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Mini-review

A review of the current trends in high-temperature electrocatalytic ammonia production using solid electrolytes

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ABSTRACT

High-temperature solid-state electrochemical synthesis of ammonia is a promising route for clean, sustainable and on-demand small-scale production of ammonia with lower energy consumption compared to the conventional Haber-Bosch process. Despite of its significant potential, there are still many aspects of this process that remain unexplored. In this mini-review article, the literature on high-temperature solid-state electrochemical ammonia production was summarized, the current state of the process was discussed and the necessary steps that should be taken to move the solid-state electrochemical ammonia synthesis concept forward were discussed while addressing the current issues and concerns.

1. Introduction

Ammonia (NH_3) is of utmost importance for the human civilization. Fixing nitrogen in the form of ammonia has been a crucial development for feeding the world population [1,2]. In fact, the dependence on ammonia will grow even further as the growing world population increases the demand for fertilizer and food. Ammonia also attracts attention as a carbon neutral fuel with high energy density.

Industrially, ammonia is produced by the Haber- Bosch process, which is named after Fritz Haber and Carl Bosch who developed this technology of producing ammonia from nitrogen and hydrogen, an accomplishment that brought them the Nobel prizes in 1918 and 1931, respectively [1,3]. In this process, nitrogen and hydrogen molecules react over an iron-based catalyst (recently Ru-based catalysts started to be used in ammonia production due to their high activity for N_2 activation) at high pressure (100–200 atm) and high temperature (400 °C–500 °C) according to the following reaction:

$$N_2 + 3\,H_2 \leftrightarrow 2\,NH_3$$

The ammonia production reaction from N_2 and H_2 is a thermodynamically-limited reaction. The gas volume decreases as the reaction proceeds. Therefore, very high pressures are needed to force the equilibrium conversion towards the product side according to the Le Chatelier principle. Also, due to the exothermicity of the reaction (−109 kJ/mol at 500 °C), a low temperature is desired to obtain higher equilibrium conversions [4]. However, the kinetics is very slow at low temperatures, and that necessitates the use of high temperatures to obtain industrially relevant production rates. The effect of the temperature and pressure on the equilibrium mole fraction of ammonia can be seen in Fig. 1. The equilibrium mole fractions of ammonia were calculated using the Gaseq program. As seen, due to the exothermic nature of the process and the decomposition of NH_3 at high temperatures, NH_3 equilibrium mole fraction decreases with increasing temperature. With increasing overall pressure of the system, it is possible to shift the industrially relevant production rates to higher temperature ranges where the kinetics are faster.

The energy need for the overall process including the production of hydrogen needed for the Haber-Bosch is quite high. The main energy intensive processes are (1) hydrogen production via reforming of fossil fuels which is an endothermic process, (2) extensive purification of the product stream of the reforming process to remove the potential catalyst poisons such as carbon monoxide and sulfur and (3) the compression of the reactant gases to achieve industrially-feasible conversion values. In addition to the high energy intensive nature of these steps, the reforming process emits significant amount of carbon dioxide to the atmosphere.

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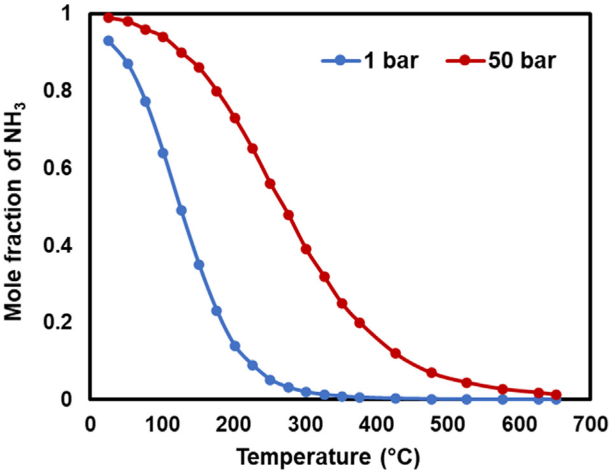

Fig. 1. Equilibrium mole fraction of ammonia versus temperature under total pressures of 1 bar and 50 bars when starting with an initial mixture of 25% N_2 and 75% H_2 by mole.

It has been reported that the Haber-Bosch process accounts for approximately 2% of global energy consumption and around 3% of global greenhouse gas emission [1,3]. Due to extensive upstream and downstream processes, low equilibrium conversion (~15%) in spite of gas recycling and extreme operating conditions, a Haber- Bosch plant is highly capital intensive; and a large-scale plant is required to meet economic profitability [1]. Economics of the process and the necessity for large scales have limited the availability of ammonia production to selective geographic locations.

Even though the Haber-Bosch process has been serving the mankind for almost a century, the abovementioned drawbacks have prompted scientists to find an alternative process that would be suitably scalable, environmentally friendly, and with lower energy requirements. There are various alternative ammonia synthesis processes such as chemical, biochemical, photochemical, thermochemical, electrochemical methods or combinations thereof. The electrochemical synthesis of ammonia is one of the promising routes, where nitrogen, hydrogen and water can be used to produce ammonia with the help of electrical energy [4–6]. Since this process can potentially use water as the source of hydrogen and the required energy to split water can come from renewable electricity, zero carbon dioxide emission is a possibility. Another advantage of the electrochemical system is its scalability. Installations ranging from small distributed facilities to large-scale production plants can be built with the electrochemical process. This can lead to production of ammonia locally in various regions of the world, which will curb the requirement of transportation of ammonia from large-scale facilities, thereby reducing the emissions accompanying the transportation sector. Having said that, the technological advances in the field of electrochemical ammonia production is still in its infancy, and nowhere near commercialization [7]. However, the need for a greener and more efficient NH_3 production process alternative to Haber-Bosch process has spurred significant research efforts in recent years.

Most of the current research is focused on low-temperature (<100 °C) ammonia production in aqueous media [8]. There are also a number of studies investigating ammonia production at intermediate temperatures (200 °C–500 °C) using molten salt electrolyte and at higher temperatures (>400 °C) using solid state electrolyte. A high-temperature route has the potential to increase catalytic activity, decrease the power consumption due to a lower kinetic overpotential, and improve Faradaic efficiency for ammonia formation. The focus of this review article will be on high-temperature ammonia production in a solid oxide electrochemical cell (SOEC).

