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Pt/MWCNTs nanocomposite: a durable electrocatalyst for proton exchange membrane fuel cells

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Abstract

Extensive research and development efforts are being under taken in recent year in the field of PEM fuel cell (PEMFC) systems to make them commercially viable. In proton exchange membrane fuel cells, stability and durability are important objects for commercialization. It is well-known that catalyst degradation and carbon-support corrosion are the main factors reducing stability, and using Pt nanocatalyst on carbon nanotube supports instead of Pt/C increase stability and durability after long-term aging. In this work, a hydrothermal method was employed to prepare Pt nanoparticles dispersed highly on multiwalled carbon nanotubes with 19.4 wt. % Pt. Membrane electrode assemblies (MEAs) from tow catalyst fabricated with thin film method. In fuel cell test station, the polarization, ac impedance and cyclic voltammetry experiment of MEAs and also ADT test was done. The Pt/C catalyst showed no activity in fuel cell testing after 2000 potential cycles due to severe carbon corrosion, Pt dissolution, and catalyst particle sintering. Conversely, the Pt/MWCNT catalyst showed better electrochemically active surface area and also durability after a potential cycling. The analysis of ac impedance spectra associated revealed that the presence of CNTs significantly reduced increasing of activation resistances. The performance of fresh MEA fabricated from Pt/c was better than fresh Pt/MWCNT MEA, but after ADT test had more reduce. Loss electrochemical active surface area of Pt/C catalyst was higher than Pt/MWCNT catalyst due to more catalyst particle sintering.

Keywords: Proton Exchange Membrane Fuel Cell (PEMFC), durability, ADT test, Pt nanocatalyst on carbon nanotube supports, performance.

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1 Introduction

In recent years, a great deal of research has been done on fuel cells. Polymer electrolyte membrane fuel cells (PEMFCs), due to their high energy efficiency, excellent response characteristics, low operating temperature, rapid start-up and etc. are the major types of fuel cells. To remove trade barriers to commercialization of PEMFC especially cost and durability, development of new catalysts with high efficiency and long lifetime are required. Corrosion of electrocatalyst layers is one of the fundamental mechanisms which strongly influences the long term performance and is considered the main obstacle to development of PEM fuel cells. To improve PEMFC performance and durability, and to reduce the catalyst cost, many studies have focused on building new and renitent anode and cathode catalysts. Recently, alternative supports have been applied to improve corrosion resistance, mass transfer and to reduce Pt loading [1]. Carbonaceous materials used as support for platinum nanoparticles and alloys have attracted much attention, because their degradation affects negatively the performance and durability of PEMFCs. In fact, the extreme operating conditions found in a PEMFC, which include high humidity, low pH (<1), and strongly oxidizing (O₂) or reducing (H₂) atmosphere at the cathode or at the anode, respectively, contribute to accelerate carbon corrosion [2]. Carbon corrosion leads to the agglomeration of platinum particles, their dissolution into the ionomer phase or even their washing out of the system. Moreover, oxygen-containing surface groups can be formed on the carbon surface, thus increasing its hydrophilic character and affecting the water removal and gas transport through the catalyst and the gas diffusion layers. In addition, surface group scan decrease the conductivity of carbon. Carbon oxidation decreases the thickness of the catalyst layer, increasing the bulk electrode resistance and/or the electric contact resistance with the current collector [2]. One of the most attractive catalyst support materials is carbon nanotubes (CNTs) due to their large surface areas, high chemical stability, high electric conductivity and fantastic mechanical strength. Moreover, to increase the Pt specific surface area and lower its cost, highly dispersed Pt-NPs have been employed as catalysts supported by CNTs to facilitate the oxygen reduction reaction (ORR) process. ORR is the rate limiting step, which dominates the PEFMC efficiency due to its 4-electron involvement and large activation energy for reaction [1]. Thus, it is necessary to functionalize the surface of CNT prior to their use as catalyst support, because the deposition, distribution and size of metal nanoparticles strongly depend on the surface properties. In fact, the hydrophobic nature of CNT surface hinders their dispersion in polar solvents and prevents a uniform distribution of catalyst particles on the carbon support [2]. When CNTs are refluxed with a mixture of HNO₃–H₂SO₄, the surface graphitic layers would react with the oxidants and produce a high density of various surface functional groups, such as carboxyl, carbonyl and phenolic groups. When the Pt ions were introduced into the system, they would interact with and attach to these surface functional groups through an ion exchange or coordination reaction, and serve as nucleation precursors. A well-dispersed deposition of the Pt metal nanoparticles on the surface of CNTs was obtained after the reduction of the surface Pt²⁺ ions by hydrogen [3].

