A comprehensive investigation of direct ammonia-fueled thin-film solid-oxide fuel cells: Performance, limitation, and prospects

Highlights

- Thin-film SOFCs and a commercial SOFC are tested for direct-ammonia and H2 operation
- Record-high performance for direct-ammonia operation achieved with thin-film SOFC
- 2D multi-physics modeling explained the performance gap between NH3 and H2 fuel
- NH3 decomposition activity and gas transport are the main causes of the performance gap
A comprehensive investigation of direct ammonia-fueled thin-film solid-oxide fuel cells: Performance, limitation, and prospects

Seongkook Oh,1,2,6 Min Jun Oh,1,4,6 Jongsup Hong,4 Kyung Joong Yoon,1,5 Ho-Il Ji,1,2 Jong-Ho Lee,1,2 Hyungmook Kang,1,* Ji-Won Son,1,2,3,7,* and Sungeun Yang1,2,*

SUMMARY
Ammonia is a promising carbon-free hydrogen carrier. Owing to their nickel-rich anodes and high operating temperatures, solid oxide fuel cells (SOFCs) can directly utilize NH₃ fuel—direct-ammonia SOFCs (DA-SOFCs). Lowering the operating temperature can diversify application areas of DA-SOFCs. We tested direct-ammonia operation using two types of thin-film SOFCs (TF-SOFCs) under 500 to 650 °C and compared these with a conventional SOFC. The TF-SOFC with a nickel oxide gadolinium-doped ceria anode achieved a peak power density of 1330 mW cm⁻² (NH₃ fuel under 650 °C), which is the best performance reported to date. However, the performance difference between the NH₃ and H₂ operations was significant. Electrochemical impedance analyses, ammonia conversion quantification, and two-dimensional multi-physics modeling suggested that reduced ammonia conversion at low temperatures is the main cause of the performance gap. A comparative study with previously reported DA-SOFCs clarified that incorporating a more active ammonia decomposition catalyst will further improve low-temperature DA-SOFCs.

INTRODUCTION
Ammonia (NH₃) and solid oxide fuel cells (SOFCs) are ideal combinations for tackling de-carbonization in transportation sectors, such as the shipping, heavy-duty vehicle, and aviation sectors. Ammonia is easily liquefied at approximately 10 bar under ambient temperature and has one of the highest gravimetric H₂ (17.8 wt %) and volumetric H₂ (108 kgH₂ m⁻³ at 8.6 bar and under 20 °C) densities among carbon-free energy carriers (Kobayashi et al., 2019; Mukherjee et al., 2018). This makes it a suitable fuel for mobile electricity generation. SOFCs are energy conversion devices that typically operate under ≥ 650 °C and possess the highest electrical efficiency among all fuel-cell technologies (Sharaf and Orhan, 2014). Ammonia can be directly fueled into SOFCs without pretreatment or external reactors; these fuel cells are thus called direct ammonia SOFCs (DA-SOFCs).

The ammonia decomposition reaction is thermodynamically and kinetically favored under the typical operating temperature of SOFCs, that is, ≥ 650 °C. The thermodynamic equilibrium composition of NH₃ is already as low as 0.13% under 500 °C and 0.03% under 650 °C. The anode of SOFCs generally consists of a few hundred micrometers thick and porous Ni-YSZ (yttria-stabilized zirconia) cermet, in which Ni is used as a cheap and active catalyst for the ammonia decomposition reaction (Boisen et al., 2005; Mukherjee et al., 2018). Therefore, the thick and porous Ni-YSZ cermet can function as an internal ammonia decomposition reactor.

Two or three reactions are required for the direct utilization of ammonia: (1) the ammonia decomposes into N₂ and H₂ inside the anode at the catalyst surface; (2) the produced H₂ generates electricity via an electrochemical oxidation reaction at the anode functional layer; (3) direct electrochemical oxidation of NH₃. However, if the ammonia decomposition reaction is fast enough to produce a sufficient amount of hydrogen, reactions (1) and (2) dominate the SOFC anode reactions.

\[
\text{NH}_3 \rightarrow 0.5\text{N}_2 + 1.5\text{H}_2 \quad \text{(Equation 1)}
\]

\[
\text{H}_2 + \text{O}_2^- \rightarrow \text{H}_2\text{O} + 2\text{e}^- \quad \text{(Equation 2)}
\]
The use of ammonia fuel also increases the device efficiency more than the use of H₂ fuel. The ammonia decomposition reaction is endothermic, where heat is required, and the electrochemical reaction is exothermic, where heat is generated. When ammonia is directly fueled into the SOFC, the heat generated from the electrochemical reaction can be directly used to decompose ammonia, thereby increasing its efficiency (Luo et al., 2022; Zendrini et al., 2021). DA-SOFCs are not only carbon-free but also perform better than traditional methane fuels. The hydrogen formation rate on the Ni surface is much faster for ammonia decomposition than for methane steam reforming (Molouk et al., 2015). In addition, the heat required to produce one mole of H₂ is 36.4 kJ mol⁻¹ for the ammonia decomposition reaction (1) and 47.1 kJ mol⁻¹ for the methane steam-reforming reaction (CH₄ + 2H₂O → 4H₂ + CO₂) under 650°C.

SOFCs are also superior to other energy-conversion devices that use ammonia. Ammonia can be directly used in traditional gas turbines. However, the combustion of NH₃ inevitably emits harmful NOx species in excessive amounts, creating a need for a separate unit to reduce NOx emissions (Kobayashi et al., 2019). Proton-exchange membrane fuel cells (PEMFCs) are another alternative. However, ammonia-fueled PEMFCs require a separate ammonia decomposition reactor that operates under a much higher temperature than the operating temperature of PEMFCs (80°C), thereby reducing the overall efficiency. The catalysts and membranes of PEMFCs also suffer from ammonia poisoning; thus, they require thorough ammonia purification (Cha et al., 2018; Verdaguer-Casadevall et al., 2012). DA-SOFCs can operate free of external catalytic reactors, purifiers, and NOx reduction devices.

