



# Electrochemical synthesis of ammonia based on a carbonate-oxide composite electrolyte

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## ABSTRACT

Electrochemical synthesis of ammonia based on carbonate electrolyte is presented in this paper. Spinel oxide CoFe<sub>2</sub>O<sub>4</sub> was synthesised via a co-precipitation method and characterised by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Ammonia was successfully synthesised from hydrogen and nitrogen under atmospheric pressure using CoFe<sub>2</sub>O<sub>4</sub> as catalyst (primary particle size 10–20 nm) together with silver at the cathode, Ag–Pd at the anode and carbonate–LiAlO<sub>2</sub> composite as electrolyte respectively. Ammonia formation was observed at 400, 425 and 450 °C and the maximum rate of ammonia production was found to be  $2.32 \times 10^{-10}$  mol s<sup>-1</sup> cm<sup>-2</sup> at 400 °C and 0.8 V. The AC impedance measurements were recorded before and after the ammonia synthesis at 400, 425 and 450 °C. The electrolytic cell during the ammonia synthesis process was more stable at 450 °C and 0.8 V over a period of 2 h. This experiment also indicates that the carbonate–LiAlO<sub>2</sub> composite electrolyte exhibits proton conduction.

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## 1. Introduction

Ammonia is one of the most widely produced chemicals worldwide, and it is not only a major end product but also an important intermediate. So ammonia plays an important role in the national economy [1].

At the present time, ammonia is synthesised predominantly via Haber's process which involves the reaction of gaseous nitrogen and hydrogen on a Fe-based catalyst at 450–500 °C under high pressure (150–300 bar). Furthermore, the conversion to ammonia is limited by thermodynamic requirements [2]. Marnellos and Stoukides [3] demonstrated an alternative route to synthesise ammonia electrochemically under atmospheric pressure using solid state proton (H<sup>+</sup>) conductors by which the requirement for high pressure is eliminated or even reversed. Since then, several proton conductors have been utilised for the synthesis of ammonia [4–11].

Mixed transition metals or ternary oxides with the general formula AB<sub>2</sub>O<sub>4</sub> have the structure of mineral spinel (MgAl<sub>2</sub>O<sub>4</sub>). Generally, A ions that occupy the tetrahedral sites are divalent cations (Fe<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Mn<sup>2+</sup>, Mg<sup>2+</sup>, Cd<sup>2+</sup>, etc.) whereas B ions that occupy the octahedral sites are trivalent cations (Co<sup>3+</sup>, Fe<sup>3+</sup>, Cr<sup>3+</sup>, Al<sup>3+</sup>, Mn<sup>3+</sup>, Ga<sup>3+</sup> etc.) [12–14]. Transition metal oxides such as spinel ferrites (CoFe<sub>2</sub>O<sub>4</sub>) are chemically and thermally stable [15]. Thus, they have

exhibit great potentials for application in gas sensors, high quality ceramics, super magnetic materials [16–18] and catalysis such as ammonia synthesis using the conventional method [19]. The typical cathode catalysts for electrochemical synthesis of ammonia are palladium and silver–palladium [2,3,5]. However, to the best of our knowledge, there is no report on the electrochemical synthesis of ammonia based on spinel-type oxides. The present work is the first report on the electrochemical synthesis of ammonia from H<sub>2</sub> and N<sub>2</sub> using an CoFe<sub>2</sub>O<sub>4</sub> spinel catalyst in a solid state electrolytic cell under atmospheric pressure. On the other hand, although various proton conductors have been used for the electrochemical synthesis of ammonia, to the best of our knowledge, there is no reports on electrochemical synthesis based on carbonate electrolyte. In this paper, a carbonate–LiAlO<sub>2</sub> composite electrolyte was employed for the electrochemical synthesis of ammonia. The proton conduction of the carbonate-oxide composite is also demonstrated.

