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Short communication

Low platinum loading for high temperature proton exchange membrane fuel cell developed by ultrasonic spray coating technique

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HIGHLIGHTS

- Low Pt loading GDEs were first inspected for HT-PEMFC.
- Four different Pt loadings (from 0.138 to 1.208 mg cm^{-2}) were investigated.
- The optimal Pt loading was found to be 0.350 mg cm^{-2}.
- The peak cathode mass power is as high as 0.967 W mg_{Pt}^{-1}.

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ABSTRACT

This paper reports use of an ultrasonic-spray for producing low Pt loadings membrane electrode assemblies (MEAs) with the catalyst coated substrate (CCS) fabrication technique. The main MEA subcomponents (catalyst, membrane and gas diffusion layer (GDL)) are supplied from commercial manufacturers. In this study, high temperature (HT) MEAs with phosphoric acid (PA)-doped poly(2,5-benzimidazole) (AB–PBI) membrane are fabricated and tested under 160 °C, hydrogen and air feed 100 and 250 cc min^{-1} and ambient pressure conditions. Four different Pt loadings (from 0.138 to 1.208 mg cm^{-2}) are investigated in this study. The experiment data are determined by *in-situ* electrochemical methods such as polarization curve, electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). The high Pt loading MEA exhibits higher performance at high voltage operating conditions but lower performances at peak power due to the poor mass transfer. The Pt loading 0.350 mg cm^{-2} GDE performs the peak power density and peak cathode mass power to 0.339 W cm^{-2} and 0.967 W mg_{Pt}^{-1}, respectively. This work presents impressive cathode mass power and high fuel cell performance for high temperature proton exchange membrane fuel cells (HT-PEMFCs) with low Pt loadings.

1. Introduction

Due to the high power density, high efficiency, zero emissions, high-quality power, scalability and fast start-up, proton exchange membrane fuel cells (PEMFCs) are considered as promising future power sources [1].

High temperature proton exchange membrane fuel cell (HT-PEMFC) is a relatively new research area which has gained considerable interest recently with over 2000 research articles published since 2012. Among these researches, phosphoric acid (PA)-doped polybenzimidazole (PBI) system is considered as the most promising candidate for HT-PEMFC with the capability of operating up to 200 °C [2–5]. Important properties, e.g. the proton conductivity of and the conduction mechanism in the membranes [6–11], their mechanical properties and gas permeability as well as the development of membrane electrode assemblies (MEAs) based on this type of membrane and their electrochemical performance at various operating conditions have been studied extensively [4,5,12–15]. The high operating temperature of this PA-doped PBI-based fuel cell system offers several advantages: (i) no need for water management systems, (ii) high tolerance for fuel impurities (up to 3% CO in the fuel stream enabling the use of a simple reformer system), (iii) high quality heat that can be utilized for cogeneration purposes, (iv) simplified Flow Field Plate (FFP) design due to improved transport of vapour water in the structures, (v) minimized BoP requirements in turns allowing simpler system designs [16].

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MEA is the core component of a PEMFC, which plays an important role in determining the whole cell performance. A MEA is a composite of gas diffusion layer (GDL), catalyst layer (CL) and proton exchange membrane (PEM). Generally, a MEA can be prepared by the three following methods: (i) Catalyst coated membrane (CCM), i.e. CLs were deposited onto a membrane directly, (ii) Decal transfer CCM, i.e. coating CL on a substrate and then transferring the CL onto a membrane, and (iii) Catalyst coated substrate (CCS), which deposits CL on GDL (a GDL with CL is called a gas diffusion electrode (GDE)). A MEA is fabricated by either sandwiching a CCM between two GDLs or sandwiching a PEM between two GDEs.

In a MEA, the electrochemical reaction occurs in the CL and it needs a three-phase boundary (TPB) where the catalyst, electrolyte, and gas are all in physical contact. The amount of TPB strongly affects the fuel cell performance [1,17–19]. The TPB is mainly dominated by the CL deposit method and the properties of the catalyst ink being used, by which the CL properties are determined. Therefore, the CL deposit technique and the formula of the catalyst ink dominate not only the fuel cell performance but also the cost. At present, the Pt loading (both cathode and anode) for HT-PEMFC is normally above 0.7 mg cm^{-2} [3,19–21]. For mass production, the catalyst ink cost is approximately 34% of the total stack cost [22]. Thus, lowering Pt loadings of MEAs is becoming one of the most important issues for PEMFCs [23–28]. For HT-PEMFC based on PA-doped PBI membrane, it is a further challenge because liquid PA in the CLs could make the gas transport difficult and impede the electrode reactions by phosphate anion adsorption on the platinum catalyst [12,13]. This could be the reason why currently no literature were found on preparing low Pt loading MEAs for HT-PEMFC even it has become a hot topic in fuel cell area. Good CL deposit techniques are required to create more available TPB and porous structure to mitigate the effect of PA, thereby reaching satisfactory performance with reduced catalyst loading.