The first DA-SOFC reported dates back to 1980 when Harr and Vayenas used DA-SOFC to produce NO and electricity (Vayenas and Farr, 1980). The use of DA-SOFC solely to produce electricity has only been studied since the early 2000s (Wojcik et al., 2003). Most of the studies on DA-SOFCs used SOFCs that were optimized for H₂ fuel and compared H₂ fuel operation with that of NH₃ fuels. Dekker and Rietveld (2006) and Stoeckl et al. (2019) used conventional large-area anode-supported SOFCs for the direct-ammonia operation. Ammonia decomposition was almost complete at 700°C, and its performance was almost the same as that of H₂ operation under ≥750°C (Dekker and Rietveld, 2006). The temperature decrease inside the cell owing to the ammonia decomposition reaction was the main reason for the slight performance loss during the direct-ammonia operation (Stoeckl et al., 2019). We note that if the performance loss is solely owing to the lowered temperature of the cell, the loss of performance can be compensated by increasing the operating temperature without compromising efficiency. Although the performance of DA-SOFCs under high temperatures (≥750°C) is almost as good as that of H₂, the operating temperature should be lowered to diversify the application of SOFCs. The high operating temperatures of SOFCs raise serious concerns such as the need for expensive constituent materials, cell degradation, and slow startup-shutdown cycles. Reducing the operating temperature of DA-SOFCs without compromising their performance will be beneficial for lowering the cost of constituent materials, improving durability, and enabling faster startup-shutdown cycles.

Different types of SOFCs were tested to lower the operating temperature of DA-SOFCs. Direct-ammonia operation showed a dramatic decrease in performance of the high-performance cell (Ni-SDC|SDC|BSCF) between 550 and 650°C (Meng et al., 2007). The cell exhibited a peak power density of 1872 mW cm⁻² with H₂ fuel and 1190 mW cm⁻² with ammonia under 650°C. The authors suggested that the decrease in temperature caused by the endothermic ammonia decomposition reaction is the main reason for the performance gap. Protonic ceramic fuel cells (PCFCs) are promising candidates for the direct operation of ammonia. PCFCs do not suffer from fuel dilution at the anode and show higher efficiencies than do SOFCs (Ni et al., 2009). Moreover, PCFCs may be operated free of NOx emissions because oxygen species are absent in the anode compartment. In addition, proton-conducting oxides improve ammonia decomposition by reducing the hydrogen-poisoning effect on Ni (Miyazaki et al., 2017, 2020; Yang et al., 2015a). Ni-BCZY|BCY20|BCY20-LSCF demonstrated a peak power density of approximately 250 mW cm⁻² under ammonia using under 650°C, and the direct-ammonia operation performed slightly worse than did the H₂ operation; the authors suggested insufficient ammonia conversion was the main reason for this (Miyazaki et al., 2020). Recently, high-performance DA-PCFCs with the incorporation of catalysts have been reported. A Pd exsolution catalyst combined with a PCFC (He et al., 2021), tubular PCFC combined with an Fe catalyst layer (Pan et al., 2022), and an Fe-infiltrated PCFC (Zhang et al., 2022) under 650°C showed peak power densities of 724 mW cm⁻², 685 mW cm⁻², and 1257 mW cm⁻², respectively. Although high-performance cells with the addition of catalysts have been reported, the exact role of the catalyst and

\[ \text{NH}_3 + 1.5 \, \text{O}^{2-} \rightarrow 0.5 \text{N}_2 + 1.5 \, \text{H}_2\text{O} + 3 \, \text{e}^- \] (Equation 3)
the limitation of performance enhancement compared to that of H₂ fuel have not been studied in detail for high-performance DA-SOFC/PCFCs.

Our team has been developing high-performance thin-film-based-SOFCs (TF-SOFCs) for use under low-temperature operations (<650°C) using pulsed laser deposition (PLD). Nanostructure incorporation of both the anode and cathode with reduced electrolyte thickness improved the performance of low-temperature SOFCs (Bae et al., 2017; Chao et al., 2011; Karimaghaloo et al., 2019; Kim et al., 2011; Myung et al., 2011; Thieu et al., 2017). The performances of our TF-SOFCs using hydrogen and butane fuels are among the best reported under <650°C (Park et al., 2021; Thieu et al., 2020, 2022). The coupling of TF-SOFCs with ammonia fuel is an excellent combination for low-temperature DA-SOFCs.

In this study, we compared three different SOFCs to systemically study DA-SOFCs under low-temperature: a commercial SOFC optimized for high-temperature H₂ operation, a TF-SOFC with a Ni-YSZ anode, and a high-performance TF-SOFC with a Ni-GDC (gadolinium-doped ceria) anode. The electrochemical performance and electrochemical impedance spectroscopy results were compared between the direct-ammonia and hydrogen operations, and unreacted ammonia was collected to measure the ammonia conversion inside the cell. Furthermore, a two-dimensional (2D) multi-physics numerical model was developed to observe kinetics and electrochemical reactions inside the cells. The model was validated with experimental results and then suggested key parameters which are able to improve the performance of DA-SOFCs toward that under the pure H₂ condition.

RESULTS

Microstructure of the tested solid oxide fuel cells

The thin-film-based SOFCs (TF-SOFCs) prepared via PLD showed very high performance at low temperatures with H₂ fuel (Park et al., 2021; Shin et al., 2020). We tested the direct-ammonia operation of TF-SOFCs to demonstrate the possibility of using TF-SOFCs as low-temperature DA-SOFCs (Figure 1A). Two types of TF-SOFCs based on Ni-YSZ and Ni-GDC were employed and denoted as TF-Ni/YSZ and TF-Ni/GDC,
respectively. A commercial SOFC cell denoted as bulk-Ni/YSZ was tested to determine the effect of high performance on the direct-ammonia operation. All three samples were fabricated on the same commercial substrate consisting of an anode support layer and an anode functional layer.

Figures 1B–1D show the cross-sectional SEM (scanning electron microscope) images of the bulk-Ni/YSZ, TF-Ni/YSZ, and TF-Ni/GDC cells after the direct-ammonia operation. Bulk-Ni/YSZ consists of an anode support layer, anode functional layer, electrolyte, buffer layer, cathode functional layer, and current-collecting layer (Figure 1B, from bottom to top). The anode consisted of approximately 1 μm-sized Ni and YSZ particles. The difference between the anode support layer and the anode functional layer is that the former contains porous gas channels that facilitate fuel gas transport. The LSCF-GDC cathode functional layer consisted of submicron-scale fine particles on a 2-μm-thick porous GDC buffer layer and 6-μm-thick dense YSZ electrolyte layer.

