Journal of Power Sources 398 (2018) 1–8

Contents lists available at ScienceDirect

Journal of Power Sources

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

Novel interfacial bonding layers with controlled gradient composition profile for hydrocarbon-based membrane electrode assemblies

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HIGHLIGHTS

- Novel interfacial bonding layer for hydrocarbon-based MEA in PEMFC is developed.
- Bonding layer with a compositional gradient can be fabricated by a spraying method.
- 14 times improved interfacial adhesion strength is obtained.
- Excellent MEA durability is achieved via the stable membrane-electrode interface.

ARTICLE INFO

Keywords:
Interfacial bonding layer
Gradient composition
Membrane electrode assembly
Polymer electrolyte membrane fuel cell

ABSTRACT

We develop a novel approach to improve the robustness of the interface between the hydrocarbon (HC) membrane and the perfluorosulfonic acid (PFSA) ionomer-based catalyst layer (CL) in membrane electrode assemblies (MEAs). This approach involves the creation of a gradient-composition interfacial bonding layer, in which the HC and PFSA contents are gradually varied along the thickness direction. The layer is fabricated using a simple spray-coating method, in which HC and PFSA ionomer mixtures with different compositions are sprayed stepwise onto both sides of the HC membrane surface. The interfacial structure developed in this process minimizes the chemical incompatibility between the HC and PFSA polymers. Owing to the tightly bound sub-layers resulting from the intertwined HC and PFSA microdomains, the gradient-composition bonding layer provides a significantly improved interfacial adhesion strength (14 times higher than that of the pristine membrane without bonding layer) between the HC membrane and the PFSA-based CL. Finally, the fabricated MEA exhibits a > 433% higher durability in humidity cycling tests compared with the pristine MEA without interfacial bonding layer, together with a better retention of its initial performance.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are considered promising alternative energy sources for stationary and automotive applications due to their high efficiency and zero pollutant emissions [1–3]. Perfluorosulfonic acids (PFSAs) such as Nafion have been widely used as the membranes of PEMFCs, owing to their high proton conductivity and mechanical stability. However, PFSA membranes suffer from several critical drawbacks, such as high cost, low temperature resistance, and high fuel permeability, which underscore the need for the development of other types of membranes [4–6]. Various sulfonated hydrocarbon (HC) membranes have been intensively investigated as alternatives to PFSA ones, including sulfonated poly (arylene ether sulfone)s (SPAESs) [7–9], poly (ether ether ketone)s (SPEEKs) [10,11], poly (phenylene)s (SPPs) [12–14], and polyimides (SPIs) [15], as well as their composites [16–18]. Even though several HC-based membranes with good proton conductivity, mechanical properties, and high thermal stability have been developed, suitable technologies for their application in efficient and stable membrane electrode assemblies (MEAs) are still lacking, which significantly limits their widespread use

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https://doi.org/10.1016/j.jpowsour.2018.07.045
Received 31 March 2018; Received in revised form 9 July 2018; Accepted 10 July 2018

in PEMFCs.

Conventional HC polymers possess extremely low oxygen permeability (approximately nine times lower than that of PFSA ionomers), which prevents their use as binder materials in the catalyst layer (CL), resulting in poor performance of the fabricated MEAs [19]. To overcome this issue, the use of PFSA ionomers as catalyst binders is still unavoidable, even for the fabrication of MEAs based on HC membranes. However, the poor compatibility between HC membranes and PFSA ionomers results in a poor interfacial adhesion between the two corresponding layers during the operation of the cell, which leads to a significant decrease in the performance and durability of the PEMFC [20,21]. These interfacial issues derive from both chemical (compatibility) and physical (preparation techniques) factors. Owing to its perfluorinated structure, Nafion (used in the CL) has very poor chemical affinity for HC membranes, which normally have a fully aromatic rigid structure [22]. Moreover, when the decal transfer method (considered the most convenient process for mass production of MEAs) is employed, it is difficult to achieve a conformal interfacial contact between HC membranes and the PFSA ionomer-based CL, because the temperature used for the thermal lamination process is much lower than the glass transition temperature (T_g) of the HC membrane [23–25].

