



Synthesis of ammonia directly from wet air at intermediate temperature



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ABSTRACT

For the first time, ammonia has been directly synthesised from wet air at intermediate temperature. $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ (CGO)– $(\text{Li},\text{Na},\text{K})_2\text{CO}_3$ electrolyte together with a new perovskite oxide $\text{Pr}_{0.6}\text{Ba}_{0.4}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_{3-\delta}$ were used for electrochemical synthesis of ammonia. An ammonia formation rate of $1.07 \times 10^{-6} \text{ mol s}^{-1} \text{ m}^{-2}$ was obtained at 400°C when applied a voltage of 1.4 V, while wet air was introduced to the single chamber reactor. This is just slightly lower than the value of $1.83 \times 10^{-6} \text{ mol s}^{-1} \text{ m}^{-2}$ when wet N_2 was fed under the same experimental conditions. These values are two to three orders of magnitude higher than the reported ammonia formation rates when synthesised from N_2 and H_2O at $\sim 600^\circ\text{C}$. The perovskite catalysts are also low cost compared to the Ru/MgO and Pt/C catalysts in previous reports.

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1. Introduction

Nitrogen fertiliser has supported approximately 27% of the world's population over the last century, equivalent to around 4 billion people born (or 42% of the estimated total births) since 1908 [1]. Although over 78% of the atmosphere is composed of nitrogen, it is difficult to use N_2 directly by plants as plants can only use fixed nitrogen. The breakthrough in nitrogen fixation took place a century ago, the well-known Haber–Bosch process, operating at high temperature ($\sim 500^\circ\text{C}$) and high pressure (150–300 bar) [2]. Fritz Haber and Carl Bosch won Nobel prize in chemistry in 1918 and 1931 respectively for their contributions in industrial production of ammonia.

In the Haber–Bosch process, the required hydrogen is produced through the steam reforming of natural gas or coal and consumed more than 1% of world power generation [3]. In addition, 1.87 tons of CO_2 is released per ton of ammonia produced [4]. Globally 131 million tons of ammonia was produced in 2010 [5]. 245 million tons of CO_2 was released from ammonia industry which is equivalent to 0.77% of the world total CO_2 emission (31.78 billion tons) in 2010 [6]. In order to reduce the current dependency on the fossil fuels and to reduce carbon emissions associated with their use, it is essential to introduce new ammonia synthesis process and break the link between fossil fuels and ammonia industry [7]. The electrochemical synthesis processes are among the promising

alternatives in particular if the hydrogen required for ammonia synthesis is produced from non fossil fuel resources [2,8–11]. Recently, it has been reported that ammonia can be directly synthesised from air and water at ambient conditions, bypassing the N_2 separation and hydrogen production stage [2]. In a recent experiment, it was found that ammonia formation rates were even higher at 80°C than those at room temperature which means reasonably higher working temperature facilitates the ammonia formation [3]. Thermodynamic analysis shows that the equilibrium conversion of ammonia decreases with temperature. Therefore, the higher the temperature, the higher the extent of ammonia decomposition [2]. However, it has been widely reported that ammonia can be synthesised at a temperature as high as $\sim 600^\circ\text{C}$ [8,10,12–15]. The possible reason is that, the decomposition of ammonia at high temperature is kinetically slow thus ammonia can still be collected if it is removed from the reactor in time. Synthesis of ammonia directly from air and water at elevated temperatures would be possible if the oxidation of ammonia is also slow. In this paper, for the first time, we report the synthesis of ammonia directly from wet air at 400°C and ambient pressure. For comparison, ammonia was also synthesised from wet N_2 under the same conditions. Double chamber reactors were previously used for electrochemical synthesis of ammonia from N_2 and H_2O [10] or air and H_2O [2,3]. In this study, a simple single chamber reactor was used to simplify the synthesis process.