The main difference between bulk and thin-film SOFCs is their size scale. The PLD process enables the fabrication of nanostructured electrodes with thin electrolytes on commercial anode substrates. Figure 1C shows the TF-Ni/YSZ fabricated with the same material as the bulk-Ni/YSZ. A thin-film nano anode functional layer with a thickness of 3 μm was deposited using PLD. This layer was composed of Ni-YSZ with a particle size of approximately 100 nm so that the triple-phase boundary could be increased, thereby improving the low-temperature performance (Park et al., 2016). However, the pore size was reduced to several tens of nanometers. A 1-μm-thick dense YSZ was deposited on top of the anode, and a 200-nm-thick dense GDC buffer layer was deposited between the YSZ electrolyte and LSC cathode. Finally, a 3-μm-thick LSC was deposited as an approximately 800 nm-wide columnar and porous layer to facilitate the oxygen reduction reaction (Noh et al., 2011).

The third cell, TF-Ni/GDC, was optimized for high-performance H2 fuel operation (Figure 1D). First, the PLD nano anode functional layer consisted of a Ni-GDC cermet on the same commercial NiO-YSZ substrate with a thickness of 3 μm. The higher ionic conductivity of GDC compared to that of the YSZ increased the activity of the electrochemical reactions. For the electrolyte, the optimized sandwich structure (GDC-YSZ-GDC) was applied to minimize the thickness of the YSZ while maintaining its dense structure (Oh et al., 2018). The cathode performance was further improved by modifying the deposition conditions to increase the surface roughness.

High performances of thin-film-solid oxide fuel cells with direct ammonia fuel

Three cells were first tested with wet H2 fuel (3% H2O) to verify the integrity of each cell and compare its performance with that of the ammonia fuel. The open-circuit voltages (OCV) of all three cells were 1.10 V under 650°C, which is close to the theoretical OCV of 1.13 V and a reasonable value for SOFC cell testing. The dotted lines in Figures 2A–2C show the I-V (current-voltage) and I-P (current-power) curves of H2 operation. After the electrochemical test using H2 fuel under each temperature, dry NH3 was directly fueled into the same cell for subsequent DA-SOFC tests. The solid lines in Figures 2A–2C show the I-V and I-P curves of the direct-ammonia operation.

A commercial cell, bulk-Ni/YSZ, shows a peak power density (PPD) of 394 mW cm⁻² under 650°C with H2 fuel, which is a suitable value for commercial SOFC. Bulk-Ni/YSZ cells with ammonia recorded OCVs of 1.24, 1.24, 1.22, and 1.22 under 650, 600, 550, and 500°C, respectively. Lower OCV with decreasing temperature is unusual for H2-fueled SOFCs. But for direct ammonia operation, ammonia conversion decreases with decreasing temperature (Figure 2F). Decreased ammonia conversion lowers pH2 at the electrochemical interface resulting in lower OCV with decreasing temperature. The PPDs of the bulk-Ni/YSZ were 394-147 mW cm⁻² with H2 and NH3 under 650, 600, 550, and 500°C, respectively (Figures 2A and 2D). The PPDs were compared between NH3 and H2 operation with respect to the PPD ratio, that is, PPDH2/PPD NH3 (%) (Figure 2E); PPDH2/PPD NH3 values were 87.3, 82.0, 82.6, and 80.0% under 650, 600, 550, and 500°C, respectively.

Unlike for the bulk Ni/YSZ, the I-V curves were slightly deflected at high current densities, especially with ammonia fuel. These deflections indicate the existence of mass transport limitations, an insufficient supply of fuel, in the TF-Ni/YSZ. The ratio of PPDH2/PPD NH3 was much lower (73.2, 50.2, 42.2, and 37.3% under 650, 600, 550, and 500°C).
The performance gap between NH₃ and H₂ increased as the operating temperature decreased. A TF-Ni/GDC cell, the most optimized cell for low-temperature H₂ operation, exhibited OCVs of 1.11, 1.10, 1.09, and 1.08 V under 650, 600, 550, and 500 °C, respectively, with ammonia. Highest PPDs were obtained for the cells tested for TF-Ni/GDC: 1961-1330, 1587-557, 1220-342, and 833-204 mW cm⁻² with H₂ and NH₃ under 650, 600, 550, and 500 °C respectively (Figures 2C and 2D). A PPD of 1330 mW cm⁻² was the highest ever reported value under 650 °C for a SOFC. Although the TF-Ni/GDC showed the highest performance, the PPDΝΗ₃/PPDH₂ ratio decreased even further: 67.8, 35.1, 28.0, and 24.5% under 650, 600, 550, and 500 °C, respectively. Similar to the observation with TF-Ni/YSZ, the performance gap widened as the temperature decreased. The I-V curves also showed a more dramatic deflection than that observed for TF-Ni/YSZ. Mass transport limiting currents were reached under all temperatures with ammonia fuel, indicating that the performance was entirely limited by fuel starvation at high current densities. We assumed that the H₂ provided by the ammonia decomposition reaction did not match the H₂ required to reach such high current densities.

Figure 2. Performances of the tested SOFCs under ammonia and hydrogen fuel operation
(A–C) I-V-P graphs of bulk-Ni/YSZ, TF-Ni/YSZ, and TF-Ni/GDC with hydrogen (dotted line) or ammonia (solid line) fuel.
(D) Peak power density comparison of each cell with hydrogen (filled) or ammonia (slashed) fuel.
(E) Peak power density ratio, PPDΝΗ₃/PPDH₂ (%), comparison.
(F) NH₃ fuel conversion measured by capturing unreacted ammonia at the exhaust of each cell at OCV.
Figure 2D compares the PPDs of the three cells in each fuel, and the TF-SOFCs presented higher power densities than the bulk-Ni/YSZ under each condition. The performance of the TF-Ni/GDC was noticeably better than that of the TF-Ni/YSZ under H2 fuel operation. However, the difference between the two TF-SOFCs decreased for the ammonia fuel, and the gap narrowed with decreasing temperature. Because both cells have similar ammonia conversions (Figure 2F) and show mass transport limiting currents, we assumed that insufficient H2 supply was the main limitation of the performance at low temperatures.

