Electrochimica Acta 285 (2018) 47–59

Contents lists available at ScienceDirect

Electrochimica Acta

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

Self-humidifying manganese oxide-supported Pt electrocatalysts for highly-durable PEM fuel cells

Aristatil Ganesan [a, b], Mani Narayanasamy [b, *], Karthikeyan Shunmugavel [c]

[a] Research & Development Centre, Bharathiar University, Coimbatore 641 046, India
[b] Ingsman Energy and Fuel Cell Research Organization Private Limited, Chennai 600096, India
[c] Madras Christian College, Department of Physics, Tambaram East, Chennai 600 059, India

ARTICLE INFO

Article history:
Received 19 February 2018
Received in revised form
27 July 2018
Accepted 1 August 2018
Available online 2 August 2018

Keywords:
Manganese oxide
Electrodeposition
Platinum
Fuel cell
Self-humidification

ABSTRACT

In this paper, we report on the synthesis and function of self-humidifying nature of manganese oxide supported platinum (Pt/Mn_xO_x) electrocatalyst under dry gas condition in proton exchange membrane fuel cells (PEMFC) with excellent electrochemical stability, long-term durability and remarkable fuel cell performance. The high-surface area nano-petal shaped manganese oxide (Mn_xO_x) clusters are synthesized by anodic deposition and the Platinum (Pt) nanoparticles are electrodeposited on diffusion layer (GDL) having two-layers of Mn_xO_x coating. The morphology and self-humidifying nature of Pt/Mn_xO_x were extensively studied through HR-SEM, HR-TEM, XPS, XRD, and water uptake studies. The electrochemical stability and long-term durability were investigated through cyclic voltammetry (CV) studies and single cell fuel cell performance. The MEAs using the spherical clusters of clump-like Pt/Mn_xO_x exhibited a peak power of 0.65 W/cm^2 at 0.48 V under dry gas condition without humidification. Also, the fuel cell delivered stable power output at a constant current density of 0.8 A/cm^2 for about 150 h with a negligible potential drop of 26 μV h^{-1}. The long-term durability, excellent electrochemical activity and self-humidifying nature of Pt/Mn_xO_x may be attributed to the formation of hydroxyl groups on Pt/Mn_xO_xwhich facilitates the proton conductivity.

1. Introduction

Interest on hydrogen fuel cells are growing faster in recent time due to the advancements in PEM fuel cell technology and its applications such as automobiles, telecom backup, portable power pack, etc. The catalyst support materials have a great influence on the cost, performance, and durability of PEMFC. The stability and catalytic activity of the fuel cell catalyst are improved by the addition of catalyst support [1]. Generally, a catalyst supp should have high conductivity, high surface area, good water management, high electrochemical stability, strong interaction to catalyst, strong corrosion resistance and ability to maximize the triple-phase boundary for the fuel cell. Also, catalyst support materials play a vital role in reducing the catalyst poisoning thereby improving the catalytic activity for longer life cycles.

Carbonaceous, Non-carbonaceous and ceramic-based materials were used as a catalyst support for PEM based fuel cells [2,3]. Among all the materials, metal oxide based catalyst support has more attraction due to its long life cycle stability [4,5]. Recently, catalyst support materials like SiO_2 are chosen for the self-humidifying anode to make internal humidification in PEMFC [6,7]. Most of the self-humidified anodes were prepared using the powder coating method which incorporates metal oxide as water retaining support [8,9]. The powder coating is a conventional brush coating method which involves the preparation of ink/paste using electrocatalysts, carbon powder, solvent, water retaining agent (Metal oxide like SiO_2), and a binder. However, this method suffers low platinum utilization, higher production cost and has a limited solubility of Pt/C, i.e. ratio of Pt/C cannot be increased beyond 30–40% [10].