In our previous papers, we reported electrochemical synthesis of ammonia from N_2 and H_2 using $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ – $(\text{Li},\text{Na},\text{K})_2\text{CO}_3$ composite electrolyte. $(\text{Li},\text{Na},\text{K})_2\text{CO}_3$ ternary molten salts have an eutectic point of 396°C [16,17]. The low melting point of

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mixed (Li,Na,K)₂CO₃ salts makes the composite to exhibit high ionic conductivity at relatively low temperature which can minimise the operating temperature of the cell, reducing the potential thermal decomposition of ammonia. It has been reported that the ionic conductivity of Ce_{0.8}Sm_{0.2}O_{2-δ}-(Li,Na,K)₂CO₃ composite reached 0.1 S/cm at a temperature around 400 °C [18]. The total ionic conductivity composed those from Li⁺, Na⁺, K⁺, H⁺, HCO₃⁻, CO₃²⁻ and O²⁻ ions. Good fuel cell performance based on Ce_{0.8}Sm_{0.2}O_{2-δ}-(Li,Na,K)₂CO₃ composite electrolyte indicates high H⁺/O²⁻ ionic conductivity in this type of composite materials [18–21]. Either H⁺ or O²⁻ ionic conduction can be used for electrochemical synthesis of ammonia [22]. Therefore a similar composite electrolyte Ce_{0.8}Gd_{0.2}O_{2-δ}-(Li,Na,K)₂CO₃ was used as electrolyte in this study. As for electrocatalysts, ammonia was successfully synthesised using Fe-containing perovskite oxide La_{0.6}Sr_{0.4}Fe_{0.8}Cu_{0.2}O_{3-δ} [14]. Barium is a well known catalytic promoter for ammonia synthesis catalysts therefore strontium was replaced by barium in the new perovskite [23]. Lanthanum was also replaced by multi-valent praseodymium to improve the electronic conductivity. Therefore a new perovskite Pr_{0.6}Ba_{0.4}Fe_{0.8}Cu_{0.2}O_{3-δ} (PBFCu) was synthesised as electro-catalyst for synthesis of ammonia from air/N₂ and water. Pr_{0.6}Ba_{0.4}Fe_{0.8}Cu_{0.2}O_{3-δ} was used as both cathode and anode and a single chamber reaction was used for the synthesis. The concept for synthesis of ammonia directly from wet air at intermediate temperature has been successfully demonstrated.

2. Experimental

2.1. Materials synthesis

For synthesis of Ce_{0.8}Gd_{0.2}O_{2-δ}, calculated amounts of Gd₂O₃ was dissolved in hot dilute nitric acid to form gadolinium nitrate aqueous solution. Then an appropriate amount of Ce(NO₃)₃·6H₂O was added into the solution. 1 M (NH₄)₂CO₃ solution was slowly added dropwise with vigorous stirring until pH value reached 7–8, after that vigorous stirring was continued for another 30 min. The formed precipitate was then collected by vacuum filtration and washed several times with deionised water then dried at 100 °C overnight. The obtained powder was calcined in air at 650 °C for 2 h to obtain ultrafine CGO powder.

Ce_{0.8}Gd_{0.2}O_{2-δ} and ternary carbonate mixture (Li,Na,K)₂CO₃ (32.1 wt% Li₂CO₃; 34.5 wt% K₂CO₃; 33.4 wt% Na₂CO₃) powders were mixed together with weight ratio of oxide to carbonate 7:3. The mixture was put in ball miller (Planetary Mono Mill Pulverisette 6) for mixing with speed of 400 rpm for 4 h. The ball-milled powder was then heated at 600 °C for 1 h.

For synthesis of Pr_{0.6}Ba_{0.4}Fe_{0.8}Cu_{0.2}O_{3-δ}, praseodymium oxide (Pr₆O₁₁) was dissolved in diluted nitric acid to form praseodymium nitrate under heating and stirring. Calculated amounts of nitrates Ba(NO₃)₂, Fe(NO₃)₃·9H₂O and Cu(NO₃)₃·2.5H₂O were dissolved in deionised water and were added to the above prepared solution. Appropriate amounts of citric acid and EDTA (ethylenediaminetetraacetic acid) were then added as complexing agents with a molar ratio of citric acid:EDTA:metal cations of 1.5:1:1. Dilute aqueous ammonia solution was then added to the mixed solution to adjust the pH value to around 6. By further heating and calcined in air at 900 °C for 2 h, single phase Pr_{0.6}Ba_{0.4}Fe_{0.8}Cu_{0.2}O_{3-δ} was obtained.

