Available online at www.sciencedirect.com
ScienceDirect
Electrochimica Acta 52 (2006) 1627–1631
ELECTROCHIMICA Acta
www.elsevier.com/locate/electacta

Study of direct type ethanol fuel cells Analysis of anode products and effect of acetaldehyde

Kento Taneda *, Yohtaro Yamazaki

Department of Innovative and Engineered Materials, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259, Nagatsuta-cho, Midori-ku, Yokohama, Kanagawa 226-8502, Japan

Received 6 November 2005; received in revised form 16 February 2006; accepted 5 March 2006
Available online 11 May 2006

Abstract

The anode products are observed when ethanol fuel is circulated in the direct ethanol fuel cell system using Nafion® as an electrolyte. The main products are CO_2 and acetaldehyde. *I–V* characteristics of a direct type fuel cell using ethanol and acetaldehyde as fuels are investigated. Anode and cathode overpotentials are also measured to analyze the characters of the polarization curves obtained for both fuels. The MEA consisted of PtRu anode catalyst. The voltage drops as the concentration of acetaldehyde solution increases. In the case of ethanol solution, the voltage increases as the concentration increases. The anode overpotential increases as the concentration of acetaldehyde increases although the increase of cathode overpotential is smaller than that of anode overpotential. The opposite result is observed for ethanol solutions, i.e., the anode overpotential increases as the concentration of ethanol decreases. This result shows that the voltage drop observed for acetaldehyde solution results from the anode overpotential. Rotating disc electrode (RDE) measurements and polarization curve measurements were also performed to confirm the relation between acetaldehyde concentration and overpotentials. It is supposed that the electrocatalytic oxidation mechanism of acetaldehyde on PtRu catalyst is different from that of ethanol.

Keywords: DEFC; Ethanol; CO_2; Acetaldehyde; DMFC; Adsorption of acetaldehyde

1. Introduction

As is known, direct type fuel cell is one of the candidates for an electric power source of the next generation, especially for compact system. It has merit that additional equipment, like a fuel reformer, is not necessary. Direct methanol fuel cell (DMFC) is the most intensively investigated one as the direct type fuel cell. However, there is a problem that methanol is toxic for human. Additionally, ruthenium, which is one of the precious metals existing rarely than platinum, is essential for the anode catalyst of DMFC. Based on these aspects of DMFC, there are several materials, which are investigated as a fuel of direct type fuel cell. Ethanol is one of them [1–8].

It is well known that ethanol is not toxic for human and is easily produced from biomass. This means that carbon dioxide (CO_2) emitted from direct type fuel cell using ethanol as a fuel can be recycled by planting. This CO_2 recycling leads to decreasing or keeping constant the amount of CO_2 emitted into the air. Moreover, it is reported recently that tin, which is one of the common metals, is more effective co-catalyst for the anode catalyst than ruthenium [3,5].

Electrocatalytic oxidation of ethanol using platinum or platinum alloy catalyst has been investigated [9–13], and the products formed by the electrocatalytic oxidation of ethanol and the oxidation reactivity of ethanol were discussed from many aspects. Iwasita and Pastor studied the adsorb behavior of ethanol on a polycrystalline platinum using a differential electrochemical mass spectroscopy (DEMS) and FTIR [9]. They reported many adsorbed species formed by the oxidation of ethanol and observed the evolution of CO_2. Fujiwara et al. also investigated the oxidation reactions of ethanol on a PtRu catalyst using DEMS, and concluded that ruthenium promotes the oxidation reactions of chemical species formed from the ethanol [11].

Direct type ethanol fuel cell (DEFC) has been investigated mainly from the sight of its *I–V* characteristics. However, the

* Corresponding author. Tel.: +81 45 924 5411; fax: +81 45 924 5433.
E-mail address: taneda@iem.titech.ac.jp (K. Taneda).

0013-4686/$ – see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2006.03.093

anode products, which are observed during DEFC operation, are not investigated well yet now. Wang et al. investigated the anode products observed when thick ethanol fuel is used and they concluded that the main product is acetaldehyde, which is one of the oxidative derivatives of ethanol [1]. On the other hand, Aricò et al. reported that the main anode product is CO_2 when thin ethanol fuel is used [2]. In these studies, fuel is used in one path, not circulated. However, it is very important for elucidating the working mechanism of DEFC to use ethanol fuel in circulating mode and to investigate the anode products.

