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Membrane Electrode Assembly Manufacture by Simultaneous Forming of Catalyst Coated Layer and Gas Diffusion Layer

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Summary

The high costs of perfluorinated membranes have prompted research for alternative membranes in production of hydrogen and ozone by water electrolysis. We have prepared new composite membranes using sulfonated polyether ether ketone (sPEEK) polymer and inorganic proton conducting fillers. And we have decreased consumption of the noble metal by means of composite catalysts based on carbon nanotubes (CNTs), graphene and noble metal. Especially, we have applied simultaneous forming of catalyst layer and gas diffusion layer on ZrO_2–sPEEK composite membrane in membrane electrode assembly (MEA) manufacturing. With this MEA, the performance of the electrolysis cell improved considerably at room temperature and atmospheric pressure. The performance of this MEA is studied by varying voltage range at current density of 0~2A/cm^2.

Keywords: water electrolysis cell; Composite membrane; Hydrogen, Ozone
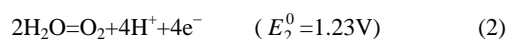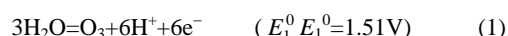
1. Introduction

Nowadays, hydrogen, clean and eco–friendly energy carrier, is attracting attention owing to exhaustion of the fossil fuel and growing of the greenhouse effect. However, hydrogen surely has to be made from other resources. Various approaches such as gasification, pyrolysis, and electrolysis of natural gas, coal and water etc. are available.[1] Currently, steam reforming of natural gas is considered as the most economic approach for large scale hydrogen production.[2~4]
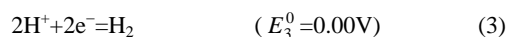
Producing hydrogen with renewable energy such as solar energy and wind energy is very cost–effective and eco–friendly in storage of natural energy. Ozone is a strong oxidizer, and whose oxidation reduction potential (2.07V, in water) is greater than that of chlorine dioxide (1.5V) or chlorine (1.36V).

Water electrolysis is a process in which water is split into oxygen and hydrogen electrically. In a special case, ozone could be produced with oxygen, and the main electrode reaction and its standard electrode potentials are as below.[11~16]

Anode

$$3H_2O=O_3+6H^++6e^- \qquad (E_1^0\ E_1^0=1.51V) \qquad (1)$$

$$2H_2O=O_2+4H^++4e^- \qquad (E_2^0=1.23V) \qquad (2)$$

Cathode

$$2H^++2e^-=H_2 \qquad (E_3^0=0.00V) \qquad (3)$$

Ozone evolution efficiency depends on various factors such as anodic material, electrode morphology, cell configuration, current density, temperature and flow rate. [16] The electrolysis of water using proton exchange membrane (PEM) has been a novel approach for developing a technology for hydrogen and ozone production. The key component of the so–called solid polymer electrolyte water electrolysis is said to be this PEM, which transports protons from the anode to the cathode and prevents the produced gases from mixing. Currently, the most widely used PEM material is Nafion (Dupont Co.) due to its moderate proton conductivity and chemical stability. Nafion–like have a few drawbacks such as high cost, water

dragging during operation and these have prompted research for alternative membranes based on hydrocarbon polymer and composite membrane.[5~10]

Walid Mabrouk et al., have synthesized new ion exchange membranes from chlorosulfonated polyether sulfone (SO_2Cl–PES) crosslinked by polyaminated crosslinking reagents.[17] And the crosslinked membranes have exhibited improved mechanical properties and shown a decreased hydrophilic character. But in this case, the MEA has not currently been optimized and many parameters have to be studied, such as membrane thickness, cross–linking rate, and etc. Helen Prifti et al., have reported the characteristics of sandwich–type sPEEK/tungstophosphoric acid (TPA)/polypropylene (PP) composite membrane.[18] And they have used this membrane in direct methanol fuel cell.

More recent research about sPEEK membranes has occurred in the field of fuel cell applications. And further work has been on the way to expand application domains of the membranes, like electrolysis. The aim of the present work is to manufacture the MEA for water electrolysis using sPEEK and to determine the parameters of the process.

2. Experiments

Multi–walled carbon nanotubes(MWCNTs) was purchased from Ryomyong Technological Agency(DPRK), with diameters between 90 to 110nm, surface area of about 100m^2/g. Graphene was also purchased from Ryomyong Technological Agency, and other reagents were purchased from Sigma Aldrich Co. Ltd.

2.1 Preparation of ZrO_2–sPEEK composite membrane.

For the preparation of sPEEK membrane, 5g of PEEK powder (Victrex, 450P) was dispersed in 100mL of 95% sulfuric acid maintaining under stirring for 3h at 70°C. After this reaction time the sulfonated polymers were precipitated in cold water, washed thoroughly to remove excess acid until the pH of the wash solution was 6 and completely dried[19].

For composite membrane preparation, 3g of sPEEK was dissolved in 35mL dimethylformamide (DMF) and added with a known amount of ZrO_2. The solution was then filtered and

sonicated in an ultrasonic water bath. After membrane casting, they were left to dry on a glass plate at 60°C. The thickness of the membranes are approximately 70~90μm.

