



# Electrochemical synthesis of ammonia from wet nitrogen via a dual-chamber reactor using $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}-\text{Ce}_{0.8}\text{Gd}_{0.18}\text{Ca}_{0.02}\text{O}_{2-\delta}$ composite cathode



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## ABSTRACT

A  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}-\text{Ce}_{0.8}\text{Gd}_{0.18}\text{Ca}_{0.02}\text{O}_{2-\delta}$  composite cathode was used to investigate the electrochemical synthesis of ammonia from wet nitrogen. Wet nitrogen was flown through a dual chamber reactor under atmospheric pressure leading to the successful synthesis of ammonia. Ammonia was synthesised at a rate of  $1.5 \times 10^{-10} \text{ mol s}^{-1} \text{ cm}^{-2}$  at 400 °C when applying a dc voltage of 1.4 V, which is the highest reported to date. This rate is twice that of the observed ammonia formation rate ( $7 \times 10^{-11} \text{ mol s}^{-1} \text{ cm}^{-2}$ ) when Co-free cathode,  $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}-\text{Ce}_{0.8}\text{Gd}_{0.18}\text{Ca}_{0.02}\text{O}_{2-\delta}$  was used as the cathode catalyst. A higher catalytic activity for ammonia synthesis may be obtained when using a catalyst with high oxygen vacancies, with the introduction of oxygen vacancies at the cathode being a good strategy to improve the catalytic activity of ammonia synthesis.

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## 1. Introduction

With a global production of around 150 million tons produced annually, ammonia is the second most produced inorganic chemical in the world [1–3]. The conventional Haber-Bosch process for ammonia synthesis uses fossil fuels such as natural gas or coal as its energy sources which lead to the release of about 300 million tons of  $\text{CO}_2$  per year [4]. To reduce  $\text{CO}_2$  from the ammonia industry, it is desired to replace the current energy sources with low carbon renewable resources such as renewable electricity. However, the development of energy storage for renewable electricity is still an urgent challenge. This is due to the nature of intermittence of energy sources such as wind and solar making it difficult to predict when they will be available. In Germany, for a certain period of time, the integration of large scale renewable electricity from solar and wind cause a negative electricity price [5]. In the UK, because they produced more electricity than the UK Grid could handle, wind farms were paid £30 million in 2013 and £53 million in 2014 to stand idle [6]. These problems remain unresolved and turbines have to be shut down at certain periods of time because the produced

power is too much for Britain's electricity network to cope with. With the integration of low carbon renewable electricity, energy storage is becoming an urgent challenge. In various energy storage technologies, pumped hydro has proven to be the most useful, however, its implementation is limited due to restrictions imposed by location and available capacity. New technologies such as battery, flow battery, supercapacitor, flying wheel, compressed air etc. have also been investigated for energy storage, however; none of these new technologies can meet the requirements on cost and durability. Hydrogen production from the electrolysis of water has been demonstrated in Germany to adsorb the 'extra' electricity but it is still quite expensive. While the existing global market and infrastructure are already in place it has been proposed that it may be more viable to produce ammonia instead of hydrogen [7]. The electrochemical synthesis of ammonia using renewable electricity is one of the promising alternatives which will alleviate the pressure on renewable energy storage while also generating a new ammonia industry with a low carbon footprint [8–19]. It has been reported that if the cost for renewable electricity is not high then the cost from the electrochemical synthesis of ammonia will be comparable to that of the existing methods [20]. This technology will prove to be very attractive if we consider the negative price for renewable electricity. In early studies,  $\text{H}_2$  and  $\text{N}_2$  were normally used as the precursors in the electrochemical synthesis of ammonia. In

