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A pressurized ammonia-fueled anode-supported solid oxide fuel cell: Power performance and electrochemical impedance measurements

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HIGHLIGHTS

- A pressurized ammonia-fueled anode-supported SOFC (ASC) is measured at 750–850 °C.
- We report detail power and electrochemical impedance of pressurized ammonia ASC.
- Gas diffusion and conversion resistances are individually analyzed and compared.
- A stability test of ammonia ASC at 3 atm at 750 °C shows little degradation.
- Pressurized ammonia SOFC integrating with micro gas turbines should be feasible.

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ABSTRACT

Ammonia is recognized as a useful fuel for high-temperature solid oxide fuel cell with advantages over hydrogen. The challenge of ammonia solid oxide fuel cell is its performance durability especially at elevated operating pressure, which motivates this work to measure power and impedance of a pressurized anode-supported solid oxide fuel cell (530-μm-Ni-YSZ/3-μm-YSZ/15-μm-LSC-GDC) using ammonia as a fuel at both 1 atm and 3 atm, each pressure with three operating temperatures (750, 800, 850 °C). Results show that both pressurization and increasing temperature enhance the ammonia-fueled cell power densities which are closely matching with that of hydrogen, indicating an almost 100% ammonia conversion to hydrogen and nitrogen at $T \geq 750$ °C. From Bode and Nyquist plots, we find that the polarization impedance is primarily contributed by the gas diffusion impedance with summit frequencies around 5–24 Hz and secondarily due to the gas conversion with summit frequencies around 0.03–0.07 Hz. When pressure increases, the gas diffusion impedance decreases noticeably, while the gas conversion impedance increases slightly. Moreover, a stability test shows little degradation even at 3 atm, suggesting that pressurized ammonia solid oxide fuel cell is feasible for future development of the hybrid power system integrating with micro gas turbines.

1. Introduction

To fulfill tomorrow's energy and environment requirements, it is crucial to develop low carbon power generation technologies, such as solid oxide fuel cells (SOFCs) having advantages of high-energy efficiency and great fuel flexibility [1]. Furthermore, pressurized SOFCs integrating with gas turbine (GT) or micro gas turbine (MGT) can achieve very high efficiency up to 70% [1], a highest-efficiency hybrid power generation system known today [2,3]. Using hydrogen as a fuel in SOFCs or in internal combustion engines can avoid carbon emission during the power production. Unfortunately, the technological challenges and difficulties in storage and transportation of hydrogen as well as its safety risk are still the obstacles that need to be overcome before the wide applications of hydrogen fuel cells become feasible. Recently, ammonia, as an alternative source of hydrogen, has been proven to be a useful fuel for high temperature SOFCs [e.g. [4–13]], because ammonia has advantages over hydrogen. For instances, ammonia can be easily stored in its liquid form at ambient temperature when a pressure of 8.6 bars is applied. In comparison, hydrogen requires an extremely low temperature of about 20 K and very high cost tank in order to keep it in liquid form [4]. Also, ammonia has much lower production cost than that of hydrogen [8]. Moreover, ammonia, a carbon free fuel like hydrogen, has relatively high energy density as compared to that of methane [9]. These advantages could make the pressurized ammonia-fueled SOFC be an excellent candidate for further development of the hybrid pressurized SOFC-MGT power generation system, provided that

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the performance of ammonia-fueled SOFC has little degradation due to pressurization during loaded operation. This is an open issue, because the pressurization effect on ammonia-fueled SOFC has not yet been reported in the literature. Hence, the objective of this study is to measure cell performance and electrochemical impedance spectra (EIS) of a pressurized ammonia-fueled SOFC and to test its stability by measuring the degradation rate of the cell power densities for the first time.

