Journal of Power Sources 352 (2017) 165–173

Contents lists available at ScienceDirect

Journal of Power Sources

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

Effect of the thickness of the anode electrode catalyst layers on the performance in direct methanol fuel cells

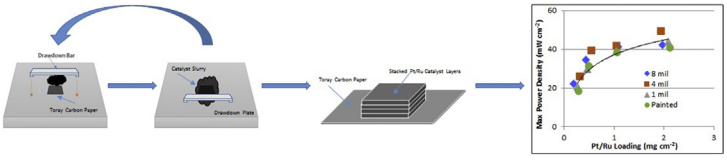
Dean E. Glass, George A. Olah, G.K. Surya Prakash*

Loker Hydrocarbon Research Institute, Department of Chemistry, University of Southern California, 837 Bloom Walk, Los Angeles, CA, 90089, USA

HIGHLIGHTS

- A drawdown method to vary catalyst layer thicknesses in DMFCs is used.
- Effect of Pt-Ru catalyst layer thickness and loading on DMFC efficacy is evaluated.
- Larger individual anode thickness layer MEAs showed higher performance.
- 49 mW cm^{-2} highest power density achieved with 4 mil layers at 2.0 mg cm^{-2} loading.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 22 November 2016
Received in revised form
20 March 2017
Accepted 22 March 2017

Keywords:
Direct methanol fuel cell (DMFC)
Platinum
Ruthenium
Spreading
Catalyst loading
Layers thickness

ABSTRACT

For the large scale fuel cell manufacture, the catalyst loading and layer thickness are critical factors affecting the performance and cost of membrane electrode assemblies (MEAs). The influence of catalyst layer thicknesses at the anode of a PEM based direct methanol fuel cell (DMFC) has been investigated. Catalysts were applied with the drawdown method with varied thicknesses ranging from 1 mil to 8 mils (1 mil = 25.4 μm) with a Pt/Ru anode loading of 0.25 mg cm-2 to 2.0 mg cm-2. The MEAs with the thicker individual layers (8 mils and 4 mils) performed better overall compared to the those with the thinner layers (1 mil and painted). The peak power densities for the different loading levels followed an exponential decrease of Pt/Ru utilization at the higher loading levels. The highest power density achieved was 49 mW cm-2 with the 4 mil layers at 2.0 mg cm-2 catalyst loading whereas the highest normalized power density was 116 mW mg-1 with the 8 mil layers at 0.25 mg cm-2 loading. The 8 mil drawdowns displayed a 50% and 23% increase in normalized power density compared to the 1 mil drawdowns at 0.25 mg cm-2 and 0.5 mg cm-2 loadings, respectively.

1. Introduction

Ever since its successful demonstration in 1994 [1], direct methanol fuel cells (DMFCs) have found many practical applications [2,3] and promises to be a solution for providing a practical electrical power source. Many patents have come from this technology globally, some notably from our own research group [4–8]. One of the appealing aspects of DMFCs is the portability as well as the ease of fuel storage and transportation. DMFCs are compact, lightweight, and can be quickly reloaded as well as being able to operate at relatively low temperatures (around 30 °C–90 °C) [9–12]. There are many factors however, that can hinder DMFCs performance. Some of these include methanol crossover in the membrane [13], catalyst poisoning [14], and catalyst leaching [15]. Platinum is the preferred catalyst for DMFCs but is costly and prone to CO poisoning on the surface [16]. Of all the catalysts that were

* Corresponding author.
E-mail address: gprakash@usc.edu (G.K.S. Prakash).

http://dx.doi.org/10.1016/j.jpowsour.2017.03.106
0378-7753/

studied, Pt/Ru seems to perform the best due to the stabilizing and anti-poisoning effects that ruthenium has on platinum [17,18]. Pt/Ru however is also expensive and can suffer from the ruthenium leaching into the proton exchange membrane.

One of the aspects of DMFCs and other fuel cells that is often overlooked is the overall three-dimensional structure of the catalyst layer in the fuel cell. Much of the mathematical modeling of the fuel cells performed in the past is based on one- and two-dimensional layers and processes [19–23], accounting for factors such as porosity, ionomer integration, reactant flow fields, and triple phase boundaries. There have also been a few in-depth three-dimensional modeling studies carried out with various aspects of the DMFCs [24,25]. These show that the catalyst layers are much more complex and cannot be easily modeled as previously thought. Such aspects of the fuel cell catalyst layers can have significant effects on the charge and mass transfer resistance, conductivity, and overall performance and lifetime of the fuel cell. As these simulations become more complex, more subtle, variable aspects of fuel cell performance become evident. Some of these subtle, yet pertinent variables to the catalyst layers such as the MEA hot pressing temperature and pressure [26], the catalyst support and percentage [27], catalyst ink pretreatment [28], pore size and structure [29], multilayer design [30], and ionomer content, can vary the performance of the fuel cell, sometimes considerably.

