Short communication

An intermediate-temperature direct ammonia fuel cell with a molten alkaline hydroxide electrolyte

Jason C. Ganley *

Department of Chemical Engineering, Howard University, 2013 Lewis K. Downing Hall, 2300 6th Street NW, Washington, DC 20059, USA

Abstract

This paper describes the development and testing of a direct ammonia fuel cell utilizing a molten alkaline hydroxide electrolyte at temperatures between 200 and 450 °C. The advantages of a molten hydroxide fuel cell include the use of a highly conductive and very low-cost electrolyte, inexpensive base metal electrocatalysts, a wide operating temperature range, fuel flexibility, and fast electrode kinetics. The direct use of ammonia in such a fuel cell, even at temperatures as low as 200 °C, is made possible due to the very chemically aggressive nature of the melt. A test cell was constructed using a KOH–NaOH eutectic mixture and produced approximately 40 mW cm^{-2} of power at 450 °C while operating on a stream of pure ammonia fed to the anode and compressed ambient air fed to the cathode.
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1. Introduction

Today, hydrogen remains the most popular fuel for fuel cell applications due to its inherently fast kinetics at a fuel cell anode and high energy content by mass [1,2]. Additionally, hydrogen fuel cells are desirable in that they produce water as the only reaction byproduct, without the generation of pollutants or greenhouse gases such as CO_2. Unfortunately, the problems related to the production, transport, and storage of hydrogen continue to delay the realization of the hydrogen economy [3].

Ammonia, supplied in either an anhydrous or aqueous form, has been proposed as an alternate fuel for fuel cell systems due to its high hydrogen content, mild enthalpy of formation, convenient storage as a refrigerated or compressed liquid, and extremely narrow flammability limit [4,5]. Ammonia is also readily available, with an annual worldwide production of over 100 million metric tonnes [6]. Although the catalytic decomposition of ammonia may be used for the fueling of hydrogen fuel cells [7–10], ammonia has also been used directly within fuel cell systems. Recent examples include direct ammonia solid oxide fuel cells (SOFCs) [11,12], and protonic ceramic fuel cells

[13,14]. Molten carbonate fuel cells (MCFCs), which operate at sufficiently high temperatures to internally decompose ammonia to its constituent elements [15], should also be suitable for use with ammonia fuel. Indeed, each of these cells relies on a high operating temperature to assist in the utilization of ammonia through internal decomposition, but their high operating temperatures also require the use of expensive materials for cell fabrication. These include materials such as ceramics or exotic alloys for structural, sealing, and interconnect materials. Additionally, high operating temperatures may cause extreme demands to be placed on the cell with respect to thermal cycling [16–18]. Lower temperature conventional alkaline fuel cells, while employing an ammonia-tolerant aqueous electrolyte, do not operate at a sufficiently high temperature to liberate hydrogen atoms from an ammonia molecule at the anode surface and must rely on an external ammonia reformer [19]. Proton exchange fuel cells which rely on acidic electrolytes, such as the polymer electrolyte membrane and phosphoric acid cells, are in fact poisoned by ammonia and are intolerant of any residual ammonia in a reformed fuel stream [8,20], requiring further treatment of the fuel stream by absorption or sieving.

The present work illustrates the construction and performance of a direct ammonia fuel cell operating at temperatures between 200 and 450 °C using a molten alkaline hydroxide electrolyte. To date, molten alkaline hydroxide salts have only been

* Tel.: +1 202 806 4796; fax: +1 202 806 4635.
 E-mail address: jganley@howard.edu.

employed in direct carbon fuel cell prototypes [21,22], despite their long-known advantages of low cost, high ionic conductivity [23], and efficient fuel oxidation [24]. Molten hydroxide fuel cells are most similar in nature to molten carbonate fuel cells. However, hydroxide melts may achieve high ionic conductivities at far lower temperatures than carbonate melts. For example, a molten potassium hydroxide (KOH) melt exhibits an ionic conductivity of about $2.5\,S\,cm^{-1}$ at $400\,°C$ [25], while a potassium carbonate (K_2CO_3) melt would require a temperature of over $1000\,°C$ to achieve the same ionic conductivity [26]. In this paper, it is illustrated that the high ionic conductivity, favorable electrode kinetics, and flexible operation temperature of a molten hydroxide electrolyte will allow for effective cell performance in direct ammonia operation with air.

