Electrocatalytic Process for Ammonia Electrolysis: A Remediation Technique with Hydrogen Co-Generation

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Alkaline ammonia electrocatalysis offers a favorable technique for hydrogen generation and simultaneous conservation of environmental sustainability. In this work, the electrooxidation of ammonia on platinum-Iridium (Pt-Ir) electrocatalyst was studied in 5 M potassium hydroxide (KOH) solution. The effects of operating conditions such as, temperature and ammonia (NH_3) concentration were investigated. Ammonia electrooxidation current density increased at elevated temperature and ammonia concentration. The maximum ammonia conversion was 78 % for 2300 ppm ammonia. Furthermore, the maximum hydrogen flow rate obtained was 25 L/ h and the corresponding energy consumption is 1.6 W h/ L-H_2. The hydrogen purity obtained from the gas chromatography was 86 %. Ammonia is poisonous to the proton exchange membrane (PEM), hence ammonia ion selective electrode was used to determine the amount of ammonia present in H_2 gas stream produced and was found to be < 0.1ppm.
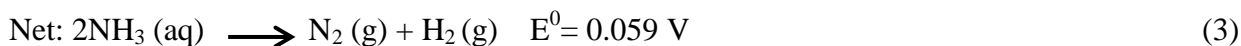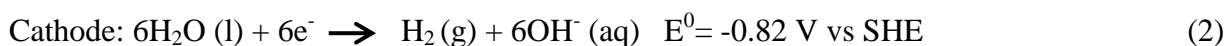
1. INTRODUCTION

Ammonia emissions from agricultural operations and industries could lead to ground water contamination and severe health problems to living organisms [1-4]. Ammonia is also an excellent hydrogen carrier containing high hydrogen capacity of 17.6 wt. % and a specific energy density of 50 % more than liquid hydrogen [5, 6]. The hydrogen produced via ammonia vector is envisaged for use in fuel cells to produce electric power or directly in internal combustion engines, for mobile and stationary applications such as in the telecommunication sector. To date, there are two methods for ammonia decomposition to produce hydrogen and nitrogen [7]. One is ammonia cracking and the other

is ammonia electrolysis. However, ammonia cracking requires an operation temperature higher than 500 ∘C [8]. Ammonia electrolysis can be done through direct liquid ammonia electrolysis and alkaline ammonia electrolysis, Little et al. [9]. For direct liquid ammonia electrolysis, a potential of 2 V is applied on Pt electrodes immersed in ammonia liquid (99.99 %) in the presence of metal amide (e.g. KNH_2) as a supporting electrolyte [9]. Though, in this method, the experimental electrolysis voltage of more than 1 V is high for practical use.

In this work, we present alkaline ammonia electrolysis where potassium hydroxide (5 M KOH) is used as an electrolyte, while Pt-Ir alloy is used as an electrocatalyst for both cathode and anode. This technology has the ability to eliminate ammonia in water, thereby solving pollution problem while simultaneously producing hydrogen [10, 11]. However, the ammonia concentration is limited to $\leq$ 3000 ppm to avoid damage to the electrodes. The mechanism of ammonia oxidation is 1) the adsorption of ammonia on to Pt surfaces, 2) dehydrogenation of ammonia into various adsorbed intermediates (N, NH, NH_2), 3) reaction of the intermediates to form $N_2H_{2,ad}$, $N_2H_{3,ad}$ and $N_2H_{4,ad}$ which then react with OH^- to produce nitrogen [12]. At the anode side, OH^- abstract protons from ammonia to form water and the nitrogen atoms adsorbed on the electrode surface are oxidized into N_2, Eq. (1).

Anode: $2NH_3$ (aq) + $6OH^-$ (aq) $\longrightarrow$ N_2 (g) + $6H_2O$ (l) + $6e^-$ E^0= -0.77 V vs SHE   (1)
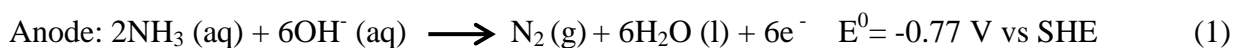
Water molecules dissociate into hydrogen and hydroxyl ions at the cathode side, and this resembles alkaline water electrolysis, Eq. 2.

