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A numerical investigation of nitridation in solid oxide fuel cell stacks operated with ammonia



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- Numerical investigation of Ni nitriding in an ammonia-fueled SOCF stack.
- Nitriding occurs in the first few cm of the fuel electrode for base case operation.
- Higher temperatures and counter-flow configuration reduce the nitriding.
- Nitriding happens in the fuel active electrode for inflow temperatures up to 700 °C.
- Nickel coating over the fuel inlet header reduces nitriding significantly.

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ABSTRACT

Operating solid oxide fuel cell (SOFC) stacks with ammonia induces the risk of nitriding in the fuel electrode and other metallic surfaces in the stack. This study aims to investigate the nitriding in the fuel electrode of an ammonia-fueled SOFC stack using a 3D Multiphysics model of a full stack. Based on the resulting species concentrations, a so-called nitriding potential is determined and compared to its critical level for various operating conditions and design modifications. The effects of the gas inflow temperatures, counterflow configuration, and nickel coating over the inlet header of the stack are investigated. The results show that nitriding occurs in the first few centimeters of the fuel electrode for all investigated operating conditions considered in this study. Moreover, it is indicated that higher gas inflow temperatures and counter-flow configuration reduce the nitriding in the fuel electrode for the gas inflow temperatures up to 700 °C. Finally, a significant reduction in nitriding in the fuel electrode is shown for a proposed nickel coating over the metallic inlet header due to a spreading of the ammonia decomposition.

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1. Introduction

The continuous high carbon-based fossil fuel consumption causes global warming, glaciers melting, and rising sea levels [1,2], leading to an urgent demand for low-carbon energy technologies. As an attractive power-generation technology, fuel cells are known for their clean, green nature and high conversion efficiency [3,4]. High operating temperatures in SOFCs lead to fast kinetics, lower internal resistance, and thus higher efficiencies in comparison to other fuel cell

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Abbrevia	Abbreviation			
DOF)F Number of degrees of freedom			
FCC	C Face Centered Cubic			
FEM	Finite element method			
HCP Hexagonal Close Packed				
Ni	Nickel			
SOFC	Solid oxide fuel cell			
YSZ	Yttria-Stabilized Zirconia			
nlpm	Normal liter per minute [293.15 K & 1 atm]			
Symbols				
J	Load current density			
Kn	Nitriding potential			
ṁ	Mass flow rate			
р	Pressure			
Т	Temperature			
х	Mole fraction			
Subscripts and superscripts				
dec	Decomposition			
crt	Critical			
in	Inlet			
Ni	Nickel			
ор	Operation			

technologies [5,6]. Another advantage of SOFCs is their capability to use various fuels such as hydrogen, methane, and ammonia [7]. Ammonia (NH_3) as a carbon-free fuel has started to be considered a promising fuel for SOFCs due to its higher volumetric energy density and feasible transportation compared to hydrogen [8].

SOFCs with Ni-based anode can directly utilize ammonia, as Ni also acts as a catalyst that decomposes ammonia to hydrogen and nitrogen inside the SOFC [9]. This gives a large advantage over low-temperature fuel cells as the needed external cracking and consequent cleaning of hydrogen, which would require a large share of the generated power (or additional ammonia for an autothermal reforming). Furthermore, in direct ammonia-fueled SOFCs, the internal endothermic decomposition of ammonia facilitates the cooling of the stack by absorbing the heat from the ohmic resistances and electrochemical reactions [10]. Therefore, the cooling system (blowers, heat exchangers) can be scaled down in direct ammonia-fueled SOFCs, and less energy is wasted by the air flow applied for stack cooling, which leads to higher system efficiencies [10,11].

Besides the advantages, the internal reforming of ammonia in direct ammonia-fueled SOFCs also results in some drawbacks, such as high thermal stresses caused by high temperature gradients due to high ammonia decomposition rates for the typical operating temperatures used for the SOFCs [12]. In addition, the ammonia-fueled operation of the SOFCs leads to nitriding of nickel used in the fuel electrode, i.e. support layer and the active electrode, which is believed to result in the degradation of the SOFC performance [13]. In the Nickel/Yttria-Stabilized Zirconia (Ni/YSZ) cermet anode, Ni particles can be nitrided in a pure ammonia atmosphere [13]. The formed nickel-nitride (Ni₃N) is not completely stable and can be decomposed in a reducing atmosphere or at a higher temperature. Therefore, nitriding of the metallic Ni leads to the formation of Ni₃N which is simultaneously decomposed and reduced back to its metallic phase during the NH₃ decomposition process [14]. The Ni₃N takes up a relatively higher volume as compared to Ni, leading to a local expansion in the anode. After Ni₃N decomposition, the volume change creates some pits in the Ni surfaces in the stack. The Ni meshes used in the cell tests crumple after exposure and disassembly. Therefore, the repetitive nitriding-reduction cycles of Ni deform the microstructure of the anode, which is an irreversible degradation and decreases the cell performance and possibly also the cell integrity [14].

There are several experimental studies on the Ni nitriding in ammonia-fueled SOFCs and its effect on the performance of SOFC. Yang et al. [13] performed a comprehensive stability analysis on a direct-ammonia SOFC with Ni/YSZ anode. Their results revealed that Ni was partially nitrided under an ammonia atmosphere, which led to a considerable morphology change. Moreover, the authors performed a temperature cycling test between 600 and 700 °C. It was clarified that delamination of the support layer of the Ni/YSZ anode due to the Ni nitriding phenomenon leads to severe degradation of the cell performance [13]. A characterization and performance evaluation of direct ammonia-fueled SOFC with Ni/YSZ anodes was conducted by Stoeckl et al. [15]. The volume of the Ni in the Ni/YSZ anode and the contact mesh increased, and microscopic pores became apparent due to Ni nitriding, in which the fuel inlet region was more affected than the fuel outlet [15]. Recently, Hendriksen et al. [16] conducted an experimental study on the direct and pre-cracked ammonia-fueled SOFC under various operating conditions and temperatures. They observed morphological changes in the Ni/YSZ fuel support layer and Ni-meshes as a result of Ni nitriding.

Some solutions have been proposed to reduce the Ni nitriding problem in direct ammonia-fueled SOFCs. Increasing the operating temperature will considerably improve the Nibased anode catalytic activity, reducing the amount of ammonia, and the Ni nitriding will be correspondingly impeded [17]. Therefore, the stability of direct ammoniafueled SOFC can be improved by high-temperature operation. However, the higher temperature results in higher degradation of the steels in the stack, and a balance between the different degradation phenomena should thus be considered. Higher operating temperatures may also introduce new problems, such as thermal matching of materials, sealing, and so on [17]. Decoupling the two degradation phenomena can be addressed using an external ammonia cracker [18]. However, the external ammonia cracker adds additional costs and more complexity to the system as heat needs to be moved from the stack to the cracker. Introducing another active layer can also reduce the chance of direct contact of ammonia with Ni. Pan et al. [19] proposed a direct ammonia-fueled tubular SOFC with a Ni-based anode embedded with a catalytic iron oxide layer. The results revealed that the stability of cells with the iron oxide catalyst layer had been dramatically enhanced compared to those without the catalyst layer. The anode

Nomenclature

structure was protected owing to the reduction of direct contact between Ni and NH_3 after adding the catalytic iron oxide layer.