The other alternative and cost-effective methods are non-powder coating technique or electrodeposition method in which, the metal oxide and electrocatalyst are directly coated on the gas diffusion layer (GDL). This method of synthesizing metal oxide as a catalyst support and Pt as a catalyst on Gas Diffusion Layer (GDL) offers improved platinum utilization with low Pt loading and reduces the cost of MEA fabrication without sacrificing the fuel cell performance. Very few reports are available where the metal oxide

---

* Corresponding author.
E-mail address: manisamy@gmail.com (M. Narayanasamy).

https://doi.org/10.1016/j.electacta.2018.08.001
0013-4686/

is used as catalyst supports at the cathode (ORR) for hydrogen fuel cell and as support for methanol oxidation catalyst in methanol fuel cells [11,12]. In this work, Mn_3O_4 is used as a predominant phase in the coating as it is considered as a catalyst support material and reserving agent for the function of the self-humidifying anode in the MEA. In addition, Manganese Oxide has strong electrocatalyst support, porous structure, large electrochemical surface area, oxidation catalysis, cycling stability, mechanical strength and wear resistance. Manganese Oxide in general possesses strong electrochemical properties under different experimental conditions and hence exhibits good proton-electron intercalation properties [13]. Several reports are available on electrodeposition of Pt for fuel cell application where the researchers have optimized the Pt loading, particle size, and surface morphology by varying the plating time, duty cycle and current density [14,15]. Since the electrodeposition of Manganese Oxide changes the surface morphology of the GDL, the plating parameters such as plating time, duty cycle and current density are to be optimized for best performance. Subsequently, total charge density for electrodeposition of Pt was also optimized. Changes in the surface morphology of the GDL, after the electrodeposition of Pt/Mn_xO_x also affects the MEA hot pressing pressure which might influence the fuel cell performance. Hence, the hot pressing pressure was needed to be optimized for improving the fuel cell performance of Pt/Mn_xO_x coated electrodes. Recent research focuses on low relative humidity operated PEM fuel cells to reduce the energy input for humidification system.

The continuous fuel cell operation imparts severe electrochemical or mechanical stresses which degrade the catalyst durability and resulting decreased fuel cell performance. Hence the degradation/failure mechanism of fuel cell materials strongly depends on the operating conditions of fuel cell. Various failure mechanism such as catalyst particle coarsening, metal dissolution, Pt bands formation in membrane, carbon support corrosion and the membrane degradation were investigated and analysed in literatures [16]. The durability of PEMFCs is a necessary study for operating fuel cell at low-RH condition and to ensure the stability of the catalyst. And hence, in this study, in-situ Cyclic Voltammetry (CV) on fuel cell was conducted to characterize the electro-chemical surface area (ECSA) of catalyst before and after long-term test. To the best of our knowledge, this is the first report showing Manganese oxide supported Pt as self-humidified anode for PEM fuel cells.

2. Experimental section

2.1. Chemicals

This work uses the Manganese (II) sulfate monohydrate (Merck CAS #: 10034-96-5 Molar Mass: 169.02 g/mol Chemical Formula: $MnSO_4 * H_2O$, Purity 98%), Manganese acetate tetra hydrate (Merck CAS #: 6156-78-1 Molar Mass: 245.09 g/mol Chemical Formula: $(CH_3COO)_2\ Mn\cdot 4H_2O$, Purity 99.5%), Hexa chloroplatinic (IV) acid hexa hydrate (Merck CAS #: 18497-13-7 Chemical Formula: $H_2(PtCl_6).6H_2O$ Molar Mass: 517.94 g/mol 40% Pt) Nafion 5 wt% Solution (Sigma Aldrich CAS Number 31175-20-9).

