



Development of a direct ammonia-fueled molten hydroxide fuel cell



Jun Yang, Hiroki Muroyama, Toshiaki Matsui, Koichi Eguchi*

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan

HIGHLIGHTS

- Electro-oxidation of ammonia on Pt electrode in molten KOH–NaOH was investigated.
- Ammonia was proved to be continuously oxidized on Pt electrode at 200 °C.
- A direct ammonia-fueled molten hydroxide fuel cell was successfully operated.

ARTICLE INFO

Article history:

Received 19 March 2013
Received in revised form
14 May 2013
Accepted 25 June 2013
Available online 3 July 2013

Keywords:

Direct ammonia fuel cells
Molten hydroxides
Ammonia oxidation
Platinum electrode
Gas diffusion electrode

ABSTRACT

A fundamental study on direct ammonia fuel cells with a molten hydroxide electrolyte was conducted. The electrochemical oxidation of ammonia on Pt electrode in a molten NaOH–KOH electrolyte was investigated by cyclic voltammetry and mass spectrometry. Ammonia was proved to be oxidized to N₂ on the Pt electrode during anodic polarization in the molten hydroxide electrolyte. Furthermore, the direct ammonia fuel cell, *i.e.*, Pt gas diffusion electrode|molten NaOH–KOH electrolyte|Pt gas diffusion electrode, was assembled and operated at 200–220 °C. The cell achieved the maximum power density of *ca.* 16 mW cm⁻² at 220 °C with the supply of NH₃ and humidified O₂ to the anode and cathode, respectively. The mechanism of ammonia oxidation over Pt electrodes in a molten hydroxide electrolyte was discussed based on the results obtained.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Fuel cells can convert chemical energy to electricity efficiently with low pollutant emissions. Hydrogen is an ideal fuel for this device because of the fast kinetics of electrochemical reaction, high mass energy density, and only water in emission gas. However, the difficulties in storage and transportation of hydrogen hinder its application for commercial fuel cells [1,2]. Therefore, various kinds of hydrocarbon fuels, such as methane, methanol, ethanol, and propane, have been investigated intensively as the hydrogen carriers for fuel cells. On the other hand, the demand for a carbon-free fuel source is rising. This is because the by-products originated from the usage of hydrocarbon fuels could severely harm the performance and long-term stability, *e.g.*, CO for polymer electrolyte fuel cells (PEFCs) and carbon deposited for solid oxide fuel cells (SOFCs) [3–5]. In this respect, recently, ammonia has attracted a considerable interest as a prospective carbon-free fuel source for

fuel cells due to the low cost, ease in liquefaction and transportation at ambient temperatures, and high volumetric energy density [6,7].

Several research groups have reported the ammonia-fueled systems, *i.e.*, PEFCs with alkaline anion-exchange membranes (room temperature ~ 100 °C), alkaline fuel cells (AFC) with aqueous electrolyte (room temperature ~ 130 °C), and SOFCs with oxide ion or proton conductive electrolytes (500–800 °C) [8–12]. Unfortunately, the first two kinds of systems have the serious problem that the operating temperature is not sufficiently high for the sustainable electrochemical oxidation of ammonia on the anode. As for SOFCs, some promising performance has been obtained with the use of ammonia. However, only the hydrogen generated from the thermal decomposition of ammonia serves as the fuel. As a result, the anode material is required to be active for the ammonia decomposition as well as the electro-oxidation of hydrogen.

In addition to the systems introduced above, Ganley has developed a direct ammonia fuel cell composed of lithiated-Ni electrodes and a molten alkaline hydroxides electrolyte. The cell was operated between 200 and 450 °C, and achieved a maximum

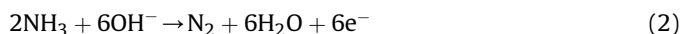
* Corresponding author. Tel.: +81 75 383 2519; fax: +81 75 383 2520.
E-mail address: eguchi@scl.kyoto-u.ac.jp (K. Eguchi).

power density of 40 mW cm^{-2} at 450°C [13]. Although the detailed investigation on the electrochemical ammonia oxidation on the electrode in a molten hydroxide electrolyte has not been conducted, the results indicated the feasibility of direct ammonia fuel cells operated at intermediate temperatures. The molten alkaline hydroxide electrolyte offers extremely high ion-conductivity at intermediate temperatures. For example, Arndt reported that the molten KOH exhibited an ionic conductivity of 2.5 S cm^{-1} at 400°C while that of yttria-stabilized zirconia was approximately 0.1 S cm^{-1} at 1000°C [14]. Secondly, the use of molten alkaline hydroxide electrolyte enables to elevate the operating temperature comparing with PEFC and AFC mentioned above. Thus, it is expected that ammonia could be continuously electro-oxidized on the anode.

The overall reaction for the direct ammonia molten hydroxide fuel cell is as follows:



The electrochemical oxidation of ammonia on the anode in the molten hydroxide is expected to be



The corresponding cathodic reaction can be expressed as



As a matter of fact, molten alkaline hydroxide eutectics have been employed in direct carbon fuel cells, and the cathode materials for the oxygen reduction reaction (ORR), such as NiO and FeTi alloys, have been well established [15,16]. However, the fundamental of ammonia oxidation on the anode has not been elucidated yet.

In this work, therefore, the mechanism for electrochemical oxidation of ammonia over Pt electrode was investigated precisely by cyclic voltammetry and mass spectrometry. Moreover, an ammonia-fueled molten hydroxide fuel cell with Pt gas diffusion electrodes (Pt GDEs) was fabricated, and its performance was evaluated at various temperatures.