In our previous works [23,28], it was found that the ultrasonic spray method can distribute the catalyst ink evenly leading to high platinum utilization due to the unusual experimental conditions caused by efficient stirring and forced convection in the form of ultrasound, cavitation and enhanced mass transport phenomenon. Consequently, it is expected that this technique possesses the ability to reduce the platinum loading of HT-PEMFC. In this paper, the CCS and ultrasonic spray coating technique were combined to fabricate low Pt GDEs for HT-PEMFC. The resultant MEAs were investigated with air oxidant and at ambient pressure for being consistent with real applications. It should be mentioned that it is the first study of low platinum loading MEAs for HT-PEMFCs.

2. Experimental

2.1. MEA fabrication

Catalyst inks consist of supported catalyst (40 wt% Pt/C, Johnson Matthey HiSpec™ 4000), PVDF solution (5 wt%), DMAc. All the contents were added to a glass vial and mixed using an ultrasonic bath. The PVDF in solid phase of catalyst ink was 15 wt%. The catalyst inks were ultrasonically sprayed onto the GDL (Freudenberg, Germany) as GDE. Run paths were created using the Sono-Tek 'Exacta-coat' ultrasonic spray instrument operating at 120 kHz. The Pt loadings were controlled by the number of passes using a given run path. The finished GDEs were heat-treated at 165 °C oven overnight to evaporate the remaining DMAc. A commercially available poly-(2,5-benzimidazole), also known as the ABPBI membrane, Fumapem AM (Fumatech, Germany) was doped in H_3PO_4 at 85 °C and doping H_3PO_4 level was controlled at 270 ± 10% prior to use. The acid-doping level was defined as the ratio of the "weight of PA doped into the membrane" to the "weight of the membrane before doping with PA".

2.2. Single cell test

Together with two gaskets (~200 μm) made of fluorinated polymer, the MEA was assembled by sandwiching the doped membrane between two GDEs impregnated with PA in a single cell fixture (BalticFuelCells GmbH, Germany) without a preceding hot-pressing step. The cell fixture consists of two graphite plates with single serpentine channels. The active area is about 5 cm^2 (23 mm × 23 mm). Electrical heaters and a thermocouple were embedded into the plates and connected to a Cell Compression Unit (Pragma Industries, France), which controlled the cell temperature at 160 °C and the piston pressure at 2 N mm^{-2} in this study.

The cells were operated in a FuelCon Evaluator C test station (FuelCon, Germany). Pure and dry hydrogen was fed to the anode with flow rates of 100 ml min^{-1}. Dry air was fed to cathode with 250 ml min^{-1}. Both the anode and cathode outlet were ambient pressure. Prior to the recording of the polarization curves, the MEAs were operated at constant load at 0.2 A cm^{-2} overnight for activation. The current–voltage polarization curves were obtained by measuring the voltage with two stepwise increments of current density. The first and second section stepwise from 0 to 0.2 A cm^{-2} and 0.2–2 A cm^{-2} with an interval of 0.01 A cm^{-2} and 0.1 A cm^{-2}, respectively. For protecting MEAs, the polarization test of the second section would be stop automatically when the cell voltage below 0.1 V.

2.3. Electrochemical measurements

Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were performed using an Autolab PGSTAT 30 Potentiostat/Galvanostat (Metrohm) equipped with a 20 A booster and a frequency response analysis (FRA) module. Because anode polarization is negligible against to cathode polarization during fuel cell operation, so the anode can be used as the counter electrode and reference electrode. The measurements were carried out at a cell voltage of 0.6 V with an amplitude of 10 mV, and in the frequency range of 0.1 Hz–20 kHz. The impedance data were obtained by calculation and simulation with Autolab Nova software.

Voltammetric measurements, undertaken to study the electrochemical active surface area (EASA), were conducted using dry N_2 at the cathode (working electrode) and dry H_2 at the anode

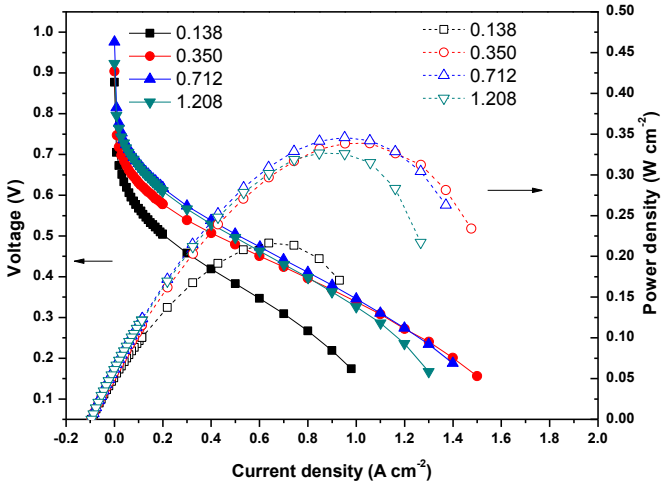

Fig. 1. Polarization curves of the GDEs with different Pt loadings.