We investigate a hydrothermal process to prepare size-controlled and well-dispersed Pt nanoparticles on MWCNTs. In this study, we showed improved long-term durability of the Pt/MWCNT catalyst. We investigated the electrochemical measurements and accelerated



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durability test of this catalyst and also for commercial catalyst (Pt/C) in two In situ and Ex situ conditions.

2 Experimental

2.1 Hydrothermal synthesis of Pt/MWCNTs nanocomposites

MWCNTs (purity min. 95%; diameter 5-20 nm; length 1-10mm) purchased from PlasmaChem GmbH were used as received. Before the deposition of Pt nanoparticle, MWCNTs were functionalized with – C=O, –COO and –COH groups by refluxing in a 65% nitric acid solution at about 110-120°C for 6h. Pt nanoparticles supported on MWCNTs were synthesized by the hydrothermal technique. 2.7 ml of an aqueous solution of H₂PtCl₆ (Merck, Art. 807340) and 80 mg of purified MWCNTs were added into glycerol (Merck, Art. 818709) in a 100 ml vessel. The aqueous NaOH solution (0.1 M) was then added to adjusted pH value at almost 9. Then the mixture was sonicated for 30 min to ensure the uniform dispersion of MWCNTs in the solution. Seventy-five milliliters of mixture solution was transferred into a 100 ml teflonlined high pressure reactor (BERGHOF, BR e100) and maintained for 5h under stirring. Finally, the product was collected through vacuum filtration using glass microfiber filter with a pore size of 0.7 mm. The solid phase was washed with ethanol and deionized water, and then dried at 100 °C [4].

2.2 Fabrication of the membrane electrode assembly

Nafion polymer electrolyte membranes (ElectroChem, EC-NM-117) were used for all experiments. After cutting, the samples were cleansed and treated in the following way to ensure that the membrane is completely in the Na⁺ form: boiling in 3 wt.% H₂O₂, cleaning in approximately 80 °C hot Millipore water, boiling in 50% NaOH and cleaning in hot Millipore water again. Catalyst slurry include deionized water, isopropanol, 5 wt.% solubilized Nafion (ElectroChem, EC-NS-05), catalyst (Pt/MWCNT or Pt/C(40 wt.%, Aldrich)). For the preparation of MEA by the thin film method, catalyst slurry was sprayed on both side of the Nafion membrane in the Na⁺ form and then dried in vacuum oven at 140°C. The active electrode area was 5 cm² with catalyst loading of 0.2 mg Pt cm⁻² for anode and cathode. The MEA was pressed with carbon paper (ElectroChem, Teflon treated) as gas diffusion layers at 60 bar for 150s maintaining the temperature at 120 °C. For MEA fabrication of commercial catalyst Pt/C, all this process was repeated.

2.3 Accelerated durability test

Electrocatalyst degradation mechanisms depend on factors such as potential, temperature, humidity, contaminants, and carbon support stability. Accelerated durability test (ADT) can be any combination of these factors when testing is conducted in a complex environment. In this work the acceleration tests is done in two ways: In situ and EX Situ experiments. In situ



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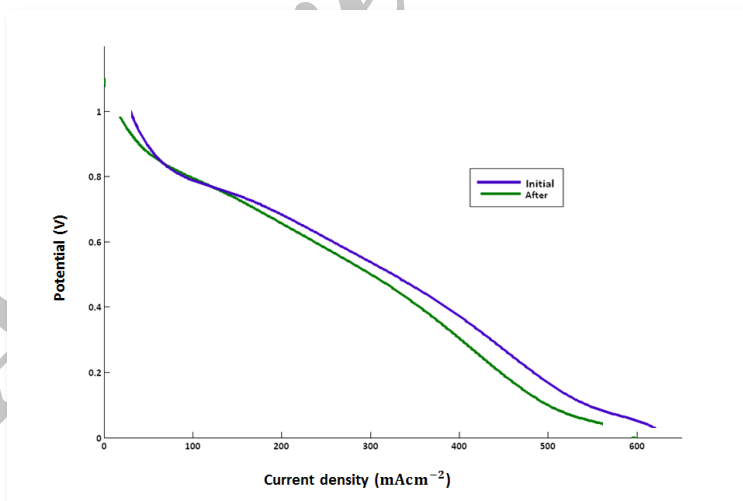
acceleration tests were performed for 6 hour under a constant high potential (1.3 V). The polarization tests, ac impedance and cyclic voltammetry (CV) were reperformed before and after acceleration tests to determine the durability of the each MEA. Ex situ acceleration tests were performed by three electrode system as mentioned in section 2-4. CV analysis was carried out for 4000 cycles and the specific electrochemical active area (ECA) was calculated before and after cycling.

3 Results and discussion

3.1 Durability experiment results

Polarization results for Pt/MWCNT and Pt/C MEA before and after high potential operation for 6 h are shown at Fig. 1 . It is well known that high potential quickly corrodes the carbon catalyst support and results in rapid degradation of fuel cell performance by the loss and agglomeration of Pt particles.