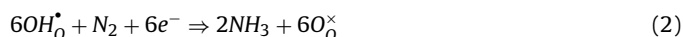
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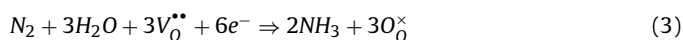
2009, for the first time, Skodra and Stoukides studied electrochemical synthesis of ammonia from steam ( $\text{H}_2\text{O}$ ) and  $\text{N}_2$ . They achieved this using a ceramic electrolytic cell based on either a proton ( $\text{H}^+$ ) or oxygen ion ( $\text{O}^{2-}$ ) conducting oxide electrolyte with a Ru/MgO catalyst as the working electrode (cathode), by using steam as the hydrogen source they thereby successfully eliminated the hydrogen production stage [21]. This will provide a more efficient process for ammonia production with a few papers already published on using steam and  $\text{N}_2$  to electrochemically synthesise ammonia based on an oxide cathode [13,22,23]. In a previous report, we found that  $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}\text{-Ce}_{0.8}\text{Gd}_{0.18}\text{Ca}_{0.02}\text{O}_{2-\delta}$  composite is a reasonably good cathode catalyst for electrochemical synthesis of ammonia from wet  $\text{N}_2$  with a maximum rate of ammonia formation of  $7 \times 10^{-11} \text{ mol s}^{-1} \text{ cm}^{-2}$  observed at a temperature of  $400^\circ\text{C}$  when the applied voltage was 1.4V [24]. On the other hand, it has been recognised that oxygen vacancies may play a key role in achieving a high catalytic activity for ammonia synthesis. It has been reported that surface hydroxyl radicals, which were formed on reduced  $\text{CeO}_2$  through the reaction between steam and oxygen vacancies in Co/ $\text{CeO}_2$  ammonia synthesis catalyst, could enhanced the catalytic activity [25]. This increase in activity was explained through the dissociation of hydrogen atoms on the Co surface reacting with hydroxyl species on the  $\text{CeO}_2$  surface forming water, thereby leaving the Co surface for the competing reaction, the dissociation of nitrogen to nitrogen atoms which is the rate-determining step [25]. When using perovskite oxide cathodes accompanying with oxygen vacancies in the lattice for electrochemical synthesis of ammonia from wet  $\text{N}_2$ , the oxygen vacancies in oxide cathode will react with  $\text{H}_2\text{O}$  to form charged protons according to the following reaction [26],



Due to their positive charge the formed proton defects  $\text{OH}_0^{\bullet}$  will be more prone to receiving electrons than neutron  $\text{H}_2\text{O}$ . In the presence of  $\text{N}_2$ , these defects may further react with  $\text{N}_2$  to form  $\text{NH}_3$  at the cathode,



Therefore oxygen vacancies can be potential reaction sites at the cathode. Combining reactions (1) and (2), the reaction at the cathode is:



At the anode,  $\text{O}_2$  is formed through lattice oxygen losing electrons according to the following reaction,



The formed oxygen vacancies  $V_{\text{O}}^{\bullet\bullet}$  will transfer to the cathode to further react with  $\text{H}_2\text{O}$  forming proton defects according to reaction (1).

Combining reactions (3) and (4), the overall reaction is:



From the analysis above, it can be seen that oxygen vacancies may play an important role in the electrochemical synthesis of ammonia, this is due to the formation of charged proton defects  $\text{OH}_0^{\bullet}$  as intermediates according to reaction (1). From this point of view, the presence of oxygen vacancies at the cathode may facilitate the enhanced catalytic activity of ammonia synthesis.

Although there are a significant amount of oxygen vacancies in  $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ , the partial replacement of Fe at the B-site by Co forming  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$  has been reported to significantly increase of the concentration oxygen vacancies with a larger  $\delta$  in LSCF [27]. In the  $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$  series,  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  (LSCF) has been widely studied as a cathode for solid oxide fuel

cells and membrane materials used for oxygen separation [28–30]. Therefore a higher catalytic activity is expected to be exhibited by LSCF than that of the Co-free perovskite oxide  $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ .

