed on NiCu/ NF. The felt showed good activity towards AOR, with a high current density of 71 mA $\rm cm^{-2}$ at 0.7 V vs Hg/HgO. The test demonstrated that the use of nickel substrate can lead to improved AOR efficiency. CV of Ni/NF showed a much higher current density for the Ni redox couple, due to the increased surface area of the electrode. Similar to the NiCu/NF, the peak for the AOR was located after the NiOOH formation peak, confirming the NiOOH was the active species. Accordingly, the Ni/NF electrode demonstrated a high AOR activity and a prominent peak at 0.62 V vs Hg/HgO was observed, reaching a current density of 63 mA cm⁻². Lastly, the CV curve of the Cu/ NF electrode showed similar activity toward the AOR as Ni/NF. However, the AOR peak was shifted to a more positive potential of 0.70 V vs Hg/HgO but demonstrated a similar current density of 68 mA cm⁻². The redox peaks before the AOR reaction also display higher current densities and are consistent with published literature on CuO electrodes [74] that attributed the peaks to the formation and reduction of copper oxidation species, see Eq. (7). Therefore, Cu(OH)₂ was likely responsible for the enhanced AOR activity on the Cu/NF electrode. As Cu is considered too weak to bind the N atoms of ammonia itself, as demonstrated by Xu et al. [42], the observed high current density of a NiCu/NF electrode was likely the result of the synergistic effect of the interaction between the hydroxides of Ni and Cu present on the surface of the felt. This is demonstrated by the Cu/NF electrode having relatively good performance for AOR when deposited onto nickel felt as opposed to showing no AOR activity when deposited onto carbon felt as reported by Xu et al.

Additionally, the effect of temperature on ammonia oxidation reaction was studied by performing cyclic voltammetry at 20 °C, 40 °C, and 60 °C. With increasing temperature, a higher current density was seen for the ammonia oxidation reaction at 0.8 V, Fig. 4(d). At 60 °C, the current density reached

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Fig. 4 – (a) Cyclic voltammograms of NiCu/NF in 1 M KOH with and without the addition of ammonia, recorded at 20 °C. (b) CVs of NiCu/NF and NiCu/CP in 1 M KOH + 0.3 M NH₃, T = 20 °C. (c) CVs of NF, Ni/NF and Cu/NF in 1 M KOH + 0.3 M NH₃, T = 20 °C (d) CVs of NiCu/NF in 1 M KOH + 0.3 M NH₃ at various temperatures, the dotted line presents CV of NiCu/NF in 1 M KOH at 60 °C. All CV measurements were recorded at a scan rate of 25 mV s⁻¹.

325 mA cm⁻². However, it should be noted that at higher temperatures the oxygen evolution reaction is a significant contributor to the current density seen at 0.8 V, as seen in the cyclic voltammograms recorded in 1 M KOH, Fig. S12.

NiCu/NF anode short-term stability

The stability and activity of a NiCu/NF electrode in an ammonia-containing electrolyte are important properties which require further investigation. To determine short-term stability, chronoamperometry experiments were performed. Fig. 5(a) shows the current response of NiCu/NF polarised at 0.7 V vs Hg/HgO for 3600 s. The potential was chosen for analysis, as no current was observed at said potential when no ammonia was added to the electrolyte and the A₂ peak, Fig. 4(a), was almost at the maximum. A sharp current decay was observed in the first few seconds of the experiment, as the ammonia in the vicinity of the electrode was depleted and the diffusion layer expanded. It was observed that with an addition of ammonia, the current density was much higher compared with the background current under identical conditions. In fact, it reached 133 mA cm⁻² before it

started decaying slowly. The decay can be attributed to the electrooxidation of ammonia. In contrast, the electrode in 1 M KOH reached only 2.5 mA cm⁻². Furthermore, the electrode activity was compared with Pt and IrO_2 electrodes, known for their good activity for ammonia oxidation [29,31,46,75]. With the addition of ammonia, Pt and IrO_2 electrodes showed a much lower current density compared to the NiCu electrode, exhibiting 1 mA cm⁻² and 39 mA cm⁻² respectively, Fig. 5(a).

