Journal of Power Sources 345 (2017) 221–226

Contents lists available at ScienceDirect

Journal of Power Sources

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

Improvement in the solid-state alkaline fuel cell performance through efficient water management strategies

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HIGHLIGHTS

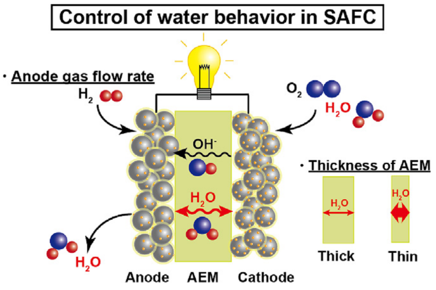
- Water transport was controlled to suppress the anode flooding in SAFCs.
- MEA with thin AEM improved cell performance at high current densities.
- Increasing the anode flow rate improved cell performance at high current densities.
- Flooding can be suppressed by using thin AEM and increasing the anode flow rate.

ARTICLE INFO

Article history:
Received 17 November 2016
Received in revised form
4 January 2017
Accepted 25 January 2017

Keywords:
Solid alkaline fuel cells
Water management
Thin anion exchange membrane
Flow rate
Flooding

GRAPHICAL ABSTRACT



ABSTRACT

In solid-state alkaline fuel cells (SAFCs), water is generated at the anode and is reacted at the cathode; as such, flooding occurs much more easily at the anode than it does in proton-exchange membrane fuel cells (PEMFCs). Anode flooding is a reason for the low performance of SAFCs, and so it is important that this flooding phenomenon is mitigated. In this study, we control water transport to suppress anode flooding. We do this through two approaches: changing the thickness of the anion exchange membrane (AEM) and changing the anode flow rate. Among two AEMs with two different thicknesses (27 μm and 6 μm) prepared, thinner AEM shows improved fuel cell performance. Increasing the anode flow rate also improved the performance of SAFCs. To find out what caused this, the water transport inside the membrane electrode assembly (MEA) was analyzed. The flooding region was estimated using calculated relative humidity at anode outlet. On the basis of our experimental and calculation approaches, flooding can be suppressed by using thin AEMs and increasing the anode flow rate.

1. Introduction

Fuel cells convert chemical energy directly into electrical energy, and they are considered to be a promising technology because of their high efficiency and cleanliness [1–3]. Recently, solid-state alkaline fuel cells (SAFCs) with anion-exchange membranes (AEMs) have attracted considerable attention as next generation fuel cells, because they have several advantages over proton-exchange membrane fuel cells (PEMFCs). As SAFCs operate under alkaline conditions, the electrochemical kinetics of both the anode and the cathode are faster than those in acidic conditions [4–6]; furthermore, low cost non-noble metal (platinum-free)

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http://dx.doi.org/10.1016/j.jpowsour.2017.01.111
0378-7753/

catalysts can be employed at the electrode [7–12]. Compared to PEMFCs, SAFCs are still in the early stages of development, and their performance is comparatively low [4,13–15]. Although the durability of AEMs is a primary issue that SAFCs need to solve, recent reports have shown improvements in their durability [15–18]. However, development of AEMs that exhibit high performance does not always lead to high cell performance.

Water behaves differently in SAFC systems than it does in PEMFC systems; to put it briefly, the electrode where water is produced, and the direction of water transport in the polymer electrolyte membrane, are opposite [19]. In PEMFCs, water is generated at the cathode (Eq. (2)):

$$\text{Anode: } 2H_2 \rightarrow 4\,H^+ + 4e^- \tag{1}$$

$$\text{Cathode: } 4H^+ + O_2 + 4e^- \rightarrow 2H_2O \tag{2}$$

$$\text{Total: } 2H_2 + O_2 \rightarrow 2H_2O \tag{3}$$

In contrast, in SAFCs, water is reacting with oxygen at the cathode (Eq. (5)) and the amount of water generated at the anode (Eq. (4)) is twice as large as the amount generated at the cathode in PEFCs:

$$\text{Anode: } 2H_2 + 4OH^- \rightarrow 4H_2O + 4e^- \tag{4}$$

$$\text{Cathode: } O_2 + 2H_2O + 4\,e^- \rightarrow 4\,OH^- \tag{5}$$

$$\text{Total: } 2H_2 + O_2 \rightarrow 2H_2O \tag{6}$$

The relative humidity (RH) at the cathode therefore decreases much faster than in PEMFCs, which leads to a decrease in both the ion conductivity of AEMs and cell performance. However, at the anode, flooding occurs more easily and induces a fast drop in cell performance in the high current density region; this is because the flooding at the anode reduces the gas transportation to the reaction sites. This flooding phenomena at the anode greatly affects the performance of SAFCs [20]. For this reason, water management is very important for improving the performance of SAFCs [20–22].