Another aspect that is often overlooked is the deposition method of the catalysts involved that also introduces many variables into the catalyst layer morphology and composition. Many methods have been used including painting, sputtering [31,32], screen-printing [33,34], spraying [35,36], and spreading [37], each having their own benefits and drawbacks. The method being described herein is a form of spreading the catalyst using a drawdown bar rather than a doctor blade. This method consists of spreading a fine, uniform layer of catalyst slurry onto the electrode surface with multiple layers of equal thicknesses. The goal of this work is to determine how the thickness of the individual layers of catalyst affect the overall performance of the DMFCs and what would be the optimal layer size and thickness for deposition as well as catalyst loading. Many of the aspects of the DMFCs discussed previously have gone into optimization processes, yet there are numerous others that still haven't been considered. In this study, we are examining another aspect dealing with the effect of different individual catalyst thickness layers with various catalyst loadings upon the overall performance of the DMFCs.

2. Experimental

2.1. Preparation of catalyst slurry

20% wt-Pt and 10% wt-Ru on carbon black (Alfa Aesar) was used as the anode catalyst. A slurry was prepared by following a procedure reported by Park et al. [37] comprising of a 1:10:7:1:0.5 wt ratio of catalyst, Millipore water (Direct-Q UV, 18.2MΩ), 5% Nafion® ionomer solution (Ion Power), DMSO (Macron), and isopropyl alcohol, respectively. The Nafion® ratio was set at 26% based on the equation:

$$W_{Naf} / (W_{Naf} + W_{Cat}) \times 100 \quad (1)$$

where W_{Naf} is the weight of the dry Nafion® and W_{Cat} is the weight of the catalyst and carbon support [38] The slurry was sonicated and aggressively stirred until a homogenous colloidal solution was obtained.

A cathode catalyst slurry was prepared with platinum black (Alfa Aesar), Millipore water, and 5% Nafion® ionomer solution in a 1:3:1 ratio, respectively. The solution was sonicated and painted on the cathode with a Pt loading of 3.7 mg cm^{-2}.

2.2. Deposition of the catalyst

The drawdowns were performed via a square drawdown bar (BYK) with 8 different thicknesses ranging from 1 mil to 8 mils (1 mil = 25.4 μm). A stainless steel plate was custom made for this process measuring 20.32 cm × 20.32 cm and 1.27 cm thick. In the middle of the plate was a hole 2.3 mm × 2.3 mm to position the electrode as shown in Scheme 1. The electrode consisted of Toray carbon paper (E-Tek, TGP-H60, 6% wet proofing) with an active area of 5 cm^2. The electrode was positioned exactly in the plane of the plate to ensure an accurate drawdown height of the catalyst on the electrode. A small amount of catalyst slurry was micropipetted on the plate in front of the electrode. The drawdown bar was then positioned at the desired thickness and manually run through the slurry down the plate at a speed of 7 cm s^{-1} in order to fully cover the electrode. The electrode was then removed from the plate and dried in an oven at 110 °C. This process was repeated until the desired catalyst loading for the sample was achieved as shown in Table 1. The catalyst slurry was also painted on the anode and dried in the oven between each layer deposition until the desired catalyst loading was achieved.

2.3. Fuel cell fabrication

Protonated Nafion-117® was cut into 10.16 cm × 10.16 cm pieces and sandwiched between the anode and cathode and hot pressed at 140 °C for 5 min with 250 kg of force. The resulting MEA was then fitted inside the fuel cell housing and hydrated overnight with Millipore water at 60 °C.

2.4. Electrochemical measurements

The polarization measurements were performed using a Fuel Test System 890B (Schribner Associates Inc.). The fuel cells were tested with a 0.5 M methanol (Macron) solution pumped at 90 mL min^{-1} at 60 °C on the anode side and O_2 flowing at 100 mL min^{-1} at the cathode. The cell temperature was maintained at 50 °C and will be referenced as such in the remainder of the paper. The discharge current was scanned from the open circuit voltage (OCV) to zero volts.

2.5. Electrochemical impedance spectroscopy (EIS) measurements

EIS measurements were performed with a Solartron SI 1287 and SI 1260 Impedence-Phase Analyzer (Solartron Analytical). EIS measurements were performed with a 0.5 M methanol solution pumped at a rate of 90 mL min^{-1} and O_2 at a flow rate of 100 mL min^{-1} with the cell temperature of 50 °C. Impedance measurements were taken at 0.3 V versus OCV with an AC amplitude of 100 mV with frequencies ranging from 100 kHz to 0.01 Hz. The resulting impedances were analyzed and equivalent circuits were fitted from the Z-Plot software (Schribner Associates Inc.).

2.6. Scanning Electron Microscope (SEM) measurements

SEM measurements were performed on a JEOL JSM-7001F electron microscope with an acceleration voltage of 6.0 kV. SEMs of the cross sections were taken from cutouts of the middle of the electrode aligned vertically on the plate to measure the thickness as well as to measure the cross-section of the catalyst layer on the carbon paper.