2. Experimental

A molten hydroxide mixture of NaOH–KOH (Wako Pure Chemical Industries) with a weight ratio of NaOH:KOH = 43:57, which has the lowest melting point (168.8°C) in this binary system [17], was kept in a container fabricated by commercial Monel[®] alloy. The configuration of the cell inside the container is schematically illustrated in Fig. 1(a). Each electrode with a Pt lead wire was inserted into the electrolyte through a Teflon tube (inner diameter: 8 mm; outer diameter: 10 mm). The electrode area was defined as the area immersed in the liquid electrolyte (illustrated as the oblique-line region in Fig. 1(a)). As a result, the electrode was isolated from the ambient atmosphere by the liquid electrolyte and the Teflon tube. The gas was supplied to the electrode via a thin Teflon tube (inner diameter: 1 mm; outer diameter: 3.2 mm). The distance between the two electrodes was *ca.* 25 mm. A polytetrafluoroethylene (PTFE, Aldrich)-film-sealed Ag wire (diameter: 0.5 mm) was immersed into the electrolyte to serve as a reference electrode, which exhibited large exchange current and stable potential in molten KOH–NaOH electrolyte [18]. The Teflon tubes, Ag reference electrode, and PTFE film were proved to be stable in the molten hydroxides throughout the tests at the operating temperature range of $200\text{--}220^\circ\text{C}$.

Pt plate electrode cut from the commercial product (0.1 mm in thickness and 0.2 cm^2 in electrode area, Nilaco Corp.) was used as a working electrode. The electrochemical measurements for the Pt

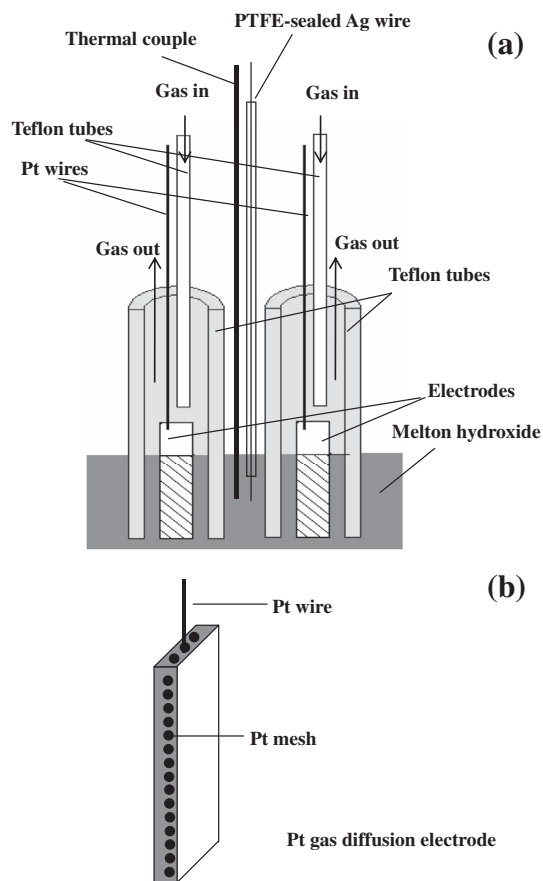


Fig. 1. Schematic illustration of (a) the molten hydroxide fuel cell and (b) the gas diffusion electrode.

plate electrode were carried out at 200°C . Cyclic voltammetry was performed on the Pt plate electrode between -0.9 to 0.3 V vs. Ag reference electrode under a flow of ammonia or argon at a sweep rate of 20 mV s^{-1} . Subsequently, the Pt plate electrode was polarized at -0.25 and 0 V vs. Ag reference electrode with ammonia, and the current density was measured as a function of time. In addition, the product of ammonia oxidation over the Pt plate electrode with an electrode area of 1.0 cm^2 was investigated by mass spectrometry. Ammonia was constantly supplied to the Pt plate electrode. After held at OCV for 10 min, the Pt plate electrode was polarized at -0.25 V for 30 min, and then held at OCV again. The outlet gas was analyzed by a mass spectrometer (OmniStar GSD 320, Pfeiffer Vacuum AG) throughout the test.

In order to obtain larger current density than the plate electrode, Pt gas diffusion electrode (Pt GDE, 0.2 cm^2 in electrode area) was prepared following the procedure in Ref. [19], as is shown in Fig. 1(b). Platinum powders (300 mesh, Nilaco Corp.) and PTFE powders ($1 \mu\text{m}$ in diam, Aldrich) with a volume ratio of PTFE:Pt = 3:2 were mixed in ethanol by ultrasonic radiation for 15 min. Subsequently, ethanol was vaporized and the resultant powder was pressed into a pellet (10 mm in diam.). The as-prepared pellet was hot-pressed into a film (*ca.* 0.1 mm in thickness) together with a piece of Pt mesh at 300°C . The Pt GDE was constantly polarized at -0.25 V . Simultaneously, Ar was flowed to the working electrode for *ca.* 4 min at first, and then was switched to ammonia for 2 min. Finally Ar was supplied again. Moreover, the stability of the Pt GDE under polarization was investigated. In these electrochemical measurements, the counter electrode was a Pt plate electrode in $97\% \text{ O}_2\text{--}3\% \text{ H}_2\text{O}$, which was prepared by bubbling

Download English Version:

<https://daneshyari.com/en/article/7738688>

Download Persian Version:

<https://daneshyari.com/article/7738688>

[Daneshyari.com](https://daneshyari.com)