Lithium Nitride is a viable alternative source of ammonia

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Abstract
The major process of synthetically fixing nitrogen to ammonia is the Haber process. It contributes to half of the total required nitrogen input to world agriculture. However, this process is expensive as it requires high reaction conditions of pressure and temperature. Previously, research focused on search for catalysts for ambient nitrogen fixation, often with the aim of reducing the energy required for this conversion to replace chemical nitrogen fixation by the Haber process. In this work, relatively pure oxygen-free nitrogen has been prepared by passing air over copper fillings, heated in the temperature range $300^oC – 500^oC$ on a charcoal heat exchanger. The nitrogen has been reacted with Lithium to form Lithium nitride which on hydrolysis gives ammonia. The ammonia thus produced is reacted with ortho-phosphoric acid recovered from bones to make diammonium phosphate. The process realized 88.87 % N_2 separation from air, 94.74 % lithium conversion to lithium nitride and 94.75% lithium nitride conversion to ammonia.
Key words: *Nitrogen fixation, lithium nitride, ammonia*

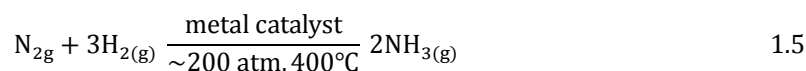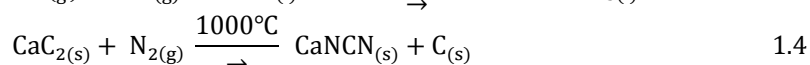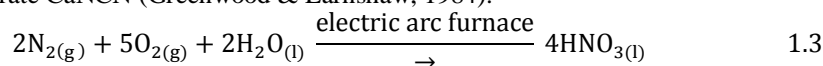
I. Introduction

Nitrogen is an essential element in the chemistry of life and it is the initial source of all nitrogen in organisms (Fryzuk & Johnson, 2002). However, this ubiquitous molecule is not easily taken up by all living organisms the way oxygen is taken up by living organisms. The process by which N2 is incorporated into biological systems is referred to as nitrogen fixation and involves the nitrogenase enzymes that contain a metal–sulfide cluster at the active site in certain plants. N2 fixation is defined as any natural or industrial process that causes free nitrogen, which is a relatively inert gas plentiful in air, to combine chemically with other elements to form more reactive nitrogen compounds such as ammonia, nitrates or nitrites.

The report of the X-ray crystal structure (Kim & Rees, 1992) of one such enzyme cofactors has inspired increased interest in the mechanism by which nitrogenase converts N_2 to ammonia. Moreover, since the discovery of the first dinitrogen complex, $[(H_3N)_5Ru(N_2)]^{2+}$, in 1965 (Allen & Senoff, 1965), the coordination chemistry of this simple molecule has flourished, and dinitrogen compounds of almost every transition element have been prepared with the hope that it may be possible to find a system that would catalytically reduce dinitrogen to produce nitrogen containing compounds under mild conditions still remains one of the loftier goals in chemistry (Fryzuk & Samuel, 2000).

At the turn of the last century, the imminent need for a source of fixed nitrogen became apparent, as natural sources of nitrogen compounds, used largely for fertilizers, were being depleted (Crookes, 1898). Three processes were developed that utilize the highly abundant feedstock, dinitrogen gas (N_2). The Birkeland–Eyde arc process (Greenwood & Earnshaw, 1984) as shown in equation 1.1 generates nitric acid via electric discharge into an oxygen–nitrogen mixture. The electric arc furnace required to overcome the activation barrier to this reaction proved too expensive to operate and hence rendered this process obsolete. The Frank–Caro cyanamide process (equation 1.2) utilizes calcium carbide, CaC_2, which reacts with nitrogen under harsh conditions (1000°C) to generate CaNCN (Greenwood & Earnshaw, 1984).

$$2N_{2(g)} + 5O_{2(g)} + 2H_2O_{(l)} \xrightarrow[\rightarrow]{\text{electric arc furnace}} 4HNO_{3(l)} \qquad 1.3$$

$$CaC_{2(s)} + N_{2(g)} \xrightarrow[\rightarrow]{1000°C} CaNCN_{(s)} + C_{(s)} \qquad 1.4$$

$$N_{2g} + 3H_{2(g)} \xrightarrow[\sim 200\,\text{atm}, 400°C]{\text{metal catalyst}} 2NH_{3(g)} \qquad 1.5$$

The Haber–Bosch process (equation 1.3), which has proven the most successful commercially, reacts N_2 gas with three equivalents of H_2 gas over a metal catalyst to produce ammonia (Greenwood & Earnshaw, 1984).