Under atmospheric pressure condition, ammonia has recently attracted a lot of attention as a fuel in high temperature SOFCs [e.g. [4–13]]. It should be noted that a few consensuses based on these previous studies have been obtained. First, ammonia fuel can be directly used in high temperature SOFCs. Second, the nickel material is a very efficient anode catalyst to allow very high ammonia decomposition. Third, the oxidation of ammonia in a nickel-based anode at common operating temperature of SOFCs follows the two-step process as shown in Eqs. (1) and (2) below.

$$2NH_3 \rightarrow N_2 + 3H_2 \quad (1)$$

$$2H_2 + O_2 \rightarrow 2H_2O + 4e^- \quad (2)$$

The first process is the cracking of ammonia that is catalytically decomposed to H_2 and N_2 (Eq. (1)), while the second process is the oxidation of hydrogen to water (Eq. (2)). Fourth, when the operating temperature is as high as 750 °C and above, 100% decomposition of ammonia can be achieved in Ni-YSZ anode [12]. Here it is interesting to know whether these consensuses will be still held for *pressurized* ammonia-fueled SOFCs using Ni-YSZ anode at 750 °C and above. In this paper, we shall report power performance and detail EIS measurements including Bode and Nyquist plots of a pressurized anode-supported SOFC (Ni-YSZ/YSZ/LSC-GDC) using both ammonia and hydrogen as a fuel. Hydrogen is used as the benchmark fuel for comparison. Experiments are conducted in a recently established pressurized full button cell test rig that overcomes the stagnation flow problem in the classic button cell rig [14]. There are two operating pressures to be tested (1 and 3 atm), each pressure condition having three different operating temperatures (750, 800, 850 °C).

2. Experimental methods

The present ammonia-fueled SOFC experiments are conducted in a recently-established pressurized full button cell platform, which has been used to measure cell performance, impedance, and various resistances of an anode-supported cell (ASC: Ni-YSZ/YSZ/LSM-GDC-LSM) using hydrogen as a fuel at 1–5 atm and 750–850 °C [14]. For completeness, we briefly describe such a testing platform upon here. The platform consists of several major parts. From inside out, a specially thread-designed ceramic full button cell test rig is connected to a serpentine heating pipe system for uniform heating of the supplied fuel and oxygen gases in a temperature-controlled furnace which is resided in a large high-pressure outer vessel together with measuring devices (please see Fig. 1 of [14] for details). The specially thread-designed rig has separated anode and cathode chambers that can prevent leakages of fuel and oxygen, and most importantly, it has a zero-stand-off distance design with guided flow passages that allow ammonia and oxygen to flow uniformly within Pt and/or Ni meshes. As such, the overestimation of the anode diffusion in the bulk gas due to the stagnation flow problem commonly occurred in the classic button cell rig can be thus greatly minimized [14]. In this study, we apply a Ni-YSZ anode-supported full button cell with a different cathode material of LSC-GDC, as shown in Fig. 1, where the corresponding SEM cross-sectional morphology image of the cell as well as its material and thickness information are presented, i.e. 530 μm Ni-YSZ (anode), 3 μm YSZ (electrolyte), and 15 μm LSC-GDC (cathode). Why using the cathode material of LSC (Lanthanum-Strontium-Cobalt, $La_{0.6}Sr_{0.4}CoO_3$)? This is because LSC has much higher ion conductivity than LSM ($La_{0.81}Sr_{0.09}MnO_3$). As pointed out by Yamada and his co-workers [15], the higher ion conductivity of the electrode, such as $La_{1-x}Sr_xCoO_3$, the higher performance of the electrode. Since the rate-determining step of the cathode electrode reaction is either by the absorption of oxygen onto the electrode surface or by the gas-phase diffusion of oxygen molecules [15], the high-performance electrode results in a higher cell performance.