Figure 2F shows the ammonia conversion, measured by trapping ammonia from the outlet gas at the OCV. Ammonia decomposition mainly occurred at the Ni catalyst surface. The three cells were fabricated on the same anode support with a thickness of approximately 700 μm, and the TF-SOFCs had an additional Ni-YSZ or Ni-GDC cermet prepared via PLD with an approximate thickness of 3 μm. Because the area of the total Ni surface was more or less similar for all three cells, the ammonia conversion was more or less the same for all cells. Ammonia conversion decreased from approximately 80 to 20% from 650 to 500 °C, indicating that the ammonia decomposition reaction was incomplete for the typical anode-supported type cell below 650 °C. However, the production rate of hydrogen measured at the outlet at OCV was 0.152, 0.092, 0.057, and 0.035 mmol H2 sec⁻¹ at 650, 600, 550, and 500 °C, respectively. If these are converted to the current density, they can draw 29.28, 17.74, 11.19, and 6.69 A cm⁻² at 650, 600, 550, and 500 °C, respectively. The maximum current density we have drawn from the best performing cell, TF-Ni/GDC, were 2.165, 0.875, 0.565, and 0.365 A cm⁻² at 650, 600, 550, and 500 °C, respectively. That is, the maximum current density measured in our experiment is very small compared to the value of total hydrogen produced at the outlet. Therefore, ammonia conversion measured at the outlet does not explain H2 starvation occurring at the TF-SOFCs.

Studies have suggested that the decreased temperature owing to the endothermic ammonia decomposition reaction is the main reason for the decreased performance of the DA-SOFC (Meng et al., 2007; Stoeckl et al., 2019). However, this explanation does not explain our data because the performance gap increased with decreasing temperature; lower temperatures reduced the extent of the decomposition reaction (Figure 2F), resulting in a smaller temperature gap. Moreover, it was clear from the I-V curves that mass transport limitations were present, particularly for high-performance cells with ammonia fuel. An improved ammonia decomposition reaction rate in the cell will further increase the performance of the TF-SOFCs with ammonia fuel.

**Electrochemical impedance spectrum analysis**

Electrochemical impedance spectroscopy was used to analyze the cause of the performance difference between the ammonia and H2 fuels. The electrochemical impedance spectrum (EIS) was analyzed from 650 to 500 °C at 0.75 V in a 3% wet H2 fuel and NH3 fuel atmosphere. The EIS of the H2-NH3 mixed fuel was further analyzed to investigate the effect of H2 concentration on EIS; 33 sccm of H2 was added to 160 sccm of NH3. Figure 3 shows representative EIS data under 550 °C and 0.75 V in Nyquist and Bode plots and the comparison of ohmic and polarization area-specific resistances for each fuel and temperature condition. Additional data are presented in Figures S1 and S2. Figures 3A–3C show the EIS data for the bulk-Ni/YSZ. Under 550 °C, the bulk-Ni/YSZ exhibited an 82.6% performance with NH3 compared to that with H2. The total resistance increased from 3.483 to 4.023 Ω cm². The ohmic resistance with NH3 fuel increased by 0.028 Ω cm² compared with that with H2 fuel. This difference seems to be caused by a temperature drop owing to the endothermic NH3 decomposition reaction; however, it is a small value compared to the total resistance increase of 0.540 Ω cm². The Bode plot in Figure 3B shows that the impedance increased in the low-frequency range (10⁶ to 10² Hz). Low-frequency impedance is generally attributed to gas diffusion of reactants (Gasper et al., 2020; Jeanmonod et al., 2020; Miyazaki et al., 2020; Thieu et al., 2022). Adding hydrogen gas to the ammonia fuel slightly decreased the low-frequency impedance. We assume that the low ammonia conversion (34.4%) was the main reason for the increased impedance in the low-frequency region and the total resistance. The gap between the NH3 and H2 fuels was greater for the TF-SOFCs, as seen in the I-V curves (Figure 2). The total resistance increased from 0.378 to 0.807 Ω cm² for the TF-Ni/YSZ and from 0.193 to 0.775 Ω cm² for the TF-Ni/GDC. Again, the contribution from the ohmic resistance increase was minimal (0.026 and 0.007 Ω cm² for the TF-Ni/YSZ and the TF-Ni/GDC, respectively), confirming that the decrease in temperature was insignificant in these cells. Deflection of the I-V curves, that is, mass transport limitation, was already present at 0.75 V for both the TF-SOFCs (Figures 2B and 2C). The Bode plots (Figures 3E and 3H) show that the impedance dramatically increased in the low-frequency range (10⁶ to 10² Hz), confirming that the supply of fuel—H2 from ammonia decomposition—is insufficient for both
TF-SOFCs. The current densities at 0.75 V were 0.07, 0.29, and 0.42 A cm$^{-2}$ for the bulk-Ni/YSZ, TF-Ni/YSZ, and TF-Ni/GDC, respectively, which means that a high-performing cell demands more and thus, falls short of H$_2$ during the operation. Therefore, a better catalyst is required to improve the performance. The low-frequency impedances were lowered by introducing additional hydrogen gas to the ammonia fuel for both TF-SOFCs, thereby compensating for the insufficient supply of H$_2$. 