Cathode: $6H_2O$ (l) + $6e^-$ $\longrightarrow$ H_2 (g) + $6OH^-$ (aq) E^0= -0.82 V vs SHE   (2)

Net: $2NH_3$ (aq) $\longrightarrow$ N_2 (g) + H_2 (g) E^0= 0.059 V   (3)

The ammonia oxidation potential at 25°C is -0.77 V (vs. standard hydrogen electrode SHE) which is 59 mV less negative than the value of -0.83 V (vs. SHE) for hydrogen evolution in alkaline solution [13]. Therefore, thermodynamic values favor the combination of hydrogen production and ammonia electrooxidation than for production of hydrogen via water electrolysis, of which the cell voltage is 1.23 V.

2. EXPERIMENTAL/ MATERIALS AND METHODS

All chemicals used in this study are of standard grade and were used as received. Aqueous ammonia 28 % and ≥85 % potassium hydroxide pellets were purchased from Sigma Aldrich. The ammonia electrolyser system was made by original equipment manufacturer (OEM), Figure 1. To execute ammonia electrolysis experiment, a desired ammonia concentration is prepared in 5 M potassium hydroxide (KOH) solution. This solution is pumped through in-line heaters to a 10 cell stack electrolyser with a volume capacity of 5 liters. The collective geometric active area of each electrode is

200 cm^2 and the volume of each electrode compartment is 90 cm^3. Where required, a continuous or batch reaction method is used. The cell stack comprises Pt-Ir electrodes separated by Celgard polypropylene diaphragm, Figure 1 (inset).
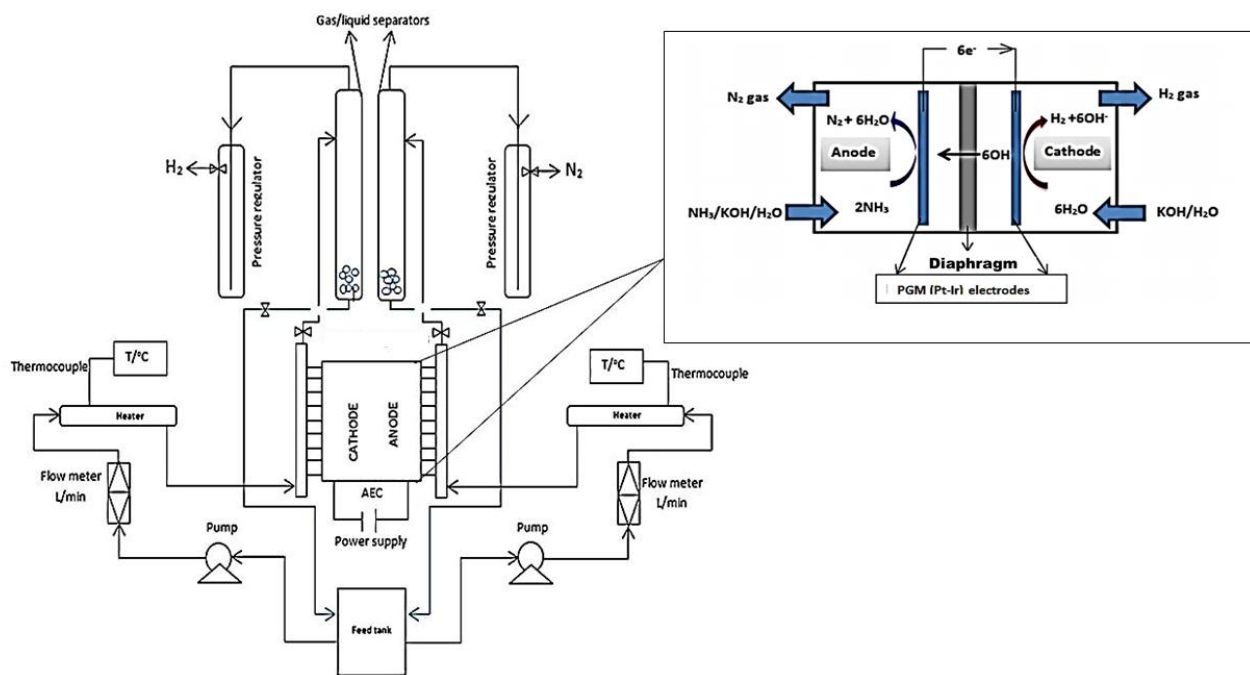

Figure 1. Schematic representation of ammonia electrolysis process for hydrogen production

In order to drive the electrochemical reactions, the solution temperature was set at 55 ^{o}C, followed by applying 0.900 V across the stack using a DC power supply (TDK-Lambda, GENH6-100). As a result, water reduction at the cathode side produced hydrogen gas and ammonia oxidation at the anode side produced nitrogen gas. A lab-view® based program was used to record the data from the power supply. The ammonia concentrations in KOH were measured in the beginning and end of each electrolysis cycle.

