



Synthesis of ammonia directly from wet air using new perovskite oxide $\text{La}_{0.8}\text{Cs}_{0.2}\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_{3-\delta}$ as catalyst



Rong Lan, Khaled A. Alkhazmi, Ibrahim A. Amar, Shanwen Tao*

Department of Chemical & Process Engineering, University of Strathclyde, Glasgow G1 1XJ, UK

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ABSTRACT

Single phase perovskite oxide $\text{La}_{0.8}\text{Cs}_{0.2}\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_{3-\delta}$ was synthesised to be used as electrocatalyst for electrochemical synthesis of ammonia directly from wet air. It exhibits an orthorhombic structure with space group $Pnma(62)$; $a = 5.5493(5)\text{Å}$, $b = 7.8352(10)\text{Å}$, $c = 5.5295(5)\text{Å}$, $V = 240.42(4)\text{Å}^3$. Composite made of $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ (CGO) and $(\text{Li,Na,K})_2\text{CO}_3$ was used as electrolyte. An ammonia formation rate of $9.21 \times 10^{-7}\text{ mol s}^{-1}\text{ m}^{-2}$ was obtained at 400°C when applied a voltage of 1.4 V, while wet air (3 mol% H_2O) was introduced to the single chamber reactor. This is just slightly lower than the value of $1.23 \times 10^{-6}\text{ mol s}^{-1}\text{ m}^{-2}$ when wet N_2 (3 mol% H_2O) was fed under the same experimental conditions. These values are more than two 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 catalyst is also low cost compared to the Ru/MgO and Pt/C catalysts in previous reports. This experiment indicates that ammonia can be directly synthesised from wet air using low-cost catalysts. This is a very promising simple technology for sustainable synthesis of ammonia in the future.

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1. Introduction

In the past century, the ammonia synthesis process invented by Fritz Haber has changed the world. 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]. Fritz Haber and Carl Bosch won Nobel Prize in Chemistry in 1918 and 1931 respectively for their contributions in industrial production of ammonia. However, ammonia industry also faces challenges due to the use of fossil fuels (natural gas and coal) as the energy sources and the release of CO_2 . The world CO_2 emission from ammonia industry is about 50% of the total CO_2 emission from the UK [2]. Therefore it is necessary to replace the traditional ammonia industry by a new sustainable synthesis process which does not rely on fossil fuels. Electrochemical synthesis of ammonia is an ideal solution as renewable electricity instead of fossil fuels can be used for as the energy sources [3].

There are many reports on electrochemical synthesis of ammonia using solid state electrolytes. The precursors used for ammonia synthesis were dominantly N_2 and H_2 [3–8]. However, H_2 can be produced from splitting of water or steam under a certain applied

voltage, therefore ammonia can be synthesised directly from N_2 and H_2O , bypassing the hydrogen production stage. The electrocatalytic synthesis of ammonia from steam and nitrogen was studied in oxygen ion (O^{2-}) and proton (H^+) conducting solid electrolyte cells at $450\text{--}700^\circ\text{C}$ and at atmospheric total pressure. A Ru-based industrial catalyst was used as the working electrode [9]. In that study, a two chamber electrochemical cell was used. The ammonia formation rates was around $1.0 \times 10^{-12}\text{ mol s}^{-1}\text{ gcat}^{-1}$ when either proton-conducting oxide $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\delta}$ or O^{2-} ionic conducting oxide yttria stabilised zirconia (YSZ) was used as the electrolyte [9]. To make the synthesis process more practical, it is necessary to use a low-cost catalyst and the ammonia formation rates need to be enhanced.

The N_2 for ammonia synthesis is normally from separation of air. It would be better if air can be directly used for ammonia synthesis, bypassing the N_2 separation stage. Recently, we reported synthesis of ammonia directly from air and water using an electrochemical cell based on Nafion electrolyte and Pt/C catalysts [2,10]. During the experiments, it was found that ammonia formation rates was higher at 80°C than that at room temperature. Therefore reasonably higher operating temperature of the cell may facilitate the formation of ammonia. Also it is necessary to use low-cost catalysts instead of expensive Pt/C used in previous reports [10]. The operating temperature of cells based on Nafion electrolyte is limited to 80°C . The fact that higher ammonia formation rate at 80°C that that at room temperature encouraged us to explore low cost catalysts for synthesis of ammonia from air/ N_2 and H_2O

* Corresponding author. Department of Chemical and Process Engineering, University of Strathclyde, Glasgow G1 1XJ UK, Tel.: +44 0 141 548 2361; fax: +44 0 141 548 2539.

E-mail address: shanwen.tao@strath.ac.uk (S.W. Tao).

at higher temperature using different electrolyte materials. It has been reported that carbonate-oxide composite electrolyte exhibits higher proton and O^{2-} conductivity at relatively low temperature and were used as electrolyte for intermediate temperature fuel cells [11–13]. In our previous research, carbonate-oxide composites were also used as electrolytes for electrochemical synthesis of ammonia, taking advantage of the relatively low working temperature, in order to minimise the thermal decomposition of produced ammonia [7,8]. In these carbonates, $(Li,Na,K)_2CO_3$ ternary molten salts exhibits an eutectic point of 396 °C [14,15]. The low melting point of mixed $(Li,Na,K)_2CO_3$ salts makes the composite to exhibit high ionic conductivity at relatively low temperature which can minimise the operating temperature of the cell, reducing the possible thermal decomposition and oxidation of ammonia. Therefore, in this study carbonate-oxide composite $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ - $(Li,Na,K)_2CO_3$ was selected as electrolyte for synthesis of ammonia from air/ N_2 and steam.