**Figure 3.** Electrochemical impedance analyses of DA-SOFCs
(A and B) Nyquist and Bode plots of the bulk-Ni/YSZ cell with H$_2$, H$_2$-NH$_3$ mixed, and NH$_3$ fuels, respectively.
(C) The distinguished ohmic, polarization resistance of the bulk-Ni/YSZ cell.
(D and E) Nyquist and Bode plot of the TF-Ni/YSZ cell with H$_2$, H$_2$-NH$_3$ mixed, and NH$_3$ fuels, respectively.
(F) The distinguished ohmic, polarization resistance of the TF-Ni/YSZ cell.
(G and H) Nyquist and Bode plot of the TF-Ni/GDC cell with H$_2$, H$_2$-NH$_3$ mixed, and NH$_3$ fuels, respectively.
(I) The distinguished ohmic, polarization resistance of the TF-Ni/YSZ cell.
Nickel nitride (NiN) formation can also reduce low-temperature performance. Ni forms NiN upon exposure to ammonia under the temperature range of 700 to 500°C, and the amount of nitride increased with lowering of the temperature (Yang et al., 2015b). The Ni-YSZ anode also suffered from Ni agglomeration by NiN formation after the DA-SOFC operation (Stoeckl et al., 2019). Therefore, NiN can be formed under low temperatures, which may have increased the anodic charge-transfer resistance at 10^3-10^5 Hz (Park et al., 2016). A slight increase in the impedance in this high-frequency region, although the contributions were small, was observed for both TF-SOFCs. Incorporating a better catalyst may also reduce this high-frequency impedance, where the unreacted ammonia reaching the anode functional layer would be smaller.

Two-dimensional multi-physics numerical model

Two-dimensional (2D) multi-physics modeling was used to obtain a more detailed perspective on what limits the performance of DA-SOFCs, especially at low temperatures. Several previous studies studied the operation of DA-SOFCs using multi-physics modeling ranging from the high operating temperature range of 700-1000°C (Ilbas et al., 2020; Kishimoto et al., 2017) to the low operating temperature range of 500-600°C (Ilbas et al., 2022; Ni, 2011). These models showed no dramatic performance reduction for direct ammonia operation in contrast to our experimental results. The difference in our result is presumed to be originated from the remarkably high performance of TF-SOFCs. Therefore, we built a model that well describes the high performance of TF-SOFCs.

Schematic diagrams for the 2D model and the validity of the model are summarized in Figure 4. Based on the SOFC cell dimension and the jig design which were used for the experiments, the representative pathway of flow was selected and is expressed as the red line on the real jig picture in Figure 4A. The sides a-b and e-f, in addition to the channel (side b-e), were also considered to reflect the ammonia decomposition reaction extent appropriately. The NH3 decomposition reaction occurs along the entire pathway while the electro-chemical reaction only occurs on side c-d of 10 mm in the active zone. The configuration of the 2D model is depicted in Figure 4B. The electrochemical sites in the active zone consisted of two nanofunctional layers for cathode and anode (prepared by PLD), a bulk anode functional layer, and an anode support layer. Please note that this study focused on the anode side for electrochemical reactions.
of the fuels. This model solved convective and diffusive flows of fuel and air at flow channels and the current-collecting layers contacting the channels and electrodes. The thickness and length of each layer refer to the cell denoted as TF-Ni/YSZ and the value of each parameter is detailed in Table S1.

First, the electrochemical model for the TF-Ni/YSZ was validated using the experimental results under the standard 3% wet hydrogen fuel condition (denoted as the pure hydrogen condition here). As shown in Figure 4D-left, the developed 2D multi-physics model simulated the electrochemical performance results with an outstanding agreement with the experimental results: 6% or less error of current density under 0.7 V condition. We then checked the validity of the decomposition equation and its parameters used in this study by comparing the overall NH3 conversion at the OCV (Figure 4C). The 2D model expected a reliable conversion rate of NH3 with 5% or less error for the temperature range. Finally, the NH3 fuel condition was applied to the 2D TF-SOFC model. The current density under the direct NH3 fuel condition was distinctly lower than that under the pure H2 condition, as observed in the experiments (Figure 4D-right). Furthermore, the 2D model accurately depicted the trend of the performance difference, which was larger at lower temperatures and higher current densities.

Gas behavior inside the thin-film-solid oxide fuel cell

We examined the behavior of the gas species inside the cell, especially in the active zone, to figure out the reason for the lower performance under the NH3-fueled condition. In Figure 5A, the overall mole fraction of hydrogen at the anode side when using NH3 for fuel under 550 °C is plotted. The mole fraction of the hydrogen appeared sufficient near the active zone under the high-potential, low-current condition (1 V, 0.75 V). In Figure 5B, the mole fraction of each gas species at the interface between the nano anode functional layer and electrolyte in the active zone (sites c to d) is compared under the H2-fueled and NH3-fueled conditions. Figure 5C shows the local current density at the interface in the active zone (sites c to d) under the H2-fueled and NH3-fueled conditions. In Figure 5D, the H2 mass flux under the H2-fueled and NH3-fueled conditions is compared. The results indicate that the hydrogen mass flux is lower under the direct NH3 fuel condition, which contributes to the lower performance of the TF-SOFC under the NH3 fuel condition.
0.057 A cm⁻². On the contrary, the hydrogen concentration in the active zone decreased under the low-voltage, high-current condition (0.75 V, 0.377 A cm⁻²). As the interface between the electrolyte and nano anode functional layer is most electrochemically active, the mole fractions of all species at the interface were analyzed in the flow direction (Figure 5B). The mole fraction of hydrogen was higher than 0.9 along the path at 1 V under the H₂-fueled condition, and decreased to approximately 0.7 at 0.75 V, indicating a sufficient supply of hydrogen. On the other hand, the mole fraction of hydrogen was much lower under the direct NH₃ operation, being below 0.3 at 1 V, and around 0.1 at 0.75 V. Even though the continuous NH₃ decomposition contributed to the increased hydrogen partial pressure, the insufficient hydrogen supply caused a much lower current density than that of the H₂-fueled condition as shown in Figure 5C. Note that not only the partial pressure of hydrogen but also the water vapor directly affected the potential and the activity of the fuel cell, as explained below in Equations (M2) and (M3). The relatively small difference between the hydrogen fraction and the water vapor fraction impacted the performance.

The mole fraction of hydrogen at the interface is determined by its supply and release via diffusion and electrochemical reactions at the functional layer. Figure 5D presents an investigation of the amount of hydrogen diffusion to the nano-anode functional layer from the anode support layer to determine whether the H₂ supply is sufficient. The amount of hydrogen consumed was directly calculated from the current density under the voltage conditions.