An SOEC is made up of three components, namely an electrolyte and two porous electrodes (cathode and anode) [9]. The electrolyte conducts ions from one electrode to the other and the electrodes provide the conductive and catalytic surfaces needed for oxidation and reduction reactions during the electrochemical process. The electrodes are electronically sealed from each other due to the presence of the electronically insulating electrolyte. However, they are connected through an external electrical circuit that transfers electrons from one electrode to the other to obtain a closed circuit. They should exhibit high electrocatalytic activity, high electrical and ionic conductivity and be stable under operating temperature and gas environment. The electrolyte material should be very stable under both reducing and oxidizing environments and should be highly dense to avoid gas permeation between electrodes and leaks between the system and outside environment. It should also exhibit very high ionic conductivity and negligible electrical conductivity at the operating temperature range. Thermal expansion coefficients of electrolyte and electrodes should match in order to avoid any structural damage during heating/cooling.

Two different classes of SOEC systems can be used for ammonia synthesis, which are distinguished based on the type of electrolyte used, i.e., proton (H^+) conducting and oxide ion (O^{2-}) conducting electrolytes, as shown in Fig. 2(a) and (b), respectively. In an SOEC containing a proton conducting electrolyte, wet or dry H_2 gas can be converted into protons on the anode, and these protons can then travel through the electrolyte to the cathode, where they combine with N_2 to form ammonia. In the oxide ion conducting SOEC, a combined stream of N_2 and H_2O is introduced to the cathode side where H_2O splits to form H_2 and protons, which react with activated nitrogen to form ammonia. O^{2-} ions that are generated from H_2O splitting move through the electrolyte to the anode and combine to form oxygen molecules.

2. Brief review of the literature

2.1. Studies with proton conducting electrolytes

Research on ammonia production in a solid oxide electrolyte cell gained momentum with the advent of proton conducting solid oxide electrolytes. Iwahara and coworkers [10] reported for the first time in the 1980′s that $SrCeO_3$-based perovskite oxides can conduct protons

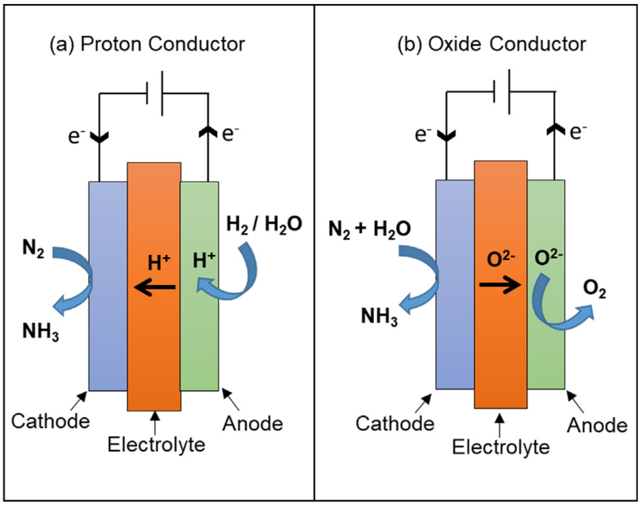

Fig. 2. Solid oxide electrochemical cell for ammonia production.

at high temperatures when exposed to a hydrogen-containing atmosphere. Work that followed this early discovery brought into light a few other oxides such as $BaZrO_3$, $BaCeO_3$ and $SrZrO_3$ that possess proton conductivity [11]. Doping the B-site of these perovskite oxides with a small fraction of trivalent rare earth metals improves the proton conductivity [11]. In a solid oxide electrolyte cell consisting of a proton conducting electrolyte, H_2 or H_2O serves as the source of protons, and these protons travel through the electrolyte to the other electrode (cathode) to react with activated N_2 forming ammonia.

The first study on production of ammonia in such a reactor was carried out by Marnellos and Stoukides [4,12], who used a $SrCe_{0.95}Y_{0.05}O_3$ proton conducting electrolyte and Pd electrodes. A small flowrate of 5.0×10^{-7} m^3/s of pure hydrogen was introduced to the anode side and an 8.3×10^{-7} m^3/s mixture of 1.8% N_2 in He was passed over the cathode at 570 °C and atmospheric pressure. With the assumption that the proton transference number is unity, this study reported that at least 78% of the H_2 was converted into NH_3 with rates shown in Fig. 3. It was also shown that the NH_3 production rate obtained here was at least three orders of magnitude higher than the maximum NH_3 production possible in a conventional catalytic reactor at atmospheric pressure. Ammonia production rates in such a hypothetical conventional reactor is shown by the line termed as CCR in Fig. 3, assuming equilibrium is attained in the process. On the other hand, the reactor pressure needed for a conventional catalytic reactor to match the production rates obtained electrocatalytically would be in the order of 10^6 bar, as shown by the line denoted as PCCR. Therefore, electrochemical ammonia production was shown to eliminate the thermodynamic requirement of a high- pressure process. Another finding of this study was that the production rate of NH_3 showed a direct dependence on the H_2 availability at the cathode which is the limiting reactant under the process conditions used here, however it did not show any dependence on the N_2 partial pressure, as shown in Fig. 3. A control experiment to investigate ammonia decomposition at 570 °C operating temperature showed that it varied between 15% and 30%, and the extent of decomposition decreased with increase in current density.

The pioneering work of Stoukides's research group was followed by many other studies on ammonia production using various compositions of the proton conducting membrane [13–35]. The majority of these proton conducting membranes were of perovskite oxide structure along with a few studies on electrolytes with pyrochlore and fluorite crystal structure. Some of these studies are summarized in Table 1. The production rate of ammonia is reported as amount of NH_3 produced per unit time per geometric area of the working electrode in Table 1, since it is the most common way of reporting the electrocatalytic activity of the electrodes used in studies cited 1. The reason for normalizing the rates with respect to the geometrical surface area of the working electrode is related to the nature of the high-temperature electrocatalysis field. In order to obtain a good contact between the solid oxide electrolyte and the electrodes, in most of the high-temperature electrocatalysis studies, the electrode/electrolyte assemblies (button cells) are sintered at very high temperatures (≥1000 °C). When the electrodes subject to the high-temperature treatments, they sinter and lose most of their porosity, therefore it is a common practice to normalize the production rates using the geometrical surface area of the electrodes.

$BaCe_{0.8}Gd_{0.2}O_{3-\delta}$, $BaCe_{1-x}Y_xO_{3-\alpha}$, $BaCe_{1-x}Ca_xO_{3-\alpha}$, $Ba_3(Ca_{1.18}Nb_{1.82})O_{9-\delta}$, $SrZr_{0.95}Y_{0.05}O_{3-\delta}$, $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\alpha}$, $La_{0.9}Ba_{0.1}Ga_{1-x}Mg_xO_{3-\alpha}$, $BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{2.9}$ are examples of perovskite oxide proton conductors that have been used for ammonia production [13,19–34]. Pyrochlore-type electrolytes such as $La_2Ce_2O_7$, $La_2Zr_2O_7$ and $La_{1.9}Ca_{0.1}Zr_2O_{6.95}$ and fluorite- type such as $Ce_{0.8}M_{0.2}O_{2-\delta}$ (M = La, Y, Gd, Sm) have also shown promise for application in ammonia production [14,17,18]. In fact, a study done by Wang and his coworkers showed that a solid electrolyte cell with fluorite-type proton conductor (ca. 8×10^{-9} mol s^{-1} cm^{-2}) can provide comparable ammonia production rates with the ones obtained with perovskite or pyrochlore-structure proton conductive electrolytes under similar conditions (400–800 °C, 0–1 V) [18].

