Journal of Power Sources 268 (2014) 50–55

Contents lists available at ScienceDirect

Journal of Power Sources

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

Corrosion protection of aluminum bipolar plates with polyaniline coating containing carbon nanotubes in acidic medium inside the polymer electrolyte membrane fuel cell

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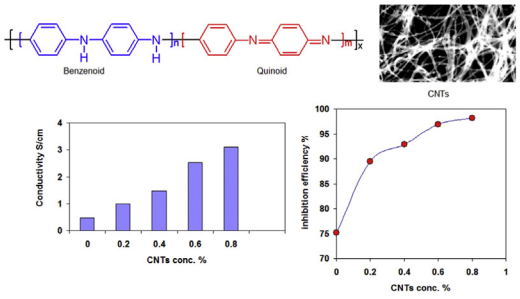
HIGHLIGHTS

- We examine the effect of addition of CNTs on the corrosion resistance of polyaniline in PEM fuel cell.
- The addition of CNTs to polyaniline coating enhanced conductivity of polyaniline.
- The addition of CNTs increases the inhibition efficiency of polyaniline coating.
- Inhibition efficiency is close to 98% when CNTs concentration is 0.8%.
- The techniques include electrical conductivity, polarization, EIS and SEM.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 4 February 2014
Received in revised form
22 April 2014
Accepted 4 June 2014
Available online 12 June 2014

Keywords:
Carbon nanotubes
Conductive polymer
Aluminum
Corrosion
Coating

ABSTRACT

The effect of addition of carbon nanotubes (CNTs) on the corrosion resistance of conductive polymer coating (polyaniline) that coated aluminum bipolar plates in acidic environment inside the PEM fuel cell (0.1 M H_2SO_4) was investigated using electrical conductivity, polarization and electrochemical impedance spectroscopy (EIS) measurements. Scanning electron microscopy (SEM) was used to characterize the coating morphology. The results show that the addition of CNTs to polyaniline coating enhanced the electrical conductivity and the corrosion resistance of polyaniline polymer. The inhibition efficiency of polyaniline polymer increased with increasing CNTs concentration. The best inhibition was generally obtained at 0.8% CNTs concentration in the acidic medium. This was further confirmed by decreasing the oxygen and water permeability and increasing coating adhesion in the presence of CNTs. EIS measurements indicated that the incorporation of CNTs in coating increased both the charge transfer and pore resistances while reducing the double layer capacitance.

1. Introduction

Polymer electrolyte membrane (PEM) fuel cells are a type of fuel cell being developed for transport applications as well as for stationary fuel cell applications and portable fuel cell applications [1]. PEM fuel cell transforms the chemical energy liberated during the electrochemical reaction of hydrogen and oxygen to electrical energy, as opposed to the direct combustion of hydrogen and oxygen gases to produce thermal energy [2]. A stream of hydrogen is delivered to the anode side of the membrane electrode assembly (MEA). At the anode side it is catalytically split into protons and electrons. This oxidation half-cell reaction is represented by [3]:

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http://dx.doi.org/10.1016/j.jpowsour.2014.06.021
0378-7753/

$$H_2 \rightarrow 2H^+ + 2e \text{ (at the anode)} \quad (1)$$

The newly formed protons permeate through the polymer electrolyte membrane to the cathode side. The electrons travel along an external load circuit to the cathode side of the MEA, thus creating the current output of the fuel cell. Meanwhile, a stream of oxygen is delivered to the cathode side of the MEA. At the cathode side oxygen molecules react with the protons permeating through the polymer electrolyte membrane and the electrons arriving through the external circuit to form water molecules. This reduction (half-cell reaction) is represented by:

$$1/2O_2 + 2H^+ + 2e \rightarrow H_2O \text{ (at the cathode)} \quad (2)$$

The polymer membrane must conduct hydrogen ions (protons) but not electrons as this would in effect "short circuit" the fuel cell. The membrane must also not allow either gas to pass to the other side of the cell. Finally, the membrane must be resistant to the reducing environment at the cathode as well as the harsh oxidative environment at the anode [4].

The bipolar plates perform as the current conductors between cells, provide conduits for reactant gases flow, and constitute the backbone of a power stack [5]. They are commonly made of graphite composite for high corrosion resistance and good surface contact resistance; however their manufacturability, permeability, and durability for shock and vibration are unfavorable in comparison to metals [5].

Increasing attention is being paid to the use of metallic materials such as Fe, Al, Cu, Ni, Ti-based alloys in bipolar plates for PEM fuel cells [6–9]. Aluminum and its alloys have excellent physical and chemical properties and presently find extensive industrial as well as domestic applications and in spite of this, there is a few of work reported on using Aluminum bipolar plates [10].