Numerical models can be regarded as complementary tools for gaining further insights into the complex Multiphysics phenomena in direct ammonia-fueled SOFCs. In addition to considering all the governing physics in SOFCs, it is crucial to account for the decomposition of ammonia and the associated thermal sinks resulting from the endothermal decomposition process. Several numerical studies on ammonia-fueled SOFCs are available in the literature. A 2D model is developed by Ni [12] to investigate ammonia thermal decomposition in a planar SOFC at the cell level. The results of this work revealed the temperature gradient in the ammoniafueled SOFC is considerably higher, particularly near the inlet of the SOFC. Kishimoto et al. [20] compared direct and predecomposed ammonia-fueled SOFCs using a 2D model. The authors modeled the ammonia decomposition rate with a correlation developed in their previous study [21]. Results showed that the direct ammonia-fueled operation has comparable performance to the pre-decomposed operation. It is concluded that the slight decrease in the performance of direct ammonia-fueled SOFC can be attributed to the temperature reduction due to the endothermic ammonia decomposition reaction [20].

A numerical investigation of the direct ammonia-fueled operation of thin-film SOFC was conducted by Oh et al. [22], employing a 2D Multiphysics model. The outcomes of their study revealed that inadequate hydrogen supply resulting from the limited ammonia decomposition reaction at temperatures below 650 °C, combined with poor mass transport, led to a significant decline in performance for direct ammonia-fueled thin-film SOFCs at lower operational temperatures. Asmare et al. [23] performed a comparative analysis between direct ammonia-fueled protonic and oxygen-ion conducting tubular SOFCs, employing a detailed 3D model. Their findings indicated the superiority of the direct ammonia-fueled oxygen-ion conducting SOFC variant over its protonic-ion conducting counterpart at temperatures exceeding 1073 K. This superiority was attributed to the boosted conductivity of the oxide-ion electrolyte and the reduction of ohmic loss at elevated temperatures [23]. Additionally, a separate investigation detailed in Ref. [24] used a 3D numerical simulation at the cell level and experimental validation of microtubular SOFCs fueled by ammonia and hydrogen. The results demonstrated that the maximum attainable power densities for direct ammonia and hydrogen utilization were 628.92 mW/cm² and 622.28 mW/cm², respectively.

Recently, Rizvandi et al. [38] developed a stack-scale model aimed at investigating the performance of an SOFC stack under direct and pre-cracked ammonia operations. Moreover, the model was used to study the effects of various factors, including co- and counter-flow configurations, gas inflow temperatures, current density, and air flow rate, on the stack performance under direct ammonia-fueled operation. The ammonia cracking across the thickness of the fuel electrode was included through ammonia penetration depth within the fuel electrode where ammonia decomposition occurs. The relationship for ammonia penetration depth within the fuel electrode was validated via a thorough comparison of its predictions against a detailed 2D model representing the cross-section of a half-cell. The results revealed that high ammonia decomposition rates at the typical operating temperatures of the SOFCs led to a significant reduction in temperature at the stack inlet, consequently giving rise to thermal stresses. Notably, it was observed that power densities for direct and pre-cracked ammonia operations exhibited disparities of less than 5% when gas inflow temperatures exceeded 750 °C. Furthermore, the study highlighted that the thermal stresses were lowest in the co-flow configuration, and they decreased with declining gas inlet temperatures and current density, as well as with increasing air flow rate. The study also demonstrated that, under the typical operating conditions of SOFCs, the risk of mechanical cell failure under direct ammonia-fueled operation remained small.

According to the authors' literature review, there is no numerical study on determining Ni nitriding in the fuel electrode of the SOFCs.

To regulate the nitriding process, the nitriding potential is commonly employed to determine the phase stability at the surface of steels [25]. The Lehrer diagram [26] is originally used to describe the phase stabilities in pure iron under different nitriding potentials and temperatures. With the development of thermodynamic calculation, customized Lehrer diagrams have been widely used to provide the process control parameters for the gas nitriding process for the steels [27,28]. The literature demonstrates that the calculated customized Lehrer diagrams for steels exhibit a high level of agreement with experimental data. This agreement serves as evidence for the validity and reliability of the customized Lehrer diagrams when applied to steels [27–29]. In the current study, a similar approach is utilized to predict the nitriding potential of Ni. This approach follows a methodology similar to that used in customized Lehrer diagrams for steels.

Flow direction in SOFCs has been demonstrated to have a significant impact on their performance. Lee et al. [30] compared three different flow directions including co-flow, counterflow, and cross-flow in a hydrogen-fueled SOFC. The study concluded that the average cell temperature was the lowest in the co-flow configuration and the highest in the counterflow configuration. Additionally, it was observed that the temperature distribution in the counterflow configuration exhibited the most uniform distribution among the different flow directions. These findings highlight the importance of flow direction in influencing the temperature profiles and thermal management of hydrogen-fueled SOFCs [30]. Fardadi et al. [31] proposed a counter-flow configuration combined with partial internal reforming of methane as a solution to address controlling the temperature gradients and minimizing the thermal stresses in SOFC. This approach demonstrated potential for improving the overall performance and durability of SOFCs. Flow direction studies specifically focused on ammonia-fueled SOFCs are limited. Stoeckl et al. conducted a study where they compared counter-flow and coflow configurations in a direct ammonia feed SOFC. The authors concluded that the counter-flow operation was more favorable compared to the co-flow configuration. This preference was attributed to the lower ohmic and diffusion resistances observed in the counter-flow configuration [15].

3D stack-scale models can simulate the variations of the modeling variables along the stack height. This valuable information is missing in the models at the cell and repeating unit scales. Nonetheless, the computational cost of the SOFC stack models is rather high [32]. In our recent studies [33–37], we have used a multi-scale approach to make the stack-scale simulations of SOCs feasible on typical computational work-stations. In our recent study, this approach was employed to investigate the operation of an ammonia-fueled SOFC stack [38]. The utilization of this approach enabled us to explore numerous design options and operating conditions within a short timeframe due to the efficiency of the model.