In order for the influence of anode flooding to be excluded in SAFCs, two different approaches for controlling water behavior have been suggested. One approach is to control the thickness of AEM. Some previous reports suggest the improved current–voltage (I–V) performance while using thin AEMs [21,23], but the reason behind it is not proven so far. When thinner AEMs are used, water transport from the anode to the cathode is accelerated. As a result, water distribution between the two electrodes is uniform, and the phenomena of cathode drying and anode flooding is mitigated. The other approach is to control the operating conditions of the fuel cell such as the RH of both electrodes, which affects the performance of the SAFCs [20,24]. In PEMFCs, water is generated at the cathode, and it has been reported that increasing the gas flow rate at the cathode improves cell performance due to water being more effectively removed from the cell [25,26]. As water is generated at the anode in SAFCs, increasing the gas flow rate at the anode would be an effective way to suppress the flooding. At the same time, it is necessary to make use of the changes in the water behavior when the thickness of the AEM and the flow rate at the anode are changed.

In this work, we focus on managing the water behavior in SAFCs so that the influence of the anode flooding can be mitigated. Water management was controlled through two approaches: changing the thickness of the AEM and changing the anode flow rate. AEMs with different thickness were prepared using a pore-filling technique that we had previously reported [18,27–30]; in this technique, an inert and stable porous substrate is used to fill the polyelectrolyte inside the pores. The thin polymer electrolyte membrane is around 6 μm thick, and it can be prepared without any loss in its mechanical strength; this cannot be achieved by the normal solution casting method. We also conducted water transport measurements of membrane electrode assembly (MEA) to evaluate the effect of the water management on the performance of the fuel cell.

2. Experimental section

2.1. Materials and chemicals

All reagents for the synthesis were used as received from the provider. Vinyl benzyl trimethyl ammonium chloride (VBTAC), divinyl benzene, and poly(vinylbenzyl chloride) (PVBC, 60/40 mixture of 3- and 4-isomers, average M_n 55,000, average M_w 100,000, measured by GPC/MALLS) were purchased from Sigma-Aldrich. 2,2'-azobis(2-methylpropionamidine)dihydrochloride (V-50), ethanol, ethyl acetate, 30% trimethylamine solution, and potassium hydroxide were obtained from Wako Pure chemical Industries Ltd. Carbon-supported platinum catalyst powders (TEC10E50E; Pt/C ratio of 46.5 wt %, TEC10E10E; Pt/C ratio of 9.8 wt %) were supplied by Tanaka Kikinzoku Kogyo Co. Ltd., and a gas diffusion layer (GDL, carbon paper with a microporous layer, SIGRACET® GDL 24 BC) was supplied by the SGL Group. The polyethylene (PE) porous substrates were provided by Toray Battery Separator Film Co Ltd., Japan (thickness = 25 μm, porosity = 46%; thickness = 5 μm, porosity = 46%)

2.2. Membrane preparation

AEMs with different thicknesses were prepared using the pore-filling technique outlined in the Introduction; VBTAC was used as an electrolyte, and two kinds of porous PE substrates with different thicknesses, 25 μm and 5 μm, were used. The PE substrates were soaked into monomer solution that contained 10.6 g VBTAC, 0.106 g divinylbenzene as a cross-linker, 1.6 g V-50 solution (10 wt%) as an initiator, and 10.6 g of ethanol as a solvent for 2 h. After immersion, the membranes were sandwiched between glass plates, and cross-linking polymerization was conducted at 60 °C for 16 h. After the polymerization, the membranes were converted into the OH^- form by immersing them in 1 M potassium hydroxide solution for 16 h.

The volumetric filling ratios of the VBTAC were calculated using the following equation:

$$\text{Volumetric filling ratio}[\%] = \frac{\text{Volume of filled polymer } \left[\text{cm}^3\right]}{\text{Substrate pore volume } \left[\text{cm}^3\right]} \times 100 \tag{7}$$

Prepared pore-filling AEMs were measured by Fourier transform infrared (FTIR) spectroscopy (FT/IR-6200V, JASCO Corp., Japan) to confirm the filling of the VBTAC into the pores of the PE substrate. The thickness of each AEM was measured using a High-Accuracy Digimatic Micrometer (MDH-25 M, Mitsutoyo Corp., Japan) at five different points and the average thickness was then calculated.

2.3. MEA fabrication and single-cell MEA tests

For the anode catalyst, a catalyst ink containing 0.64 g TEC10E10E (Pt 9.8 wt%), 19.9 g ethyl acetate, and 0.1 g PVBC was ball-milled with φ 1 mm of zirconia balls at 400 rpm for 2 h (Planetary Mono Mill Pulverisette 6, Fritsch). For the cathode