For the H₂-fueled condition (Figure 5D-top), a sufficient amount of hydrogen was supplied to the functional layer, which was much larger than that required for the electrochemical reaction. In other words, it was operated under low-fuel-utilization conditions. However, in the NH₃-fueled condition (Figure 5D-bottom), the fuel supply was relatively insufficient under all temperature conditions, which resulted in the harsh condition of locally high fuel utilization. Fuel depletion was more obvious at lower temperatures, which led to the experimentally observed trend of lower performance at lower temperatures with NH₃ as a fuel. The amount of H₂ decomposed from NH₃ was also investigated, as indicated by the red lines. Both the total decomposed amount through the entire path (sites A to F) and the amount by the end of the active zone (sites A to D) were considered. Despite the exclusion of back-diffusion from the side E-F, the decomposed amount of hydrogen seems relatively sufficient compared to the diffused hydrogen to the nano anode functional layer. This analysis raises the issue of inferior mass transport in the layers.

The mass transport of species in the micro-porous layers is mainly dominated by the diffusion mechanism. Specifically, the anode support layer with a few hundred µm thickness is the main region where the NH₃ decomposition reaction occurred during the diffusive transport. Note that the heavy NH₃ molecules move slower than the lighter and smaller H₂ molecules, and the byproduct N₂ also disturbs the efficient supply of H₂ to the nano anode functional layer.

Figure 6 shows the current density and ammonia conversion rate with respect to parameters mainly affecting gas diffusion: thickness and tortuosity of the porous anode support layer. We first checked the performance under ideal situations, that is, excluding the local effect of the decomposition reaction. The fully decomposed NH₃ before the active zone was mimicked by the input conditions of 25% N₂ and...
75% H2. The ideally fully decomposed NH3 condition shows slightly lower performance than that of the pure H2 condition (gray lines in Figure 6), and much higher performance than the DA-SOFC operation at varying thickness and tortuosity of the anode support. Therefore, enhancing the NH3 decomposition reaction is one way to achieve a performance close to that under H2-fueled conditions.

Increased thickness and tortuosity only have a negative effect on diffusion under the reference conditions of pure hydrogen and fully decomposed NH3. In contrast, for the NH3-fueled condition, the effect of a thicker anode support layer, which increased the volume participating in the decomposition reaction, enhanced the total ammonia conversion rate, as shown in Figure 6A. Nevertheless, the sequential effect on the current density was not significant because the increased thickness negatively influenced diffusion. The effect of diffusion was more clearly observed by adjusting the tortuosity of the anode support layer (Figure 6B). Although lowering the tortuosity for efficient diffusion had little effect on NH3 conversion, it improved the current density more sensitively, resulting in higher performance. To improve the performance of direct NH3-fueled TF-SOFCs, a better design for efficient catalytic reaction and diffusive gas transport should be considered simultaneously.

**DISCUSSION**

**Comparison with state-of-the-art direct-ammonia-solid oxide fuel cells**

The PPDs of state-of-the-art DA-SOFCs are compared in Figure 7A, and the PPD ratio between NH3 and H2 operation, PPD_{NH3}/PPD_{H2} (%), is compared in Figure 7B. DA-SOFCs have recently attracted much attention because of the potential of NH3 as a hydrogen carrier, and most studies, especially high-performance ones, have been reported since 2019. The TF-SOFCs reported in this work present among the best performance under low temperatures (≤650°C), and TF-Ni/GDC shows record-high performance under 650 and 500°C. As described in earlier sections, the main limitation of our TF-SOFCs was the low ammonia conversion in the low-temperature range and the large difference between the H2 operation. Therefore, the development of
TF-SOFCs with better internal ammonia decomposition and gas transport ensures even better performance for the direct-ammonia application.

The PPD ratio between the NH₃ and H₂ operations, PPDₙH₃/PPDₙH₂, is 80% or more under temperatures above 750°C, which is the conventional temperature for SOFCs. Ammonia conversion in this temperature range using anode-supported SOFCs is near its thermodynamic limit, indicating that ammonia conversion is not an issue during high-temperature operations (Dekker and Rietveld, 2006). However, PPDₙH₃/PPDₙH₂ dramatically decreased below 700°C, similar to our TF-SOFCs. Although high-performance DA-SOFCs have been reported (Figure 7A), there is room to improve the performance of DA-SOFCs at lower temperatures, as shown in Figure 7B. The PPDₙH₃/PPDₙH₂ values for almost every cell decreased as the operating temperature decreased. Because the performances were directly compared with H₂ operation using the same cell, the performance drop (low PPDₙH₃/PPDₙH₂ value) was entirely related to the anode. The decrease in PPDₙH₃/PPDₙH₂ could be explained by the reduced ammonia conversion, insufficient H₂ diffusion to the functional layer, poisoning effect of ammonia, and stability issues related to ammonia corrosion. Although the issues raised are different, we suggest that incorporating a highly active catalyst can solve the issues—a highly active decomposition catalyst will increase the ammonia conversion reaction to produce a sufficient amount of H₂ and inhibit potentially poisonous ammonia from reaching the electrochemically active region. The numerical model supported the fully decomposed NH₃ before the active zone can achieve high performance close to that of H₂-fueled condition by neglecting the diffusion issue as well (Figure 6).

We observed (Figure 2) that high-performance TF-SOFCs suffer more severely from low ammonia conversion than did the low-performance bulk-Ni/YSZ. We attempted to verify whether performance under H₂ operation is an essential factor when determining PPDₙH₃/PPDₙH₂. Data in Figures 7A and 7B under 600°C were rearranged, and PPDₙH₃/PPDₙH₂ was plotted against PPDₙH₂ (Figure S3). Figure S3 shows that PPDₙH₃/PPDₙH₂ decreased as PPDₙH₂ increased, and linear fitting yielded an adjusted R² value of 0.671. We suggest that an improved ammonia decomposition catalyst is critical for high-performance cells.

Various factors may contribute to the PPDₙH₃/PPDₙH₂ ratio. First, most cells differ in the anode support area per cathode area and thickness of the anode support. Because ammonia decomposition takes place at the anode support, its thickness and area relative to the cathode area will affect the extent of ammonia conversion and, thus, the PPDₙH₃/PPDₙH₂ ratio. Second, the ammonia decomposition activity may differ from cell to cell. The performance of the reported cell was improved by adding a secondary catalyst or using protonic oxide. The particle size and porous structure of Ni may also affect the extent of the ammonia decomposition reaction and mass transport of converted H₂.