This paper concerns a numerical investigation of the Ni nitriding in the fuel electrode in an ammonia-fueled SOFC stack. The simulation is based on a 3D model of a 90-cell SOFC stack, which was presented in our recent study on the degradation of an SOFC stack [34]. Here we model the nitriding of the fuel electrode for an SOFC stack operating under the direct-ammonia operation. A nitriding potential is used to determine where nitriding occurs in the fuel electrode. The nitriding is illustrated for a base case operating conditions considered in this study. Moreover, the effects of the gas inflow temperature, counter-flow configuration, and nickel coating over the inlet header on the nitriding are investigated.

2. Methodology

The methodology section is organized as follows:

- Section 2.1: describing the stack-scale model.
- Section 2.2: describing the Ni nitriding criteria.
- Section 2.3: describing the numerical solution approach.

2.1. Stack model

A 3D SOFC stack model, shown in Fig. 1, is used to study the stack performance under the ammonia-fueled operation. The modeling domain includes the active area, headers, sealing domains, and manifolds. The multi-scale model is based on a homogenization approach for the transport equations of mass, momentum, species, charges, and heat in the layered domains of the stack, i.e. all domains except the manifolds. A detailed description of the governing equations for the active area and extension of the model to the other domains are given in Refs. [33–35], respectively.

The stack model used in this study is the same as the one used in our recent study on the ammonia-fueled operation of the SOFC stack [38]. The geometric and modeling parameters used in this study are the same as those used in Ref. [34]. The governing equations for the stack-scale model are given in Table 1. The base operating conditions and geometry and modeling parameters are listed in Table 2.

Our stack-scale model [33–35] adopts a homogenization approach that shares similarities with the approach used for single-cell electrodes. Instead of solving transport equations over a detailed electrode geometry encompassing all phases and pores, an equivalent domain with effective modeling variables is employed. In the stack-scale model, the repeating units in the active area are substituted with an equivalent domain possessing average or effective properties (thermal conductivity, permeability, etc.). The model then solves for average variables (temperature, species composition, etc.) over this equivalent domain [33]. To homogenize the headers and sealings, a similar approach is employed, considering their respective dimensions and material properties [35]. This approach has also been utilized by other research groups and European companies, as demonstrated in Ref. [40] for SOFC stacks and a simpler version in Ref. [41] for polymer electrolyte fuel cells. In our recent work [34], we validated our stack-scale model against experimental data from the 18-cell FZJ Mark-F SOFC stack [39].

Although all the parameters solved for are thus homogenized values (average values in many cases) then the local values in the repeating unit can be obtained again – either through a numerical sub-model but in many cases also through analytical expressions. It is for instance possible to determine the distribution of gas species through the electrodes, knowing the local current density and gas specie concentration in the gas channels, as these serves as local boundary conditions for the gas transportation through the porous electrodes. This concept is however challenged if any chemical reactions, such as ammonia cracking, are occurring through the thickness of the electrode. This challenge is however addressed analytically [38], enabling fast computations without employing much more computationally demanding numerical sub-models.

A description of the effective volume within the fuel support/active electrode, where ammonia decomposition effectively occurs at all x,y-locations in the stack, was developed in our recent study [38]. In the model, this effective volume is characterized by the penetration depth of ammonia at each point across the fuel electrode. By utilizing this approach, the ammonia decomposition rate at different locations in the homogenized stack model can be described without the need for discretizing every cell and its layers, resulting in a significant reduction in computational time. The accuracy of the ammonia penetration depth relationship was validated by comparing its predictions against a detailed 2D model of the cross-section of a half-cell [38].

In this study, the simulation of stresses in the fuel support layer is included due to the steep thermal gradients owing to the fast ammonia cracking over the active area, which can result in mechanical failures in the cells. The method for calculating mechanical stresses in the homogenized description has been previously described in Ref. [33] and is not repeated here. The concept is as for the other physics to describe the average stiffness of the repeating unit and from this obtain the average stresses, solving the global set of equations. From the average stresses, the local stress can be obtained by applying the average stress on a sub-model containing the actual layers of the repeating unit. This can be done numerically [35] but due to the layered structure of the stack, the classical laminate theory can also be applied [33].

The fuel support layer is specifically investigated in this study as it significantly dominates the structure, being over 10 times thicker than any other cell layers. If the integrity of this layer is maintained, thermally induced in-plane cracks within the cell plane will most likely not propagate to other layers.



Fig. 1 – Schematic of the stack configuration, adapted from Ref. [34]. The modeling domain is the right half of the stack with symmetry boundary condition on the middle surface in the x-direction.

However, if it fails, other layers are unlikely to withstand failure. It is important to note that this study does not aim to provide an extensive mechanical analysis but rather to obtain an indication of whether the thermal gradients pose problematic or manageable conditions. For a specific stack geometry, the numerical approach shown in Ref. [35] should be extensively used for all components and junctions.

The application of homogenization to laminar flows in the manifolds [34] is currently not feasible, although attempts have been made to homogenize them as shown in Ref. [50]. Laminar flows are utilized to resolve the flow distribution in the fuel and air manifolds. In contrast, the flow distribution in the headers is modeled using Darcy's Law, which involves homogenization and replacement with a porous domain. To ensure the coupling of flows in the manifolds and headers at their shared interfaces, the continuity of flows is maintained by equating their mass fluxes and pressures [34].

To reduce the computational cost of the model, the right half of the stack in the x-direction is modeled, taking advantage of the symmetry of the molding domain. The air inflow and outflow occur through the front and back manifolds, respectively; the air flow in the front manifold is depicted by blue arrows in Fig. 1. The fuel enters and exits the stack through the side manifolds located at the front and back of the stack, respectively; the fuel flow in the front-left manifold is illustrated by red arrows in Fig. 1. Consequently, the configuration in the base case exhibits a co-flow arrangement. It is worth noting that the inlets and outlets are positioned at the bottom of the manifolds. Moreover, the origin of the coordinate system is set at the center of the active area at the bottom of the stack.

2.2. Ni nitriding

Two stable phases exist in the Ni-rich part of the Ni–N system: the terminal solid solution phase, which is FCC (Face Centered Cubic), and the Ni3N phase, which is HCP (Hexagonal Close Packed) [43]. Nitrogen can dissolve in pure Ni forming the FCC solid solution first, and then the Ni₃N phase begins to form with the increase of nitrogen concentration in the binary system. The stability of the FCC solid solution is determined by temperature and nitrogen concentration.