To confirm the NiCu/NF current density was decreasing in response to a change in ammonia concentration and not catalyst dissolution, the chronoamperometry experiment at 20 °C was repeated with additional dosing of concentrated aqueous ammonia. The ammonia in the electrolyte was replenished by 0.1 M NH₃ after 1000 and 2000 s, as seen in Fig. 5(b). With every injection of ammonia, the current density increased close to the original values. The experiment has illustrated that the electrode maintained its integrity and activity towards ammonia oxidation in a highly alkaline environment. Furthermore, the high current density achieved by the NiCu/NF electrode suggests the anode can be used for large-scale commercial applications.



Fig. 5 – (a) Chronoamperograms of various electrode materials in 1 M KOH with an addition of 0.3 M NH₃, recorded at 20 °C at a fixed voltage where maximum AOR current density was observed ($E_{Pt} = -0.1$ V, $E_{IrO2} = 1.6$ V, $E_{NiCu} = 0.7$ V). (b) Chronoamperogram of NiCu/NF electrode recorded at 0.7 V in 1 M KOH + 0.3 M NH₃ with additional injections of NH₃, T = 20 °C. (c) Chronoamperograms of NiCu/NF in 1 M KOH + 0.3 M NH₃ at various temperatures, recorded at a fixed potential of 0.7 V.

To study the NiCu electrode's stability and activity at higher temperatures, chronoamperometry experiments were performed at 40 °C and 60 °C. The chronoamperometric analysis confirmed the cyclic voltammetry results and a significant increase in current density was seen at both, 40 °C (166 mA cm⁻² at 1000 s) and 60 °C (214 mA cm⁻² at 1000 s) when compared to room temperature experiments (122 mA cm⁻² at 1000 s), Fig. 5(c). In agreement with chronoamperometry performed at 20 °C, the current density decreased with time at the elevated temperatures, which can be attributed to depleting ammonia concentration due to electrooxidation and a degree of evaporation, especially at higher temperatures.

To further analyse the catalyst's electrochemical durability, a galvanostatic bulk electrolysis experiment was performed in 1 M KOH +0.3 M NH₃ electrolyte at 20 °C. During the experiment, 100 mA cm⁻² current was applied for 30 h and cell voltage was monitored regularly. At the beginning of the experiment, cell voltage for ammonia electrolysis was 1.80 V, considerably lower compared with water electrolysis of 2.15 V. For ammonia electrolysis, cell voltage increased slowly over several hours, see Fig. 6(a). Each time the electrolyte was refreshed with ammonia, cell voltages dropped to original

values, indicating the increase in cell voltages correlated to the decreasing ammonia concentration.

To determine the stability of the catalytic coating ICP-OES analysis of the electrolyte throughout the 30-h electrolysis was performed, as shown in Fig. 6(b). After placing the electrode in the electrolyte, a sample was taken before current was applied. It showed that 2.9 ng cm^{-2} (1.5%) of the Cu in the catalyst has been lost before the galvanostatic experiment started. This initial loss was probably due to poorly adherent particles on the surface of the electrode. Up to 10 h into the experiment a dissolution rate of 5 ng cm⁻² h⁻¹ was recorded for Cu. The dissolution stabilised after 10 h of electrolysis and no further significant Cu dissolution was observed. Ni presented no considerable dissolution throughout the duration of the experiment with <1% dissolved after 30 h. Overall, the catalyst maintained 73.2% of the copper and 99.9% of the nickel after the experiment commenced, demonstrating good stability in a highly corrosive media. Additionally, SEM images of the electrode after the 30 h galvanostatic electrolysis showed no significant change in the number of cauliflowerlike island on the electrode surface, indicating good longterm stability of the electrode up to 30 h, see Fig. 6 (c) and (d). However, at high magnification, it was observed that



Fig. 6 – (a) Cell voltages recorded during a 30 h galvanostatic electrolysis at 100 mA cm⁻², T = 20 °C. The right-hand Y axis shows ammonia concentration throughout the experiment. (b) Dependence on galvanostatic electrolysis time on dissolution of catalyst material. The inset shows Ni and Cu dissolution rate (solid line) and percentage of Ni and Cu remaining in the catalyst (dashed line). (c) and (d) SEM images of the NiCu/NF after 30 h galvanostatic electrolysis.

nano-plate structures were formed on the surface of the cauliflower-like formations. This is in good agreement with previous literature, denoting formation of a thicker $Ni(OH)_2$ layer [76,77].

