Journal of Power Sources 236 (2013) 17–24

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Performance degradation of a direct borohydride fuel cell

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HIGHLIGHTS

- ► Catalyst erosion from anode substrate is a major cause of performance degradation of the direct borohydride fuel cell.
- ► Cooperative interaction among Co, N, and C contributes to the good performance stability of $Co(OH)_2$–PPY/BP.
- ► $Co(OH)_2$ and CoOOH in $Co(OH)_2$–PPY/BP disappear after long time of operation.

ARTICLE INFO

Article history:
Received 12 September 2012
Received in revised form
21 January 2013
Accepted 22 January 2013
Available online 24 February 2013

Keywords:
Direct borohydride fuel cell
Performance degradation
Hydrogen evolution
Hydrophobic anode
Electrode polarization
Cooperative interaction

ABSTRACT

This study explores the performance degradation mechanism of direct borohydride fuel cells (DBFCs) by investigating the catalyst surface characteristics, electrode structure, and electrode polarization after cell operation. Catalyst erosion from the anode substrate is a major cause of DBFC performance degradation. The depression of hydrogen evolution effectively stabilizes DBFC performance. DBFCs using Ni–Pd/C as the anode catalyst and polypyrrole-modified carbon-supported $Co(OH)_2$ [$Co(OH)_2$–PPy/BP] as the cathode catalyst exhibit high performance stability. The performance stability of $Co(OH)_2$–PPy/BP is similar to that of commercial Pt/C, although only a small amount of Co remains after operation. The cooperative interaction among Co, N from polypyrrole, and C from the carbon supporter plays a very important role in the performance stability of a DBFC cathode.

1. Introduction

Direct borohydride fuel cells (DBFCs) are an emerging type of fuel cell that uses alkaline borohydride solutions as fuel [1,2]. DBFCs are attracting interest as a potential power source because of their high electromotive force of 1.64 V and high theoretical energy density (9.3 Wh g^{-1} of $NaBH_4$). Most recent studies have aimed at improving cell performance and depressing hydrogen evolution [1–3]. However, little attention has been paid to the performance stability of DBFCs, particularly to their long-term performance stability.

Generally, the performance degradation of a fuel cell is characterized by one of four loss mechanisms: (a) ohmic, (b) activation, (c) mass transportation, and (d) fuel efficiency losses. Performance degradation is usually caused by a combination of these losses. Hydrogen evolution in a DBFC is susceptible to performance degradation because hydrogen bubbles generated during operation block the anolyte flow in the channels of a bipolar plate (in short-term cell performance deterioration) [4–7] and erode catalyst particles away from the anode (in long-term cell performance deterioration). A three-dimensional Os anode has been developed to prevent catalyst erosion and improve the durability of DBFC anodes [8]. A special anode structure with upper and lower parts for the electrooxidation of borohydride [9] may be used to decrease the effects of hydrogen evolution on catalyst erosion.

Apart from hydrogen evolution at the anode, the anolyte crossover, hydrophobic characteristics of cathode, and nature of cathode catalyst also affect the performance stability of DBFCs [10,11]. Pt/C has higher electroactivity toward oxygen reduction reaction (ORR), as well as better performance stability, than Pd/C, Ag/C, and Ni/C [10]. Some non-precious catalysts such as iron tetramethoxyphenyl porphyrin have high borohydride tolerance, exhibiting activity and performance stability similar to Pt/C [12]. Previous studies [13–15] show that polypyrrole-modified carbon-supported cobalt hydroxide [$Co(OH)_2$–PPy/BP] catalysts have fairly high electroactivity toward ORR. However, the long-term

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http://dx.doi.org/10.1016/j.jpowsour.2013.01.175

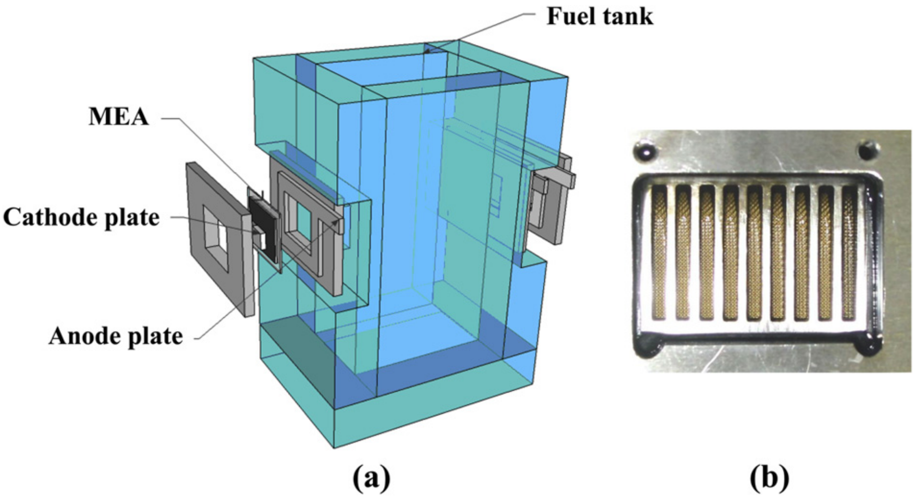

Fig. 1. (a) Schematic of the DBFC test module for performance degradation evaluation, and (b) top view of the single cell.

performance stability of these catalysts has not yet been evaluated. The effects of $Co(OH)_2$ on the performance stability of $Co(OH)_2$–PPy/BP catalyst are also unclear.