While the Haber–Bosch process differs substantially from the biological fixation of dinitrogen, both of these processes involve the activation of N_2 by a transition metal-containing catalyst.

This study was undertaken with the following objectives.

First, it was of interest to find out the possibility of separating nitrogen from air using low cost equipment. Second, it was of interest to find out whether one can take advantage of the lithium properties and convert this nitrogen to ammonia and then re-generate the lithium cheaply to make the process continuous. A third objective of the study was to react the ammonia produced with enhanced phosphoric acid to produce diammonium phosphate. The phosphate to be used was to be recovered from bones.

II. Materials and Methods

2.1 The electrolysis set up and pre - electrolysis

The electrolysis cell consisted of a three chamber arrangement involving the electrolytic cell (4595 cm^3 in volume), a separator compartment (2486 cm^3), a buffer compartment (994.78 cm^3) which were fabricated at Kenyatta University engineering workshop out of stainless-steel sheets as described by Jean – Michel Verdier *et al.*, (1986). The electrolytic cell comprised of a stainless steel housing equipped with a single anode/cathode pair. The cathode was a perforated cylindrical stainless sheet welded to the bottom of the cell. The perforations permit the circulation of the electrolytic medium within the electrolyser. The height was such that the upper end electrode would continuously remain under the surface of the electrolyte (when the cell is in operation). The anode was cylindrical graphite, rod positioned within the cathode but not touching the bottom of the cell. It was protected from Cl_2 attack by alumina sheathing over the surface area extending above the electrolytic medium and slightly below the surface of the medium (when the cell is in operation). The graphite electrode was held onto the cell head cylinder using high temperature aluminium oxide/ cement/ clay paste.

The temperature of the cell was monitored by a temperature probe thermocouple in a stainless-steel sheath located 2 cm above the bottom of the electrochemical cell. Scotch tape was wound round the electrolytic cell housing before the heating nichrome wire was wound round to avoid possible short circuiting. A layer of ceramic based flexible furnace grade insulation was also wrapped around the cell. The cell was heated at a rate of 10 ^{o}C/min from room temperature to 450 ^{o}C as recorded by the thermocouple. The gas outlet was dipped into a solution of concentrated sodium hydroxide to absorb the chlorine gas that resulted during electrolysis.

The electrolyte concentration was kept at 58 mol % LiCl- 42 mol % KCl mixture through addition of lithium chloride depleted through the buffer vessel. The graphite electrode was held into the cell head cylinder using high temperature aluminium oxide/ cement/ clay paste. Electrical connections were supplied by use of crocodile clips crimped to the electrodes and connected to the battery. Pre – electrolysis was first performed to test the influence of applied voltage on current efficiency of the cell. Predetermined amounts of lithium chloride and potassium chloride were weighed and placed into the cell and sealed. Argon gas was purged into the cell before heating was started to drive out any air available in the cell. Argon gas was continuously passed into the cell during the pre - electrolysis period. The cell was connected to the battery power source where voltage was programmed to vary from 1.2 V – 2.7 V. Then the melting began by raising the temperature to 456°C. The results determined the applied voltage that was used in the main electrolysis process.

The pump

This was used to effect circulation of the molten electrolyte during electrolysis. It was made of a seamless stainless rode 2" in diameter and 1ft long. The motor had a gearing system to reduce the speed from 1500 revolutions to 750 revolutions per minute a reverse interlocking system.