The transfer of oxygen vacancies from the anode to the cathode surface to complete the cathode reaction may also be facilitated by the oxygen vacancies in doped  $\text{CeO}_2$  such as  $\text{Ce}_{0.8}\text{Gd}_{0.18}\text{Ca}_{0.02}\text{O}_{2-\delta}$  [31]. In this paper, results for the electrochemical synthesis of ammonia using wet nitrogen in via a dual-chamber reactor using  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}\text{-Ce}_{0.8}\text{Gd}_{0.18}\text{Ca}_{0.02}\text{O}_{2-\delta}$  composite cathode are presented. The catalytic activity of  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  was found to be higher than that of Co-free analogue  $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ .

## 2. Experimental

### 2.1. Materials synthesis

A combined EDTA-citrate complexing sol-gel process was used to synthesise the  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  (LSCF) catalyst. Lanthanum oxide ( $\text{La}_2\text{O}_3$ , Alfa Aesar, 99%), strontium nitrate ( $\text{Sr}(\text{NO}_3)_2$ , Alfa Aesar, 99%), cobalt nitrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , Sigma Aldrich, 98+%) and iron nitrate nonahydrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , Alfa Aesar, 98%) were used as starting materials. To remove the absorbed water  $\text{La}_2\text{O}_3$  was first dried at  $700^\circ\text{C}$  for 2 h. A lanthanum nitrate aqueous solution was then formed by dissolving  $\text{La}_2\text{O}_3$  in diluted nitric acid. Calculated amounts of  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  were dissolved in deionised water before being added to the lanthanum nitrate solution. Citric acid and ethylenediaminetetraacetic acid (EDTA), with a molar ratio of citric acid: EDTA: metal cations of 1.5:1:1 were then added as complexing agents. The pH value was then adjusted to around 6 through the addition of dilute aqueous ammonia solution to the mixed solution. A black sticky gel was then obtained by evaporating this solution on a hot plate. The as-prepared gel was pre-fired and then transferred to an alumina crucible and calcined in air at  $900^\circ\text{C}$  for 2 h with heating/cooling rates of  $5^\circ\text{C min}^{-1}$  to obtain single phase LSCF.

$\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$  (SSCo) has been previously reported as an excellent cathode for intermediate temperature SOFCs [32]. Therefore in the ammonia electrochemical synthesis cell used in this study, SSCO was used as the anode. The activity of the oxygen evolution reaction at the anode was further increased by combining SSCO with an  $\text{O}^{2-}$  ionic conductor, ceria co-doped with Ca and Gd  $\text{Ce}_{0.8}\text{Gd}_{0.18}\text{Ca}_{0.02}\text{O}_{2-\delta}$  (CGDC) powders, to form a composite anode. CGDC was also synthesised via the previously described combined citrate-EDTA complexing sol-gel process [24]. In order to prepare the composite electrolyte, CGDC was mixed in a weight ratio of 70:30 with the ternary carbonate ( $(\text{Li}/\text{Na}/\text{K})_2\text{CO}_3$ ) as previously described [22]. In order to improve the transfer of oxygen ions in the form of oxygen vacancies and thereby improve the ammonia synthesis activity, CGDC was also integrated to the cathode to form a composite cathode.

### 2.2. Materials characterisation

A Panalytical X'Pert Pro diffractometer with Ni-filtered  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ), using 40kV and 40 mA, fitted with a X'Celerator detector was used to obtain X-ray diffraction (XRD) data at room temperature. The  $2\theta$  range  $20\text{--}80^\circ$  was used to record absolute scans, with a step size of  $0.0167^\circ$ .

A Hitachi SU6600 Scanning Electron Microscope (SEM) was used to examine the cross-sectional area of the single cell and the microstructures of the prepared catalyst.

A Stanton Redcroft STA/TGH series STA 1500 was used to perform Thermogravimetry and differential scanning calorimetry analyses. RSI Orchestrator software was used to control the Rheometric Scientific system interface used in the operation. A

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