2.2. Materials synthesis

2.2.1. MEA preparation

The membrane electrode assembly (MEA) is the heart of the fuel cell which is prepared by sandwiching a proton conducting membrane (Nafion 212) between an anode and a cathode. The anodes were prepared by coating anode electrode with 5% Nafion solution as a binder using the brush coating method where the dry Nafion content was maintained at about 1 mg/cm^2. Then it was dried at 100 °C ± 0.1 °C for 1 h in the N_2 atmosphere. Commercial electrodes with a Pt loading of 0.5 mg/cm^2 was used as the cathodes for all MEAs used in this study. The membrane (Nafion 212) was sandwiched between the electrodes and pressed at 130 °C ± 0.1 °C for 3 min at different pressures for various MEAs. Once the MEA was prepared, it was post treated to open up the active catalyst site in the membrane-catalyst layer interface by massaging thereby the catalyst utilization was enhanced. MEA preparation was successfully done by optimizing hot pressing pressure for various MEA active surface areas (8.41 cm^2 and 25 cm^2) (Supplementary Fig. S1).

2.2.2. Electrochemical deposition of first- and second-layer MnxOx

Mn_xO_x was synthesized by anodic deposition with a current density of 5 mA/cm^2 at constant current mode [17]. The first layer of Mn_xO_x was coated directly on GDL using an electrolytic bath containing manganese acetate of 0.01 M (±4.2%). A GDL was used as working electrode and a graphite plate was used as a counter electrode which was placed vertically, 20 mm away from the working electrode. The temperature of the bath was maintained at 60 °C (±0.1 °C). Electrolyte pH value was measured as 4.0 (±0.1) at 60 °C (±0.1 °C). Deposition time was maintained for about 10 min. After electrodeposition, the working electrodes were rinsed with deionized water, dried in an oven at 60 °C (±0.1 °C) and then stored in a vacuum desiccator.

The second layer of Mn_xO_x was coated over the first layer using acidic electrolyte constituents of 0.1 M (±2.4%) Manganese sulphate and 0.1 M (±4.8%) H_2SO_4 dissolved in a de-ionized water [18]. Electroplating setup has two electrodes separated by a vertical distance of 10 mm. Before coating, the pH of the solution was maintained at 1.4 (±0.1) at room temperature. Mn_xO_x was electroplated at a galvanostatic condition of 0.5 mA/cm^2 for 33 min. (Supplementary Fig. S2) on the first layer with anodic deposition followed by rinsing of the electrodes with de-ionized water and then dried at 100 °C (±0.1 °C) in nitrogen atmosphere for 1 h to eliminate the water and to remove the impurities formed during plating.

2.2.3. Platinum electrodeposition on Mn_xO_x-coated electrode

Platinum was electrodeposited on Mn_xO_x coated electrodes (working electrode) using electrolyte bath (Supplementary Fig. S3) consisting of 10 g/L (±0.001 g) of H_2PtCl_6 and 1.64 M (±1.66%) of HCl at room temperature [10]. Here Electroplating of Pt was done in Pulse deposition mode with the following pulse parameters: (1) peak current density 400 mA/cm^2, (2) T_{on} = 3 ms, and (3) T_{off} = 100 ms with a total charge density varied from 1.6 C/cm^2 to 8 C/cm^2 (Supplementary Fig. S4). The electrodes were dried at 100 °C (±0.1 °C) in the N_2 atmosphere for 1 h after Pt deposition.

2.3. Material characterization

The Physical Characterizations of Electrodes and MEA's were done using the following techniques. The crystal structure of Pt and MnxOx on GDL were examined using X-ray diffraction (XRD) analysis (PANalytical Japan (Spectris Co. Ltd)). Surface characterization of the catalyst was studied by Scanning Electron Microscopy (SEM) Hitachi Model S-4800 with EDX analysis using EMAX ENERGY, Horiba which coupled with SEM. The morphology and the particle size at nanoscale were determined by Tunnelling Electron Microscopy (TEM) (JEOL 3010). The various chemical oxidation states of elements present in the catalyst were determined by X-ray photoelectron spectroscopy (XPS) (Kratos Analytical Ltd, UK). Thermogravimetric Analysis (TGA) had done by TGA Q500 V20.10 Build 36 thermal analyzers, TA Instruments, USA. The catalyst loadings were determined by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) analysis based on optical emission spectrometry, which was done using Perkin Elmer Optima 5300 DV, Perkin Elmercorporate, USA. The in-situ cyclic