The separator

This was a cylindrical decantation compartment equipped with an outlet for discharging the upper light phase (the lithium metal) by overflow and an outlet for discharging the dense bottom phase that is the mixture of molten salts for recycling, to the buffer. It was made of stainless steel cylinder measuring 50 cm (height) x 25 cm (diameter) and a 0.75 cm pipe that would act as an inlet for withdrawal of lithium from the main cell during electrolysis. Inside the cylinder was a thin circular shaped sheet then inserted which would act as a separator for the light and denser phase of the electrolyte.

The buffer

This cylindrical compartment was used to replace the amount of LiCl in the electrolyte that was consumed as a result of electrolysis. The buffer vessel was made from a cylindrical stainless steel sheet measuring 25 cm (height) x 20 cm (diameter) and 0.75" diameter pipe from the separator and another pipe that would be used to feed the depleted electrolyte.

The battery

A wind-solar hybrid system was connected to a storage battery type N100 manufactured by Associated Battery Manufacturers (ABM), Kenya. The DC outputs' voltages from individual solar PV, wind and battery bank stream through individual DC/AC and AC/DC units, were integrated on the DC side and went through one common DC/AC inverter which acted as an interface between the power sources and the grid to provide the desired power. It had a storage capacity of 200 Ah which was used as storage medium and a voltage stabilizer. The battery rating was voltage of 12V with a current of 3.54A.

2.2 Electrolysis of molten KCl – LiCl mixture

Energy for electrolysis was drawn from a storage battery, type N100 (Associated Battery Manufacturers, Kenya) continuously charged by a wind-solar hybrid system. It had a storage capacity of 200 Ah, output 12V and 3.54A current.

Lithium chloride, LiCl (3859 g) and KCl (3150 g) were dried separately at 480 ^{o} C in an oven to a constant weight. They were mixed while in the oven and transferred to the electrolyte cell. The temperature of the cell was raised to 450 ^{o} C, the temperatures at which electrolysis of the molten mixture takes place. The temperature of the molten salt was measured with an R- type thermocouple placed in an alumina sheath immersed in the melt.

The electrolysis was carried out continuously for five days and the mass of lithium collected by overflow method from the separator at an average rate of 23.02 g after every five days. The lithium metal obtained was collected in the receiver flask that was maintained under a continuous flow of argon gas until when dry and kept tightly closed pending reaction with nitrogen. After five days the experiment was stopped to remove and safe guard the lithium formed. Heating resumed to raise the temperatures of the electrolysis cell and other components to resume the process again. The separator was heated through two points to maintain the same temperature as that of the electrolyte. There was also a provision for addition of depleted LiCl at the buffer vessel. The amount if lithium depleted was calculated using the equation:

$$\text{Number of moles of electrons transferred} = \frac{It}{F} \qquad 3.1$$

Where,

I = current

t = time

F = Faraday's constant = 96485C/mol.

From the quantitative aspects of electrolysis as developed by Faraday (1907), Strong, (1961) & Ehl, (1954), the mass of product formed at an electrode is proportional to both the amount of electricity transferred at the electrodes and the molar mass of a substance.

The anode reaction includes: $Cl^- \rightarrow Cl_2 + 2e^-$ 3.2

The cathode reaction includes: $Li^+ + e^- \rightarrow Li$ 3.3

The overall reaction: $2LiCl \rightarrow 2Li + Cl_2$ 3.4

Mass of lithium deposited was calculated using the equation;

$$\frac{Q}{F} \times \frac{M}{Z} \frac{(3.54 \times 3600)}{96485} \times \frac{6.947}{1}$$

Where Q = charge, F = Faradays constant, M = RMM of Lithium metal and Z = number of electrons.

The total charge, Q, which passes through an electrolytic cell can be expressed as the current It or nF. These equations can be used to determine things like amount of material used or generated during electrolysis, how long the reaction must proceed or what value of the current is required.

2.3 Separation of N$_2$ from compressed air and its reaction with Lithium

Nitrogen was obtained from commercial compressed air through the set-up presented in Figure 2.2. The compressed air was bubbled through a concentrated NaOH solution to scrub CO_2. The CO_2 - free air was through a column of P_2O_5 on pumice stones to remove any moisture in the air.