2. Experimental

A schematic for the liquid–electrolyte fuel cell is shown in Fig. 1. The cell container was machined from 7 cm diameter Nickel-400 (66.5% Ni, 31.5% Cu, 1.2% Fe, 1.1% Mn) bar stock cut to 15 cm in length. Nickel-400, also known as the commercial Monel® alloy, was chosen due to its resistance to corrosion by molten hydroxides. The bar was internally bored to a depth of 11 cm with a diameter of approximately 3.8 cm. This central well served to store the molten electrolyte. The cell was heated by three 200 W cartridge heaters inserted into the bottom of the container. The top of the cell container was machined with a knife edge and bolt holes designed to mate with a standard 7 cm stainless steel conflat flange with copper gasket, which served as a cap for the container. The cap provided conduits for fuel

Fig. 1. Schematic diagram of the molten hydroxide direct ammonia fuel cell.

and oxidant entry, as well as a combined vent and thermocouple access port.

The anode and cathode electrodes (Mott Corporation) were each 6.4 mm diameter nickel tubes, 18 cm in length, each with a 1.9 cm porous nickel cup (also 6.4 mm in diameter) welded to the end of the tube to create a porous metal sparger at the tube end. The porous spargers had an external superficial surface area of approximately $4\,cm^2$, and this area was used for the calculation of the current and power densities produced by the cell. The electrode tubes were isolated from one another and the cell housing by Teflon® tubing sleeves placed at the top of each electrode, approximately 3 cm above the cell cap. During cell operation, the top of each electrode was cooled externally by flowing tap water to prevent melting the Teflon® sleeves. While immersed in the molten electrolyte, the two porous electrode ends were submerged to a depth of 10 cm and were separated by a lateral center-to-center distance of 2 cm. A direct electrical connection to the cell housing served as a reference electrode. This design proved to be reliable for cell operating temperatures of up to $450\,°C$.

The cell was operated over a range of temperatures from 200 to $450\,°C$. In each experiment, a stream of technical grade (99.99%) anhydrous ammonia was provided to the anode tube at a rate of 15 standard cubic centimeters per minute (sccm), which was automatically regulated by a calibrated mass flow controller. The oxidant provided to the cathode tube was a slight stoichiometric excess (60 sccm) of compressed air. The compressed air was supplied at room temperature and approximately 10% relative humidity. The air flow was manually adjusted and was measured with a calibrated mass flow meter. The molten electrolyte for each experiment was a eutectic mixture of sodium and potassium hydroxides (51 mol% NaOH, 49 mol% KOH, Alfa Aesar). This eutectic has the benefit of a much lower melting temperature ($170\,°C$) compared to the melting temperatures of pure sodium and potassium hydroxides (323 and $360\,°C$, respectively).

Fuel cell testing was accomplished by measuring the electrical current–potential (polarization) relationship by placing the cell in series with a controlled electronic load (TL5 Test Load, Astris Energi Inc.). The cell was monitored by defining an electric current to be produced by the cell, which the test load resistance was automatically adjusted to allow. The test current was increased from 0 (open circuit) to 200 mA by small steps, and at each prescribed current a resistance-free electrochemical potential measurement was made by interrupting the current for 0.1 ms. These *I–V* data allowed for the construction of polarization and power production plots.