Although non-noble catalysts have been reported on electrochemical synthesis of ammonia from H_2 and N_2 [3], reports on electrochemical synthesis of ammonia from air/ N_2 and H_2O based on solid electrolytes are limited and the explored catalysts Ru/MgO [9] or Pt/C which are quite expensive [2,10]. In our previous report, an iron-containing perovskite oxide $La_{0.6}Sr_{0.4}Fe_{0.8}Cu_{0.2}O_{3-\delta}$ was used as cathode catalyst for electrochemical synthesis of ammonia from N_2 and H_2 [8]. It has also been reported that Fe-containing perovskite $SmFe_{0.7}Cu_{0.3-x}Ni_xO_3$ ($x = 0-0.3$) exhibits good catalytic activity on ammonia synthesis from N_2 and H_2 when Nafion membrane was used as the electrolyte [5]. However, the chemical compatibility between $SmFe_{0.7}Cu_{0.3-x}Ni_xO_3$ and acidic Nafion member might not be good. On the other hand, it has been demonstrated that Cs-containing chemicals such as $CsNO_3$ is an excellent catalyst promoter for ammonia synthesis [16]. As $CsNO_3$ will decompose to Cs_2O and NO_x at high temperature, it would be better to integrate Cs_2O into the perovskite lattice. Therefore a new perovskite $La_{0.8}Cs_{0.2}Fe_{0.8}Ni_{0.2}O_{3-\delta}$ was synthesised to be used as catalysts for both cathode and anode for electrochemical synthesis of ammonia. Instead of two chamber reactors used in previous reports, a simple single chamber reactor was used (Fig. 1). Wet air or wet N_2 was used as the precursors. Ammonia was successfully synthesised from either precursors when a symmetrical cell using $La_{0.8}Cs_{0.2}Fe_{0.8}Ni_{0.2}O_{3-\delta}$ as the catalyst.

2. Experimental Section

2.1. Materials synthesis

2.1.1. Synthesis of $Ce_{0.8}Gd_{0.2}O_{2-\delta}$

Calculated amounts of Gd_2O_3 was dissolved hot dilute nitric acid to form gadolinium nitrate aqueous solution. Then an appropriate amount of Ce (NO_3) $_3 \cdot 6H_2O$ was added into the solution. 1 M $(NH_4)_2CO_3$ solution was slowly added dropwise with vigorous stirring until pH value was 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 hours with a heating/cooling rate of 2 °C min^{-1} . Finally, ultrafine powder of (GDC) was obtained.

2.1.2. Preparation of CGO- $(Li,Na,K)_2CO_3$ composite electrolyte

$Ce_{0.8}Gd_{0.2}O_{2-\delta}$ and ternary carbonate mixture (Li,Na,K) $_2CO_3$ (32.1 wt% Li_2CO_3 ; 34.5 wt% K_2CO_3 ; 33.4 wt% Na_2CO_3) powders were mixed together with weight ratio of oxide to carbonate 7:3. The mixture was mixed and grounded with the use of 25 ml isopropanol. Then the mixture was put in ball miller (Planetary Mono Mill Pulverisette 6) for mixing with speed of 400 rpm for 4 hours.

The number of balls were used with a 1:1 weight ratio with the powders grinded. Then the mixture was heated at hot plate magnetic stirrer at 150 °C to release and get rid of isopropanol. The powder was then heated at 600 °C for one hour then quench in air to room temperature. The as-prepared oxide-carbonate composite electrolyte will be used for ammonia synthesis.

2.1.3. Synthesis of $La_{0.8}Cs_{0.2}Fe_{0.8}Ni_{0.2}O_{3-\delta}$

Calculated amounts of La_2O_3 and Cs_2CO_3 were weighed and dissolved in diluted nitric acid to form mixed nitrates under heating and stirring. Then calculated amounts of $Fe(NO_3)_3 \cdot 9H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ 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 and a dark green clear solution was obtained. The solvent was evaporated on a hot-plate at 200–250 °C under stirring and then gradually changed into a dark sticky gel before complete drying. By further heating the gel converted to black. The brown ash was grounded and subsequently calcined in air at 700 °C for 2 hours with heating/cooling rates of 5 °C min^{-1} to obtain a single phase of $La_{0.8}Cs_{0.2}Fe_{0.8}Ni_{0.2}O_{3-\delta}$.

2.2. Materials characterisation

2.2.1. X-ray powder diffraction

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

2.2.2. Thermal analysis

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} .

2.2.3. Conductivity measurement

Total conductivity measurements were carried out by a pseudo-four-terminal method using a computer-controlled Solartron Analytical® SI 1470A electrochemical interface by applying a constant current. The $La_{0.8}Cs_{0.2}Fe_{0.8}Ni_{0.2}O_{3-\delta}$ powder fired at 900 °C was pressed into pellets with diameter of 13 mm and thickness around 2 mm then fired at 1100 °C for 5 hours. 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 was placed in a self-designed single chamber reactor as shown in Fig. 1. Electrolytic 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 $La_{0.8}Cs_{0.2}Fe_{0.8}Ni_{0.2}O_{3-\delta}$ plus 0.2 g composite electrolyte to form a composite electrode materials. The composite anode, composite electrolyte and composite cathode (LCF Ni/CGO/LCF Ni) 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 cm^2 . Silver paste was painted on each electrode surface of the cell as a

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