As tabulated in Table 1, the majority of the high-temperature electrochemical ammonia synthesis studies include Pd or Ag-Pd type standard electrocatalysts. The ammonia production rates obtained using these standard working electrodes are in a range of 2×10^{-9} – 9×10^{-9} mol $NH_3/s.cm^2$. The differences in the ammonia production rates, even when the same electrocatalyst is used, can be attributed to the utilization of different solid electrolytes with different proton conductivities. Li et al. evaluated the performance of three different composition of electrolytes: $Ba_3(Ca_{1.18}Nb_{1.82})O_9$, $Ba_3CaZr_{0.5}Nb_{1.5}O_9$, $Ba_3Ca_{0.9}Nd_{0.28}Nb_{1.82}O_9$ for ammonia production from H_2 and N_2 over Ag-Pd electrodes [15]. It was found that the ammonia production rate was a function of the electrolyte composition, meaning that the protonic conductivity of the electrolyte can influence the ammonia production. In addition to that, the results given in Table 1 show that there is no universal optimum temperature and voltage/current for maximizing electrochemical ammonia production. Each electrochemical cell

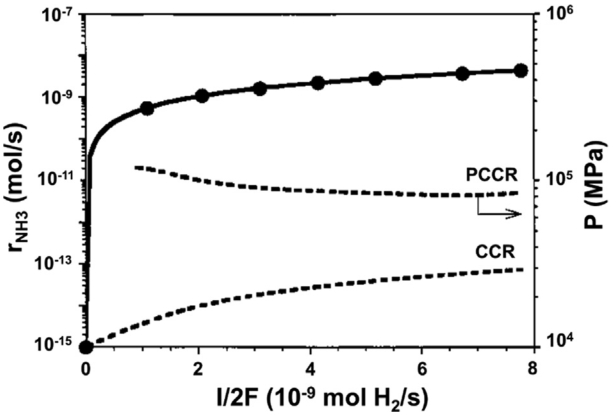

Fig. 3. Electrochemical ammonia production rates as a function of H_2 supply to the cathode at 570 °C and partial pressure of N_2 = 1.8 kPa. CCR curve is the ammonia production rate obtained in a conventional catalytic reactor under similar conditions. PCCR curve is the pressure required for attaining rates similar to the electrochemical production rates in a conventional reactor. Reprinted from [4], Copyright 1998, with permission from Elsevier.

is unique and the ammonia production rate is a function of several parameters such temperature, electrical bias, proton conductivity, etc. which also have an effect on each other.

The recent studies showed that H_2O can be used instead of H_2 as a proton source. If H_2O is used as the proton source, more advanced electrocatalysts will be needed, otherwise the ammonia production rate will be very low (~10^{-12} mol s^{-1} cm^{-2}) to have any practical relevance. In recent years, therefore, the focus has shifted towards developing more efficient electrode catalysts for ammonia production in

Table 1
Summary of high-temperature and atmospheric pressure electrochemical ammonia synthesis studies.