High performance ammonia ion selective electrode (ISE) (No.9512HPBNWP) in conjunction with ISE/pH meter (Thermo Scientific Orion STAR A214) was used to determine ammonia concentration. This electrode was calibrated prior use, and 1 ml of the NH$_3$/KOH solution was diluted to reduce the pH and ammonia concentration to the measurable range of the instrument. The anode and cathode gases were analyzed using an online SRI-8610C GC equipped with two TCDs, one HID, two molecular sieve columns (6' 13x and 6' 5A), and one HayeSep D column (6').

3. RESULTS AND DISCUSSION

3.1. The effect of temperature and ammonia concentration

Figure 2 shows voltage against current density at different temperatures. The conductivity of the electrolyte (KOH) increases at elevated temperatures. Thus, ammonia electrooxidation is

accelerated by increasing the temperature. This trend is observed when the current density increases with increasing temperature [14]. Furthermore, at high concentration of ammonia, more NH_3 will be adsorbed on the electrode surface, and the current density increases as seen in Figure 3. However, at high concentration of ammonia the electrodes become saturated and the intermediates (NH and NH_2) block the catalytic sites [15]. As a result, the current density is no longer enhanced anymore.
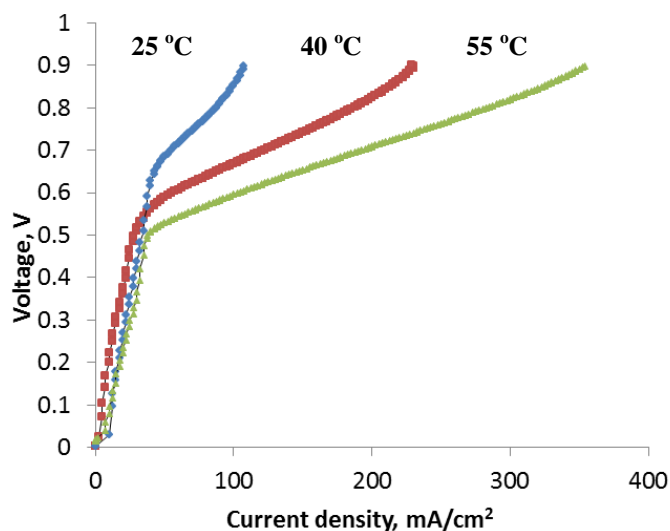

Figure 2. Shows the effect of temperature on current density. The cell retention time (Rt) was 12.5 min at 0.4 L/min using a continuous reaction mode with applied voltage of 0.900 V.
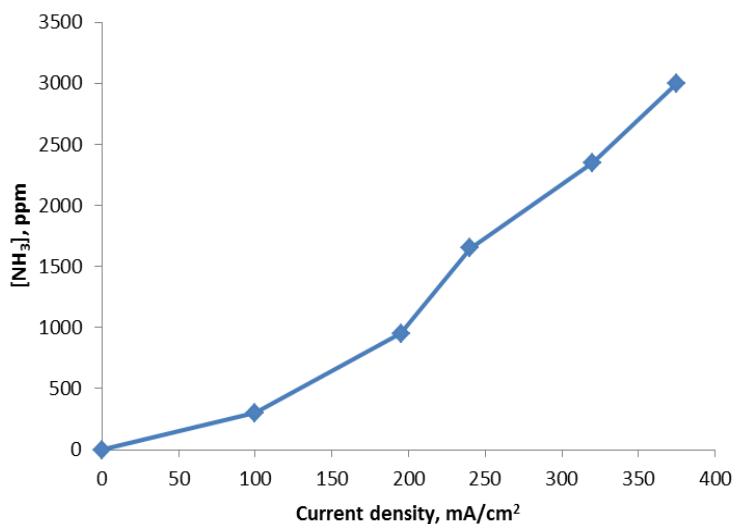

Figure 3. The effect of ammonia concentration on current density. The cell retention time (Rt) was 25 min at 0.2 L/min and 55 ^{o}C using a continuous reaction mode with applied voltage of 0.900V.