Table 1 – Governing equations.						
Description	Transport equation	Eq. #				
Mass Momentum	$\nabla \cdot (\rho \mathbf{u}) = S_m$ Darcy's Law (homogenized domains): $\nabla p = \frac{\mu}{K} u_{av}$ Navier-Stokes (manifolds): $\rho(\mathbf{u}.\nabla)\mathbf{u} = -\nabla p + \mu \nabla^2 \mathbf{u}$	(1) (2)				
Species	$ abla \cdot \left(- ho oldsymbol{\omega}_i \sum_j \!$	(3)				
Heat Charge	$ \begin{aligned} (\rho c_p)_{eff} \mathbf{u} \cdot \nabla T + \nabla \cdot (-k_{eff} \nabla T) &= S_T \\ \nabla \cdot (-\sigma \nabla V + J_e) &= S_j \end{aligned} $	(4) (5)				

Table 2 – Base operating conditions and geometry and modeling parameters.					
Parameter	Value	Description			
T _{in}	750 C	Gas inflow temperature			
p _{op}	1 atm	Operating pressure			
m _{in.fuel}	$1.1 imes 10^{-4}~{ m kg~s^{-1}}$ (0.26 kg m $^{-2}~{ m s^{-1}}$)	Fuel mass flow rate (mass flux) at the inlet			
m _{in air}	$3 \times 10^{-3} \text{ kg s}^{-1}$ (2.99 kg m ⁻² s ⁻¹)	Air mass flow rate (mass flux) at the inlet; oxygen stoichiometric ratio of			
,		7.5			
J	0.25 A cm^{-2}	Load (/average) current density			
X _{NH3,in}	0.99	Ammonia mole fraction at the inlet			
X _{H2O,in}	0.01	Steam mole fraction at the inlet			
X _{H2,in}	0	Hydrogen mole fraction at the inlet			
x _{N2.in}	0	Nitrogen mole fraction at the inlet			
x _{O2.in}	0.21	Oxygen mole fraction at the inlet			
N _{cell}	90	Number of the cells			
W _{stack}	0.1 m	Width of the stack			
d _{stack}	0.1 m	Depth of the stack			
$w_{sealing}$	0.015 m	Width of the sealing domain			
h _{ch}	$1.3 imes 10^{-3} \text{ m}$	Height of the channel			
w _{ch}	0.6×10^{-3} and 3.2×10^{-3} m	Widths of the bases of the channel			
h _{fuel}	$3.5 imes 10^{-4} \text{ m}$	Height of the fuel electrode (support layer $+$ active electrode)			
h _{air}	$4 \times 10^{-5} \text{ m}$	Height of the air electrode			
h _{elect}	$1 \times 10^{-5} \text{ m}$	Height of the electrolyte			
h _{IC}	$3 \times 10^{-4} \text{ m}$	Height of the interconnect			
E _{felec}	207.1 GPa	Young's modulus for the fuel electrode [52]			
alfelec	$13.1 \times 10^{-6} \ \mathrm{K}^{-1}$	Thermal expansion coefficient for the fuel electrode [52]			
v _{felec}	0.32	Poisson's ratio for the fuel electrode [52]			
Ê _{IC}	200 GPa	Young's modulus for the interconnect [35]			
α _{IC}	$12 \times 10^{-6} \text{K}^{-1}$	Thermal expansion coefficient for the interconnect [35]			
$\nu_{\rm IC}$	0.3	Poisson's ratio for the interconnect [35]			
E _{cell}	200 GPa	Young's modulus for the cell [35]			
α_{cell}	$12.3 imes 10^{-6} \ \mathrm{K}^{-1}$	Thermal expansion coefficient for the cell [35]			
Vcell	0.3	Poisson's ratio for the cell [35]			

As mentioned in the introduction section, the Lehrer diagram and nitriding potential can be used to control the nitriding process on steels [27–29]. The so-called nitriding potential can be used to determine if nitriding occurs. The nitriding potential is defined by the mole fractions of ammonia, x_{NH_4} , and hydrogen, x_{H_2} , as follows:

$$K_n = \frac{X_{\rm NH_3}}{X_{\rm H_2}^{1.5}} \tag{6}$$

To investigate the equilibrium phase for Ni and N at different nitriding potentials and temperatures, a customized Lehrer diagram for pure Ni is calculated according to a thermodynamic database [44], as shown in Fig. 2. The stability of the FCC phase decreases with the temperature increase, which means that the FCC phase is easier to transform to the HCP phase at higher temperatures even with a low Nitrogen concentration.

The Ni nitriding potential diagram (Fig. 2) is calculated using the Thermo-Calc software and the associated TCFE8 database [44]. The thermodynamics in the Ni–N system, i.e. Gibbs energy functions of relevant phases adopted from TCFE8, is established by CALPHAD (CALculation of PHAse Diagram) modeling of the Ni–N system and validated with experimental thermodynamic and phase diagram data [45–48]. The Ni nitriding potential was experimentally validated by Fonovic et al. [48]. All these have been incorporated in the TCFE8 database which is used to calculate Fig. 2.

To avoid nitridation, the HCP phase should be avoided, and safe operation criteria can thus be stated as:

$$K_n < K_{n,crt}$$
 (7)
or

$$\frac{K_n}{K_{n,crt}} < 1 \tag{8}$$

where $K_{n,crt}$ is the critical nitriding potential, which is the K_n values at the interface between the FCC and HCP phases, given in Fig. 2.

Fig. 3 shows a flowchart illustrating the calculation of nitriding potential (K_n) and its critical limit ($K_{n,crt}$) using results from the multi-scale stack model. The ammonia and hydrogen mole fractions are used to calculate K_n , and linear



Fig. 2 – Ni nitriding potential (K_n) vs temperature.



Fig. 3 – Flowchart illustrating the calculation of nitriding potential (K_n) and its critical limit ($K_{n,crt}$) using results from the multi-scale stack model.

interpolation is used to evaluate the $K_{n,crt}$ values based on the temperature distribution obtained from the multiscale stack model.

It should be noted that the nitriding potential given in Eq. (6) solely represents the feasibility of nitriding and does not encompass the aspect of nitriding kinetics, which pertains to the time required for the nitriding process to occur. Stoeckl et al. [51] demonstrated that after 100 h of testing, the ammonia-fueled operation of a single-cell SOFC caused the formation of microscopic pores and the enlargement of nickel particles in the inlet region of the fuel electrode. They also found that the significant increase in the fuel electrode volume led to cracks in the electrode. In addition, the nickel mesh used in the fuel flow field exhibited a large volume increase, microscopic pores, and stress-related cracks. The observation of nitriding effects after only 100 h supports the assumption that nitriding will occur soon after the nitriding potential exceeds its critical limit, which is the assumption considered in this study.

2.3. Numerical solution approach

The software COMSOL Multiphysics is used to couple the governing equations and solve them numerically via the finite element method (FEM). A non-uniform quadrilateral mesh is applied to the top surfaces of the active domain, headers, and sealing domains, while a triangular mesh is employed for the top surfaces of the manifolds and their adjacent sealing domains, as shown in Fig. 4. This mesh is then non-uniformly swept throughout the modeling domain. A detailed description of the mesh is given in our previous study [34]. Linear shape functions are used for the physics used in the model. The number of degrees of freedom (DOF) is 451 thousand. A Segregated solver with four steps solving for the modeling variables of flow distribution, mass transport, charge transfer, and heat transfer is used. A detailed description of the numerical approach is given in our previous study [34].