The initial current density of MEA-1 and MEA-2 at 0.6 V were 259 and 378 mA cm⁻² , respectively, which were reduced to 238 and 283 mA cm⁻² , respectively.



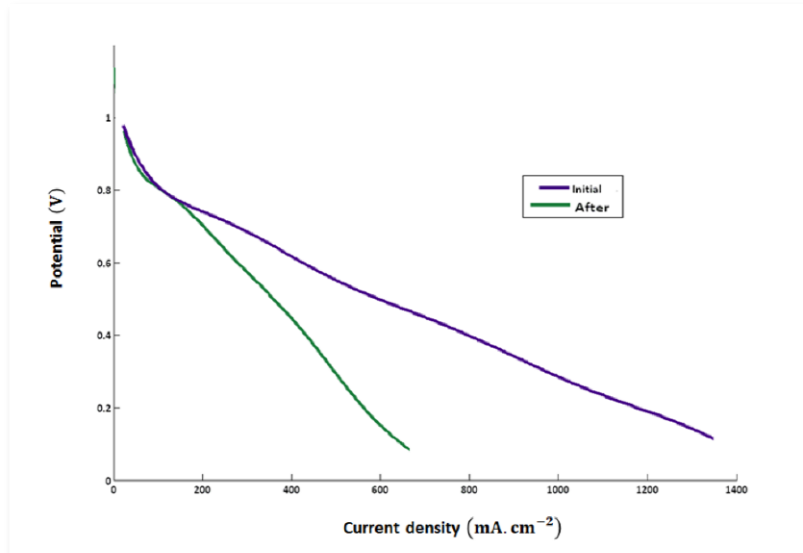
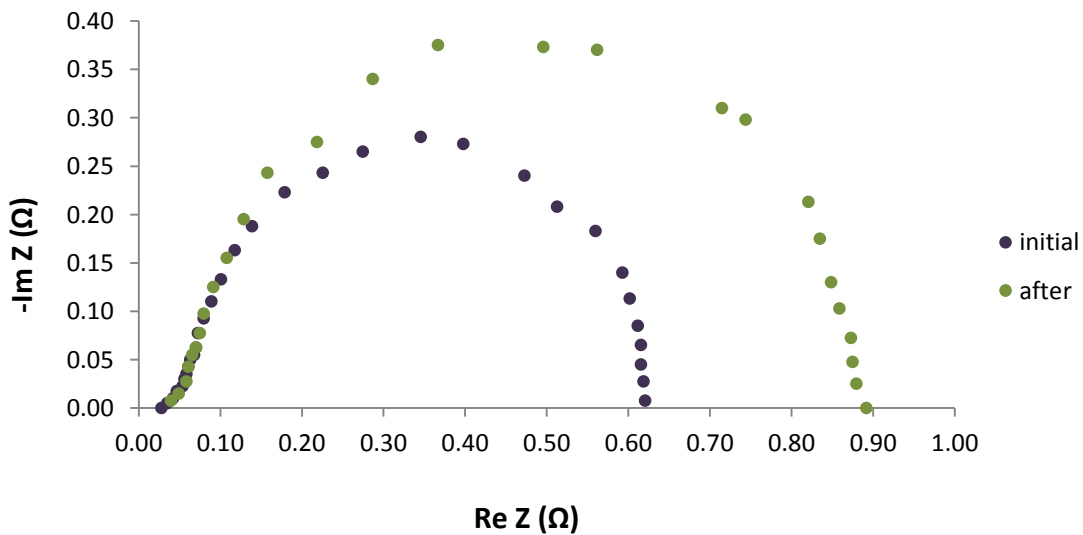


Fig. 1- Polarization curves of MEAs before and after acceleration test, (a) Pt/MWCNT, (b) Pt/C.

To understand the degradation mechanism, EIS measurements results before and after durability tests are shown in fig. 2.