In this study, the anode products formed during the DEFC operation in fuel circulating mode are investigated. Actually, it is shown that the main anode products are CO_2 and acetaldehyde. Acetaldehyde is known to be oxidized on platinum based catalysts [14–16] and it is strongly expected that acetaldehyde formed by anodic reaction of ethanol and accumulated in the fuel line affects the total cell performance of DEFC with fuel circulation. Based on the results of fuel circulating operation, the *I–V* and overpotential curves are measured for acetaldehyde and ethanol solutions. Additionally, the rotating disc electrode (RDE) and polarization curve measurements are performed for acetaldehyde solutions with PtRu/C working electrode to confirm the relation between the concentration of acetaldehyde and anode overpotential.

2. Experimental

2.1. Fuel circulating operation

The MEAs consisted of anode catalyst of PtRu/C (Pt loading: 2 mg cm^{-2}, Ru loading: 1 mg cm^{-2}), cathode catalyst of Pt/C (Pt loading: 2 mg cm^{-2}) and Nafion 117® as an electrolyte. The concentration of ethanol was 0.5 mol dm^{-3} (M). The cell temperature was 80 °C and fuel flow rate was 5.0 ml min^{-1}. Humidified O_2 was supplied as the cathode gas and flow rate was set at 50 ml min^{-1}. The applied cell voltages to investigate anode products were 0.3 and 0.05 V. The liquid and gas products were analyzed by gas chromatograph (Shimadzu GC-8AIT). The fuel circulating system is shown in Fig. 1. The ethanol fuel is stored in the reservoir first, and then pumped into the anode of the cell. The anode exhaust, which is liquid and gas mixture, is put into the liquid–gas separator. The gas products are stored in the gas trap and liquid products are returned to the reservoir.

2.2. I–V curve and polarization curve measurements

The MEAs used for *I–V* curve measurements were the same for the fuel circulating operation. The operating conditions are also the same for the case of fuel circulating operation. The concentrations of acetaldehyde and ethanol were 0.1, 0.5 and 1.0 M. No backpressures were applied for both fuel and cathode gas supplying systems. This means all experiments were performed under the atmospheric pressure. Dynamic hydrogen electrode (DHE) was used to measure the anode and cathode overpotentials. AuPd foil was used as the electrodes of DHE. Applied voltage and current for the DHE circuit were 1.2 V and 4 μA, respectively.

2.3. RDE and polarization curve measurements

The working electrode for RDE and polarization curves measurements consisted of PtRu/C pasted by Nafion solution (5 wt.%, Aldrich). The atomic ratio of platinum and ruthenium in PtRu/C is 1:1. Pt wire was used as the counter electrode and silver chloride electrode with saturated potassium chloride solution (Ag|AgCl) was for the reference electrode. All potentials shown in this study is based on Ag|AgCl. The support electrolyte was 0.1 M Na_2SO_{4aq}. The potential sweeping rate was 10 mV s^{-1} for both RDE and polarization curve measurements

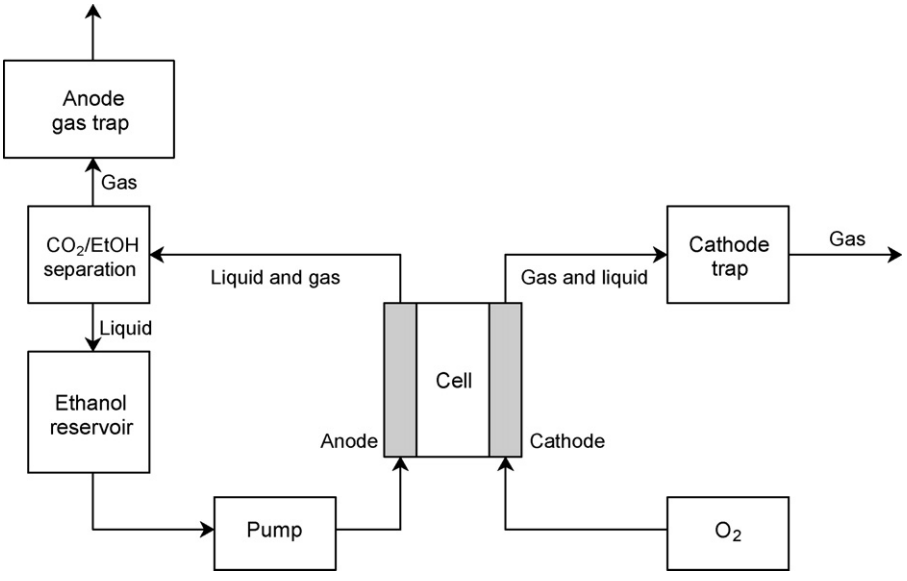

Fig. 1. The image of fuel circulating operation with ethanol fuel. The anode exhaust, which is liquid–gas mixture, is put into the liquid–gas separator and liquid products are returned to the reservoir.