To assess the change in the composition of the catalyst of the electrode, before and after bulk electrolysis experiments, XPS was performed. The XPS analysis of the as-prepared NiCu/NF electrodes revealed high features at binding energy (BE) of 856 eV and 932.5 eV for Ni 2p and Cu 2p regions respectively, Fig. 7(a), (b), suggesting the presence of hydroxide species, formed on the as-prepared NiCu catalyst. In good agreement with the literature [78,79], the peaks revealed the NiCu catalyst was oxidised when exposed to air after preparation. Elemental nickel peak can be observed in the Ni 2p region, indicating the passivation layer (nickel oxide/hydroxide) was thinner than the XPS sampling depth. For copper, the Auger region data confirmed that copper (I) oxide and copper (II) hydroxide were the major phase, Fig. S13. After 30 h of electrolysis, the response to NiO was reduced, indicating the formation of thicker Ni(OH)₂ layer Eq. (4), Fig. 7(c), confirming the results of the SEM analysis described above. Overall, in the Ni 2p region, Ni(OH)₂ remained the presiding species present. The fact that the NiOOH peak was not present indicates that the oxyhydroxide had reacted with ammonia and was reduced back to the hydroxide species [33]. Similarly to Ni results, in the Cu 2p region, the Cu₂O has been converted to Cu(OH)₂, Fig. 7(d).

To conclude, after 30 h of electrolysis in an alkaline ammonia electrolyte, $Ni(OH)_2$ and $Cu(OH)_2$ are the dominant

species on the NiCu/NF catalyst surface. The fact that XPS confirmed both hydroxides are present at the end of the experiment and ICP-OES has shown good electrode stability, merits the further testing of this system in an anion exchange membrane electrolyser.

Flow cell electrolyser for ammonia oxidation and hydrogen production

Upscaling the ammonia electrooxidation reaction from a bulk electrolysis cell to a zero-gap flow cell is a critical step. It allows a more rigorous study of electrode activity, stability, and mass transport effects. Previous work with NiCu catalysts has used electrodes of only 2 cm² active electrode area and typically bulk electrolysis cells where the mass transport process is not representative of a full-scale cell. Electrolysis in an undivided cell is possible because nitrogen is produced at the anode (rather than oxygen), lowering the risk of explosion. However, if nitrogen oxyanions (NO₂⁻ and NO₃⁻) are produced at the anode, they could be reduced at the cathode, resulting in a decrease in hydrogen production efficiency. Lastly, the mass transport in three-electrode cells is not representative of a full-scale electrolyser. Accordingly, as illustrated in Fig. 8(a), a zero-gap 5 cm² electrolyser was set up in which the prepared NiCu/NF electrode was used as an anode/GDL and a commercial NiFeCo as a cathode/GDL. The electrodes were separated by an anion exchange membrane to support the selective transfer of OH⁻ from the anode to the cathode. This electrolyser (which we have called an AEMAE), allows



Fig. 7 – XPS spectra of NiCu/NF electrode (a) Ni 2p_{3/2} region before electrolysis; (b) Cu 2p_{3/2} region before electrolysis; (c) Ni 2p_{3/2} region after 30 h ammonia electrolysis at 60 °C; (d) Cu 2p_{3/2} region after 30 h ammonia electrolysis at 60 °C.

separation of the anode and cathode off-gas, improves cell resistance, and represents electrolysers typically used in hydrogen production industry. To determine the practicability and benefits of the NiCu/NF electrode, several parameters, including ammonia concentration, operating temperature and current density were investigated and to benchmark the process, alkaline ammonia electrolysis was compared with water electrolysis.

A plot of cell voltage versus current density, recorded at room temperature, for different concentrations of ammonia (0.1-1 M) in 1 M KOH anolyte is shown in Fig. 8(b). For low ammonia concentrations, cell voltages increased after 50 mA $\rm cm^{-2}$, probably because of hydroxide ion oxidation competing with ammonia oxidation at the anode. With higher concentrations of ammonia, a decrease in cell voltage at higher current densities was observed. For example, the cell voltage at 200 mA cm^{-2} was 1.90 V, and 1.81 V for 0.3 M and 1.0 M respectively. As a benchmark, cell voltages were recorded in the absence of ammonia. The presented data showed that cell voltages were higher for all current densities tested. In addition, electrochemical impedance analysis was conducted at a cell voltage of 1.7 V, for a 1 M KOH electrolyte with and without the addition of 1 M ammonia, see Fig. S14. Ammonia electrolysis was the more favourable reaction, with

a much lower cell resistance. This also matched with the observation of lower cell voltages at high ammonia concentrations. Cathode off-gas flow rates were also monitored and followed closely the calculated theoretical values, Fig. 8(c). Cell voltages recorded in this work were compared to cell voltages obtained for alkaline water electrolysis using a commercially available laboratory scale Dioxide Materials AEM water electrolyser (WE) process. The cell voltages from the commercial AEMWE were, on average, 105 mV higher for all current densities tested, at 20 °C, in comparison with the AEMAE presented in this work, Fig. 8(d).