2.2. Materials characterisation

TG/DSC analyses were performed using a Stanton Redcroft STA/TGH series STA 1500 operating through a Rheometric Scientific system interface controlled by the software RSI Orchestrator in flowing air at a flow rate of 50 ml min⁻¹.

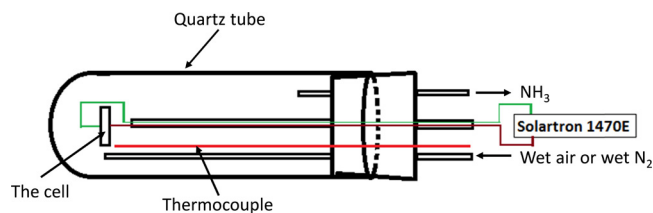


Fig. 1. Schematic diagram of the single chamber reactor used for ammonia synthesis.

X-ray data were collected on a PANalytical X'Pert Pro in the Bragg–Brentano reflection geometry with a Ni-filtered Cu K α source (1.5405 Å), fitted with a X'Celerator detector and an Empyrean CuLFF XRD tube. Absolute scans in the 2 θ range of 5–100° with step sizes of 0.0167° were used during data collection.

Conductivity measurements were carried out by a pseudo-four-terminal method using a computer-controlled SolartronAnalytical® SI 1470E electrochemical interface by applying a constant current. The Pr_{0.6}Ba_{0.4}Fe_{0.8}Cu_{0.2}O_{3-δ} powder fired at 900 °C was pressed into pellets with diameter of 13 mm and thickness of around 2 mm then fired at 1100 °C for 5 h. A silver coated pellet was fitted into the measuring apparatus and measurement was carried out in ambient air.

2.3. Fabrication of the single cell

The cell for ammonia synthesis was a tri-layer single cell which fabricated by a cost-effective one-step dry-pressing and co-firing process. The anode and cathode material was 0.8 g Pr_{0.6}Ba_{0.4}Fe_{0.8}Cu_{0.2}O_{3-δ} plus 0.2 g composite electrolyte to form a composite electrode materials. The composite anode, composite electrolyte and composite cathode (PBFCu/CGO-(Li,Na,K)₂CO₃/PBFCu) were fed into the die, layer by layer, with the aid of a sieve to ensure uniform powder distribution, and then uniaxially pressed at pressure of 300 MPa by cold pressing into 13 mm pellets. The pellets were sintered at 600 °C for 2 h. The thickness of the anode, electrolyte and cathode was approximately 0.6, 1.0 and 0.6 mm respectively. The catalyst surface area of the cathode and anode was 1.281 cm². Silver paste was painted on each electrode surface of the cell as a current collector. Ag wires were used as output terminals for both electrodes.

2.4. Ammonia synthesis and measurement

The as-prepared cell was put inside a quartz tube sealed by a rubber bung at the cold end. The schematic diagram of the single chamber reactor used for ammonia synthesis is shown in Fig. 1. Compressed air or N₂ was passing through room temperature water before imputing to the single chamber reactor. The flow rate of air (or N₂) was 50 ml min⁻¹. The steam concentration in air (or N₂) was 3 mol%. A dc voltage was applied to the cell using a Solartron 1287E electrochemical interface. The synthesised ammonia was absorbed by 25 ml of diluted sulphuric acid (0.001 M) for 60 min as described before [2,14]. The concentration of NH₄⁺ in the absorbed solution was analysed using Orion Application solution for low adjusting ISA. The produced ammonia was detected using an ammonia meter (ISE Thermo Scientific Orion Star A214) and the rate of ammonia formation was calculated using the following equation [2].

$$r_{\text{NH}_3} = \frac{[\text{NH}_4^+] \times V}{t \times A} \quad (1)$$

where [NH₄⁺] is the measured NH₄⁺ ion concentration, V is the volume of the dilute H₂SO₄ for ammonia collection, t is the adsorption time, A is the effective area of the cell.

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