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Factors in electrode fabrication for performance enhancement of anion exchange membrane water electrolysis

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HIGHLIGHTS

- Effects of MEA fabrication parameters on alkaline AEMWE performance were examined.
- Optimal PTFE binder content in the anode is 9 wt% within the range of 5–20 wt%.
- Hot-pressing the MEA at 50 °C, 669 psi improved the performance by 12%.

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ABSTRACT

To improve the cell performance for alkaline anion exchange membrane water electrolysis (AEMWE), the effects of the amount of polytetrafluoroethylene (PTFE) non-ionomeric binder in the anode and the hot-pressing conditions during the fabrication of the membrane electrode assemblies (MEAs) on cell performances are studied. The electrochemical impedance data indicates that hot-pressing at 50 °C for 1 min during MEA construction can reduce the polarization resistance of AEMWE by ~12%, and increase the initial water electrolysis current density at 1.8 V (from 195 to 243 mA cm^{-2}). The electrochemical polarization and impedance results also suggest that the AEMWE performance is significantly affected by the content of PTFE binder in the anode electrode, and the optimal content is found to be 9 wt% between 5 and 20 wt%. The AEMWE device fabricated with the optimized parameters exhibits good water splitting performance (299 mA cm^{-2} at 1.8 V) without noticeable degradation in voltage cycling operations.

1. Introduction

The emission of greenhouse gases, mainly from the combustion of fossil fuels, has become a serious issue while global energy consumption is rapidly increasing [1]. The accumulated carbon dioxide in the atmosphere is considered as the main cause of global warming and climate change [2]. To mitigate the environmental impact of greenhouse gases by reducing the use of fossil fuels, research on alternative energy has been actively pursued for decades [3,4]. Among the various energy carriers, hydrogen is not only abundant, but also has high power and fuel efficiency. However, it is currently produced mainly by steam reforming of natural gas, a process that creates carbon dioxide or hydrocarbons as byproducts. Therefore, cleaner alternatives such as water electrolysis, water gasification, and photolysis are clearly needed [5]. Water electrolysis has advantages over other hydrogen production technologies, primarily by using renewable power sources (e.g., wind, geothermal, or solar energy) to yield high-purity hydrogen without

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greenhouse gas emission. Additionally, on-site hydrogen generation fueling stations using water electrolysis require relatively less space due to the low operating temperature, and they could also use the existing water and electricity infrastructure [6].

Recently, water electrolysis using a solid polymer electrolyte membrane has been extensively investigated [7,8]. Compared to conventional alkaline water electrolysis that uses alkaline solution electrolytes with porous diaphragm separators, the polymer electrolyte membrane-based systems offer advantages with regard to safety, efficiency, and separation of the product gases [9]. Two kinds of solid polymer electrolytes are used: proton exchange membranes (PEMs) [10] and alkaline anion exchange membranes (AEMs) [11]. PEM-based water electrolysis (PEMWE) has shown high performance in producing hydrogen without emitting pollutants. However, it requires acid-resistant noble metal catalysts, e.g., platinum, and expensive perfluorinated membranes such as Nafion® in the water splitting device [9,12]. On the other hand, as AEMWE systems are operated under high pH, inexpensive non-noble metal electrocatalysts can be utilized towards oxygen evolution and hydrogen evolution reactions [13]. Therefore, AEMWE should resolve the cost issue of the PEMWE system while satisfying the environmental requirements.

However, the water splitting performance of AEMWE is currently much lower than that of PEMWE. Hence, performance enhancement through developing new materials and membrane electrode assemblies (MEAs) are highly desirable. There have been many studies to develop AEMs with high ionic conductivity and stability [14–19], as well as catalysts with improved activity and durability in alkaline conditions [20–23]. Moreover, the optimization of electrode/MEA fabrication is also very essential for improving the performance and durability of electrochemical devices [24–26]. An et al. have developed mathematical modeling for AEMWE to predict the performance. Their results represented that the performance reduction in AEMWE is mainly caused from the activation polarization of the hydrogen and oxygen evolution reactions [26] which represents the importance of electrode optimization to produce high performance MEAs. Nevertheless, only a few studies have examined the effects of relevant factors, such as catalyst loading [27], hydroxide ion-conducting inorganic binder with pore formers [28], and electrodeposited low-loading electrodes [29,30] for AEMWE devices. Therefore, further optimization of MEA fabrication methods is urgently needed.