In this paper, we design and assemble a DBFC test set for performance degradation evaluation. The performance degradation behaviors of anode and cathode catalysts are investigated by electrode polarization measurements and physical characterizations. The effect of $Co(OH)_2$ in $Co(OH)_2$–PPy/BP on ORR during cell operation is discussed.

2. Experimental

Fig. 1 shows the test set for cell performance stability evaluation. Two single cells with a similar structure to a previously described microcell [16] were used. The cells were mounted 12 cm apart on the walls of a fuel tank to ensure the same environmental conditions. The prismatic fuel tank was made of acrylic and had a fuel reservoir capacity of 1.44 L ($L \times W \times H = 12 \times 6 \times 20$ cm^3). In the middle of the tank, two windows ($L \times W = 3.5 \times 3$ cm^2) facing each other were opened for anolyte transportation. Each single cell consisted of anode and cathode plates with slits for fuel and air transportation, and the entire anode–membrane–cathode assembly had an active area of 6 cm^2. To improve contact between the end plate and electrode, a hydrophobic gold-coated Ni grid (100 mesh) was welded to the end plate by spot welding, as shown in Fig. 1(b). The hydrophobic gold-coated Ni grid was prepared by dipping the gold-coated Ni grid in a polytetrafluorethylene (PTFE) emulsion (5 wt.%) followed by heating to 573 K under an argon atmosphere for 1 h after air drying.

The anode was prepared by pasting an anode ink onto a piece of Ni foam with a catalyst loading of 1 mg cm^{-2}. The anode ink was prepared by mixing the catalyst powders with water, ethanol, and Nafion solution (5 wt.%) or PTFE emulsion (5 wt.%) at a 1:3:3:7 mass ratio of catalyst:ethanol:Nafion solution (or PTFE emulsion):water. The cathode was prepared by painting a cathode ink onto a piece of hydrophobic carbon cloth. The cathode ink was prepared by mixing catalyst powder with water, ethanol, and PTFE emulsion (5 wt.%) at a 1:3:3:7 mass ratio of catalyst:ethanol:PTFE emulsion:water. The preparation procedure of $Co(OH)_2$–PPy/BP was as described in a previous study [13]. The electrolyte used to separate the anode from the cathode contained a cation exchange membrane (CEM): Nafion 112 membrane (Dupont) or anion exchange membrane (AEM): Neosepta AMX membrane (Tokuyama Soda). An alkaline $NaBH_4$ solution (5 wt.% $NaBH_4$–10 wt.% NaOH) was used as the fuel (anolyte). Cell performance polarization measurements and performance stability evaluation were conducted under ambient and passive conditions.

Electrode polarization measurements were conducted using the PFX2011S electrochemical workstation (Kikusui Electronics Corp.). A saturated calomel electrode (SCE) served as the reference electrode and was connected to the fuel tank with a salt bridge. The used fuel was replaced by fresh fuel at 96 h intervals.

The electrodes were subjected to cyclic voltammetry (CV) between −1.0 and 0.2 V (vs. SCE) at 25 °C with a scan rate of 50 mV s^{-1} in an alkaline O_2-saturated solution (0.1 mol L^{-1} KOH). The detailed preparation procedures of $Co(OH)_2$–PPy/BP electrodes for CV measurements are described elsewhere [15].

The microstructure of the synthesized catalysts was characterized by X-ray diffraction (XRD) using a Rigaku-D/MAX-2550PC diffractometer with Cu Kα radiation (λ = 1.5406 Å). The morphology of the anode was characterized by scanning electron

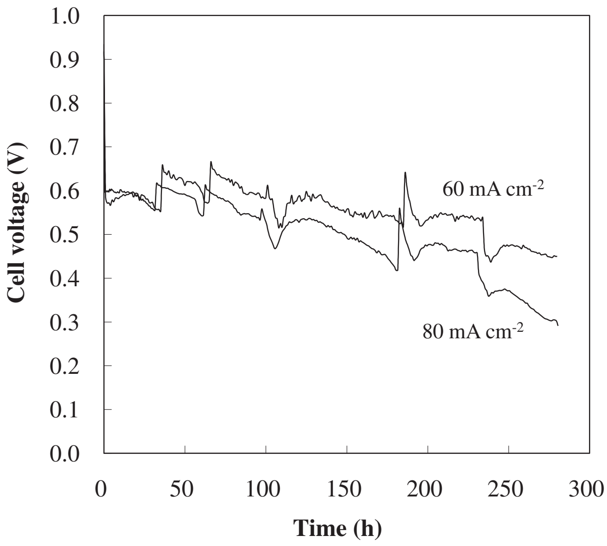

Fig. 2. Performance degradation of the DBFC using $Co(OH)_2$–PPy/BP as anode and cathode catalyst operating at a current density of 60 and 80 mA cm^{-2} under ambient conditions, respectively.