The mesh-independency of the results is confirmed by conducting simulations on a finer mesh consisting of 981 thousand DOF, which is more than twice the DOF of the base mesh. This refined simulation leads to low relative changes, specifically 0.16%, 0.01%, 0.05%, and 0.09% for the maximum values of nitriding potential, its critical limit, current density, and temperature, respectively.

3. Result

The results section is organized as follows:

- Section 3.1: presenting the results for the base case operation.
- Section 3.2: showing the effects of the gas inflow temperature on the nitriding.



Fig. 4 - Mesh distribution.

- Section 3.3: illustrating the effect of nitriding under counter-flow configuration.
- Section 3.4: indicating the alleviating effects of nickel coating of the inlet header on the nitriding.

3.1. Base case operation

Fig. 5 shows the distributions of ammonia mole fraction, temperature, first principal stress at the fuel support layer, nitriding potential (K_n), and its critical limit ($K_{n,crt}$) for the base case operation. A sharp decrease of the ammonia mole fraction is seen at the inlet of the active area, Fig. 5a, which is due to the high ammonia decomposition rate for the base case operation with a gas inflow temperature of 750 °C. Under the ammonia-fueled operation of SOFCs, the heat sink associated with the ammonia decomposition counteracts the heat sources from the overpotentials and electrochemical reactions. The ammonia heat sink makes an abrupt temperature drop at the inlet of the active area, as shown in Fig. 5b.

This high temperature gradient induces tensile stresses at the inlet of the active area, Fig. 5c. The tensile stress level is well below the Weibull strength of the fuel support layer (Ni/ YSZ) reported in Ref. [49], which is in the range of 85–120 MPa at operating temperatures of 700–800 °C. Therefore, the risk of mechanical failure of the stack under the base case operation is very low. The tensile stress in the fuel support layer is considered since it is the most dominant layer structurally as it is more than 10 times thicker than other layers of the cell. If this layer fails to resist thermal stresses, other layers would most probably not be able to resist the failure. A detailed description of the mechanical analysis in the multi-scale stack model is given in our previous studies [33,35].

Eq. (6) is used to calculate the K_n distribution over the active area, shown in Fig. 5d, based on the distributions of the ammonia and hydrogen mole fractions. It is seen that K_n has a very high value at the inlet of the active area and decreases toward its outlet, which follows the ammonia distribution over the active area, Fig. 5a. It should be noted that the hydrogen mole fraction is zero at the fuel inlet, given in Table 2 and it is generated from the ammonia decomposition in the active area. Thus, the hydrogen mole fraction is very low at the inlet of the active area and so increases the K_n significantly. Therefore, the highest level of the K_n is located at the front right corner of the active area, which is closest to the fuel inlet and so has the highest/lowest amount of ammonia/ hydrogen.

The critical nitriding potential, $K_{n,crt}$, for the base case operation is illustrated in Fig. 5e. It is higher at the inlet due to the lower temperature, where the actual nitriding potential is higher. For a better visualization of the nitriding in the active area, the ratio of the K_n and $K_{n,crt}$ along the flow at the middle, top, and bottom of the stack are shown in Fig. 5f. It should be mentioned that the ratio of the K_n and $K_{n,crt}$ significantly exceeds 10 (the upper limit of the y-axis in Fig. 5f) at the inlet of the active area at y = -0.05 cm. Nevertheless, given the assumption that nitriding occurs where the K_n and $K_{n,crt}$ ratio is higher than 1, the shift of this ratio to below one holds greater significance than its level at the inlet of the active area. Therefore, to enhance the visualization of the transition from the nitriding-prone zone within the active area to the secure zone, the maximum level of y-axis in Fig. 5f is set to 10.

Fig. 5f indicates nitriding occurs over the first 2 cm of the fuel electrode along the flow direction for the base case operation. Moreover, one can see slightly higher nitriding at the bottom of the stack, which is due to a higher ammonia concentration owing to higher fuel flows at the bottom of the stack. The shortest distance between the fuel inlets and outlets is the bottom of the stack since they are placed at the bottom of the manifolds. Thus, the fuel flow experiences lower flow resistances at the bottom of the stack, and so it has a higher fuel flow (/concentration).

3.2. Effects of gas inflow temperature

As understood from Fig. 2, the temperature plays an important role in the nitriding of the fuel electrode under ammoniafueled operation [17]. Fig. 6 shows the effects of the gas inflow temperatures on the fuel electrode nitriding and relevant modeling variables. It should be mentioned that the stack temperature is controlled through the fuel and air inflow temperatures since an insulation layer is applied to the outer boundaries of the stack, which practically prevents heat dissipating out of the stack.

The ammonia mole fraction is not included in Fig. 6, as its temperature dependence is relatively straightforward, and its significance is better demonstrated through its influence on other modeling variables. For instance, the ammonia distribution in the active area could be inferred from the



Fig. 5 – Distributions of (a) ammonia mole fraction, (b) temperature, (c) first principal stress at the fuel support layer, (d) K_n , (e) $K_{n,crt}$, and (f) the ratio of K_n and $K_{n,crt}$ along the flow at the middle, top, and bottom of the stack for the base case operation.

 $T_{in} = 800 \ ^{\circ}C$

Т (°С)

830

820

810

800

790

780

770

760

40

30 20

10

0

-10

0.06

 $\sigma_1 (MPa)$

(a")

y Z x

(b")

TR:





 K_n

300

250

200

150

100

50

0

0.2

0.18

0.16

0.14

0.12

0.1

0.08

0.06

y Z x

K_{n,crt}

(c)

y Z x

(d)

y, Z

B

7RG







0.06

y Z x

Fig. 6 – Distributions of (a, a', and a") temperature, (b, b', and b") first principal stress at the fuel support layer, (c, c', and c") K_n , and (d, d', and d") $K_{n,crt}$ for the gas inflow temperatures of 600 °C (left column), 700 °C (middle column), and 800 °C (right column).

temperature distribution within the stack. Moreover, it should be mentioned that the ammonia distribution under various inflow temperatures is presented in our recent study on the ammonia-fueled operation of SOFC stacks [38].

Fig. 6c-c" indicate that the nitriding potential K_n decreases for higher temperatures, which is owing to the higher ammonia decomposition rates. Hence, operating the SOFC at a higher temperature is a way to alleviate the fuel electrode nitriding [17]. However, higher inlet temperature leads to higher tensile stresses at the inlet of the cells, Fig. 6b-b", due to a higher temperature gradient, Fig. 6a-a", which is caused by the higher ammonia decomposition rate at higher temperatures. Nonetheless, the tensile stresses are still small compared to the Weibull strength for the fuel support layer [49].