Metals should demonstrate higher mechanical strength, higher values of electrical conductivity, better durability to shocks and vibration, no permeability, and much superior manufacturability and cost effectiveness when compared to graphite composite. However, the main disadvantage of metals is the lack of ability to resist corrosion in the harsh acidic and humid environment inside the PEM fuel cell [11]. The corrosion of bipolar plates causes the membrane poisoning and lowers the ionic conductivity of the membrane and this lead to lower the PEM fuel cell performance [12].

Several coating materials and processes have been proposed to improve the corrosion resistance of metals in the PEM environment [13–15]. One such material is a conducting polymer coating [16,17].

Conductive polymers are organic polymers that conduct electricity. Such compounds may have metallic conductivity or can be semiconductors. Conducting polymers can combine the electronic characteristics of metals with the engineering properties of polymers. Polypyrrole, polythiophene and polyaniline are common examples of conducting polymers [18].

A carbon nanotubes (CNTs) is a tube-shaped material, made of carbon, having a diameter measuring on the nanometer scale [19]. Carbon nanotubes have attracted the fancy of many scientists worldwide. The small dimensions, strength and the remarkable physical properties of these structures make them a very unique material with a whole range of promising applications. One method to improve the corrosion resistance and conductivity provided by conductive polymers coatings is the addition of carbon nanotube [20].

The aim of this work is to study the effect of addition of CNTs on the corrosion resistance of conductive polymer coating (polyaniline) that coated aluminum bipolar plates in acidic environment inside the PEM fuel cell (0.1 M H_2SO_4).

2. Experimental

2.1. Materials

Corrosion tests were performed on aluminum sheets of the following percentage composition: Al (99.89%), Si (0.03%), Cu (0.02%), Mg (0.03%) and Zn (0.01%). Prior to each experiment, the aluminum electrode with dimension 12 × 17 × 0.5 mm were first briefly ground with different grades of emery paper (120, 400, 800, 1000 and 1200) and washed thoroughly with distilled water and degreased with acetone.

Polyaniline polymer was obtained from Sigma–Aldrich Co. Xylene was received from Sciencelab.com, Inc. and used without further purification.

Carbon nanotubes CNTs that were prepared by Egyptian Petroleum Research Institute (EPRI) (diameter: 20–30 nm, length: 1–10 μm, layers: 5–20).

The aggressive solutions, 0.1 M H_2SO_4 were prepared by dilution of AR grade 98% H_2SO_4 with distilled water.

2.2. Preparation of polyaniline polymer coating

Painting of polyaniline polymer coating on aluminum was accomplished by dissolving polyaniline polymer in xylene, 1:1 ratio. The dissolved polyaniline polymer was applied on the cleaned aluminum samples by a small brush and dried overnight. The dried samples were heated at 110 °C for 5 min to remove any air bubbles that may have trapped in the coating. The coating thickness measured was 10–12 μm.

Different concentrations (0.2, 0.4, 0.6 and 0.8% by weight) of CNTs powder (average particle size = 20–30 nm) were mixed with 5% of chloroform and then they added to polyaniline polymer coating. The particles were dispersed by using a high speed mechanical stirrer. The electrical conductivity of polyaniline polymer coating in the absence and presence of CNTs was measured by using four point probe method.

The morphology of CNTs and polyaniline coating in the absence and presences of 0.8% CNTs were performed recorded using JEOL-JEM 1200 EX II scan electron microscope (SEM).

2.3. Electrochemical measurements

Electrochemical experiments were carried out in a conventional three-electrode cell with a platinum counter electrode and a saturated calomel electrode (SCE) coupled to a fine Luggin capillary as the reference electrode. To minimize the ohmic contribution, the Luggin capillary was kept close to aluminum (working electrode). Electrochemical measurements were performed using Gill AC Serial no. 947 (ACM instruments).

Potentiodynamic polarization measurements were carried out at potential range of ±200 mV with respect to the corrosion potential (E_{corr}) at a sweep rate of 0.125 mV s^{-1}. The linear Tafel segments of the anodic and cathodic curves were extrapolated to corrosion potential to obtain the corrosion current densities (j_{corr}).

EIS measurements were carried out using AC signals of amplitude 5 mV peak to peak at the open-circuit potential in the frequency range 100 kHz to 10 mHz.

2.4. Coating adhesion and permeability measurements

For Adhesion test, coated carbon steel panels were submitted to the pull-off test using the Elcometer tester model 107 (CORRPRO CO. INC.).