Column of P$_2$O$_5$

Column of copper

Iron tube

Lithium metal

Compressed air
in

Heat

Heat

Conc. NaOH

Solution of sodium
naphthalide

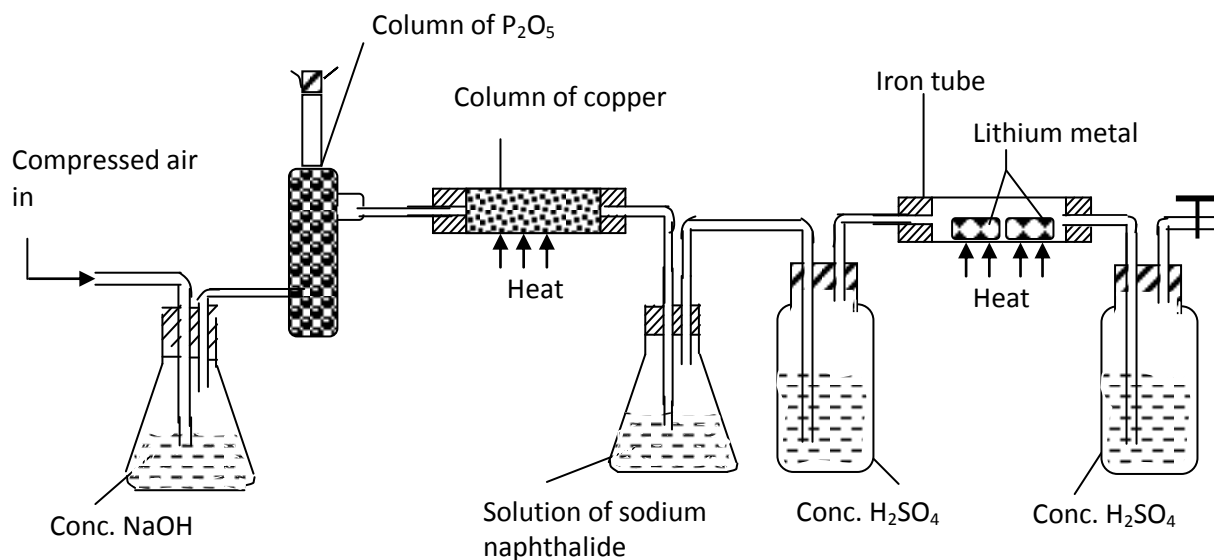Conc. H$_2$SO$_4$

Conc. H$_2$SO$_4$

Figure 2.2: Extraction of nitrogen from compressed air and preparation of lithium nitride

The dry CO$_2$ - free air was passed through a heated column of heated copper filings to remove oxygen. The hot, dry CO$_2$ - free, O$_2$ - free air exiting from the copper fillings column was bubbled through a solution of sodium naphthalide and then dried by bubbling through a conc. H$_2$SO$_4$ solution before being allowed into the vessel containing the metallic lithium for the production of lithium nitride. The set-up of apparatus for the heating of the copper filings column consisted of a clay-lined *Jiko* with a capacity to hold about 5.0 kg charcoal, a 36 mm diameter and 43.5 cm long glass column filled with about 850 g of copper fillings and closed at each end with a vermiculite clay cork. The *Jiko* was filled with about 1 kg of charcoal and lit. The temperature was raised by blowing air through the air hole. The set-up was flushed with a slow current of hydrogen gas to reduce any copper oxides in the heated copper filings until the temperature of the vessel reached 400°C.