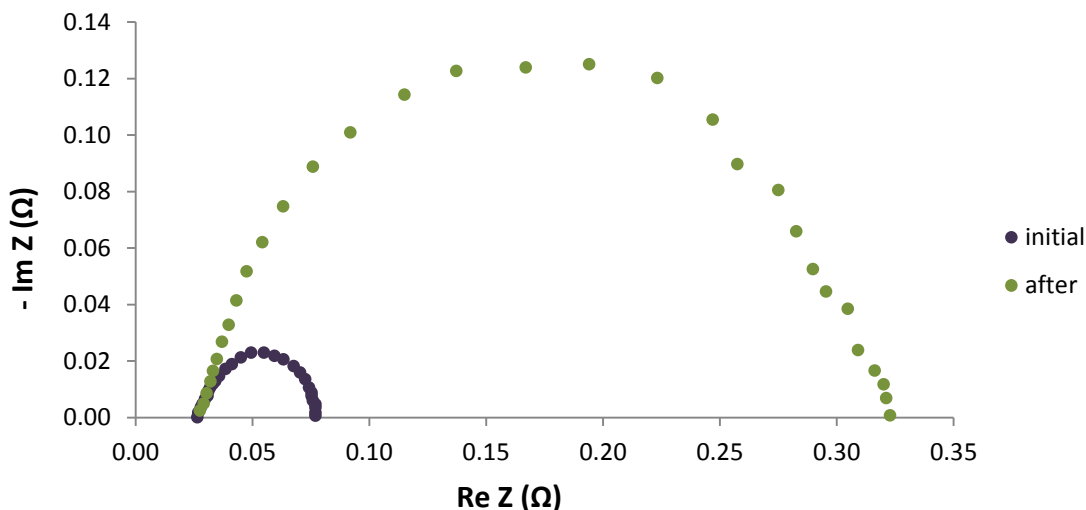
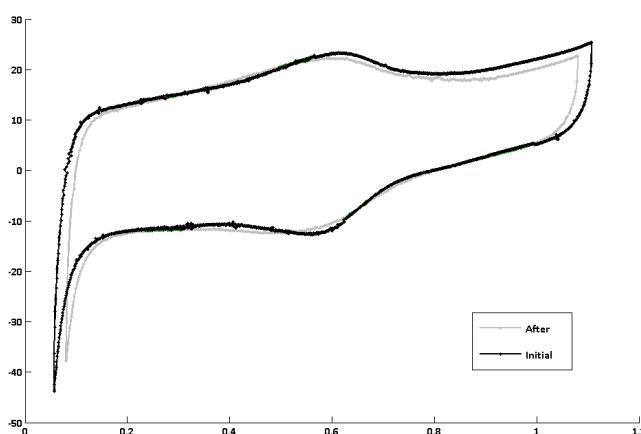


Fig. 2- EIS spectra of MEAs before and after durability test, (a) Pt/MWCNT, (b) Pt/C at voltage 0.7 V.

CVs were also measured to investigate the change of the ECSAs after acceleration test and the results were shown in Fig. 3. The ECSA of the commercial Pt/C was higher than fabricated catalysts initially due to the small Pt size, however it dropped to 74% of its original value. Instead, ECSAs of Pt/MWCNT showed 44% drop. It is believed that high carbon corrosion of carbon black caused the agglomeration of Pt, the collapse of carbon supports, the loss of support porosity and blocking of the mass transfer pathway, which resulted in the reduced active surface area.





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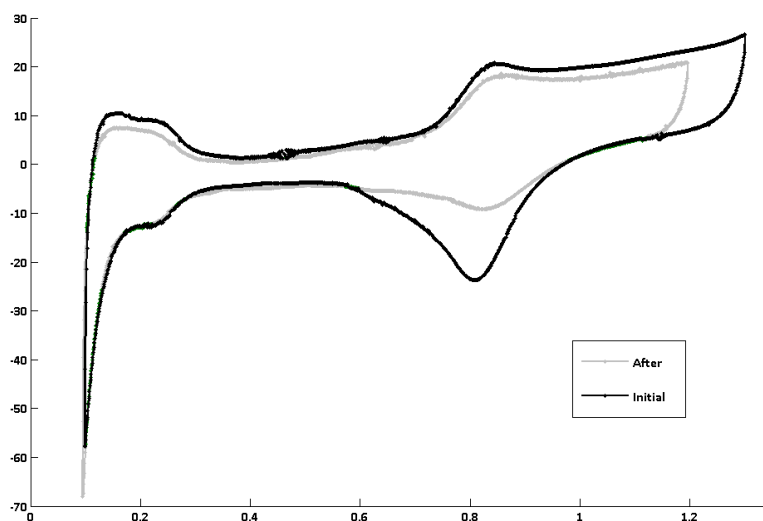


Fig. 3- Cyclic voltammograms of MEAs before and after durability test, (a) Pt/MWCNT, (b) Pt/C.

4 Conclusion

To achieve the commercialization of PEM fuel cell technology, durability, cost, and reliability are the main issues to be solved. Most of all, long-term durability is considered as the most critical issue that influences the other two. In this study, we showed improved durability of the Pt/MWCNT catalyst. The cell performance of Pt/MWCNT catalyst showed less activity loss (8%) compared to that of commercial Pt/C catalyst (25%) after high voltage acceleration test. The polarization resistance increased only 43% for Pt/MWCNT but 300% for commercial Pt/C. Thus, the Pt/MWCNT catalyst showed better durability after a potential cycling.

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