3.2. Hydrogen production and energy consumption

Figure 4 shows the consumption of energy and power for ammonia electrolyser cell at different hydrogen production rates. As the hydrogen flow rate increases due to applied current, the power and energy consumption to generate hydrogen increases, Figure 4. The highest volumetric hydrogen

production rate (25 L/ h) was obtained when the cell was operated at a constant current density of 250 mA/ cm^2. The corresponding power and energy requirement is 43 W and 1.6 W h/ L-H$_2$, respectively.
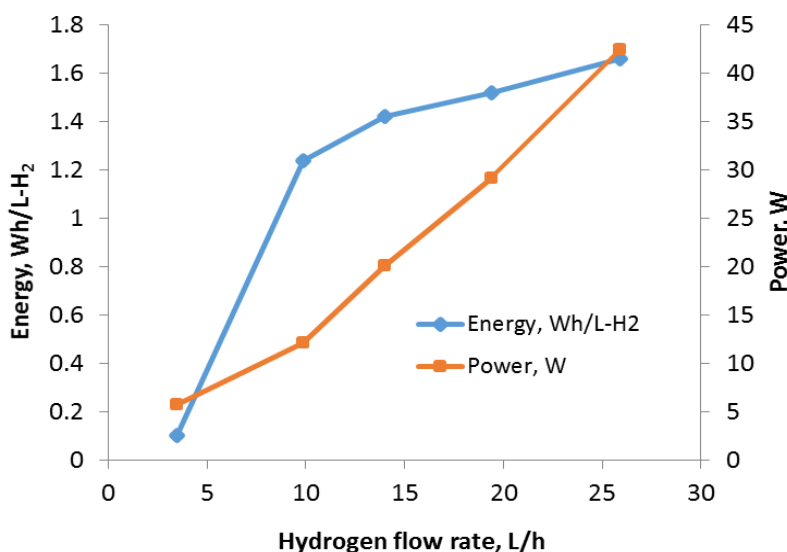

Figure 4. Volumetric hydrogen production rates and the required energy and power input for the hydrogen production. The cell retention time (Rt) was 12.5 min, 2000 ppm NH$_3$ in 5 M KOH at 55 ^{o}C using a batch reaction mode.

3.3. Kinetics for ammonia electrooxidation

The ammonia electrolyser can remediate water at the same time producing hydrogen, it is therefore important to study the kinetics for ammonia removal. However with this technology, KOH will still need to be separated from water after ammonia removal. Hence, Palaniappan et al. developed this technology to utilise solid alkaline polymer electrolyte gel instead of KOH solution [16]. Figure 5 shows the ammonia degradation with time at different current densities. As the current density is elevated, ammonia concentration reduced per electrolysis time. At low current density i.e. 75 mA/cm^2, ammonia degradation was not effective. However, when the current density is increased to 150 mA/cm^2 the electrolysis process was effective, resulting in almost complete removal of ammonia. Ammonia degradation effectiveness can be investigated by means of pseudo first-order kinetics [17]. Therefore the rate of ammonia degradation can be expressed as:

$$d\,[NH_3]/dt = -k\,[NH_3] \qquad (4)$$

Integration of the above equation gives:

