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Demonstrating hydrogen production from ammonia using lithium imide – Powering a small proton exchange membrane fuel cell

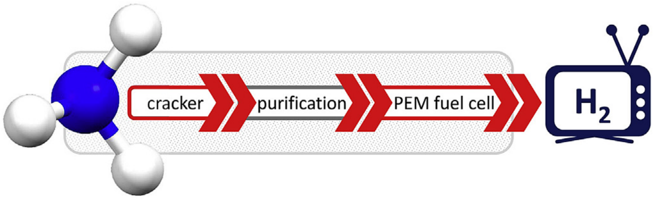
Hazel M.A. Hunter [a, *], Joshua W. Makepeace [b], Thomas J. Wood [a], O. Simon Mylius [c], Mark G. Kibble [a], Jamie B. Nutter [a], Martin O. Jones [a], William I.F. David [a, b]

[a] *ISIS Facility, STFC Rutherford Appleton Laboratory, Harwell Campus, Didcot, OX11 0QX, UK*
[b] *Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QR, UK*
[c] *Arcola Energy Ltd, 24 Ashwin Street, Dalston, London, E8 3DL, UK*

HIGHLIGHTS

- A first bench-top demonstrator showing hydrogen production from ammonia by Li_2NH.
- Catalytic decomposition of ammonia by lithium imide powers a PEM fuel cell.
- Effective ammonia scavenging achieved using anhydrous $MgCl_2$ powder.
- Dynamic PEM fuel cell purge strategy created for use with a 75% H_2/25% N_2 gas mix.

GRAPHICAL ABSTRACT



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ABSTRACT

Accessing the intrinsic hydrogen content within ammonia, NH_3, has the potential to play a very significant role in the future of a CO_2-free sustainable energy supply. Inexpensive light metal imides and amides are effective at decomposing ammonia to hydrogen and nitrogen ($2NH_3 \rightarrow 3H_2 + N_2$), at modest temperatures, and thus represent a low-cost approach to on-demand hydrogen production. Building upon this discovery, this paper describes the integration of an ammonia cracking unit with a post-reactor gas purification system and a small-scale PEM fuel cell to create a first bench-top demonstrator for the production of hydrogen using light metal imides.

1. Introduction

Environmentally benign, sustainable and economically favourable alternatives to fossil fuels are required if the ever increasing demand for energy worldwide is to be satisfied, while addressing the global impact of a changing climate. In this regard, hydrogen is considered as a promising fuel and energy vector. However, its safe and effective storage remains a key scientific and technological challenge that must be overcome before widespread adoption can be realised. One route to working with hydrogen is to consider liquid ammonia as an approach to storing hydrogen.

Ammonia, NH_3, is an attractive, ubiquitous and sustainable energy vector if its intrinsic hydrogen content can be accessed for use. Among hydrogen storage candidates, ammonia has one of the highest volumetric (121 kg H_2 m^{-3} at 10 bar) and gravimetric (17.8 wt%) hydrogen densities and it can be liquefied under

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* Corresponding author.
E-mail address: hazel.hunter@stfc.ac.uk (H.M.A. Hunter).

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relatively mild conditions (<10 bar at room temperature). In addition, its widespread use as an industrial chemical (and fertilizer feedstock) means that the safety hazards are well understood, the handling protocols are defined and documented, and distribution networks already exist – all key considerations if ammonia (as a hydrogen energy vector) is to be adopted in transport and off-grid applications. With nitrogen and water as clean combustion products and with physical properties similar to liquid petroleum gas, ammonia is, in many ways, the ideal non-carbon hydrocarbon.

Indeed ammonia-coal gas mixtures were used as the motor fuel [1] for the Belgian bus fleet during the straitened times of World War II. From 1943 up to the end of the war in 1945, these buses carried passengers for tens of thousands of miles without incident, in a real demonstration of the use of ammonia as an automotive fuel in standard internal combustion engines. More recently, Thomas and Parks have described [2] ammonia as having the potential for use as an energy carrier, particularly in the transition to a hydrogen economy. However, in addition to safety concerns, they identified both the size and cost of current ammonia cracking units and their successful integration with a proton exchange membrane (PEM) fuel cell as potential showstoppers when considering the use of ammonia for on-board vehicular hydrogen storage. This paper addresses these challenges.

We have recently shown [3–5] that light metal imides and amides define a new class of catalyst for the effective and efficient decomposition of NH_3 into H_2 and N_2 (Equation (1)), and that this represents a low-cost approach to on-demand hydrogen production.

$$NH_{3\ (g)} \rightarrow \frac{3}{2}H_{2\ (g)} + \frac{1}{2}N_{2\ (g)} \qquad \Delta H = 46\ \mathrm{kJ\ mol^{-1}} \qquad (1)$$

Thus integrating an ammonia decomposition reactor based on a light metal imide-amide catalyst into a small-scale power generation system provides an opportunity to illustrate and assess the practicality of this innovative hydrogen production method and to address, in part, the concerns of Thomas and Parks [2].