When the temperature was about 400 $^{\circ}$C (measured using a pocket-sized thermocouple, Probe M), the hydrogen gas was closed and replaced with compressed air from a cylinder a rate of 290 ml/sec as measured using an airflow metre and controlled by the regulator for five minutes. The dry nitrogen from the air was then allowed to enter the reaction chamber (an iron tube 90 cm in length × 5 cm in diameter) containing lithium metal in two stainless steel boats. The external temperature of the reaction tube was determined by means of a thermocouple placed between the tube and the source of heat. The boat nearer the point of entry of the nitrogen held only 3.0 g of lithium and served as a final protection against oxygen and water vapour while the second vessel contained the 20.0 g of lithium required for the preparation of lithium nitride. The temperatures of heated lithium in the two stainless steel boats were maintained at 250 $^{\circ}$C (using a hot plate) and each experiment lasted on average five minutes. After the experiment, the hot plate was withdrawn and nitrogen gas continuously passed to allow the lithium nitride formed to cool under the inert atmosphere. The boat containing the reddish – brown formed was removed and the sample transferred to a flat bottomed flask where the hydrolysis was to take place. This procedure was repeated till all the lithium prepared was used.

The mass of nitrogen separated was estimated from the known volume of air passed over the heated copper granules and the mass of copper oxide formed. The amount of oxygen removed by heated copper was calculated as the difference between mass of the cooled copper oxide and that of un-reacted copper. When the copper filings in the first half of the column showed signs of darkening, the air flow was stopped and reducing agent hydrogen passed over the hot copper oxide/ copper mixture to regenerate the copper which had been oxidized. The amount of heat energy used in separation of air was calculated using the following *Fourier* series equation (Mills, 1995)

$$q = \left\{ \frac{4\pi k(T1 - T0)}{\left[\frac{1}{r1} - \frac{1}{r0}\right]} \right\}$$

Where,
 q = amount of heat transferred
T$_1$ = temperature inside the column
T$_0$ = temperature outside the column = constant (thermal conductivity of the column)
r$_1$ = inner radius of the column
r$_0$ = outer radius of the column

k = thermal conductivity

III. Results

3.1 Pre – electrolysis and electrolysis of molten LiCl – KCl mixture

The working conditions that is, applied voltage, time and current density were obtained and recorded as summarized in Table 3.1.

Table 3.1: Change in voltage with time and current

Cell voltage (V)	Current density(A)/M^2	Current (A)	Time (min)	Resistance	Current efficiency (%)
1.20	0.85	4.49	17.4	0.267	89.0
1.40	0.94	4.06	21.3	0.345	87.9
1.53	1.06	3.60	27.6	0.425	88.0
1.85	1.08	3.54	46.5	0.522	89.9
2.00	1.09	3.50	43.9	0.571	81.6
2.19	1.18	3.24	42.2	0.676	78.9
2.20	1.57	2.43	42.4	0.905	75.0
2.27	1.32	2.89	42.7	0.978	73.0

It was observed that current efficiency decreased with decreasing current applied from 89.0 – 73.0 %) and that current efficiency also increased with increase in time and voltage. This was because as time passes, the electrolyte depletes and an increase in current density increases molecular movements hence reducing the contact time of the electrolyte with the electrodes. The high current efficiency was also influenced by lower viscosity of the electrolyte which also influences mass transport including delivery of ions to the electrodes. The best current density observed in production of lithium was 3.54A. The decreasing current from 4.49A **s**how that the salt has a greater electric conductivity at increased potential meaning that more current may be wasted by just passing through the salt. It is also noted that the energy consumption in electrolysis is predominantly dependent on the current. The voltage also changed by a small margin as the current decreased rapidly an indicator that the system resistance was very low. After establishing the voltage (1.85V) and current (3.54A) to be applied on the electrolysis cell, the process of electrolysing lithium chloride/ potassium chloride mixture was allowed to run continuously for five days and the mass of lithium was collected by overflow method.

3.2 Separation of nitrogen from air and its reaction with lithium metal

This was achieved by removing oxygen, CO_2 and water vapour from air. The optimum working temperature for maximum oxygen removal from the air was determined by varying the working temperature and measuring the percent oxygen removal. Table 3.2 gives results of percentage O_2 separated when air was passed over heated a constant mass of copper filings (850g) for 300 seconds at different temperatures.