Ref#	Cell Configuration Anode|Electrolyte|Cathode	Anodic Flow	Cathodic Flow	Temperature	Cell Voltage/ Current Density	Production Rate of Ammonia	Faradaic efficiency for NH_3 production (%)
Studies using proton conducting electrolytes							
[4]	Pd |$SrCe_{0.95}Y_{0.05}O_3$ |Pd	H_2	N_2	570 °C	2 mA/cm^2	3×10^{-9} mol/cm^2/s	78
[13]	Ag-Pd |$SrCe_{0.95}Y_{0.05}O_3$ |Ag-Pd	H_2/H_2O	N_2	480 °C	0.6 V	3.09×10^{-9} mol/cm^2/s	–
[14]	Ag-Pd |$SrCe_{0.95}Y_{0.05}O_3$ |Ag-Pd	H_2/H_2O	N_2	520 °C	0.6 V	1.756×10^{-9} mol/cm^2/s	–
[15]	Ag-Pd |$Ba_3(Ca_{1.18}Nb_{1.82})O_9$ |Ag-Pd	H_2/H_2O	N_2	620 °C	0.6 V	7.82×10^{-9} mol/cm^2/s	–
[15]	Ag-Pd |$Ba_3CaZr_{0.5}Nb_{1.5}O_9$ |Ag-Pd	H_2/H_2O	N_2	620 °C	0.6 V	7.96×10^{-9} mol/cm^2/s	
[15]	Ag-Pd |$Ba_3Ca_{0.9}Nd_{0.28}Nb_{1.82}O_9$ |Ag-Pd	H_2/H_2O	N_2	620 °C	0.6 V	8.36×10^{-9} mol/cm^2/s C	–
[16]	Ag-Pd |$Ce_{0.8}Y_{0.2}O_{1.9}$-$Ca_3(PO_4)_2$-K_3PO_4 |Ag-Pd	Natural Gas	N_2	650 °C	1.0 V	6.95×10^{-9} mol/cm^2/s	–
[17]	Ag-Pd |$La_{1.95}Ca_{0.05}Zr_2O_7$|Ag-Pd	H_2	N_2	520 °C	0.6 V	2.0×10^{-9} mol/cm^2/s	–
[17]	Ag-Pd |$La_{1.95}Ca_{0.05}Ce_2O_7$|Ag-Pd	H_2	N_2	520 °C	0.6 V	1.3×10^{-9} mol/cm^2/s	–
[18]	Ag-Pd |$Ce_{0.8}La_{0.2}O_2$|Ag-Pd	H_2/H_2O	N_2	650 °C	1.0 V	7.2×10^{-9} mol/cm^2/s	–
[18]	Ag-Pd |$Ce_{0.8}Y_{0.2}O_2$|Ag-Pd	H_2/H_2O	N_2	650 °C	1.0 V	7.5×10^{-9} mol/cm^2/s	–
[18]	Ag-Pd |$Ce_{0.8}Gd_{0.2}O_2$|Ag-Pd	H_2/H_2O	N_2	650 °C	1.0 V	7.7×10^{-9} mol/cm^2/s	–
[18]	Ag-Pd |$Ce_{0.8}Sm_{0.2}O_2$|Ag-Pd	H_2/H_2O	N_2	650 °C	1.0 V	8.2×10^{-9} mol/cm^2/s	–
[19]	Pd |$SrZr_{0.95}Y_{0.05}O_3$ |Fe	H_2	N_2	450 °C	1.0 V	2.2×10^{-9} mol/s	–
[20]	Ag-Pd|$La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_3$|Ag-Pd	H_2	N_2	550 °C	1.0 mA/cm^2	2.37×10^{-9} mol/cm^2/s	70
[21]	Ag-Pd|$La_{0.9}Ba_{0.1}Ga_{0.8}Mg_{0.2}O_3$|Ag-Pd	H_2	N_2	520 °C	1.0 mA	1.89×10^{-9} mol/cm^2/s	60
[22]	Ni-$BaCe_{0.85}Gd_{0.15}O_3$|$BaCe_{0.85}Gd_{0.15}O_3$|Ag-Pd	H_2/H_2O	N_2	480 °C	1.5 mA	4.63×10^{-9} mol/cm^2/s	70
[23]	Ag-Pd|$BaCe_{0.85}Gd_{0.15}O_3$| Ag-Pd	H_2/H_2O	N_2	500 °C	0.75 mA	2.1×10^{-9} mol/cm^2/s	60
[24]	Ag-Pd|$BaCe_{0.9}Ca_{0.1}O_3$|Ag-Pd	H_2/H_2O	N_2	480 °C	0.8 mA	2.69×10^{-9} mol/cm^2/s	50
[25]	Ni-$BaCe_{0.85}Gd_{0.15}O_3$|$BaCe_{0.85}Gd_{0.15}O_3$|Ag-Pd	H_2/H_2O	N_2	530 °C	1.0 mA	4.1×10^{-9} mol/cm^2/s	–
[2]6	Ag-Pd|$BaCe_{0.85}Dy_{0.15}O_3$| Ag-Pd	H_2/H_2O	N_2	530 °C	1.2 mA	3.5×10^{-9} mol/cm^2/s	–
[27]	Rh-$BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{2.9}$|$BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{2.9}$| Ni-$BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{2.9}$	H_2	N_2	550 °C	2.1 V	2.9×10^{-9} mol/cm^2/s	6.2
[28]	$La_{0.3}Sr_{0.6}TiO_3$-$BaCe_{0.9}Y_{0.1}O_3$|$BaCe_{0.9}Y_{0.1}O_3$|Pt	H_2O, Ar	H_2O, N_2	500 °C	0–1.0 V	3.8×10^{-12} mol/cm^2/s at 0.1 V and 500 °C	–
[29]	Ag-Pd|$BaCe_{0.8}Gd_{0.1}Sm_{0.1}O_3$|Ag-Pd	H_2	N_2	620 °C	0.6 V	5.82×10^{-12} mol/cm^2/s	–
[30]	Cu-$BaZr_{0.7}Ce_{0.2}Y_{0.1}O_{2.9}$|$BaZr_{0.7}Ce_{0.2}Y_{0.1}O_{2.9}$ |Ni-$BaZr_{0.7}Ce_{0.2}Y_{0.1}O_{2.9}$	H_2	N_2, H_2	620 °C	2.3 V	4.1×10^{-9} mol/cm^2/s	2.6
[31]	Ni-$BaCe_{0.8}Y_{0.1}Ru_{0.1}O_3$| $BaCe_{0.9}Y_{0.1}O_3$|Ni-$BaCe_{0.9}Y_{0.1}O_3$	H_2/H_2O	N_2	500 °C	0.6 V	5.3×10^{-10} mol/cm^2/s	2.6
[33]	Ni-$BaCe_{0.8}Y_{0.1}Ru_{0.1}O_3$| $BaCe_{0.9}Y_{0.1}O_3$|Pt	H_2/H_2O	N_2, H_2O	500 °C	0.3 V	1.1×10^{-11} mol/cm^2/s	<1
[34]	Ni-$BaCe_{0.9}Y_{0.1}O_3$| $BaCe_{0.9}Y_{0.1}O_3$|Ni-$BaCe_{0.9}Y_{0.1}O_3$	H_2/H_2O	N_2	500 °C	0.2 V	3.36×10^{-10} mol/cm^2/s	<1
Studies using oxide ion conducting electrolytes							
[36]	Pd|$Zr_{0.92}Y_{0.08}O_2$|Ru-MgO	He	N_2, H_2O	650 °C	2.0 V	1.4×10^{-12} mol/g cat./s	–
[37]	Pt| $Ce_{0.9}Gd_{0.1}O_{1.95}$|Pt	–	H_2O, N_2	600 °C	2.0 V	3.67×10^{-11} mol/cm^2/s	<1

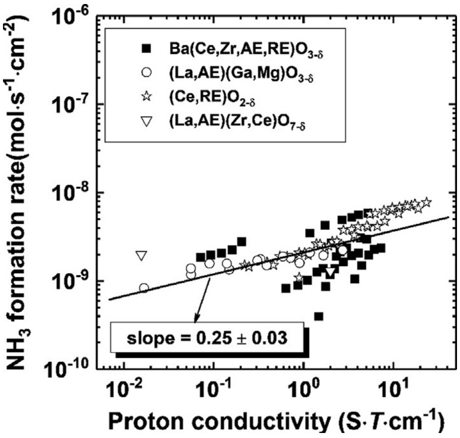

Fig. 4. Dependence of ammonia production rates on proton conductivity of selected electrolytes using a Ag-Pd cathode in the temperature range 350 °C–650 °C. Reprinted with permission from [35]. Copyright 2017 American Chemical Society.

proton conducting solid electrolyte cells. Kobayashi et al. compared the performance of Ag-Pd with that of Ni-$BaCe_{0.9}Y_{0.1}O_{3-\delta}$ and Ni-$BaCe_{0.8}Y_{0.1}Ru_{0.1}O_{3-\delta}$ cermet electrodes for ammonia production in a cell with $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ as the proton conducting electrolyte and 2.3% H_2O/H_2 as the anode gas [31]. The Ni-$BaCe_{0.9}Y_{0.1}O_{3-\delta}$ cathode showed two orders of magnitude higher ammonia production rate than the Ag-Pd cathode under similar conditions. On the other hand, the Ru-containing cathode Ni-$BaCe_{0.8}Y_{0.1}Ru_{0.1}O_{3-\delta}$ showed slightly higher ammonia production than the Ni-$BaCe_{0.9}Y_{0.1}O_{3-\delta}$ cathode (~10^{-10} mol s^{-1} cm^{-2}). Similar improvement in performance due to Ru addition into $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ was also reported by Otomo and coworkers [33]. Even though H_2O was used in these studies, its concentration in the gas stream was very low compared to hydrogen. In order to make electrochemical ammonia production process renewable and sustainable (carbon neutral), studies are needed looking into the feasibility of using just H_2O as the source of H_2. However, to the best of our knowledge, no such effort to use only H_2O as the proton source for ammonia production in a proton conducting cell can be found in the literature.