The $K_{n,crt}$ decreases with the temperature, as shown in Fig. 6d-d". However, the K_n reduction with the temperature is higher than $K_{n,crt}$ reduction, so higher temperatures reduce the nitriding. This can be seen in Fig. 7, comparing the ratios of the K_n and $K_{n,crt}$ for different gas inflow temperatures. The nitriding is anticipated to occur in a smaller portion of the fuel electrode at higher gas inflow temperatures.

Nitriding leads to significant morphology changes in the nickel of the fuel support layer [13]. If the ammonia could penetrate the fuel active electrode, it would also cause nitriding there. Nitriding in the fuel active electrode would be more detrimental to the SOFC performance, whereas nitriding of the fuel support layer would impact the cell integrity to a higher degree.

In the homogenized model, the species mole fractions shown in Figs. 5 and 6 represent their average levels in the channels, and the conditions in the electrodes can be obtained from that and the local current density [33]. The species mole fractions do not change notably over the channel crosssection, so their values at the channel/support layer interface are close to their average levels. Thus, the aforementioned K_n values are at the channel/support layer interface, which is the most critical location for nitriding as ammonia concentration decreases through the support layer due to its decomposition. The diffusive fluxes are used to calculate the ammonia and hydrogen mole fractions at the fuel active electrode, which are used to determine the K_n level at the active electrode.

The ratios of K_n and $K_{n,crt}$ at the fuel active electrode for different gas inflow temperatures are shown in Fig. 7. Although the decomposition occurs through the thickness of the fuel support layer, nitriding still occurs in the fuel active electrode for the gas inflow temperatures up to 700 °C, but not at 750 and 800 °C. At gas inflow temperatures of 750 and 800 °C, the ammonia undergoes complete decomposition within the fuel support layer. Consequently, the ammonia mole fraction within the fuel active electrode reaches zero, resulting in a corresponding K_n value of zero. Therefore, the ratio of the K_n and $K_{n,crt}$ is zero along the flow from the inlet to the outlet for gas inflow temperatures of 750 and 800 °C. The difference in nitriding portions gets more significant for higher temperatures due to higher ammonia decomposition rates.

To prevent the calculation of negative mole fraction values, which hold no physical meaning, and to mitigate non-physical oscillations arising from numerical errors associated with very low mole fraction values in the active electrode, a threshold is set. Specifically, the K_n value is set to zero for ammonia mole fractions below 10^{-6} . The results indicate that this threshold is reached at a specific node point, while the K_n



Fig. 7 – Comparison of ratios of K_n and $K_{n,crt}$ in the fuel support layer and active electrode along the flow at the middle of the stack (section A-A) for the gas inflow temperatures of 600–800 °C.



Fig. 8 – Distributions of (a) ammonia mole fraction, (b) temperature, (c) first principal stress at the fuel support layer, (d) K_n , (e) $K_{n,crt}$, and (f) the ratio of K_n and $K_{n,crt}$ along the flow at the middle, top, and bottom of the stack for the counter-flow configuration.



Fig. 9 – Distributions of (a) ammonia mole fraction, (b) temperature, (c) first principal stress at the fuel support layer, (d) K_n , (e) $K_{n,crt}$, and (f) and the ratio of K_n and $K_{n,crt}$ in the fuel support layer and active electrode along the flow at the middle of the stack (section A-A) for the base case operation with nickel coating over the inlet header for the gas inflow temperatures of 600–800 °C.

level at the preceding node remains non-negligible. Consequently, there is a sharp decrease in the K_n level between these nodes.

3.3. Counter-flow configuration

A way of mitigating the nitridation could be using a counterflow configuration, as the high exit temperatures on the air side could promote faster cracking of the ammonia at the fuel inlet. Here, the counter-flow configuration is made by switching the fuel inlets and outlets, i.e. the fuel flow is from the back to the front of the stack.

Fig. 8 shows the distributions of the ammonia mole fraction, temperature, first principal stress at the fuel support layer, K_n , and $K_{n,crt}$ for the counter-flow configuration. The ammonia concentration drop occurs at the back of the active area under the counter-flow configuration, as illustrated in Fig. 8a. It should be noted that the operating conditions employed under the counter-flow configuration are identical to those utilized under the co-flow configuration, given in Table 2. The counter-flow configuration has a higher ammonia decomposition rate as ammonia decomposition takes place at the outlet of the active area, which has a higher temperature level than its inlet. The higher ammonia decomposition rate leads to a higher temperature gradient, Fig. 8b, and so higher tensile stress at the outlet of the active area, Fig. 8c. The risk of mechanical failure is still low as the tensile stresses are well below the Weibull strength of the fuel support layer [49].

Comparing Figs. 8d,e and 5d,e indicates lower levels for the K_n and $K_{n,crt}$ under the counter-flow configuration compared to the base case operation with the co-flow configuration. This is due to the higher temperature level over the stack under the counter-flow operation, Fig. 8b, than the co-flow configuration, Fig. 5b. Under the counter-flow configuration, the maximum level of the K_n is located at the back right corner of the active area, which is closest to the fuel inlet. Like the co-flow configuration, Fig. 8f shows a slightly higher nitriding at the bottom of the stack for the counter-flow configuration, which is due to a higher ammonia concentration owing to higher fuel flows at the bottom of the stack.

The effect of the K_n reduction for the counter-flow configuration is higher than the effect of the $K_{n,crt}$ reduction. Therefore, as intended, the nitriding is predicted over a smaller portion of the active area for the counter-flow configuration, Fig. 8f, compared to the co-flow configuration, Fig. 5f. Nonetheless, nitriding still occurs in a portion of the fuel electrode support, so the counter-flow configuration is not a solution for preventing nitriding completely.

3.4. Nickel coating over the inlet header

Another idea for minimizing the nitriding in the fuel electrode is to coat the steel at the fuel inlet header with Ni, as this would partially crack the ammonia and act as an integrated ammonia cracker. The nitriding phenomenon is also anticipated to take place on the Ni coated over the walls of the inlet headers. However, this occurrence holds less significance compared to the nitriding observed in the fuel support layer and active electrode, as it directly impacts both the integrity and performance of the cells. For the ammonia decomposition over nickel, a relationship developed by McCabe [42], Eq. (A1) given in APPENDIX A, is used. Another catalyst could also be used, but here we use Ni as its kinetics are well known.

Fig. 9 shows the distributions of the ammonia mole fraction, temperature, first principal stress at the fuel support layer, K_n , and $K_{n,crt}$ for the base case operation with nickel coating over the inlet header. Because nickel catalyzes ammonia decomposition strongly, most of the ammonia is decomposed in the inlet header, as illustrated in Fig. 9a. Owing to lower/higher amounts of ammonia/hydrogen at the inlet of the active area, the K_n level is very low for this case, Fig. 9d, compared to the base case operation, Fig. 5d.

