Abstract

Ammonia (NH_3) is a chemical composed of 75% hydrogen and 25% nitrogen, making it a promising low-carbon alternative fuel. It has the same volumetric energy density as fuels as LNG, CNG, LPG, and hydrogen. Additionally, it can be stored under favorable conditions - approximately -33°C at 1 bar and 20°C at 10 bar. The use of ammonia in the energy industry reduces carbon dioxide emissions but its indirect combustion, for instance in internal combustion engines, increases NO_X emissions. The use of ammonia in solid oxide fuel cells, which have operating temperatures lower than those of thermal NOX formation, is being investigated in order to reduce emissions of both of these greenhouse gases and increase the efficiency of the process of converting chemical energy to electricity. Consequently, ammonia-fueled solid oxide fuel cell technology has the potential to be widely used in the decarbonization of certain energy-intensive energy processes, large-scale renewable energy storage systems, and on-board energy sources for propulsion of medium and large marine vessels. To achieve these objectives, however, a comprehensive feasibility study of using ammonia in SOFC-based systems must be conducted, taking into consideration different fuel conversion methods and measurements in off-design operating states.

The dissertation presents four sections of research: (i) a study of a 5 cm × 5 cm direct ammonia solid oxide fuel cell, (ii) a developmental study of NH3-SOFC stacks, (iii) a post-mortem analysis of cells and stacks, and (iv) a numerical study of a plant containing NH3-SOFCs. This method enabled a comprehensive and in-depth analysis of the industrial application of ammonia-fueled solid-oxide fuel cells, from fundamental research to the development of SOFC technology.

In the first part of the study, the performance of single fuel cells operating in DA-SOFC mode was characterized. Its primary objective was to determine the current-voltage dependence of the cells and the degradation rate as a function of operating time. The thickness of the anode support layer of solid-oxide fuel cells was measured at 400 and 1000 μm to identify its effect on the process of direct internal cracking occurring on the nickel catalyst, which is one of its key components. Experiments have demonstrated that, regardless of the thickness of the anode support layer, ammonia-fed cells rupture during operation. A numerical and *post-mortem* analysis of the cells was conducted to determine the reasons for their failure. OpenFoam® thermodynamic analysis and computational fluid dynamics (CFD) software developed with a kinetic method for modeling electrochemical processes has been used for numerical analysis. As a novel contribution to the OpenFuelCell module, a source component responsible for the internal cracking of ammonia on a nickel catalyst as well as additional components in the kinetic model determining concentration losses at both the air and fuel electrodes were introduced. The calculations allowed for the experimentally impossible determination of the temperature gradient inside a fuel cell operating in DA-SOFC mode. In addition, theoretical NH_3 emissions were determined by analyzing the ammonia cracking in the SOFC anode. Based on numerical analysis for three anode support thicknesses of 200, 400, and 1000 μm, it was determined that thinning the cell and decreasing its operating temperature decreases the conversion of ammonia, thereby increasing its emission. Nonetheless, a thicker substrate layer induces higher

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temperature gradients in the cell (up to 70°C), which may contribute to cell cracking during direct internal cracking operation, despite possessing greater mechanical strength.

The dissertation subsequently presents an experimental investigation of the effects of varying operating conditions, such as current load and fuel flow, on the level of degradation and performance of a 10-cell NH_3-SOFC stack integrated with an external ammonia cracking reactor. The objective of the study was to simulate the load profile of a barge propelled by an NH_3-SOFC system with a set of lithium-ion batteries allowing for the reduction of transient operation of the cell stacks. As a starting point for simulating the variable duty cycle of a barge, the propulsion power demand characteristics of this class of vessel available in the literature were used. The study demonstrated that the average stack degradation over 550 hours under varied conditions, including dynamic change in operating states, was 0.38 percent. In addition, a decrease in total area-specific resistance was observed within the first few hours of the experiment, despite alterations in operating modes and fuel supply. The lowest area-specific resistance value was observed around 200 hours, followed by a steady increase until the conclusion of the experiment. None of the selected and verified operating modes or their variants caused the stack voltage to decrease by a significant amount. The experiment revealed that the NH_3-SOFC stack's maximum measured electrical efficiency for operation at a 20% load reduction from the operating point was 62.54 percent, with a 77% of fuel utilization rate. At a nominal capacity of 24 A, the voltage of the reference cell was 0.89 volts, and the power and electrical efficiency of the stack were 204 W and approximately 60%, respectively. In this part of the investigation, DA-SOFC stacks and a stack fed with diluted ammonia simulating 50% pre-cracking (P-C, or pre-cracking) were also analyzed. In both instances, the characteristics of the dependence of the stack voltage on the current were measured and utilized in the numerical portion of the work, but the stacks themselves failed after several hours of operation.

The third section of the dissertation's observations is devoted to the post-mortem examination of individual semi-technical cells and stacks. The research revealed that operation in direct ammonia supply mode - DA-SOFC - could not be implemented in the studied cell types in such manner. However, the analysis also uncovered distinct failure causes for solitary cells and cell stacks. In the case of 5 cm × 5 cm semi-technical cells, the failures were due to mechanical failure of the cells, whereas in the case of stacks, corrosion of steel elements and, consequently, internal combustion of hydrogen or ammonia are believed to be to fault. In neither instance was nitrification of the cells observed.

The fourth section presents the results of a numerical study that analyzes the effects of changing operating states of an NH3-SOFC-based power system. The analysis describes how the system characteristics change when operating in pre-cracking (P-C) mode versus direct internal cracking (DIC) mode. The numerical study has been verified based on measurements made on cell stacks (in DIC, P-C and simulated with N_2 and H_2 ammonia modes) and uses reduced-order modeling. This method allows the experimental results of the stacks to be converted into numerical studies of the power system that determine efficiency and heat production. The presented research results address a significant absence in the limited database of analyses of NH3-SOFC plants, which includes measurements of cell stacks. The results indicate that the electrical efficiency of SOFC stacks with a total capacity of 100 kW fueled by ammonia in DIC and P-C mode can reach 60% with a net electrical efficiency of 55%, which is nearly

10% higher than when the plant is fueled by hydrogen. In addition, numerical studies based on experimental data have demonstrated that the system can operate between 20 kW and 250 kW, depending on the fuel supplied, the oxidizer, and the current load of stack. Nonetheless, a significant increase in fuel flow and operation at an excess relative to the designed operating point is associated with a decline in the electrical efficiency of the system by a few percentage points. In the final section of the paper, it is determined how the efficiency of the entire Power-to-Ammonia-to-Power cycle can be enhanced by applying certain NH_3-SOFC systems to ammonia-fueled internal combustion engines.

Krystian Machaj