The difficulty in conducting experiments of pressurized planar SOFCs should not be underestimated. Since the button cells or planar SOFCs have very small tolerance of pressure differential, a careful pressure regulation among the anode, the cathode, and the ambient in the dual-chambered constant-pressure vessel is required. Pressurization using nitrogen from the high-pressure gas bottle is applied at the inlet of the outer pressure vessel, which is constantly regulated by a nitrogen flow meter at the end of the outlet of the outer pressure vessel. The anode and cathode gases are separately monitored by ammonia (or hydrogen) and oxygen mass flow controllers that have sensors to retain fixed mass flow rates at elevated pressure. The cathode is supplied by 100% O_2 at a flow rate of 100 ml min^{-1}, while the anode is supplied by either 60% H_2/40% N_2 at a total flow rate of 100 ml min^{-1} or 66.7% NH_3/33.3% N_2 at a total flow rate of 60 ml min^{-1}. Here the gas composition of NH_3/N_2 is controlled to achieve the same hydrogen concentration and flow rate of H_2/N_2 when the complete decomposition of ammonia takes place. As such, results of the ammonia-fueled SOFC can be directly compared with that of the hydrogen-fueled SOFC. Hence, cell performance and electrochemical impedance spectra for the anode-supported Ni-YSZ fuel cell employing LSC-GDC cathode with a very thin YSZ electrolyte using both ammonia and hydrogen fuels are measured at two different operating pressures (1 and 3 atm), each pressure at three different temperatures (750, 800, 850 °C). All data of temperature, pressure, mass flow rate, voltage, and current are continuously recorded and analyzed by the computer. The same standardization of the testing procedure proposed by Haanapple and Smith [16] is applied in this study, which has also been used in our previous planar SOFCs studies [17–19], so it is not elaborated upon here.

Concerning EIS measurements, a small perturbed voltage signal with 50 mV amplitude, $V(t) = V_0\cos(\omega t + \phi)$, is applied onto the cell to measure a current response, $I(t) = I_0 \cos(\omega t + \psi)$. ω is the angular frequency ($\omega = 2\pi f$). The amplitudes (V_0; I_0) and the initial phase angles (ϕ; ψ) are respectively for the voltage signal and the current response. Further, we convert the expression of the voltage signal and the current response in the time domain into a complex frequency domain via the Fourier transformation to obtain the impedance function $Z(i\omega) = V(i\omega)/I(i\omega)$. Hence, $Z_{real}(i\omega) = |Z|\cos(\theta)$ and $Z_{image}(i\omega) = |Z|\sin(\theta)$, where the phase difference $\theta = \phi - \psi = \tan^{-1}(Z_{image}/Z_{real})$ and $|Z| = [(Z_{real})^2 + (Z_{image})^2]^{1/2}$. The plot of Z_{image} *vs.* Z_{real} is the Nyquist plot that can be used to extract the information of the ohmic (R_Ω) and polarization (R_P) resistances of the measured fuel cell [20]. Also, various Bode plots [20] with the impedance and the phase-shift as a function of the frequency are also analyzed to obtain the important characteristic frequencies (f) and phase difference (θ) associated with specific summit data points on different semi-circle impedance spectra of the Nyquist plot. This study presents both Nyquist and Bode plots of the aforesaid pressurized ammonia-fueled anode-supported SOFC over a range of temperature from 750 °C to 850 °C under loaded condition at 0.8 V. Moreover, an equivalence circuit model based on the best fit of measured impedance data is used to explain how exactly ohmic and polarization resistances vary with a change of pressure and temperature, as discussed later.

In order to test the stability of ammonia-fueled ASC under loaded condition at 750 °C, we continue to supply ammonia to the cell at a fixed anode gas flow rate of NH_3/N_2 = 40/20 ml min^{-1} and a fixed cathode gas flow rate of O_2 = 100 ml min^{-1} and the cell is operated at 0.8 V. The measuring sequences/procedures are as follows. (1) We measure continuously the cell performance at 3 atm for 90 min (2) Then we switch ammonia fuel to hydrogen fuel at a flow rate of H_2/N_2 = 60/