2.2 Preparation of electrocatalysts

Electrocatalysts were prepared by thermal decomposition of noble metal salts and sintering. MWCNTs were added in mixed acid for oxidation process and washed with deionized water. The mixture was evaporated to dryness in vacuum dryer.

Pt/CNTs catalyst was prepared by thermal decomposition method. Oxidized MWCNTs(300mg), anhydrous ethanol(5mL), isopropanol(2.5mL), n−butanol(2.5mL) and ethylene glycol(4mL) were sonicated for 30min. Chloroplatinic acid was added in this suspension , and the mixture was stirred strongly (>6 000rpm) for 2h. And then, we reduced the mixture by keeping it for 1h at 130°C. After filtration, we washed the residue with deionized water and dried it for 8h at 80°C, and then Pt/CNT catalyst was obtained. Graphene oxide was prepared by using a modified Hummers method. Nitrogen−doped graphene was synthesized from Graphene oxide and nitrogen precursor (e. g. urea). Then, N−doped graphene was mixed with chloroplatinic acid, anhydrous ethanol (4mL), isopropanol(2mL) and n−butanol(2mL), and they were sonicated for 30min. This suspension was calcined for 1h at 440°C for reduction and then washed with deionized water. At last, Pt/graphene, ozone evolution catalyst is obtained by dryness.

2.3 MEA preparation

Anders Christian and Maria A. Folgado have reported about hot pressing of catalyst coated membrane (CCM). But in the case of sPEEK membranes, this method is not appropriate, and parameters of the processes have not been reported. In this paper, we propose simultaneous assembly method of CCM and GDL in the case of sPEEK membranes to improve the performance of PEM electrolysis cell. One of above prepared catalysts was dispersed in 5% sPEEK solution followed by ultrasonic blending to achieve a catalyst ink. The catalyst ink was coated on carbon paper as GDL that was made from CNT and carbon black. Coating catalyst ink was done by drying at 70°C. On the other hand, the catalyst ink was brushed on the composite membrane pretreated with boiling H_2O_2 and H_2SO_4. Sequentially the GDL was adhered to the CCM. This procedure was repeated on the opposite side of the membrane. CCM−GDL structure was pressed at room temperature, 2kg/cm^2 pressure for 10h, and the MEA(Fig. 1.) was obtained.

Figure 1. MEA after 1 000h(total) operation at room temperature and 0.5A/cm^2

3. Results and Discussion

The performance of prepared MEA is evaluated by in−house fabricated single cell assembly with current and voltage characteristics curves generated while water electrolysis operating. Fig. 2 shows the polarization curves of commercial MEA and prepared MEA. Cell voltage at current density of 1A/cm^2 is 1.77V and 1.89V, respectively.

Results obtained with commercial MEA are slightly less efficient than those obtained with prepared MEA, i.e. at the current density of 1 A/cm^2, the operating voltage of the cell with prepared MEA is 0.12V higher compared to that with commercial MEA. But this enables us to use this as PEM.
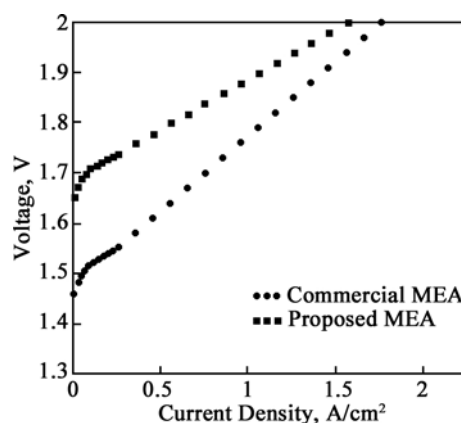

Figure 2. Polarization curves of the water electrolysis cell with the MEAs prepared by Nafion 115(commercial MEA) and ZrO$_2$−sPEEK composite membrane, operated at atmosphere pressure and room temperature. Anode Pt loading: 0.7mg/cm^2; cathode Pt loading: 0.4mg/cm^2.

The MEA prepared by ZrO$_2$−sPEEK composite membrane can be used in PEM water electrolysis. But DMF was used in the process of fabrication of MEA, and this might remain from dryness of CCM. Therefore, more research work is necessary for application to hydrogen water machine and ozone water machine etc.

4. Conclusions

This paper has proposed how ZrO$_2$−sPEEK composite membrane can be formed, and a new approach has been introduced to fabricate the MEA prepared by this composite membrane. Pt/CNTs and Pt/graphene catalysts were prepared for this MEA. The cell voltage was 1.89V at 1A cm^{-2}.

Performances of the MEA are enhanced by simultaneous assembly of CCM and GDL. This process is of a great significance in the development of cost−effective PEM water electrolysis system.

However, it remains to be further clarified whether sPEEK membranes could take the place of perfluorinated membranes.

Further studies are needed to determine whether these findings could be contributed to the commercialization of cost−effective PEM water electrolysis.

Acknowledgements

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