## 2. Experimental

### 2.1. Catalyst preparation

CoFe<sub>2</sub>O<sub>4</sub> spinel catalyst was prepared by a co-precipitation method which has been described elsewhere [17]. The oxide precursor was obtained by mixing an aqueous solution of cobalt nitrate (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Sigma Aldrich) with an aqueous solution of iron nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Alfa Aesar) at the molar ratio Co: Fe of 1 : 2. A dilute ammonia solution was then slowly added into the mixed solution

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under stirring until the pH value was about 7. A brown precipitate was obtained after vacuum filtration, washed several times with deionised water and ethanol, and then dried at 100 °C overnight. The obtained powder was calcined in air at 450 °C for 4 h with a heating/cooling rate of 2 °C min<sup>-1</sup>. Finally, ultrafine powder of CoFe<sub>2</sub>O<sub>4</sub> was obtained. A flow chart for the overall experiment is shown in Fig. 1.

## 2.2. Catalyst characterisation

X-ray diffraction (XRD) data were carried out at room temperature using a Bruker-AXS (D8 Advance) machine, controlled by DIFFRACT<sup>plus</sup>™ software, in the Bragg–Brentano reflection geometry with a CuK $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ), fitted with a LynxEye™ detector. XRD patterns were recorded in the  $2\theta$  range 5–85° with a step size of 0.009° and step time of 61.6 s were used at each step during data collection.

The microstructure of CoFe<sub>2</sub>O<sub>4</sub> catalyst was examined with a Quanta 3D FEG Scanning electron microscope (SEM) (FEI Company). It should be noted that in order to obtain better image definition the samples were coated by a thin layer of gold.

## 2.3. Ammonia synthesis

First, Li<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> were mixed at a molar ratio of 43.5:31.5:25 for Li<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub>. The carbonates were pre-mixed first then mixed with commercial LiAlO<sub>2</sub> (Aldrich) at a weight ratio 50:50. Pellets of the carbonate-LiAlO<sub>2</sub> composite were obtained after pressing the mixed carbonate-LiAlO<sub>2</sub> composite and fired at 600 °C. The formed composites were used as electrolyte for electrochemical synthesis of ammonia. CoFe<sub>2</sub>O<sub>4</sub> is a semiconductor therefore its conductivity is not high enough to be used alone as an electrode [20]. In order to increase both the electronic conductivity and adhesion, Ag paste was mixed with the as-synthesised CoFe<sub>2</sub>O<sub>4</sub> then pasted on the electrolyte surface as cathode. Ag–Pd (Johnson Matthey, 20 wt.% Pd) paste was pasted on the other side as anode. The catalyst surface area of the cathode was 0.45 cm<sup>2</sup>. Ag wires were used as output terminals for both electrodes (cathode and anode). The cell was placed in a self-

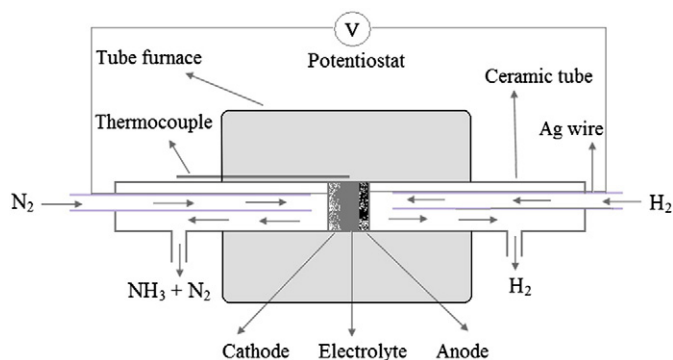


Fig. 2. Schematic diagram of the apparatus used for ammonia synthesis.

designed double-chamber reactor as shown in Fig. 2. The electrolytic cell used for ammonia synthesis was constructed as follows; H<sub>2</sub>, Ag–Pd | Carbonate-LiAlO<sub>2</sub> | CoFe<sub>2</sub>O<sub>4</sub>-Ag, N<sub>2</sub>, NH<sub>3</sub>. The cathode chamber was fed with oxygen free N<sub>2</sub> (BOC Gas), whereas wet highly pure H<sub>2</sub> (BOC, 99.995) was fed to the anode chamber. The dc potential was applied by a Solartron 1287A electrochemical interface controlled by software CorrWare/CorrView for automatic data collection. Direct potential was applied and the ammonia synthesised at the cathode chamber was absorbed by 25 ml of dilute sulphuric acid (0.001 M) for 2 h. The concentration of NH<sub>4</sub><sup>+</sup> in the absorbed solution was analysed using Nessler's reagent (Aldrich). The produced ammonia was detected using an ammonia meter (Palintest 1000) and the rate of ammonia formation was calculated using Eq. (1) [11].