In previous experiments, it was concluded that the operating temperature was a key parameter for the AOR. Therefore, flow cell experiments were carried out at 20 °C, 40 °C and 60 °C, as seen in Fig. 8(e). At 40 °C, cell voltage for ammonia oxidation decreased by an average of 28 mV across the current density range, reaching 1.78 V at 200 mA cm⁻². At 60 °C, the cell performance decreased by an average of 63 mV compared with 20 °C, with a cell voltage of 1.74 V at 200 mA cm⁻². Overall, while electrolyser performance improved with increasing temperature, the disadvantage of additional power consumption, and equipment needed to heat large volumes of electrolyte at scale must be considered. Furthermore, the performance of the NiCu/NF electrode at room temperature



Fig. 8 – (a) Schematic of the electrolyser for ammonia oxidation. (b) Cell voltage dependence on the concentration of ammonia, recorded at 20 °C. (c) Ammonia electrolyser cathode gas flow values compared to theoretical values at various current densities. (d) Comparison of AEMAE and commercial AEMWE (Dioxide Materials) cell voltages at 20 °C. (e) AEMAE cell voltage dependence on temperature.

shows promise and outperforms the work reported by Xu et al. [42] where a current density of 3.0 mA cm^{-2} was achieved at a cell voltage of 1.4 V. Our results show that using a NF substrate, an operating current density of at least 100 mA cm⁻² is sustainable in a flow cell with a cell voltage lower than that of water electrolysis at 20 °C.

Long-term stability

A long-term stability test of a NiCu/NF electrode was performed at room temperature with 1 M KOH +1 M NH₃ as an anolyte and 1 M KOH as a catholyte in the AEMAE. To select the optimal current density for the long-term test, gas chromatographs of the anode reservoir off-gases at various current densities were recorded, Fig. S15. At 200 mA cm⁻², oxygen and nitrous oxide concentrations were 26.1% and 4% respectively with a hydrogen cross-over of 4%. At 150 mA cm⁻², 12.7% of oxygen and 5.4% of nitrous oxide were observed with a hydrogen concentration of 3.8%. The optimal current density for long-term ammonia electrolysis was selected as 100 mA cm⁻² as the gas chromatography results gave the lowest oxygen and nitrous oxide content of <5% and <1% respectively, and the highest concentration of nitrogen at 93%.

Therefore, the electrolyser current was held at 100 mA $\rm cm^{-2}$ for 50 h and gas flow rates, cell voltages and ammonia consumption were monitored throughout the duration of the experiment. Fig. 9(a) shows a plot of cell voltage, ammonia concentration and Faradaic efficiency against time for ammonia electrolysis in the AEMAE. The cell voltage remained fairly stable; it increased by 30 mV over the first 30 h of the test and then by 60 mV over the last 20 h of the experiment. The cell voltage started at 1.69 V and reached 1.78 V after 50 h. This increase is due to decreasing ammonia concentration and when the ammonia was replenished at the end of the experiment, the cell voltage returned to the original value. A feed and bleed system would keep the ammonia concentration constant and maintain the low cell voltage. Ammonia consumption was approximately 0.56 M during the 50 h test, and it was consumed at an average rate of 0.011 M h⁻¹. Throughout the experiment, the concentration of ammonia decreased linearly with time. The Faradaic efficiency of the reaction was determined by comparing the ammonia consumption rate to the theoretical values and was calculated to be 87% for the experiment. The Faradaic efficiency was also calculated for every sampling interval, and it was established that the rate remained relatively constant throughout the experiment.

The gas chromatography analysis of the anode off-gases, shown in Fig. 9(b), confirmed the anode off-gases contained 92.8% nitrogen, 4.3% of oxygen, 2.8% of H₂ and 0.1% of nitrous oxide. Hydrogen cross-over to the anode chamber in traditional water electrolysers can pose a serious explosion hazard. In an AEMAE, the major gaseous product is nitrogen, and the risk of hydrogen explosion is decreased. However, it is important to note that membrane thickness in this work was only 15 μ m, and, with increasing AEM thickness, the hydrogen cross-over rate would likely be reduced. The nitrite and nitrate concentrations were also monitored, as seen in Fig. S16. The data obtained was used to calculate the average selectivity and was found to be 85.8% for nitrogen, 2.3% for NO₃⁻ and 11.9% for NO₂⁻.