As mentioned earlier, ammonia production rate is a function of the proton conductivity of the electrolyte membrane. In a study performed by Yoo et al. [35] where they surveyed the literature on electrochemical ammonia production in proton conducting cells, a linear relationship between the ammonia formation rate and proton conductivity of the electrolyte was obtained, provided the electrode catalysts remain the same. Fig. 4 shows this linear dependence of ammonia production on the electrolyte conductivity when a bimetallic Ag-Pd cathode electrocatalyst is used in the temperature range 350–650 °C. The authors hypothesized that due to the high energy need of N_2 dissociation (945.41 kJ/mol), an associative mechanism is highly probable for ammonia production where the nitrogen molecule adsorbs on the electrocatalyst surface followed by subsequent protonation steps. Although the type of mechanism (associative or dissociative) is still under debate, it is agreed that the rate determining step is the first protonation step, ($N_{ad} + H^+ + e^- \rightarrow NH_{ad}$), indicating that the rate can be expressed as $r_{NH_3} \propto \theta_{N_{ad}}\theta_{H^+}$, where $\theta_{N_{ad}}$ and θ_{H^+} are the surface coverages of adsorbed nitrogen and proton, respectively [35]. From this expression, it is clear that for a particular catalyst having a constant nitrogen coverage, the ammonia formation rate is proportional to the proton coverage. Since the concentration of proton on the catalyst surface is determined by the conductivity of the electrolyte, it is implied that the ammonia production rate would increase with increasing electrolyte proton conductivity. Having said that, it has been observed in almost all the ammonia synthesis studies that there is an optimal coverage of nitrogen and hydrogen on the electrode surface at which the ammonia production rate is the maximum. As explained by Kosaka et al. [33] using both experimental data and kinetic modeling, at lower current or cell voltage, the concentration of proton on the surface is low, and so is ammonia formation. As the current increases, proton concentration on electrode surface increases and that leads to greater production rate of ammonia. If the current is increased beyond an optimal point, protons start competing with nitrogen for adsorption sites on the catalyst and that reduces concentration of nitrogen species on the surface. As a result, ammonia formation rate starts decreasing.

2.2. Studies with oxygen ion conducting electrolytes

An alternative to electrocatalytic ammonia production in a proton conducting solid oxide cell is to use an oxide ion conducting solid oxide cell where N_2 and H_2O can be sent simultaneously to the cathode to for ammonia synthesis. One advantage of oxide ion conducting cell is that it produces pure oxygen gas as a byproduct on the anode side, thereby adding value to the process. Moreover, the prospect of using pure H_2O instead of H_2 as the proton source nullifies CO_2 emission from the process. There are not many groups working on oxide ion conducting cells for the purpose of ammonia production, possibly due to the lower rates of ammonia production in such cells compared to their proton conducting counterparts. However, the production rate in the proton conducting cells also drops to the same order of magnitude as obtained from an oxide ion conducting cell, when H_2O is used as the proton source. Therefore, with the added incentive of producing pure oxygen, the oxide ion conducting cells can be a promising alternative for electrocatalytic ammonia production.

To the best of our knowledge, there are only two high-temperature electrocatalytic ammonia production studies in the literature in which oxide ion conducting solid oxide electrolytes were used. One of the studies was published by Skodra and Stoukides in 2009 [36]. In this study, both proton ($SrCe_{0.95}Yb_{0.05}O_{3-\delta}$; SCY) and oxide ion (8% yttria-stabilized zirconia; YSZ) conducting electrolytes were used to synthesize ammonia from N_2 and H_2O. Ru-based industrial catalyst and Ag were utilized as working and counter electrodes, respectively. The low ammonia production rates obtained by both H^+ and O^{2-} conducting cells were attributed to the nature of the working electrode. It is known that Ru is a very active catalyst for ammonia synthesis, however its electrical conductivity is very low. Therefore, in order to increase the electrical conductivity of the working electrode, an inner layer of Ag was used. However, this working electrode configuration caused the surface hydrogen species formed from water electrolysis and/or dissociation to combine on the Ag phase and form gaseous H_2

before reaching the active Ru phase. The desorption of one of the reactants without reaching the active site then caused a significant decrease in ammonia production rate and Faradaic efficiency.

The second study was conducted by Jeoung et al. [37] in 2014. In this study, Pt/GDC/Pt (cathode/electrolyte/anode)-type button cell was used for electrocatalytic ammonia production from N_2 and H_2O at atmospheric pressure between 400 and 600 °C. The study showed that while the highest ammonia production rate (3.67×10^{-11} mol/s.cm^2) was achieved at the highest current applied (2 mA) and the highest temperature (600 °C), the Faradaic efficiency decreased with increasing temperature and current which can be attributed to the increase in the competing hydrogen evolution reaction (HER) that blocks the active sites needed for N_2 adsorption.

It should be noted that it would not be fair to compare the reported electrochemical NH_3 production rates in Table 1 with the rates obtained in Haber-Bosch process using the state-of-the-art catalysts. The reason is that the electrochemical production rates are reported per geometrical area of the electrode and there is limited information about the amount of catalyst used or the number of active sites to calculate the turnover frequency. In order to be able to compare the activity and efficiency of the electrocatalysts used in this nascent technology with those of the state-of-the-art catalysts used in the conventional Haber-Bosch process, more information density amount of active sites should be measured and reported.

3. Current challenges of high-temperature electrocatalytic ammonia synthesis

Although recent years have seen significant effort in producing ammonia electrochemically from its elements at atmospheric pressure in aqueous media and at ambient temperature, high-temperature application of this process is still in its infancy. As summarized in the Background section, the high-temperature electrocatalytic ammonia synthesis studies have focused on solid oxide (ceramic) proton-conducting electrolytes and precious metal-type electrodes such as Rh, Ru, Pd and Pt that provide ammonia production rates in a range of 10^{-13}–10^{-9} mol NH_3/s.cm^2 which are not high enough for a commercial ammonia production system. According to the preliminary analysis of Giddey and co-workers [38], if a current density in the range of 0.25–0.50 A/cm^2 is achieved with a current (Faradaic) efficiency higher than 50% (which can provide ammonia production rate in the range $4.3–8.7 \times 10^{-7}$ mol NH_3/s.cm^2), then the electrochemical NH_3 production can be considered as a reasonable commercial process for small scale and distributed NH_3 production. In order to achieve this targeted production rate range and Faradaic efficiency, new approaches to the working electrode and electrolyte (oxygen ion or proton conducting ceramics) development are needed.