$$\ln\,[NH_3]_o/[NH_3]_t = kt \qquad (5)$$

where $[NH_3]_0$ and $[NH_3]_t$ corresponds to the initial and final ammonia concentration, respectively.
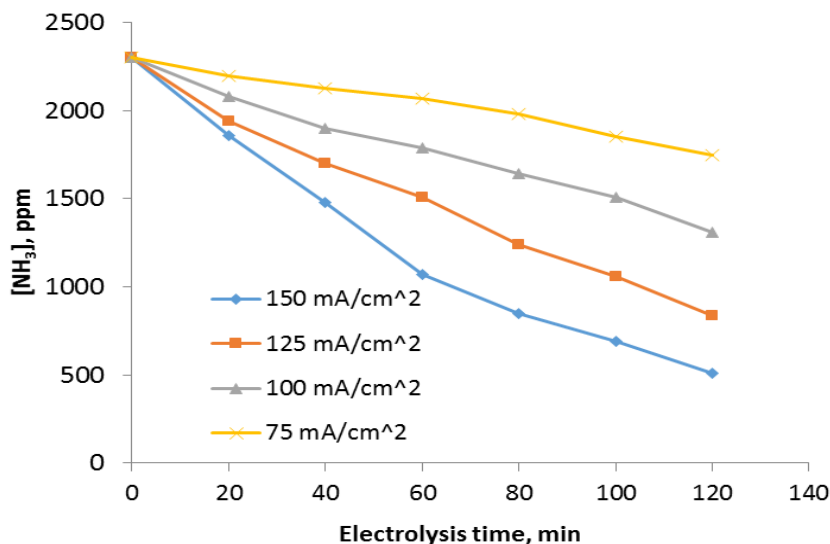
Figure 5. Ammonia decay curves at different current densities. The cell retention time (Rt) was 12.5 min at 0.4 L/min and 55 ^{o}C using a batch reaction mode with applied voltage of 0.900V.
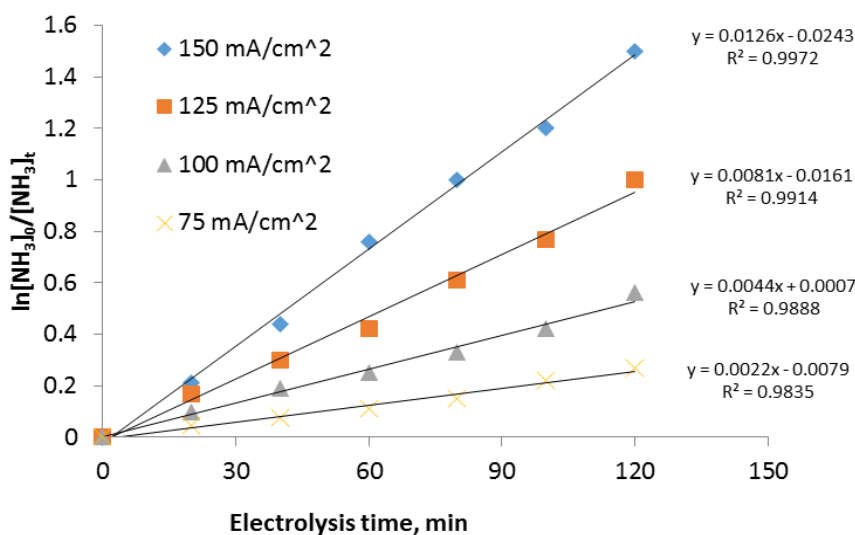

Figure 6. Pseudo first-order kinetic model of the electrochemical treatment data

The use of Eq. 5 to the ammonia degradation data produces a linear curve as shown in Figure 6. This indicates that ammonia electrooxidation obeys by pseudo first-order reaction kinetics.

The kinetic rate coefficients were calculated from the slopes of the linear curves for every set of process parameters. We observed that, ammonia consumption rate increases as the current density is increased. Figure 7 shows the electrochemical ammonia degradation efficiency against time at different current densities. At 75 mA cm^{-2}, the degradation efficiency was 24 % and at higher current density (150 mA cm^{-2}), 78 % efficiency was achieved. Table 1 shows the values of the kinetic rate coefficients and half-lives (ln2/k) obtained at different ammonia concentrations and current densities.
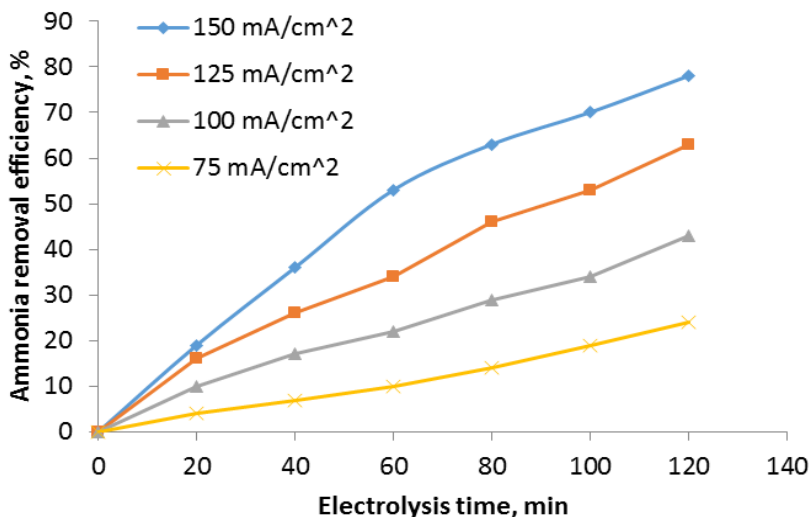
Figure 7. Ammonia removal efficiency as a function of time and current density.