Table 3.2 Mean of O_2 (%) removed from air at different temperatures

Temperature ^{o}C	Volume of air passed (ml)/sec	Total volume of air passed for 5 minutes(ml)	Mass of copper oxide formed (g)	Initial mass of copper granules (ml)	Volume of nitrogen extracted	Mean % (±SD) O_2 percentage separated
200	293.34	88002	874.51	850	68641.56	92.70 ± 1.375 [a]
250	291.72	87516	875.05	850	68262.48	95.43 ± 1.809 [b]
300	291.48	87444	875.26	850	68206.32	96.31 1.577 [bd]
350	291.12	87336	875.10	850	68122.08	95.89±1.481 [cbd]
400	290.61	87183	875.83	850	68002.74	98.79 ±1.297 [ed]

Values with similar superscript letters indicate that there was no significant difference.

From the results in Table 3.2, the amount of oxygen separated generally increased with increase in temperature. However, there was no significant increase in oxygen separated between 250 ^{o}C and 350 ^{o}C, though the increase in percentage oxygen separated between 350 ^{o}C and 400 ^{o}C was significant at (p-values = 0.000 < 0.05). The temperature of 400 ^{o}C was, therefore, used in the separation of oxygen from air. The percentages of oxygen separated ranged from 92.7 to 98.8 %, indicating that there was effective diffusion of oxygen into copper from 200 to 400 ^{o}C. However, all oxygen was supposed to be separated from air in order to get pure nitrogen which was supposed to react with lithium. To ensure that no traces of oxygen that passed without reacting with the heated copper fillings reached the reaction vessel that contained heated lithium, the gas was passed through a solution of sodium naphthalide. From the total volume of 8700 ml of air passed at a temperature of 400 ^{o}C, the volume of oxygen separated was 18081 ml (98.96 % separation) and 67860 ml of nitrogen extracted. About 1.25 kg of lithium formed during electrolysis reacted with nitrogen gas at 250 ^{o}C,

giving 1980.09 g (94.75 %) conversion of lithium to lithium nitride obtained as a reddish brown solid. Heated lithium glowed within the first one minute of the reaction an indication of rapid diffusion of nitrogen through molten lithium. An average amount (156.09 g) of lithium nitride was ground in a mortar and placed in a flat bottomed flask and a separatory funnel attached to the flask. 150 ml of deionized water was added to the flat-bottomed flask through the separatory funnel to initiate hydrolysis. The ammonia gas produced passed through a delivery tube to a beaker containing 200 ml of 4.58 M H_3PO_4 extracted from bones. This experiment was repeated eight times to enable use of all the lithium nitride solid that had been prepared. The beaker containing 4.58 M phosphoric acid (200 ml) was immersed in basin containing ice because the reaction was highly exothermic. The highest temperature recorded during the reaction was 95 ^{o}C but the crystals formed at 51 ^{o}C. The crystals formed were filtered through Whatman No 1 filter paper, air dried at room temperature for seven days and weighed. A total of 3170.60g of the crystals formed realizing a conversion of 94.75 % of Li_3N to ammonia.

IV.   Conclusion

This work presents results for processes of separating nitrogen from air and its conversion to lithium nitride, hydrolysis of the nitride to ammonia, it has been known to produce lithium through electrolysis of lithium-containing salts (Jean – Michel Verdier *et al.*, (1986)). Among the problems encountered with these approaches has been the corrosion of equipment in the recycling of chlorine and relatively high cost of production of lithium. In spite of these, there remains a real and substantial need for an effective means of producing lithium by direct electrolysis of lithium chloride – potassium chloride mixture. The overall process of separating nitrogen from air and its conversion to ammonia using this procedure has proved to be viable because of the following reasons: first, the electrolysis cell fabricated was able to be driven by a solar/wind power and it allowed the recycling of lithium hydroxide hence a guarantee to the economic feasibility of the process. The chlorine produced during the process of electrolysis reacted with sodium hydroxide forming sodium hypochlorite which has vast industrial uses. Secondly, there was the use of biomass in separation of nitrogen from air. Thirdly, the fact that the experiment is done in a centralised place increases safety as compared to use of cylinders and bulk ammonia supplied by the Haber process.

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