Cathode off-gases were monitored continuously, and it was determined the hydrogen purity was 99.6% indicating the exchange of gases from the anode to the cathode was minimal, Fig. 9(c). Gas Production flow rates from both the cathode and anode were also stable with 3.45 \pm 0.40 mL min⁻¹ of hydrogen being produced from the cathode throughout the



Fig. 9 − (a) Record of cell voltages, Faradaic efficiency, and ammonia concentration profile for 50 h ammonia electrolysis at a fixed current density of 100 mA cm⁻², 20 °C. (b) Gas chromatogram of the off-gases collected during the 50 h ammonia electrolysis experiment from the anode reservoir (c) from the cathode reservoir.

experiment. The hydrogen production rate remained close to the theoretical value (3.5 mL min⁻¹) denoting the electrolyser had high efficiency towards hydrogen production. The flow rate of the off-gases produced at the anode increased from 1.14 ± 0.27 mL min⁻¹ to 1.44 ± 0.36 mL min⁻¹ after 30 h of electrolysis, slightly higher than expected, indicating some oxygen evolution was occurring during ammonia electrolysis which may have contributed to the rising NO₃⁻ and NO₂⁻ concentration. Kapałka et al. [33] proposed that the nitrate, with Ni-based electrodes, might be generated during the oxygen transfer process involving the activation of water. This results in the transfer of an oxygen atom to the ammonia molecule, according to Eq. (8):

$$NiOOH(NH_3)_{ads} + 3H_2O \rightarrow NO_3^- + 9H^+ + 8e^-$$
 (8)

Jiang et al. [80] investigated the role of Cu in Ni-Cu bimetallic catalysts for the production of nitrite. The group determined that NO2⁻ was formed significantly in higher quantities on electrodes containing $Cu(OH)_2$ as opposed to NiOOH alone. In-situ FTIR analysis showed that *NO2 intermediate was found on both Cu(OH)2 and Ni0.8Cu0.2 electrodes, whereas *N₂H₄ was detected on NiOOH electrode only. This finding indicated that AOR utilises the Nad oxidation pathway on the Cu site and the NH_x dimerization pathway on the Ni site. The authors stated that the AOR route on Ni-Cu oxyhydroxide was highly comparable to the Cu site, which resulted in the production of nitrite. Additionally, Johnston et al. [81] have also researched Cu(OH)₂ based electrodes for nitrite production and hypothesised that nitrite is formed as the primary product of homogenous Cu^{2+/3+} mediated AOR at high KOH concentration (>0.5 M). The authors proposed that nitrite and nitrate could be formed on Cu(OH)₂ electrodes by the following mechanism:

$$NH_3 + 7OH^- \rightarrow NO_2^- + 5H_2O + 6e^-$$
 (9)

$$NH_3 + 9OH^- \rightarrow NO_3^- + 6H_2O + 8e^-$$
 (10)

The stability, activity, selectivity, and high Faradaic efficiency of the NiCu/NF electrode in an AEMAE for 50 h demonstrate the potential of the catalyst/substrate combination as a low-cost non-noble metal anode material. Furthermore, in combination with a non-noble metal cathode, the electrolyser has the capability to treat ammonia and couple this reaction with hydrogen production at low temperature.

To further assess the stability of the electrolyser, the AEMAE was operated in a typical set-up that could be used in industry. The cell was run for 8-10 h a day for 4 weeks (20 days, 170 total hours) and the ammonia was topped up daily, by additions to the anode reservoir, to 1 M. To eliminate any potential instability of a NiFeCo cathode, a Pt/Carbon cloth electrode was used as a cathode for this experiment. NiCu/NF was used as an anode and Piperion was used as a membrane, and the cell was assembled as usual (described in Methodology) and run at 100 mA ${
m cm}^{-2}$ in 1 M KOH + 1 M NH₃ anolyte. As shown in Fig. 10(a), the cell voltage remained stable for the 170 h of the experiment with the lowest cell voltage of 1.47 V and the highest of 1.50 V. The minimal variation in cell voltage of only 0.03 V demonstrated that the NiCu/NF electrode was resilient and could be employed in an industrial setting for at least 4 weeks of daily operation with an ammonia electrolyte. Moreover, due to cell compression, the catalysts transferred directly to the membrane surface during the electrolyser assembly and therefore worked similarly to a catalyst-coated membrane, Fig. 10(b).