3. Results and discussion

Initial cell tests indicated that the nickel cathode was not suitable for operation within the caustic melt. As is common in molten carbonate fuel cells [27,28], the nickel cathode quickly oxidized to nickel oxide (NiO), which has very limited electrical conductivity, as well as the propensity to dissolve in a molten salt. The oxidation of the cathode therefore caused irreversible polarization of the cell and an unacceptable reduction
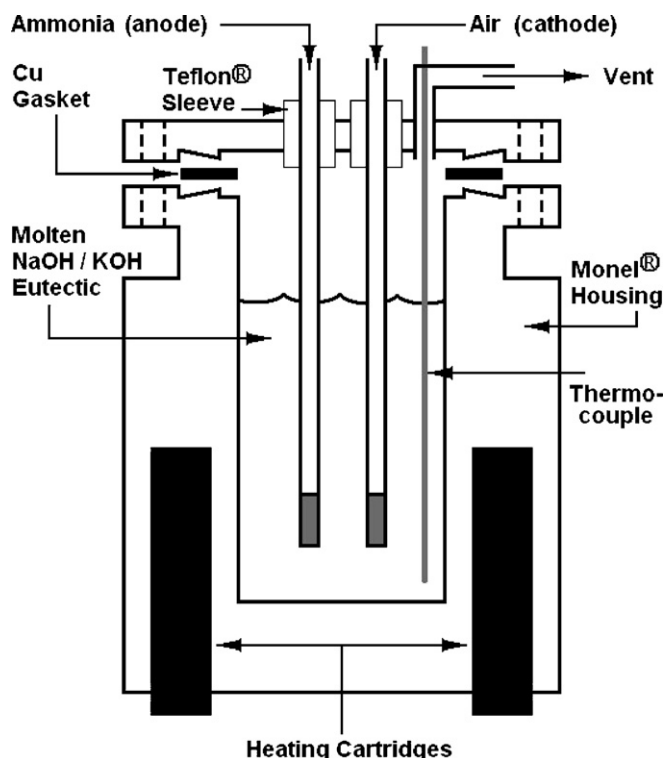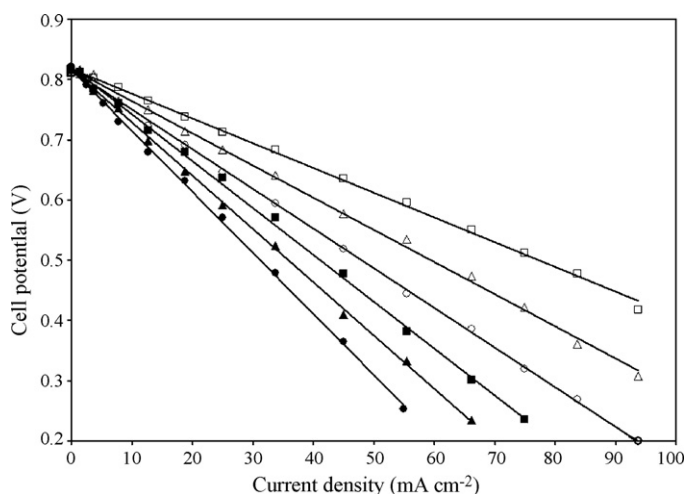
Fig. 2. Polarization behavior of the molten hydroxide direct ammonia fuel cell operating at (●) 200 °C, (▲) 250 °C, (■) 300 °C, (○) 350 °C, (△) 400 °C, and (□) 450 °C.
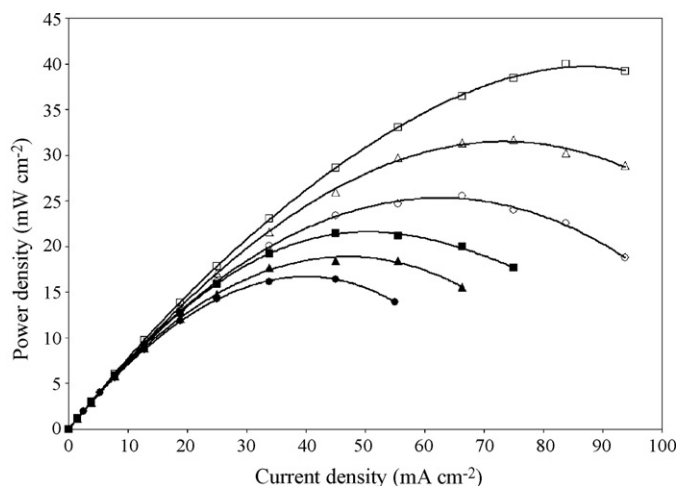