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

Where [NH<sub>4</sub><sup>+</sup>] is the measured NH<sub>4</sub><sup>+</sup> ion concentration, V is the volume of the dilute H<sub>2</sub>SO<sub>4</sub> for ammonia collection, t is the adsorption time and A is the effective area of the catalysts.

## 2.4. Impedance measurements

AC impedance spectroscopy (IS) measurements were performed using a Schlumberger Solartron SI 1250 analyser coupled with a SI 1287 Electrochemical Interface controlled by Z-plot/Z-view software. The AC impedance spectra were recorded over the frequency range 65 kHz to 0.01 Hz.

## 3. Results and discussion

### 3.1. XRD and SEM analysis

The phase identification of the CoFe<sub>2</sub>O<sub>4</sub> catalyst was determined by XRD. The obtained pattern is in good agreement with the standard XRD pattern for cobalt ferrite with cubic spinel structure (JCPDS card no. 22-1086) and the cell constant of  $a = 8.3592(1) \text{ \AA}$  (Fig. 3). The powder X-ray analysis of the commercial  $\gamma$ -LiAlO<sub>2</sub> (Alfa Aesar) and carbonate-LiAlO<sub>2</sub> composite electrolyte before and after the ammonia synthesis have been conducted and shown in Fig. 4a–c. The commercial LiAlO<sub>2</sub> are mainly composed of  $\gamma$ -LiAlO<sub>2</sub> but with some unknown weak peaks. As shown in Fig. 4, the carbonate-LiAlO<sub>2</sub> electrolyte before ammonia synthesis consists of  $\gamma$ -LiAlO<sub>2</sub>, Li<sub>2</sub>CO<sub>3</sub> and binary carbonates namely LiNaCO<sub>3</sub> and LiKCO<sub>3</sub> (Fig. 4b) formed in the reaction between the carbonates during the firing.

The microstructure of CoFe<sub>2</sub>O<sub>4</sub> powder was investigated by SEM. Fig. 5a and b show the SEM images of the CoFe<sub>2</sub>O<sub>4</sub> catalyst at  $\times 20,000$  and at  $\times 40,000$  magnification, respectively. After calcination at 450 °C for 4 h, the microstructure of CoFe<sub>2</sub>O<sub>4</sub> consists of large grains

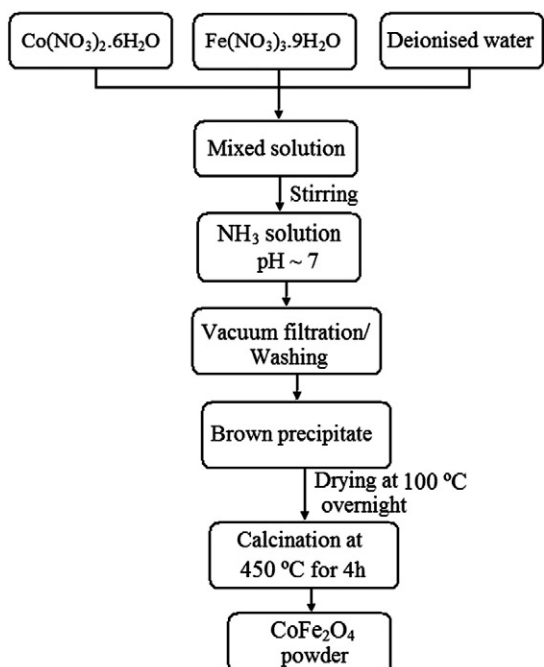


Fig. 1. A schematic diagram for preparation of CoFe<sub>2</sub>O<sub>4</sub>.

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