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Performance evaluation of an air-breathing high-temperature proton exchange membrane fuel cell

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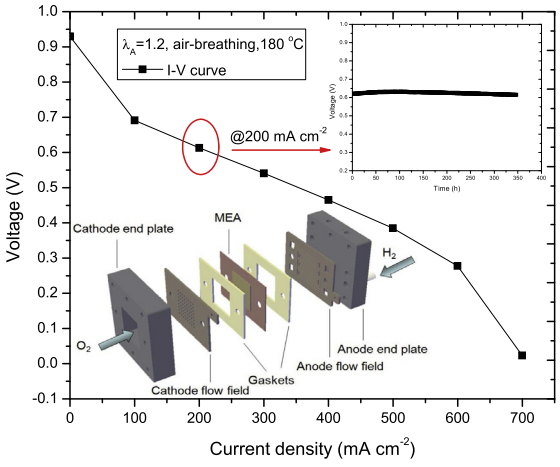
HIGHLIGHTS

- An air-breathing HT-PEMFC was designed and evaluated experimentally.
- The peak power density of the air-breathing HT-PEMFC was 220.5 mW cm^{-2} at 200 °C.
- Break-in behavior and effects of temperature and anodic stoichiometry were studied.
- The effect of cell orientations on the performance was investigated.
- The degradation rate of the air-breathing HT-PEMFC was around 58.32 μV h^{-1}.

GRAPHICAL ABSTRACT



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ABSTRACT

The air-breathing proton exchange membrane fuel cell (PEMFC) is of great interest in mobile power sources because of its simple system design and low parasitic power consumption. Different from previous low-temperature air-breathing PEMFCs, a high-temperature PEMFC with a phosphoric acid doped polybenzimidazole (PBI) membrane as the polymer electrolyte is designed and investigated under air-breathing conditions. The preliminary results show that a peak power density of 220.5 mW cm^{-2} at 200 °C can be achieved without employing any water managements, which is comparable to those with conventional Nafion® membranes operated at low temperatures. In addition, it is found that with the present cell design, the limiting current density arising from the oxygen transfer limitation is around 700 mA cm^{-2} even at 200 °C. The short-term durability test at 200 mA cm^{-2} and 180 °C reveals that all the cells exhibit a gradual decrease in the voltage along with a rise in the internal resistance. The degradation rate of continuous operation is around 58.32 μV h^{-1}, which is much smaller than those of start/stop cycling operations.

1. Introduction

Since the last decade, considerable attentions [1–3] have been paid to proton exchange membrane fuel cells (PEMFC) because of

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their appealing advantages, such as high energy-conversion efficiency (typically higher than 50%), large power density, zero pollution and low noise. These favorable features make this kind of fuel cells suitable for automobiles, backup power sources and off-grid residential power systems. In an operating PEMFC, sufficient oxygen must be fed to the electrode to sustain oxygen reduction reaction (ORR) while excess water produced by ORR needs to be removed. For a large power system, forced convection generated by blowers/compressors is usually employed to ensure the efficient supply of reactants and removal of products. Nevertheless, such auxiliary devices not only consume additional power but also are difficult to miniaturize for small power applications. Hence, air-breathing PEMFCs that make use of natural convection and molecular diffusion have been proposed [4–14] as portable power sources for smart phones, laptops and mobile chargers.

Generally, the power density of air-breathing PEMFCs is 80–350 mW cm^{-2} [4–14], around 1/3 as that of active PEMFCs. The poor performance of air-breathing PEMFCs mainly arises from two issues: (1) slow mass-transfer rate of oxygen by diffusion and natural convection; (2) difficulty in maintaining a delicate balance between drying out of membranes and water flooding without employing active water management techniques. In order to improve the performance, a number of interesting efforts have been devoted to addressing such issues in recent years. Krumbholz et al. [11] investigated the current collector design parameters of an air-breathing PEMFC and found that when the open ratio was less than 0.1, the cell impedance was substantially low as water predominately accumulated inside the electrodes. In addition to open ratios, Bussayajarn et al. [13] experimentally studied the geometry of cathode current collector and its influences on the oxygen transport and membrane resistance and found that circular holes yielded the best performance. To retain the water inside the catalyst layers (CL), Poh et al. [14] improved the hydrophilicity of Pt/C catalysts by citric acid treatment and demonstrated an increase of 23.4% in power density with such self-humidifying catalysts.