Electrolyte: The ionic conductivity of the electrolyte material in an electrocatalytic system is one of the most important parameters because in these systems, one of the reactants such as oxygen and hydrogen is supplied electrochemically through the electrolyte material. The studies conducted so far have shown that there is a linear correlation between the ionic conductivity of the electrolyte and ammonia production rate. Therefore, in order to develop a promising electrochemical ammonia production system, possible ways to enhance the ionic conductivity of the solid electrolyte materials should be investigated.

In the proton conducting perovskite-type solid oxides, the protons formed at the anode migrate through the electrolyte via hopping from one oxygen ion to another by forming an O—H bond with a lattice oxygen atom (Step 1) and breaking it to hop to the neighboring oxygen atom (Step 2) [39]. A schematic of the proton transfer within a perovskite-type (ABO_3) electrolyte is shown in Fig. 5.

The proton conduction mechanism on the perovskite-type solid oxides suggest that in order to enhance the proton conduction, the number of proton hopping sites should be increased which can be achieved by creating defects in the ideal cubic structure of the perovskite. The proton conductivity also depends on the temperature. As the temperature increases, the protonic conductivity of the solid oxide electrolyte increases. This phenomenon was studied by Chen and Ma [22] by a constant current of 1.5 mA. The study showed that the ammonia production rate increases as the temperature increases from 400 °C to 480 °C due to the increase in protonic conductivity of the BCGO electrolyte, however at higher temperatures, there was a sharp decrease in the production rate which can be attributed to the decomposition of the produced NH_3 into N_2 and H_2 at higher temperatures (Fig. 6). This result suggests that a promising electrolyte material for electrochemical NH_3 production should possess high ionic conductivity at relatively lower temperatures to prevent the ammonia loss due to decomposition.

Another parameter that affects the ionic conductivity of the solid electrolyte materials is the thickness of the electrolyte. As mentioned in a review paper of Fabbri et al. [40], the resistivity of the electrolyte can be lowered by decreasing the electrolyte thickness which provides similar or higher ionic conductivity at relatively lower temperatures. It is well known that the ohmic losses across the electrolyte increases as the thickness of the electrolyte increases which result in a decrease in the current efficiency of the cell [40,41]. Under the same conditions, when the electrolyte thickness is reduced, the electrolyte ohmic loss decreases which enhances the performance of the cell. This phenomenon can be applied to high temperature electrocatalytic ammonia synthesis. The two studies [23,25] performed using the same

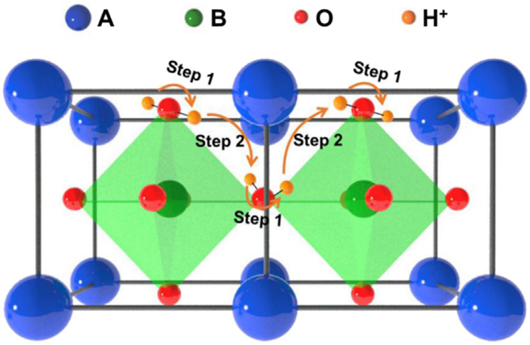

Fig. 5. Schematic of the proton transfer. Reprinted from [39], Copyright 2019, with permission from Elsevier.

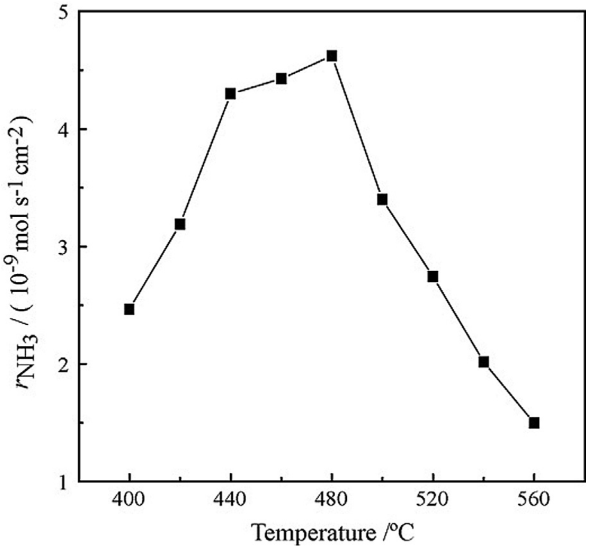

Fig. 6. The rate of ammonia formation as a function of operating temperature. The electrolytic cell: wet H_2, Ni-BCGO|BCGO|Ag-Pd, dry N_2. Reprinted from [22], Copyright 2009, with permission from Elsevier.

electrolytic system, $H_2O + H_2$, Ag-Pd|$BaCe_{0.85}Y_{0.15}O_{3-\delta}$|Ag-Pd, N_2, showed that the ammonia production rate obtained was doubled at 500 °C and 1 mA when the electrolyte thickness decreased from 0.6 mm to 0.03 mm. In conclusion, these findings suggest that, although the current ammonia production rates in the field of high-temperature solid-state ammonia synthesis are too low, the progress in the development of better electrolytes with higher ionic conductivities at lower temperatures promises a potential breakthrough in this field.

Working Electrode: As it can be seen in Table 1, in more than 75% of the high-temperature electrochemical ammonia synthesis studies, Pd-based electrocatalysts, especially Pd and Ag-Pd cathodic materials were used. It is believed that these electrodes work as a hydrogen trap, which improves the probability of hydrogen reacting with nitrogen. If the hydrogen is desorbed readily, hydrogen evolution reaction dominates over ammonia formation. Pd and Ag-Pd electrodes also possess good conductivity and activity for ammonia production. Although studies in the past fifteen years (Table 1) suggest that the above-mentioned assertion has merit and relatively high ammonia production rates and Faradaic efficiencies up to 80% can be achieved using Pd or Ag-Pd electrodes, theoretical studies show that Pd and Ag are amongst the worst surfaces for N_2 adsorption [42].

This seeming contradiction can be explained if one considers the two possible routes for electrocatalytic ammonia synthesis mechanism (Scheme 1): (i) the "dissociative" mechanism that goes through dissociative adsorption of N_2 (breakage of strong triple bond of N_2 prior to nitrogen protonation) [43] (Scheme 1-a), (ii) the "associative" mechanism in which nitrogen is protonated without prior rupture of nitrogen bonds [42] (Scheme 1-b). Although the "associative" mechanism is more favorable to low-temperature NH_3 synthesis, it can also be in operation for electrocatalytic NH_3 synthesis on Pd-based electrodes at high temperatures.