Fig. 3. Power production performance of the molten hydroxide direct ammonia fuel cell operating at (●) 200 °C, (▲) 250 °C, (■) 300 °C, (○) 350 °C, (△) 400 °C, and (□) 450 °C.

in the electrochemical potential and consequently the power available from the cell. In the operation of molten carbonate fuel cells, this situation is occasionally remedied by lithiation of the nickel oxide cathode—doping the nickel with lithium [29]. By doing so, the electrical resistance of the oxide layer is greatly decreased, and cathode dissolution is decreased. To produce lithiated nickel oxide from the porous metallic nickel electrode, a thermal–electrochemical treatment procedure was developed based on the method described by Yoshimura and coworkers. [30]. In the present study, the porous nickel cathode was treated in a 3 M LiOH solution maintained at 100 °C for 24 h while applying an anodic current of 1 mA cm^{-2}. In this single-step treatment, nickel metal is thermally and electrochemically converted first into a hydrated nickel oxide, which is further electrochemically oxidized and lithiated by cationic exchange to produce stoichiometric variants of LiNiO$_2$ [30]. The lithiated nickel sparger was much more stable in the melt and did not polarize or deactivate during the 2–4 h cell testing periods at each temperature.

The polarization and power production characteristics of the cell at various temperatures appear in Figs. 2 and 3, respectively. As the cell operating temperature increased, the open cell potential dropped slightly, which is a trend consistent with the expected electrode thermodynamics. Open cell potential at 200 °C was approximately 820 and 811 mV at 450 °C. This small thermodynamic potential loss was more than compensated for by the increased conductivity of the electrolyte as temperature increased, leading to less potential loss at higher electrical currents. Consequently, the peak cell performance was achieved at the highest temperature (450 °C), where a power density of approximately 40 mW cm^{-2} was delivered at a current density of approximately 94 mA cm^{-2}.

It should be noted that, although the cell does not currently perform with competitive power densities to commercial SOFC and MCFC devices, the electrode separation in the liquid electrolyte cell described here (2 cm) is over three orders of

magnitude greater than that common in high-power solid state fuel cells manufactured today (ca. 10 μm in anode-supported SOFC). Given the superior ionic conductivity of the hydroxide melt, it is anticipated that MCFC-like isolation of a molten hydroxide eutectic within a thin, inert ceramic matrix tile would greatly reduce ohmic potential losses. It is clear from the linear nature of the data appearing in Fig. 2 that ohmic potential losses are significant for this system. Additionally, the porous metal spargers are not constructed of a finely divided metal or metal oxide catalyst as is the case in state-of-the-art planar fuel cell stacks. Consequently, there is far less available catalytic surface area for chemical reaction, ionization, and product formation in the cell described in this study than may be possible with a more refined electrode design. Bubbling the reactant gases through the spargers had the added detriment of intermittent blockage of the electrode area from the electrolyte, likely greatly reducing the cell current density.

4. Conclusions

A direct ammonia fuel cell utilizing a molten alkali hydroxide eutectic melt was fabricated and tested at various operating temperatures between 200 and 450 °C. The use of a porous nickel anode and a porous cathode of lithiated nickel oxide provided stable cell performance for the duration of the testing. The polarization characteristics of the cell at different operating temperatures indicated that ohmic potential losses dominated the cell performance. It is likely that reduction in electrode separation distance and the use of a higher surface area, highly dispersed electrocatalyst at each electrode surface should increase overall cell performance. Now that the concept of a direct ammonia fuel cell using a molten alkali hydroxide electrolyte has been proven, ongoing research is being directed towards recasting the cell in the more traditional planar fuel cell design. This will allow a more direct comparison of the cell's performance to be made with other fuel cell types.

Acknowledgments

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