Table 1. Shows kinetic rate constants and half-lives at different ammonia concentrations and current densities. Initial ammonia concentration is 2300 ppm.

Final ammonia concentration, ppm	Ammonia removal efficiency, %	Current density mA/ cm^2	k, min^{-1}	Correlation coefficient R^2	Half life min
500	78	150	0.0126	0.9972	55
840	63	125	0.0081	0.9914	85
1311	43	100	0.0044	0.9888	158
1750	24	75	0.0022	0.9835	315

3.4. Gas Analysis

The relative humidity of produced gases is $27.5^{o}C \pm 73$ % indicating wetness, a chiller at $-5^{o}C$ was used to freeze the moisture so that further gas analysis can take place. Using gas chromatography, the gas from the hydrogen outlet shown a prominent peak at Rt =1.641 which is attributed to hydrogen and a less prominent nitrogen at Rt=2.94, Figure 8. The H_2 purity obtained is 86 %. From the nitrogen outlet, the chromatogram shown a less prominent hydrogen peak at Rt=1.45 and a nitrogen peak at Rt=2.908. The nitrogen produced at the anode side permeates through the diaphragm to the cathode side, hence nitrogen peak is observed at the hydrogen outlet. Similarly, the hydrogen generated at the cathode will possibly permeate though the diaphragm to the anodic side of the electrolytic cell. Ammonia is poisonous to PEM fuel cells [18], therefore it is important to determine the amount of ammonia in the hydrogen gas stream. Ammonia ion selective electrode was used to quantify ammonia present in the H_2 gas stream and it was found to be compatible with H_2 fuel cell, which is less than 0.1 ppm.
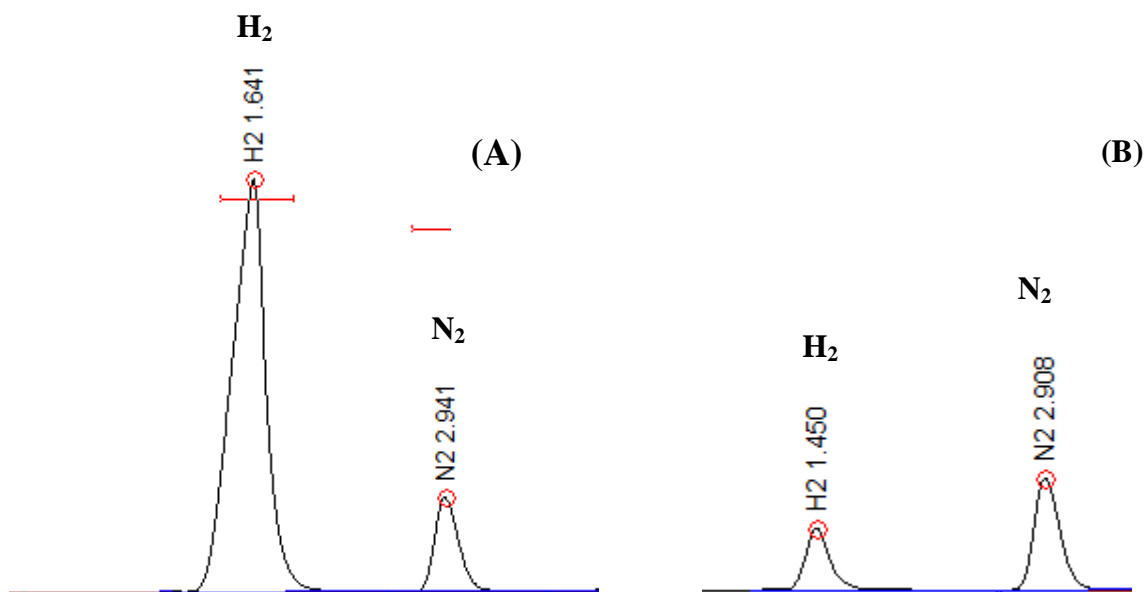
Figure 8. Chromatograms of gases evolved from H_2 outlet (A) and N_2 outlet (B).

4. CONCLUSION

The concept of alkaline ammonia electrolysis for hydrogen production and ammonia removal has been successfully proven. Elevated temperature is essential for both ammonia electrooxidation and hydrogen evolution. Kinetic investigations provided a reasonable fit to the experimental data confirming that ammonia electrooxidation obeys pseudo first-order reaction kinetics. The ammonia removal efficiency increased with increasing operating current density, and the hydrogen purity was acceptable when compared with the literature.

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