In operando/in situ studies performed under 'real' reaction conditions are needed to be able to differentiate between these two mechanisms for high-temperature electrochemical ammonia synthesis.

Another phenomenon discussed in the literature for NH_3 synthesis on metal electrocatalysts [42,44] is the restructuring of the electrode surfaces or electrode/electrolyte interphases. These theoretical studies evaluated metal electrocatalysts for electrochemical ammonia synthesis and suggested that unlike the precious metals such as Pd, Pt and Ag, early transition metals such as Sc, Y, Ti, Zr, Sr, Yb and Ce have a higher tendency to adsorb N_2 molecules than H_2, thus can catalyze the ammonia synthesis reaction effectively. Considering the fact that most of the electrolyte materials include these early transition metals such as $BaCe_{0.85}Y_{0.15}O_{3-\delta}$, $SrCe_{0.95}Yb_{0.05}$ $O_{3-\delta}$ and $SrZr_{0.95}Y_{0.05}O_{3-\delta}$, it is possible that under reaction conditions, these metals can exsolute from the electrolyte structure and form an active interlayer between the electrode and electrolyte [43,45]. As a result, the promising activity of the Pd-based electrodes could be attributed to the formation of active interlayer between the working electrode and electrolyte. Unfortunately, the lack of elaborative characterization of the electrocatalytic materials and electrode-electrolyte assemblies under reaction conditions makes it difficult to reconcile the differences between the observed activities of Pd-Ag type working electrodes and the theoretical studies.

Aside from the precious metal-type electrocatalysts, well-known Haber-Bosch catalysts, Fe and Ru were also used in solid-state electrochemical synthesis of ammonia, however due to their low electrical conductivity and very high affinity for hydrogen evolution reaction (HER), these electrocatalysts suffered from low Faradaic efficiency.

In addition to metal electrocatalysts, a relatively new group of catalysts, transition metal nitrides, has started gaining attention. The computational studies of Abghoui and Skulasson [46,47] suggest that the transition metal nitrides, especially VN, NbN, CrN and ZrN have a significant potential to activate nitrogen and catalyze the electrochemical synthesis of ammonia via Mars-van Krevelen (MvK) mechanism (Scheme 2). In Scheme 2, $^*V_N$ and $^*V_{2N}$ denote nitrogen vacancy (N-vacancy) and dimer N-vacancy, respectively. In MvK mechanism, surface nitrogen atoms are reduced by protons to NH_3 and then NH_3 molecules desorb from the electrode surface creating nitrogen vacancies which are replenished with gaseous nitrogen molecules.

Although the theoretical study results are very promising, the number of studies utilizing transition metal nitrides as working electrode in the solid-state electrocatalytic ammonia production studies is very limited. Amar and co-workers [48,49] studied Co_3Mo_3N and Fe_3Mo_3N type mixed metal nitrides for electrocatalytic ammonia production at a temperature range of 400–450 °C, however due to relatively low electrical conductivity of nitrides and low operating temperature, the ammonia production rates and Faradaic efficiencies were rather low. In the most recent study conducted by Kyriakou et al. [50], vanadium nitride-iron (VN-Fe) type composite electrode was studied for

(a)

$$2^* + N_2 \rightarrow 2^*N \tag{1}$$

$$2^*N + 6(H^+ + e^-) \rightarrow {}^*N + {}^*NH + 5(H^+ + e^-) \tag{2}$$

$${}^*N + {}^*NH + 5(H^+ + e^-) \rightarrow 2^*NH + 4(H^+ + e^-) \tag{3}$$

$$2^*NH + 4(H^+ + e^-) \rightarrow {}^*NH + {}^*NH_2 + 3(H^+ + e^-) \tag{4}$$

$${}^*NH + {}^*NH_2 + 3(H^+ + e^-) \rightarrow 2^*NH_2 + 2(H^+ + e^-) \tag{5}$$

$$2^*NH_2 + 2(H^+ + e^-) \rightarrow {}^*NH_2 + {}^*NH_3 + (H^+ + e^-) \tag{6}$$

$${}^*NH_2 + {}^*NH_3 + (H^+ + e^-) \rightarrow 2^*NH_3 \tag{7}$$

$$2^*NH_3 \rightarrow 2NH_{3(g)} + 2^* \tag{8}$$

(b)

$${}^* + N_2 \rightarrow {}^*N_2 \tag{1}$$

$${}^*N_2 + 6(H^+ + e^-) \rightarrow {}^*N_2H + 5(H^+ + e^-) \tag{2}$$

$${}^*N_2H + 5(H^+ + e^-) \rightarrow {}^*NNH_2 + 4(H^+ + e^-) \tag{3}$$

$${}^*NNH_2 + 4(H^+ + e^-) \rightarrow {}^*N + NH_{3(g)} + 3(H^+ + e^-) \tag{4}$$

$${}^*N + 3(H^+ + e^-) \rightarrow {}^*NH + 2(H^+ + e^-) \tag{5}$$

$${}^*NH + 2(H^+ + e^-) \rightarrow {}^*NH_2 + (H^+ + e^-) \tag{6}$$

$${}^*NH_2 + (H^+ + e^-) \rightarrow {}^*NH_3 \tag{7}$$

$${}^*NH_3 \rightarrow NH_{3(g)} + {}^* \tag{8}$$

Scheme 1. Possible electrocatalytic ammonia synthesis mechanisms via (a) dissociative route and (b) associative route [42]. * denotes surface sites on the electrode.

$${}^* + 6(H^+ + e^-) + N_2 \rightarrow {}^*H + 5(H^+ + e^-) + N_2 \tag{1}$$

$${}^*H + 5(H^+ + e^-) + N_2 \rightarrow {}^*2H + 4(H^+ + e^-) + N_2 \tag{2}$$

$${}^*2H + 4(H^+ + e^-) + N_2 \rightarrow {}^*3H + 3(H^+ + e^-) + N_2 \tag{3}$$

$${}^*3H + 3(H^+ + e^-) + N_2 \rightarrow {}^*V_N + NH_{3(g)} + 3(H^+ + e^-) + N_2 \tag{4}$$

$${}^*V_N + 3(H^+ + e^-) + N_2 \rightarrow {}^*V_NH + 2(H^+ + e^-) + N_2 \tag{5}$$

$${}^*V_NH + 2(H^+ + e^-) + N_2 \rightarrow {}^*V_N2H + (H^+ + e^-) + N_2 \tag{6}$$

$${}^*V_N2H + (H^+ + e^-) + N_2 \rightarrow {}^*V_N3H + N_2 \tag{7}$$

$${}^*V_N3H + N_2 \rightarrow {}^*V_{2N} + NH_{3(g)} + N_2 \tag{8}$$

$${}^*V_{2N} + N_2 \rightarrow {}^* \tag{9}$$

Scheme 2. Possible electrocatalytic ammonia synthesis mechanism via Mars-van Krevelen (MvK) route [44]. *, *H, $^*V_N$ and $^*V_{2N}$ denote surface sites, protonated surface sites, N-vacancies and dimer N-vacancies on the electrode.