For this work we selected a fuel cell as the small-scale power generating unit, however the choice of fuel cell critically influences the design of the overall system. Although a number of types of fuel cell exist, this work focussed upon low temperature, high efficiency stacks which when assembled within a complete, fully insulated, system have the potential to deliver net energy gains. Specifically, the two relevant types are alkaline fuel cells (AFCs) and PEM fuel cells. AFCs are partially ammonia compatible [6], and have a long standing reputation having been used [7] on the Apollo space missions, but currently are not readily available for purchase. Instead, a PEM fuel cell was selected because this technology is considered to be the leading low-temperature route for power generation for use with hydrogen fuel. PEM fuel cells can also be bought off-the-shelf and do not require significant lab-based infrastructure modifications for testing (unlike internal combustion engines). Moreover, because PEM fuel cells are ammonia intolerant [8] and can be irreparably damaged if more than 100 ppb NH_3 is present in the inlet gas stream, a reliable and robust gas purification method was needed to ensure that no ammonia entered the PEM fuel cell.

For this work, the complete system comprised an ammonia gas supply, an ammonia cracking reactor, a post-reactor gas purification column and a 100 W PEM fuel cell, with associated gas and electrical handling. The technological challenges that were encountered when assembling this demonstrator are discussed in detail.

2. Experimental

2.1. System description

An overview of the experimental set-up, including a photograph of the whole system, is shown in Fig. 1, with more detailed schematic descriptions given in Fig. 2.

The NH_3 decomposition reactions were performed in simple cylindrical flow reactors (316 stainless steel) of internal volume 21.3 cm^3. As described [3,4] previously, the reactor was fitted with an inlet gas pipe running from the lid to 10 mm from the base of the reactor with a thermocouple monitoring the internal temperature at 5 mm from the base of the reactor. NH_3 (99.98%, SIP Analytical) or argon (99.998%, BOC) gas was supplied to the reactor *via* a custom-designed gas control panel and the exhaust gas stream was passed through a column of anhydrous $MgCl_2$ before being quantitatively analysed by a Hiden Analytical HPR-20 mass spectrometer. Gas flow inputs were mediated by a mass flow controller (HFC-302, Teledyne Hastings Instruments) and the hydrogen-containing outlet gas flow monitored by a mass flow meter (HFM-300, Teledyne Hastings Instruments). Microfibre gas filters (Parker 05-11-BS, retain 99.99% $\geq$ 0.01 μm particles) were fitted to ensure that the gas streams were particulate-free throughout. Gas flows were recorded in standard cubic centimetres per minute (sccm) and the reactor temperature and system pressure were also logged.

Typically to run the system 1.0 g lithium imide (Li_2NH, the fine powder catalyst) was loaded and sealed into the reactor in an argon-filled glove box, and the reactor connected to the gas panel and heated at 5 °C min^{-1} under flowing argon to 585 °C. Once stable at 585 °C, the gas was switched to NH_3 and the system operated at this constant temperature while varying the NH_3 inlet flow (60–300 sccm) in order to produce sufficient hydrogen to operate the fuel cell at the desired power output. Testing was performed under autogenous pressure, up to 2.0 bar in the reactor and purification column, which was sufficient to deliver the ~0.5 bar overpressure needed to run the fuel cell. As reported [3,4] previously, ammonia conversion efficiencies were calculated using a customised computer program, which removes background contributions and determines the ammonia signal as a percentage of the total signal.

To create the ammonia-scavenging purification system, two 19 mm i.d. chromatography columns were filled with anhydrous magnesium chloride powder ($MgCl_2$, ≥98%, Sigma-Aldrich) and connected in-line (and in parallel to each other) to the reactor and gas control panel. Typically, these columns contained 130–150 g $MgCl_2$ filled to an initial height of 550–600 mm, with the air in each

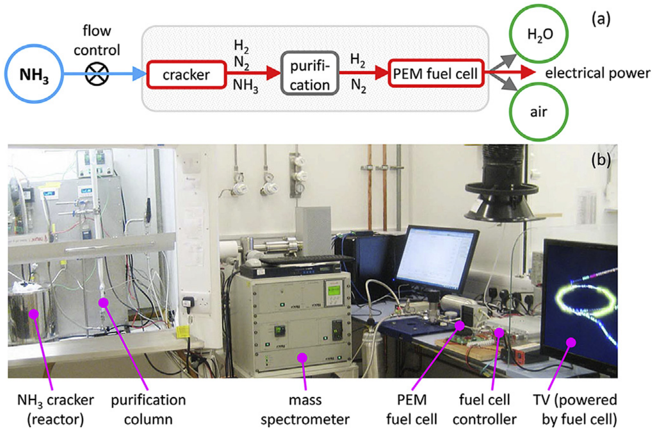

Fig. 1. Experimental set-up (a) system overview and (b) annotated photo.