Ammonia is a poisonous gas and therefore, immediately dangerous to life or health concentration of ammonia is 300 ppm (NIOSH) (Klerke et al., 2008). Therefore, exhaust gas should be thoroughly treated before exhaustion. A higher ammonia conversion is beneficial for simplifying the exhaust treatment step.

**Conclusion**

In this study, we investigated three different types of SOFCs for direct-ammonia operation: two high-performance TF-SOFCs and a commercial SOFC. The TF-SOFCs showed one of the best performances for low-temperature DA-SOFCs, albeit with a considerable performance drop from the H₂ operation. Electrochemical analyses and 2D multi-physics modeling showed that an insufficient supply of H₂ from the reduced ammonia decomposition reaction under low temperatures and poor mass transport resulted in a considerable performance drop. Our results imply that the improved ammonia decomposition reaction and appropriate cell design that facilitates the diffusion process may further increase the performance of low-temperature DA-SOFCs. Future studies should focus on implementing active catalysts inside SOFCs with adequate diffusion channels to improve the performance of DA-SOFCs to the level of H₂-fueled ones.

**Limitations of the study**

The dimension of the studied cells (4 cm² anode area and 1 cm² cathode area) is different from the commercial cells (~100 cm² anode area and ~80 cm² cathode area). The fuel utilization used in the study is smaller than the realistic fuel utilization.
STAR METHODS

Detailed methods are provided in the online version of this paper and include the following:

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SUPPLEMENTAL INFORMATION

Supplemental information can be found online at https://doi.org/10.1016/j.isci.2022.105009.

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AUTHOR CONTRIBUTIONS

Methodology, S.O. and M.J.O. and S.Y., and H.K.; investigation, S.O.; investigation administration S.Y.; modeling M.J.O; modeling administration H.K.; resources K.J.Y. and J.-H.L.; data analysis H.-J. project administration S.Y., and J.-W.S.; funding acquisition J.-W.S.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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STAR METHODS

KEY RESOURCES TABLE

| REAGENT or RESOURCE | SOURCE | IDENTIFIER |
|---------------------|--------|------------|
| Software and algorithms | COMSOL Multi-physics v5.1 | COMSOL www.comsol.com |
| Other | | |
| Scanning electron microscope, INSPECT F50 | FEI Company | www.fei.com |
| Ivium-stat electrochemical analyzer, IviumStat.h | Ivium Technologies | www.ivium.com |
| UV-vis spectrometer, UV-1900i | Shimadzu | www.shimadzu.com |
| Anode support substrate | KCeracell | www.kceracell.com |

RESOURCE AVAILABILITY

Lead contact

Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Ji-Won Son (jwson@kist.re.kr).

Materials availability

This study did not generate new unique reagents.

Data and code availability

- All data reported in this paper will be shared by the lead contact upon request.
- This paper does not report original code.
- Any additional information required to reanalyze the data reported in this paper is available from the lead contact upon request.

METHOD DETAILS

Preparation of thin-film SOFCs

Three SOFCs were prepared to study high-performance DA-SOFCs. All samples were fabricated on a commercial substrate consisting of an anode support layer (ASL) and anode functional layer (AFL). First, a commercial SOFC (KCeracell) was used to measure the performance of a conventional SOFC with a thick electrolyte (bulk Ni/YSZ). Second, a pulsed laser deposition (PLD) process was employed to prepare a high-performance TF-SOFC with materials (TF-Ni/YSZ) similar to those of a commercial cell. A NiO-YSZ (NiO:8YSZ = 56.44 wt %) with a thickness of approximately 3 μm was deposited on the AFL of a 2 × 2 cm² commercial substrate (KCeracell) under 700°C and in an oxygen atmosphere of 6.67 Pa (50 mTorr). The deposited sample was annealed under 1200°C for 1 h to agglomerate NiO. Electrolytes consisting of 1 μm-thick YSZ and 200 nm-thick GDC layers were deposited under 700°C and in an oxygen atmosphere of 6.67 Pa (50 mTorr). Subsequently, a 2.5 μm-thick LSC cathode was deposited in a 1 × 1 cm² area at room temperature in an oxygen atmosphere of 13.3 Pa (100 mTorr). Finally, the cell was heat-treated at 650°C for 1 h in air to crystallize the cathode, completing the TF-Ni/YSZ process. Third, a sample capable of producing an even higher performance was prepared by optimizing the material and structure of the anode, electrolyte, and cathode. The NiO-GDC (NiO:20GDC = 51.49 wt %) with a thickness of approximately 2.5 μm was deposited on the AFL of a 2 × 2 cm² commercial substrate (KCeracell) under 700°C and in an oxygen atmosphere of 6.67 Pa (50 mTorr). The deposited sample was annealed under 1200°C for 1 h to agglomerate NiO. To minimize the thickness of YSZ, which has lower ionic conductivity than GDC, a GDC–YSZ–GDC sandwich-structured electrolyte with a thickness of 650–300–150 nm, respectively, was deposited under 700°C and in an oxygen atmosphere of 6.67 Pa (50 m Torr). The cell was completed by depositing a 4.2 μm-thick LSC cathode under 680°C and in an oxygen atmosphere of 40 Pa (300 m Torr) (Park et al., 2016).
**Electrochemical performance and electrochemical impedance analysis**

An Iviumstat electrochemical analyzer (Ivium-stat, Ivium Technologies) was used for electrochemical analyses. For each sample, electrochemical impedance spectra (EIS) and I-V curves were measured at 50 °C intervals from 650 to 500 °C in 200 sccm of wet hydrogen (3% H2O, 97% H2) in anode atmosphere and 200 sccm of air in cathode atmosphere. Excess amount of fuel and air gases were introduced to eliminate gas starvation issues and fuel utilization remained below 11.5%. Each EIS was measured at an AC amplitude of 50 mV at OCV and 0.75 V from 10^6 Hz to 10^-1 Hz. The I-V curves were obtained from the OCV to 0.4 V. To analyze the performance of DA-SOFC, the cell temperature was raised to 650 °C again, and the fuel was converted from wet H2 to 160 sccm of dry ammonia. Excess amount of fuel and air gases were introduced to eliminate gas starvation issues and fuel utilization remained below 6.4%. Subsequently, electrochemical analyses were performed in the same way as for hydrogen fuel. To study the effect of H2 concentration, additional hydrogen flow of 30 sccm was added to 160 sccm NH3 under 550 °C for EIS analysis.