electrochemical NH_3 production in a double chamber protonic ceramic membrane reactor (PCMR). The novelty of this research comes from the fact that the whole Haber-Bosch process was squeezed into an electrochemically-driven PCMR operated at atmospheric pressure. The hydrogen needed for the NH_3 production comes from methane steam reforming and water-gas shift reactions which take place at the counter electrode chamber. The protons transfer through proton conductive electrolyte ($BaZrO_3$) and react with N_2 at the working electrode chamber.

Given the fact that high-temperature electrochemical synthesis of ammonia using solid electrolytes has been studied only for the last 20 years and still in early stages of development, the lack of information about the reaction mechanism and the behavior of the potential electrocatalysts under reaction environment is understandable. However, in order to move the high-temperature electrochemical synthesis of ammonia process one step forward, experimental and theoretical studies should be combined to design stable electrocatalysts that can activate nitrogen, catalyze the reaction between nitrogen and hydrogen and provide high electronic conductivity while suppressing the hydrogen evolution reaction. In other words, the triple-phase-boundary (TPB) of the working electrodes where the electrochemical reactions are believed to take place should be enhanced by improving the ionic and electrical conductivity of the electrode materials. The triple-phase-boundary (TPB) term is used to refer to the active sites on the electrode where the activity, ionic conductivity and electrical conductivity meet. As it can be seen from Table 1 that metallic electrodes which do not exhibit any ionic conductivity dominate the research field. Therefore, it is suggested that the working electrode development studies should shift from metallic electrodes to composite electrodes which can be modified by doping techniques to enhance their ionic/electronic conductivity, as well as their ability to activate nitrogen.

Quantification of Ammonia: Since the activity and selectivity of the electrocatalytic ammonia synthesis catalyst is directly determined by the production rate of ammonia during the electrochemical process, the method used for ammonia quantification in the product stream or in the ammonia trap is very critical. The quantification method should be very sensitive, only selective towards ammonia, accurate, reproducible, not time-consuming and economically feasible [51]. The ammonia quantification techniques including ion chromatography, spectrophotometry/colorimetry, ion-selective electrode and fluorescence methods used in both ambient and high-temperature electrochemical ammonia production studies are critically discussed in a review paper of Cui et al. [52]. Among these methods, ion chromatography with the appropriate columns provides the lowest ammonia detection limit with high reproducibility and accuracy, however the need of costly instrumentation limits the use of this technique. The most widely used quantification method is the spectrophotometric method including indophenol blue and Nessler reagent techniques due to its relatively good sensitivity and low cost [51]. In addition to these techniques, ammonia or ammonium ion-selective electrode method is also used for quantification of ammonia produced electrochemically with good precision.

All the methods mentioned above need a thorough calibration for the accurate quantification of ammonia. In order to obtain reproducible and reliable results, the calibration checks should be performed regularly.

In addition to the above-mentioned issues and concerns, research articles on ammonia production should also provide sufficient details on the experimental parameters, reactor set-up and product detection system, so that the reported data can be reproduced by other groups. Among the current literature, a significant portion does not mention the respective Faradaic efficiencies, and it is not possible to calculate it from the reported data due to incomplete information on the experimental variables.

4. Conclusions and prospects

In the present mini-review paper, the literature on high-temperature solid-state electrochemical ammonia production was summarized and the current state of the process was discussed. As mentioned earlier, the high-temperature electrocatalytic ammonia synthesis process is at an early stage of research and development, and demands collaborative effort on both theoretical and practical aspects of the process. Only through such efforts, additional insights can be acquired on how to tailor the activity, selectivity and stability of electrocatalysts, how to manipulate the ionic conductivity of the solid-state electrolytes, and how to differentiate among different mechanisms.

Realizing the full potential of high-temperature electrocatalytic ammonia production will only be possible if the following issues are addressed:

1. *Better understanding of the high-temperature electrocatalytic ammonia synthesis mechanism on different types of electrocatalysts:* Both theoretical and experimental studies should be performed to investigate the possible reaction pathways on different types of active surfaces such as precious metals, transition metals, metal/mixed metal nitrides, perovskite oxides and perovskite oxynitrides. Although there are some theoretical studies available in the literature to understand the mechanistic steps of electrochemical nitrogen reduction reaction, especially on precious metals and transition metal oxide/nitrides, the experimental backing of the proposed NRR mechanisms is still missing. It is unfortunate that despite the recent developments in the advanced characterization techniques such as in-situ/in operando near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS), in-situ transmission/scanning electron microscopy, synchrotron X-ray radiation techniques and in operando vibrational spectroscopy, the number studies applying these techniques to the high-temperature NH_3 production is limited.
2. *Better design of the working electrode:* Instead of relying on precious metal-based electrodes, as suggested by the theoretical studies, novel electrocatalysts which can provide high activity and electronic conductivity while suppressing the dominant hydrogen evolution reaction (HER) should be investigated. The computational studies showed that certain transition metal nitrides have a significant potential in nitrogen reduction for ammonia synthesis via MvK-type mechanism that provides an easier nitrogen activation.
3. *Better understanding of the overall process:* There are some concerns in the scientific community regarding the source of nitrogen in electrochemical ammonia production process. The on-going debate is that the reported values for the electrocatalytic ammonia production might be originated from the potential contamination in the reactant gases or environmental contamination or from the electrode and/or electrolyte materials including activated nitrogen in their structure such as transition metal nitride-type electrocatalysts [53]. In order to eliminate this possibility, $^{15}N_2$ isotope labelling experiments should be performed whenever a new catalytic material or electrolyte is tested to prove that the source of the nitrogen is molecular dinitrogen supplied to the system.

In conclusion, high-temperature solid-state electrocatalytic ammonia production has a significant potential for distributed, on-demand fertilizer production as well as for a cleaner ammonia production process. In order to achieve this in the near future, the theoretical and experimental efforts should be combined to design active, selective and stable electrocatalytic systems.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2020.04.025.

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