Although the performance can be increased to some extent by above mentioned methods, previous air-breathing PEMFCs still suffer from slow oxygen supply and water flooding/starvation problems. Obviously, one simple way to enhance the mass transport and avoid water flooding is elevating the cell temperature. For water starvation or drying out of polymer electrolyte membranes, employing a membrane with its conductivity independent or slightly dependent on water may be an ultimate solution. Wainright et al. [15] combined such two methods and firstly introduced acid-doped polybenzimidazole (PBI) membranes for high-temperature proton exchange membrane fuel cells (HT-PEMFC). Since this pioneering work [15], extensive attentions were paid to the proton conduction in acid-doped membranes [16–18], development of alternative acid-doped membranes [19–22], durability of HT-PEMFCs [23–25], electrode designs [26–28] and demonstration of stacks [29,30]. In addition to experimental works, numerical modeling was also of great interest to understand heat/mass transport phenomena occurring in a HT-PEMFC, including the gas crossover [31], flow field designs [32], effect of gas compositions [33] and the thermal effects [34]. However, a close look at the literature reveals that previous HT-PEMFCs rely on active supply of oxygen and their operating characteristics under air-breathing conditions remain unclear. In this work, an air-breathing HT-PEMFC based on a phosphoric acid (PA) doped PBI polymer electrolyte is designed and investigated under various operating conditions, with an aim to gain a general understanding on its performance characteristics.

2. Experimental

2.1. Fabrication of PBI based membrane electrode assemblies (MEA)

The preparation procedures of MEAs were similar to our previous work [35]. A PBI membrane with a thickness of 40 μm and a doping level of approximately 6.5 was applied as a proton-conducting membrane. A 356 μm thick AvCarb® 1071-HCB carbon cloth with a microporous layer (MPL) was employed as the gas diffusion layer (GDL); the polytetrafluoroethylene (PTFE) contents in the carbon cloth and the MPL were 5 wt.% and 15 wt.%, respectively. The CLs were fabricated by spraying catalytic inks, consisting of Hispec® 9100 Pt/C, PTFE and ethanol, onto the surface the MPLs; the metal loading and PTFE content in CLs were maintained to be about 1 mg cm^{-2} and 10 wt.%, respectively. To increase the active surfaces in the CL, all the electrodes were sprayed with additional 5 mg cm^{-2} PA before hot pressing. Finally, the electrodes and the membrane were hot pressed at 180 °C for 3 min to form a compact MEA, the active area of which was 3.0×3.0 cm^2.

2.2. Single cell design of an air-breathing HT-PEMFC

Fig. 1 shows the single cell design of the air-breathing HT-PEMFC. The present single cell consisted of an aluminum cathode end plate, a cathode flow field, a MEA, an anode flow field and an aluminum anode end plate with a hydrogen inlet and outlet. Both the anode and cathode end plates were square shape of 75 mm × 75 mm and have a thickness of 20 mm. For the cathode end plate, there was a square hole of 30 mm × 30 mm at the center for the transport of oxygen. The cathode flow field was made of 316L stainless steel with a thickness of 2 mm and an open ratio of 46.94% formed by 64 ∅ 2.9 mm drilled circular holes, while the anode flow field was a 2 mm-thick graphite plate grooved with double-pass serpentine channels; the channel depth, channel width and the rib width were 1 mm, 1.5 mm and 1.1 mm, respectively. To control the fuel cell temperature, an electrical heater and a thermal couple were inserted to the holes (∅ 6.5 mm) of the anode end plate. It should be noted that electrical heating is unnecessary in practice as high temperatures can be achieved by supplying reformates to the anode directly or by self-heating from reactions with appropriate thermal insulation.

2.3. Electrochemical characterizations and test conditions

The electrochemical impedance spectra (EIS) of the air-breathing HT-PEMFC were attained by the Zahner® Zennium workstation. To conduct the measurement, the counter and reference electrode of the workstation were connected to the anode whereas the working electrode was connected to the cathode. The measurement was performed under galvanostatic mode at 1.8 A with a perturbation amplitude of 0.1 A and the impedance data were recorded from 10^{-2} to 10^5 Hz with 8 steps per decade. For fuel cell performance test, an Arbin® BT-5HC testing system was used to control the external load and record the corresponding measured data. To attain the stable polarization curves, pure hydrogen (99.999%) with various anodic stoichiometry (λ_A) was fed to the anode and the HT-PEMFCs were discharged at a series of predefined current for 10 min until reproducible data was achieved. During the short-term durability test, the internal resistances were monitored and measured at every 24 h by the Arbin test station with the current interruption method. The environmental temperature and humidity during tests were, respectively, in the ranges of 23–25 °C and 45–55%.