The 5 cm² AEMAE tested in this work can produce 0.0187 gh⁻¹ of hydrogen at 100 mA cm⁻². With a NiFeCo cathode a specific energy consumption of 45.5 kWh kg⁻¹ H₂ was calculated using a working cell voltage of 1.69V. Replacing this with a Pt/C cathode, the electrolyser could offer a lower energy demand, with a specific energy consumption of 40.0 kWh kg⁻¹ H₂ (at a cell voltage 1.5V). Both these results surpass commercial electrolysis cells, which consume ~47.5 kWh kg⁻¹ H₂, and using a Pt/C cathode the 2050 IRENA target of <42 kWh kg⁻¹ is achieved [82]. The cost of Pt can be offset by its good performance and stability in alkaline media; the reduction in energy consumption would lead to lower electricity consumption and therefore lower OPEX costs over time.



Fig. 10 – (a) Cell voltages recorded during 20-day electrolysis at 100 mA cm⁻² T = 20 °C. (b) Piperion A15R membrane after 170 h electrolysis.

Conclusions

In this study, a new low-cost nickel-copper catalyst, electrodeposited onto a high surface area nickel felt substrate was studied as an anode for ammonia electrooxidation. Firstly, electrode preparation was optimised, and it was determined that the electrodes prepared by galvanostatic deposition on NF showed superior catalyst distribution on the substrate surface and provided a scalable method of preparing electrodes. A cauliflower-like micro-nano structure formation recorded an ECSA of 85 cm^2 cm^{-2} , higher than that achieved using less stable carbon paper. In a three-electrode cell, the NiCu/NF electrode showed excellent activity for the AOR, reaching a current density of 200 mA cm⁻² at 0.8 V vs Hg/HgO at 20 °C, the highest current density recorded for ammonia oxidation from a non-noble metal catalyst. XPS and ICP-OES analysis confirmed the electrocatalyst showed good stability after a 30 h ammonia electrolysis test at 20 °C with both Ni and Cu species present on the electrode surface at the end of the experiment.

NiCu/NF electrodes were used as a porous transport electrode in an AEMAE. A commercially available non-noble metal catalyst was used to support the hydrogen evolution reaction at the cathode. A long-term experiment at a current density of 100 mA cm⁻² showed the electrode maintained a stable ammonia oxidation rate (0.011 M h⁻¹) and high Faradaic efficiencies of >85% for at least 50 h at 20 °C. The NiCu/NF electrode has shown good selectivity of 85.8% for nitrogen production and the cathode off-gas analysis has shown the hydrogen purity to be >99% at predicted flow rates. The cell voltage was typically 105 mV lower than an equivalent water electrolysis cell operating at 20 °C.

These findings provide important information to aid the future design and scale-up of an AEMAE for ammonia removal and hydrogen production. Such a process could bring significant benefits to the water treatment industry especially with the advent of new technology to strip, recover and generate purified ammonia solutions from wastewater. Converting ammonia to nitrogen and hydrogen, for local energy use, is an attractive prospect for wastewater treatment companies particularly when ammonia concentrations in effluent are on the increase. Many have committed to achieving net zero carbon emissions over the next decade and to produce 100% of their energy needs from renewable sources. The generation of on-site hydrogen from a waste ammonia stream has the potential to help them achieve these goals in the medium/long term and reduce the environmental impact of wastewater treatment.

Author contributions

Egle Latvyte: methodology, validation, formal analysis, investigation, writing — original draft, writing — review and editing (supporting). Xuanheng Zhu: methodology, validation, investigation. Liang Wu: methodology, supervision. Rong Lan: supervision, writing — review and editing (supporting). Peter Vale: conceptualisation, supervision. John Graves: conceptualisation, writing — review and editing (lead), project management, funding acquisition.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Egle Latvyte reports financial support was provided by Severn Trent Water Ltd. John Graves, Xuanheng Zhu, Liang Wu, Peter Vale report financial support was provided by European Commission. John Graves has patent #United Kingdom - Patent Application No. 1820678.9 pending to Coventry University.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijhydene.2023.05.076.

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