To overcome the interfacial delamination issues, most earlier studies focused on introducing fluorinated moieties inside the HC membrane, in order to minimize its chemical incompatibility with the PFSA ionomers [26,27]. For example, McGrath et al. prepared SPAES-based copolymers containing partially fluorinated units, aimed to improve the chemical affinity with the PFSA ionomer-based CL. Membranes based on a blend of SPEEK and poly (vinylidene fluoride) (PVdF) were also investigated, with the purpose of improving the dimensional stability and compatibility of the HC membrane [28]. A significant improvement was achieved by incorporating additional interfacial bonding layers between the HC membrane and the PFSA ionomer-based CL [29]. Park et al. fabricated MEAs with good interfacial adhesion by introducing an additional layer with crosslinkable units on the surfaces of SPI or SPEEK membranes [30]. Our group also developed a thin interfacial bonding layer based on SPAES and PVdF blends applied on the surface of a SPAES membrane using a spraying method, which resulted in a significantly enhanced interfacial adhesion between the HC membrane and the electrodes [22]. Moreover, we recently developed a new bonding layer material based on sulfonated aromatic copolymers with flexible and partially fluorinated moieties [31]. This bonding layer was found to be very effective in enhancing the interfacial adhesive strength between an SPAES membrane and a Nafion ionomer-based CL, leading to improved performances in PEMFCs. Kim et al. proposed a novel approach based on interfacial fastening with an interlocking layer, in which micrometer-sized pillar arrays formed on one side of the HC membrane are intruded into the thin PFSA ionomer layer present at the cathode CL during a thermal lamination process [32]. The embedded pillars expand during cell humidification, generating a high friction force (with an eight-fold increase in interfacial adhesion) at the interface with the PFSA ionomer layer, and resulting in a significantly improved durability of the MEA under humidity cycling. In a collaborative study with our group, the same researchers recently expanded their approach to develop a mechanical nanofastener with a three-dimensionally interconnected ball-and-socket joint structure constructed on the HC membrane surface [33]. An unprecedented level of interfacial durability (with a 10-fold improvement with respect to the results obtained using microsized pillars) was obtained for the manufactured MEA, which remained stable for more than 3000 humidity cycles.

In the present study, we report a novel approach to develop a robust interface between the HC membrane and the PFSA ionomer-based CL through the creation of an interfacial bonding layer with a compositional gradient, in which the HC and PFSA ionomer compositions are gradually varied along the thickness direction, as shown in Fig. 1. In this way, the inner sublayer in direct contact with the HC membrane surface has a composition dominated by a HC ionomer (e.g., HC:PFSA = 7:3) with the same chemical structure as the membrane, while the outer sublayer, forming an interfacial junction with the PFSA-based CL, has a PFSA-rich composition (e.g., HC:PFSA = 3:7). Moreover, the middle sublayer has the same content of HC and PFSA ionomers, resulting in an interfacial layer with a continuously changing composition. This unique interfacial structure is expected to minimize the chemical incompatibility between the HC and PFSA polymers. Moreover, the sublayers are well interconnected with each other by HC and/or PFSA microdomains formed by phase separation between the PFSA and HC ionomers. Finally, as an overall result of the strong adhesion between adjacent sublayers, the gradient-composition interfacial bonding layer leads to a significantly improved interfacial adhesion between the HC membrane and the PFSA-based CL. Notably, the thickness of the gradient-composition interfacial bonding layer can be controlled by a simple spray-coating method where HC and PFSA ionomer mixtures with different compositions are sprayed stepwise onto both surfaces of the HC membrane. Furthermore, because the developed bonding layer possesses a PFSA-rich outer sublayer with a considerably softened surface, complete transfer of CLs during the decal transfer method could be achieved under a mild temperature and pressure condition [34]. Finally, the fabricated MEA exhibits a $>$ 300% improved durability in humidity cycling tests compared with the pristine MEA without interfacial bonding layer, together with a better retention of its initial performance.

2. Experimental

2.1. Preparation of reinforced polymer electrolyte membrane

Sulfonated poly (arylene ether sulfone) (SPAES) (degree of sulfonation = 40) copolymer was prepared following a literature [35]. Then reinforced polymer electrolyte membrane, RSPAES, was prepared using a solution casting method where a liquid crystal polymer nonwoven (LCP) was impregnated with 16wt% of SPAES solution in dimethylacetamide (DMAc, Samchun). The cast solution was dried in a convection oven at 80 °C for 6 h to complete the membrane. Fig. S1 shows the fabrication process of the reinforced membrane schematically.

2.2. Preparation of interfacial bonding layers

Ten weight percent of PFSA ionomer (D1021, Dupont) and SPAES solutions were prepared separately using dimethyl sulfoxide (DMSO, Samchun) as solvent. From these solutions, three mixture solutions with different weight ratios between SPAES and PFSA, 30:70, 50:50 and 70:30, were prepared and used for the spraying. To fabricate the gradient composition interfacial bonding layer, three mixture solutions were sprayed stepwise onto RSPAES starting from the ratio of 3:7 through 5:5 to 7:3 mixture solutions. The spray coater (LSC-300, Lithotech., Korea) was operated with an circular nozzle with a hole diameter of 0.8 mm and length to diameter (l/d) of = 8.75 equipped on a xy-robot arm in a ventilated box. The nozzle air pressure was 230 KPa and its moving speed was 60 mm s^{-1}. The mixture solutions were fed to the nozzle through tubes connected to a syringe pump. The mixture solution was injected at a rate of 0.5 ml min^{-1} using a syringe pump, and the injection interval of the spray nozzle was set at 5 mm. During the spraying the membranes were fixed on a temperature controlled vacuum chuck table. After the spraying, the sprayed membrane was then dried at 190 °C on the vacuum chuck table for 10 min. The same procedure was then repeated for three times by keeping the conditions same. The coated membranes were acid-treated by placing them in a 1.5 M H_2SO_4 bath for 24 h, and then washed with D. I water for 24 h to remove residual acid from the membrane. The thickness of the bonding layers was kept constant at 3 ± 1 μm for all prepared membranes.