The ratios of the K_n and $K_{n,crt}$ along the flow at the middle of the stack for the gas inflow temperatures of 600–800 °C are shown in Fig. 9f. It is indicated that this design eliminates fuel electrode nitriding for the gas inflow temperatures of 750 and 800 °C. Nonetheless, fuel electrode nitriding still occurs for lower inflow gas temperatures up to 700 °C. In addition, nitriding should be expected for a very limited portion of active area at its front right corner with high K_n values, Fig. 9d, for even higher inflow gas temperatures. The nitriding could most likely be removed entirely by baffles to create a more uniform flow across the stack.

4. Conclusion

In this work, Ni nitriding in the fuel electrode of an ammoniafueled SOFC stack is investigated. A stack-scale model of a 90cell stack is used to determine the nitriding based on a nitriding potential. The effects of the gas inflow temperatures, counter-flow configuration, and Ni coating over the inlet header on the fuel electrode nitriding are investigated. Based on the results, the following conclusions can be drawn:

- For the base case operating conditions considered in this study, the nitriding occurs in about the first ~2 cm of the fuel electrode. The highest level is at its front right corner, which is closest to the fuel inlet.
- The higher the gas inlet temperature, the lower the nitriding. However, the higher temperatures lead to 2.48 times higher tensile stresses due to faster cracking and higher temperature gradients. Nonetheless, the risk of mechanical failure is still low as the tensile stress level is well below the Weibull strength of the fuel support layer.
- Direct feeding of ammonia will result in nitriding over part of the cells at all gas inlet temperatures investigated.
- Nitriding would also occur in the fuel active electrode for lower operating temperatures (600-700 °C), despite passing the very large surface area of Ni in the fuel support layer.
- Comparing the co- and counter-flow configurations illustrates that the counter-flow configuration has less nitriding due to its higher temperature. However, the counter-flow configuration induces 1.4 times higher tensile stresses. Nonetheless, the tensile stress level is still well below the Weibull strength of the fuel support layer and so the risk of mechanical failure is small.

- Nickel coating of the inlet header, making it act as an integrated ammonia cracker, can effectively remove the nitriding for large parts of the considered stack design.
- The stack-scale model employed in this study proves valuable for addressing the variations in nitriding throughout the height of the stack. Additionally, it facilitates the proposal of implementing an integrated ammonia cracker by coating the stack inlet headers with Ni. Furthermore, the model captures the in-plane distribution of nitriding over the active area, providing insights into the results at the cell level.

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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijhydene.2023.09.241.

REFERENCES

- [1] Zemp M, Huss M, Thibert E, Eckert N, McNabb R, Huber J, Cogley JG. Global glacier mass changes and their contributions to sea-level rise from 1961 to 2016. Nature 2019;568(7752):382-6.
- [2] Immerzeel WW, Lutz AF, Andrade M, Bahl A, Biemans H, Bolch T, Baillie JEM. Importance and vulnerability of the world's water towers. Nature 2020;577(7790):364–9.
- [3] Khan T, Yu M, Waseem M. Review on recent optimization strategies for hybrid renewable energy system with hydrogen technologies: State of the art, trends and future directions. Int J Hydrogen Energy 2022;47(60):25155–201.
- [4] Murray EP, Tsai T, Barnett SA. A direct-methane fuel cell with a ceria-based anode. Nature 1999;400(6745):649–51.
- [5] Padinjarethil AK, Bianchi FR, Bosio B, Hagen A. Electrochemical characterization and modelling of anode and electrolyte supported solid oxide fuel cells. Front Energy Res 2021;9:668964.
- [6] Campanari S, Mastropasqua L, Gazzani M, Chiesa P, Romano MC. Predicting the ultimate potential of natural gas SOFC power cycles with CO2 capture–Part A: methodology and reference cases. J Power Sources 2016;324:598–614.
- [7] Hagen A, Langnickel H, Sun X. Operation of solid oxide fuel cells with alternative hydrogen carriers. Int J Hydrogen Energy 2019;44(33):18382–92.
- [8] Cinti G, Discepoli G, Sisani E, Desideri U. SOFC operating with ammonia: stack test and system analysis. Int J Hydrogen Energy 2016;41(31):13583–90.
- [9] Yang J, Akagi T, Okanishi T, Muroyama H, Matsui T, Eguchi K. Catalytic influence of oxide component in Ni-based cermet anodes for ammonia-fueled solid oxide fuel cells. Fuel Cell 2015;15(2):390–7.
- [10] Cinti G, Desideri U, Penchini D, Discepoli G. Experimental analysis of SOFC fuelled by ammonia. Fuel Cell 2014;14(2):221–30.

- [11] Jeerh G, Zhang M, Tao S. Recent progress in ammonia fuel cells and their potential applications. J Mater Chem A 2021;9(2):727–52.
- [12] Ni M. Thermo-electrochemical modeling of ammonia-fueled solid oxide fuel cells considering ammonia thermal decomposition in the anode. Int J Hydrogen Energy 2011;36(4):3153-66.
- [13] Yang J, Molouk AFS, Okanishi T, Muroyama H, Matsui T, Eguchi K. A stability study of Ni/Yttria-stabilized zirconia anode for direct ammonia solid oxide fuel cells. ACS Appl Mater Interfaces 2015;7(51):28701–7.
- [14] Wan Z, Tao Y, Shao J, Zhang Y, You H. Ammonia as an effective hydrogen carrier and a clean fuel for solid oxide fuel cells. Energy Convers Manag 2021;228:113729.
- [15] Stoeckl B, Subotić V, Preininger M, Schwaiger M, Evic N, Schroettner H, Hochenauer C. Characterization and performance evaluation of ammonia as fuel for solid oxide fuel cells with Ni/YSZ anodes. Electrochim Acta 2019;298:874–83.
- [16] Hendriksen PV, Mondi F, Sun X, Caldogno R, Frandsen HL, Rizvandi OB, Hansen J. Ammonia as an SOFC fuel. ECS Trans 2023;111(6):2085.
- [17] Wang B, Li T, Gong F, Othman MHD, Xiao R. Ammonia as a green energy carrier: electrochemical synthesis and direct ammonia fuel cell-a comprehensive review. Fuel Process Technol 2022;235:107380.
- [18] Okanishi T, Okura K, Srifa A, Muroyama H, Matsui T, Kishimoto M, Eguchi K. Comparative study of ammoniafueled solid oxide fuel cell systems. Fuel Cell 2017;17(3):383–90.
- [19] Pan Y, Zhang H, Xu K, Zhou Y, Zhao B, Yuan W, Liu M. A high-performance and durable direct NH3 tubular protonic ceramic fuel cell integrated with an internal catalyst layer. Appl Catal B Environ 2022;306:121071.
- [20] Kishimoto M, Kume T, Iwai H, Yoshida H. Numerical analysis of ammonia-fueled planar solid oxide fuel cells. ECS Trans 2017;78(1):2845.
- [21] Kishimoto M, Furukawa N, Kume T, Iwai H, Yoshida H. Formulation of ammonia decomposition rate in Ni-YSZ anode of solid oxide fuel cells. Int J Hydrogen Energy 2017;42(4):2370–80.
- [22] Oh S, Oh MJ, Hong J, Yoon KJ, Ji HI, Lee JH, Yang S. A comprehensive investigation of direct ammonia-fueled thinfilm solid-oxide fuel cells: performance, limitation, and prospects. iScience 2022;25(9):105009.
- [23] Asmare M, Ilbas M, Yalcin S. Numerical modelling and comparative analysis of direct ammonia fuelled protonic and oxygen-ion conducting tubular solid oxide fuel cell. Int J Hydrogen Energy 2021;46(74):36878–89.
- [24] Asmare M, Ilbas M, Cimen FM, Timurkutluk C, Onbilgin S. Three-dimensional numerical simulation and experimental validation on ammonia and hydrogen fueled micro tubular solid oxide fuel cell performance. Int J Hydrogen Energy 2022;47(35):15865–74.
- [25] Pye D. Practical nitriding and ferritic nitrocarburizing. ASM international; 2003.
- [26] Lehrer E. Über das Eisen-Wasserstoff-Ammoniak-Gleichgewicht. Zeitschrift für Elektrochemie und angewandte physikalische Chemie 1930;36(6):383–92.
- [27] Yang M, Sisson Jr RD. Modeling the nitriding process of steels. Adv Mater Process 2012;170(7):33-7.
- [28] Yang M, Sisson RD. Gaseous nitriding process control: application of customised lehrer diagrams. Int Heat Treat Surf Eng 2013;7(4):164–71.
- [29] Altinsoy I, Onder K, Celebi Efe F, Bindal C. Gas nitriding behaviour of 34CrAlNi7 nitriding steel. Acta Phys Pol, A 2014;125(2):414–6.