**Ammonia conversion measurement**

The indophenol blue method was used to analyze the ammonia decomposition rate inside the cell. HCl (37% w/w, Sigma-Aldrich, USA), NaOH pellets (≥ 98%, Sigma-Aldrich, USA), 4.00–4.99% sodium hypochlorite, and phenol nitroprusside (Sigma-Aldrich) were used. An acid trap containing 60 mL of 1M HCl was connected to the gas vent line of the anode to collect the exhaust NH3. Ammonia was captured in the OCV state at each temperature before commencing electrochemical analysis. The ammonia-captured solution was diluted from 1 to 5,000 and mixed with 1M NaOH, 4.00–4.99% sodium hypochlorite (9:1) solution, and phenol nitroprusside solution with a 4:1:1 vol ratio. The mixed solution was analyzed using a UV-vis spectrometer (UV-1900i, Shimadzu, Japan). Cross-sectional images of the tested cells were analyzed using FE-SEM (Inspect F50, FEI, USA). The ammonia conversion was calculated using Equation (M1):

\[
\text{Ammonia conversion (\%) } = \frac{(NH_3_{in} - NH_3_{out})}{NH_3_{in}} \times 100 
\]

(Equation M1)

**Two-dimensional multi-physics numerical model**

A two-dimensional multi-physics numerical model was developed on COMSOL Multi-physics. The model solved four conservation laws of mass, momentum, charge, and species as summarized in Table. Mean-while, the model adapted an isothermal condition since the size of tested cells (2 × 2 cm²) was small enough to neglect temperature distribution by exothermic electrochemical reaction and endothermic NH3 decomposition reaction.

The electrochemical reactions in the active area were determined by Butler-Volmer expressions. The current densities at anode and cathode electrode are expressed as

\[
i_a = i_{0a} \exp \left( \frac{a_a n F \eta_{act,a}}{RT} \right) - \exp \left( \frac{(1 - a_a) n F \eta_{act,a}}{RT} \right) 
\]

(Equation M2)

\[
i_c = i_{0c} \exp \left( \frac{a_c n F \eta_{act,c}}{RT} \right) - \exp \left( \frac{(1 - a_c) n F \eta_{act,c}}{RT} \right) 
\]

(Equation M3)

\[
\begin{align*}
\hat{i}_a &= \hat{i}_{0a} \left( \frac{(pH_2/pH^*_2)^{1/4}}{1 + (pH_2/pH^*_2)^{1/2}} \right)^{3/4} \\
\hat{i}_c &= \hat{i}_{0c} \left( \frac{(pO_2/pO^*_2)^{1/4}}{1 + (pO_2/pO^*_2)^{1/2}} \right)^{3/4}
\end{align*}
\]

(Equation M4)

(Equation M5)

The pre-exponential factors, \( A_a \) and \( A_c \), and the activation energies, \( E_a \) and \( E_c \), were parameterized based on the experimental data of this study and their values are summarized in Table. We followed the same details about assumptions and variables with a previously developed model in our group (Lee et al., 2018).
For the ammonia decomposition reaction, \( \text{NH}_3 \rightarrow 0.5 \text{N}_2 + 1.5 \text{H}_2 \), at the layers containing Ni catalyst, the following relation format was applied (Luo et al., 2022), which was developed for a tubular DA-SOFC design.

\[
r_{\text{de}} = \beta_{\text{de}} \exp \left( - \frac{E_{\text{act,de}}}{RT} \right) \left\{ \left( \frac{P_{\text{NH}_3}}{P_{\text{N}_2}} \right)^{\frac{\beta}{2}} \left( \frac{P_{\text{H}_2}}{P_{\text{N}_2}} \right)^{1 - \frac{\beta}{2}} \right\} \text{ where } K_{\text{de}} = \exp \left( - \frac{\Delta G_{\text{de}}}{RT} \right)
\]

(Equation M6)

The \( K_{\text{de}} \) is equilibrium constant of decomposition and we applied the same value of the free energy of decomposition, \( G_{\text{de}} \), from the reference. The \( K_{\text{de}} \) and \( \beta \) were used as tuning parameters to match with the empirical reaction rate for our planar design. The parameters are also summarized in Table.

### Table. Governing equations for 2D Multi-physics model

| Conservation equation | Charge | \( \nabla \cdot (\sigma_{\text{elec}} \nabla \varphi_{\text{elec}}) = Q_{\text{elec}} \)  
| | | \( \nabla \cdot (\sigma_{\text{ion}} \nabla \varphi_{\text{ion}}) = Q_{\text{ion}} \)  
| Mass | \( \nabla \cdot (ρ \vec{u}) = W \)  
| Momentum | \( \nabla \cdot (ρ \vec{u} \vec{u} / ε) = - ρ \vec{F} + \nabla \cdot (\rho \vec{u} \vec{u} / ε) - \frac{2}{3} \rho \vec{u} \vec{u} / ε \)  
| Species | \( \nabla \cdot (ρ w_i \vec{u}) = \nabla \cdot \left( \frac{ρ w_i D_i}{ε} \nabla x_i \right) + \dot{R} \)

### Table. Coefficients for the exchange current density and ammonia decomposition equations

| Parameters | Value |
|----------------|-------|
| \( A_a \) (A\cdot m\(^{-2}\)) | \( 2.47 \times 10^{10} \) |
| \( E_a \) (J\cdot mol\(^{-1}\)) | \( 6.02 \times 10^{4} \) |
| \( A_e \) (A\cdot m\(^{-2}\)) | \( 1.21 \times 10^{8} \) |
| \( E_e \) (J\cdot mol\(^{-1}\)) | \( 6.95 \times 10^{4} \) |
| \( β \) | 0.12 |
| \( β_{\text{de}} \) (mol\cdot m\(^{-3}\)\cdot s\(^{-1}\)) | \( 2.20 \times 10^{7} \) |
| \( E_{\text{act,de}} \) (J\cdot mol\(^{-1}\)) | \( 9.76 \times 10^{4} \) |