While many previous studies have adopted ionomeric binders in the MEA electrode of AEMWE single cells, the durability was poor [8,14,15,21,22]. Polytetrafluoroethylene (PTFE) can be used as a binder for higher durability, as its repeat unit of $-[CF_2-CF_2]-$ has high chemical bond strength and therefore excellent chemical stability [31]. For example, Pavel et al. reported that the AEMWE single cell with PTFE binder [27] delivered initial performance comparable to that with commercial anion-conducting binder (AS-4 ionomer, Tokuyama Corporation) [8], as well as high durability (voltage increase as small as 5% after 500 h). In comparison, the reported voltage increases with ionomeric binders were much higher: 53% for 27 h (AS-4) [8], 24% for 500 h (A-Radel) [8], and 9% for 500 h (polymethacrylate quaternary ammonium (QPDTB-OH^-)) [22]. Moreover, the MEA prepared using PTFE binder showed the comparable performance of approximately 460 mA cm^{-2} at 1.8 V [27], while the MEA prepared using AS-4 ionomer showed approximately 480 mA cm^{-2} at 1.8 V [8] with supplying 1 M KOH solution as an electrolyte solution. PTFE binder was also used for improved stability of AEMWE in this study. For the MEAs in polymer electrolyte membrane fuel cells (PEMFCs), the hot-pressing step has been frequently adapted when fabricating catalyst-coated substrate (CCS) using PTFE-based electrodes [32–34]. The enhanced cell performances and durability were reported to originate from the reduced resistance at the electrode/electrolyte interface and the suppressed MEA delamination, respectively [33,34]. However, the study with PTFE-based electrodes in AEMWE by Pavel et al. did not use the pressing step [27]. To the best of our knowledge, no study has been reported on the effect of the pressing process in AEMWE systems. However, it is known that when the temperature or pressure is too high, the polymer membrane can be degraded, resulting in decreased conductivity [35] or the electrodes can become significantly deformed with porosity loss [36].

Meanwhile, controlling the amount of binder in the electrodes has been used to modify the microstructure and increase the performance of various polymer membrane-based electrochemical cells, including PEMFCs [37–40], PBI-based high-temperature PEMFCs (HT-PEMFCs) [25,41,42], and alkaline direct ethanol fuel cells (ADEFCs) [43]. Especially, the pore structure changes with the amount of PTFE loading. For example, severe agglomeration of catalyst particles was observed with high PTFE loading [25,41,43]. Increased ohmic resistance with higher binder content was also commonly observed. However, the optimal content seems to depend on the electrochemical reactions in each application. In HT-PEMFCs, Jeong et al. obtained the best performance in the MEA containing 20 wt% PTFE binder, which produced the lowest charge transfer resistance and highest secondary pore volume [41]. In contrast, Li et al. reported that the ADEFC performances were the highest with 5 wt% PTFE binder in the electrode [43]. Regarding the durability, higher PTFE loading was reported to help prevent the catalyst particle loss in the out-stream during long-term operations [43]. However, the effect of binder content in AEMWE systems has not been reported, since the reported single cell performances were all based on fixed amounts of binders (PTFE: 9 wt% [27], A-Radel ionomer: 22 wt% [8], quaternary ammonium groups modified polymer: 20 wt% [15], and polysulfone quaternary benzyl trimethylammonium: 30 wt% [13]). Pavel et al. also studied the AEMWE performance with varying Non-PGM cathode (HER) catalyst loading correlated to the electrode thickness under fixed fabrication factors [27]. However, the optimized amount of catalyst can be varied with different electrode structure for either PGM or non-PGM catalyst used in AEMWE.

In this study, the effects of MEA hot-pressing and the binder content (5–20 wt%) in the anode electrode on the cell performance of AEMWE were investigated, by electrochemical analyses with voltage cycling operation. The characteristics of MEA performance with various electrode structures were observed through polarization curves and impedance. These factors were then optimized to achieve high performance for AEMWE operation, based on the measured electrochemical data.

2. Experimental

2.1. MEA preparation

Electrodes in the MEAs were fabricated via the CCS method as follows. The catalyst ink slurry was prepared with the electrocatalysts of IrO_2 (Premion®, Alfa Aesar) and Pt/C (Pt 46.5 wt%, Tanaka K. K.) for the anode and cathode, respectively. Each electrocatalyst was mixed with isopropyl alcohol (A.C.S grade, Burdick & Jackson), an aqueous solution of PTFE (60 wt% PTFE dispersion in H_2O, Aldrich), and distilled water. The amount of PTFE in the anode was varied as 5, 9, 12, and 20 wt% of the total solid weight, while the cathode binder content was fixed at 9 wt%. The prepared anode and cathode inks were homogenized in an ultrasonic bath for 1 h, and then sprayed onto titanium paper (250 μm in thickness) and carbon paper (TGP-H-120, Toray), respectively. The electrodes were dried at room temperature overnight and then sintered at 350 °C in N_2 gas. During sintering, the molten PTFE improves the binding of