- [30] Lee HL, Han NG, Kim MS, Kim YS, Kim DK. Studies on the effect of flow configuration on the temperature distribution and performance in a high current density region of solid oxide fuel cell. Appl Therm Eng 2022;206:118120.
- [31] Fardadi M, McLarty DF, Brouwer J, Jabbari F. Enhanced performance of counter flow SOFC with partial internal reformation. Int J Hydrogen Energy 2014;39(34):19753–66.
- [32] Li A, Song C, Lin Z. A multiphysics fully coupled modeling tool for the design and operation analysis of planar solid oxide fuel cell stacks. Appl Energy 2017;190:1234–44.
- [33] Navasa M, Miao XY, Frandsen HL. A fully-homogenized multiphysics model for a reversible solid oxide cell stack. Int J Hydrogen Energy 2019;44(41):23330–47.
- [34] Rizvandi OB, Miao XY, Frandsen HL. Multiscale modeling of degradation of full solid oxide fuel cell stacks. Int J Hydrogen Energy 2021;46:27709–30.
- [35] Miao XY, Rizvandi OB, Navasa M, Frandsen HL. Modelling of local mechanical failures in solid oxide cell stacks. Appl Energy 2021;293:116901.
- [36] Rizvandi OB, Jensen SH, Frandsen HL. A modeling study of lifetime and performance improvements of solid oxide fuel cell by reversed pulse operation. J Power Sources 2022;523:231048.
- [37] Rizvandi OB, Frandsen HL. Modeling of single- and doublesided high-pressure operation of solid oxide electrolysis stacksInt. J Hydrogen Energy https://doi.org/10.1016/j. ijhydene.2023.04.169
- [38] Rizvandi OB et al., Numerical performance analysis of solid oxide fuel cell stacks with internal ammonia cracking, Int J Hydrogen Energy, https://doi.org/10.1016/j.ijhydene.2023. 05.321.
- [39] Nishida RT, Beale SB, Pharoah JG, de Haart LGJ, Blum L. Three-dimensional computational fluid dynamics modelling and experimental validation of the Jülich Mark-F solid oxide fuel cell stack. J Power Sources 2018;373:203–10.
- [40] Nishida RT, Beale SB, Pharoah JG. Comprehensive computational fluid dynamics model of solid oxide fuel cell stacks. Int J Hydrogen Energy 2016;41(45):20592–605.

- [41] Kvesić M, Reimer U, Froning D, Lüke L, Lehnert W, Stolten D. 3D modeling of a 200 cm2 HT-PEFC short stack. Int J Hydrogen Energy 2012;37(3):2430–9.
- [42] McCabe RW. Kinetics of ammonia decomposition on nickel. J Catal 1983;79(2):445–50.
- [43] Wriedt HA. The N-Ni (Nitrogen-Nickel) system. Bull Alloy Phase Diag 1985;6(6):558–63.
- [44] Andersson JO, Helander T, Höglund L, Shi P, Sundman B. Calphad-based thermocalc and dictra method. Calphad 2002;26:273–312.
- [45] Fernández Guillermet A, Frisk K. Thermodynamic properties of Ni nitrides and phase stability in the Ni-N system. Int J Thermophys 1991;12:417–31.
- [46] Hull BA, Mohney SE, Liu ZK. Thermodynamic modeling of the Ni–Al–Ga–N system. J Mater Res 2004;19(6):1742–51.
- [47] Scientific Group Thermodata Europe (SGTE). Binary system Mn-Ni: thermodynamic properties. Ternary steel systems: phase diagrams and phase transition data: Part 1: binary systems and ternary systems from C-Cr-Fe to Cr-Fe-W. 2012. http://www.sgte.org. 39-39.
- [48] Fonović M, Leineweber A, Mittemeijer EJ. Experimental investigation and thermodynamic modeling of the Ni-Rich part of the Ni-N phase diagram. Metall Mater Trans 2014;45:4863–74.
- [49] Ni DW, Charlas B, Kwok K, Molla TT, Hendriksen PV, Frandsen HL. Influence of temperature and atmosphere on the strength and elastic modulus of solid oxide fuel cell anode supports. J Power Sources 2016;311:1–12.
- [50] Rizvandi OB, Miao XY, Frandsen HL. Fast and stable approximation of laminar and turbulent flows in channels by Darcy's Law. Alex Eng J 2021;60(2):2155–65.
- [51] Stoeckl B, Preininger M, Subotić V, Gaber C, Seidl M, Sommersacher P, Hochenauer C. High utilization of humidified ammonia and methane in solid oxide fuel cells: an experimental study of performance and stability. J Electrochem Soc 2019;166(12):F774.
- [52] Pihlatie M, Kaiser A, Mogensen M. Mechanical properties of NiO/Ni-YSZ composites depending on temperature, porosity and redox cycling. J Eur Ceram Soc 2009;29(9):1657–64.